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Chemistry, Process Design, and Safety for the Nitration Industry

Thomas L. Guggenheim, Editor
SABIC Innovative Plastics
Mt. Vernon, Indiana

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Foreword

The ACS Symposium Series was first published in 1974 to provide a mechanism for publishing symposia quickly in book form. The purpose of the series is to publish timely, comprehensive books developed from the ACS sponsored symposia based on current scientific research. Occasionally, books are developed from symposia sponsored by other organizations when the topic is of keen interest to the chemistry audience.

Before agreeing to publish a book, the proposed table of contents is reviewed for appropriate and comprehensive coverage and for interest to the audience. Some papers may be excluded to better focus the book; others may be added to provide comprehensiveness. When appropriate, overview or introductory chapters are added. Drafts of chapters are peer-reviewed prior to final acceptance or rejection, and manuscripts are prepared in camera-ready format.

As a rule, only original research papers and original review papers are included in the volumes. Verbatim reproductions of previous published papers are not accepted.

ACS Books Department

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James Dodgen 1921–2010

Jim Dodgen, born in Anniston, Alabama, graduated from Georgia Institute of Technology with a B.S. in Chemical Engineering in 1943, whereupon he entered the U.S. Navy. Lieutenant Dodgen was assigned to the Air Force, Pacific Fleet, managing ordnance from 1943 until March 1945 in the Marshall Islands. Jim married Charlene Ward in 1945 and they have two sons, James Jr. and Charles. From 1945 until 1946, he had assignments pertaining to bomb- and torpedo-handling equipment for the Bureau of Ordnance, and then distributing aviation armaments with the Bureau of Aeronautics.

From 1946 to 1951, Jim worked as a senior engineer for Pennsalt, where he designed chemical plants, while staying in the military as a reservist. In 1951, he was called back to military service. From 1955 to 1958, Jim was head of the propellants, explosives, chemicals, and pyrotechnic section of the Bureau of Ordnance. He then worked at the Naval Propellant plant at Indian Head in Maryland, serving as director from 1959 to 1962. During this time he worked on propellant units for multiple systems including Talos, Sidewinder, Sparrow, and Hawk. In 1962 he served as the representative of the Bureau of Naval Weapons at Hercules in Utah, where he was responsible for engineering and inspection of the second stage of Polaris. In 1965 he was transferred to the Naval Torpedo Station in Washington, working on Mark torpedoes. He retired from the Navy with the rank of Commander in 1968 and worked briefly at Lockheed, Olin, Aerojet Solid Propulsion Co., and Cordova Chemical Co.

Charlene died in 1969. He remarried Virginia Britten in 1972 and became a wonderful father to her three daughters. In 1974, Jim started Dodgen Engineering Company, a one-man operation. He then consulted with many companies involved in the manufacture of propellants, explosives, and chemicals up until his death in 2010.

In 2003, the editor, working at General Electric at the time, got to work with Jim when we started up a large-scale mixed acid nitration plant. Jim was one of several consultants hired to oversee the engineering and safety aspects of the process. He possessed the essential elements required when designing and operating a plant that handles energetic material — namely, deep practical experience and technical training. The plant started up and ran without incident; and his insight and ability to teach others lent confidence to those who ran the operation.

When a condenser failed in another nitration plant (one can read about this in one of the chapters of this book), Jim was consulted. He had data in his files on trinitromethane (the suspected culprit in the failure) that was not in the public domain. This data proved very useful, resulting in the safe redesign of the failed unit. Commander James Dodgen was a model technologist and wonderful coworker.

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Chester Grelecki 1927–2007

Chester (Chet) was born to Polish immigrants in Newton Township, Pennsylvania in 1927, learning English when he went to school. In 1945, he left high school and joined the Navy. He was discharged in 1946 and his older sister pushed him to finish high school, after which he obtained a B.S. in chemistry from Kings College (1950), an M.S. in biochemistry from Duquesne University, and his Ph.D. in physical chemistry from F.O. Rice at the Catholic University of America in Washington, D.C. (1956), whereupon he started working for Thiokol Chem. Corp. in the Reaction Motors division.

In 1959, he became a manager directing work on propellant technology, specifically mixed hydrazine fuel systems. This phase of Chet's career concluded with the successful landing of *Surveyor 1* on the moon in 1966, which employed the hydrazine fuel. Since the *Surveyor* briefly bounced on the surface during the landing, Chet liked to claim that the fuel was also responsible for the first successful launch of a vehicle from the moon's surface.

While at Thiokol, Chet began testing propellants, commercial explosives, and industrial chemicals to determine their thermal stability, detonation velocity, critical diameter, ignition mechanisms, and shock sensitivity. In 1963, he founded the Fire and Explosion Hazards Evaluation Service, a service to the chemical process industries directed to the reduction of processing accidents. In 1968, Chet was appointed Manager of Research Operation at Reaction Motors, directing work in propellant and explosives research, combustion engineering, and pilot plant process studies.

In 1970, Chet, with William Cruice, co-founded Hazards Research Corporation (HRC) to continue safety studies for the chemical industry. From that date until his death, Chet directed several thousand studies to access the safety of chemicals and chemical processes in a multitude of industries. Work was performed for the Army, Navy, Air Force, Atomic Energy Commission, Department of Transportation, the EPA, OSHA, and the chemical industry at large. HRC determined the root cause of countless failures at chemical facilities, leading to safe redesign efforts. In several cases, opposing parties hired Chet to evaluate the circumstances of the failure in question, and based on his findings settled the dispute, speaking to the high regard others placed in Chet. Chet married the chemical nature of materials with the engineering used to handle them. When interacting with him for the first time, it was not possible to discern whether he was a chemical engineer or a chemist, or a physicist for that matter.

In the early 1970s Chet developed a course in Fire and Explosion Hazards Evaluation for the American Institute of Chemical Engineers. This proved to be an effective course, and was given hundreds of times at professional meetings and companies around the world. Chet was a masterful educator, and special person and tutor to authors Odle and Guggenheim. One can only ponder how many industrial incidents and personnel injuries were averted because of the efforts of Chet and all his associates at HRC. It is expertise and experience like Chet's that is required when designing and operating complex chemical operations.

Chet was a warm individual. He was once contracted to investigate a pump explosion and he interviewed the people in the plant at the time of the event. He asked how their ears were feeling. The question was part compassion and part science: knowing the distance and orientation of the witness from the explosion, whether the ear drum was intact or not, the metallurgy, and whether the pump impellor housing failed in a brittle or ductile manner, quickly gave Chet an estimate of the amount of material that had led to the explosion and if the event was a detonation or a deflagration.

To see Chet's photograph in color in the printed book, please see the color insert.

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Preface

This is the third ACS Symposium Series book dealing with nitration, the first two having been published in 1976 and 1996. The nature of this 2013 publication reflects the changes worldwide in process safety management, and geographies of research and manufacturing. The contributions to this book were first presented at the 243rd ACS National Meeting in San Diego, California in March of 2012, in the Industrial and Chemical Engineering Division.

Several of the chapters deal with the burgeoning capacity increases in the polyurethane industry, requiring improved methods to nitrate benzene and toluene, to ultimately produce MDI and TDI. Methods to manage waste streams from these nitrations plants are also discussed. There are several chapters on process safety that discuss accident investigation, process redesign, and sensitivity testing of energetic material. Hazards of laboratory and pilot plant nitration studies are addressed. Several of the papers describe considerations which must be taken into account when analyzing nitration reaction samples.

These chapters represent practical application of known principles and concepts. Some of the chapters read more like a tutorial than a scientific paper. Those new to nitration will benefit the most from reading this book, but it will serve to remind the experienced of factors to consider when operating a nitration facility. By no means are all hazards of nitration covered in this monograph.

Two Festschrifts are included in this publication, one for James Dodgen and one for Chet Grelecki. Both these individuals were highly trained, deeply experienced technologists who studied the processing and nature of energetic materials. They remind us of the need to include minds such as theirs when designing and operating nitration facilities.

The Editor wishes to thank those who made this book possible. Mary Moore at Eastman Chemical Company assisted in organizing the nitration symposium at the 243rd ACS National Meeting. The expert staff at ACS Books streamlined the publishing process. Thanks to all the authors and reviewers who labored to produce each chapter of the book. Finally, thanks to Jacob Oberholtzer and Roy Odle, both working for SABIC, for encouragement and technical advice, and SABIC for financial support.

Thomas L. Guggenheim
SABIC Innovative Plastics
Mt. Vernon, Indiana 47620

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Chapter 1

The Adiabatic Mononitrobenzene Process from the Bench Scale in 1974 to a Total World Capacity Approaching 10 Million MTPY in 2012

Alfred Guenkel[*]

NORAM Engineering and Constructors Ltd., 200 Granville Street,
Suite 1800, Vancouver, BC, Canada V6C 1S4
[*]E-mail: aguenkel@noram-eng.com

The age of adiabatic mononitrobenzene (MNB) production began with a meeting held in July 1974 at the Canadian Industries Ltd. (CIL) Explosives Research Laboratory in McMasterville, Quebec, Canada. Two senior scientists of the American Cyanamid Company disclosed the adiabatic MNB concept, and invited CIL to contribute its sulfuric acid concentration technology, and lead the piloting of the adiabatic process. Three simple questions had to be answered at that time: What is the rate of by-products formation? Can the spent acid be recycled indefinitely? What scale-up rules should be applied to size industrial-scale stirred tank nitrators? The first adiabatic MNB plant was brought on line in 1979, in Louisiana, USA. At that time, the world's MNB production was less than 1 million metric tonnes per year (MTPY), all coming from plants based on the incumbent isothermal technology. The world capacity in 2012 for MNB is now approaching 10 million MTPY, predominantly from adiabatic plants. This paper is a review of challenges which had to be overcome to bring the now dominant adiabatic MNB process to its current state of high reliability, high yield and energy efficiency, and excellent safety record. MNB capacity estimates quoted in this paper should be viewed as "best guesses" only. Producers keep production records confidential.

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Background

The development of the adiabatic MNB process started with a meeting held in July 1974 at CIL's Explosives Research Laboratory. Two senior scientists of the American Cyanamid Company disclosed, in a half-page document, the adiabatic MNB process concept and invited CIL to participate in a joint development project, where CIL would contribute its sulfuric acid concentration technology. The process concept was simple: Nitrate benzene in a large excess of mixed acid, sufficient to absorb all of the heat of nitration, decant the crude MNB phase, then flash the spent acid under vacuum to boil off water generated chemically, charging the reconcentrated sulfuric acid with additional nitric acid, and finally sending the resulting mixed acid to the nitration stage. The potential benefits were immediately evident; the heat of nitration was about the same as the heat required to boil off the water from the spent acid. This would result in substantial energy savings relative to the isothermal process, where the heat of nitration is dissipated by cooling the nitrators and is thus wasted. Capital savings would come from the elimination of almost all the heat-transfer surface areas in the isothermal nitrators and in the associated sulfuric acid concentrator. During the meeting it was agreed that three questions would have to be answered through a pilot program. What is the rate of by-products formation? Can the sulfuric acid be recycled indefinitely? What scale-up rules should be applied to size the proposed stirred-tank nitrators? These nitrators had to achieve essentially complete conversion of nitric acid to MNB for process economics and environmental reasons.

The MNB Market

American Cyanamid disclosed in the 1974 meeting that they were contemplating building an MNB plant with a capacity of 350,000 MTPY, which seemed surprising at the time. The total US MNB production in 1974 was only 230,000 MTPY (*1*). What wasn't recognized by the CIL party, which included the author of this paper, was that a new class of polymers, namely polyurethanes, had become a commercial reality in the 1960's, and was on a rapid growth trajectory, which has continued to this day.

The first step in the synthesis of MDI-based urethanes requires MNB. In 1978 the total world production of MDI was 400,000 MTPY, which steadily increased to 2 million MTPY in 1998 (*2*). This corresponded to an average growth rate of 8.4% per annum. To support this growth it has been necessary to build a world-scale MNB plant almost every year, not counting capacity required by the replacement of inefficient isothermal plants. Some large isothermal plants were, in fact, built in the 1970's, only to be scrapped in the 1980's.

Extrapolation of production capacity through 2012 and beyond, accounting for projects known to be in planning stages, suggests that current MDI capacity may be over 6 million MTPY, and could exceed 10 million MTPY by 2015. Much of the growth will take place in China, where currently at least seven major projects are in various stages of execution. In 2010 the share of MNB production worldwide was about 25% for the USA, 30% for Europe, 25% for China and 20%

for the rest of the world (*3*). China's share will likely exceed 50% within the next three years.

MNB has become a commodity chemical, and it is safe to assume that at least one world-scale plant will be built every year for the foreseeable future. The other trend has been to build plants with large capacities, of up to half a million MTPY.

First-Generation Adiabatic MNB Technology

Based on the outcome of the CIL/American Cyanamid pilot development work, two adiabatic MNB plants came on stream in 1979, with individual capacities of 172,000 and 50,000 MTPY (*4*). These two plants immediately accounted for about a third of US capacity (*1*) and caused the subsequent shut-down of a number of isothermal plants.

The pilot work did show that the rate of formation of nitrophenol by-products was somewhat higher than that in the isothermal plants, but that it was not overly problematic at the first two plant sites given the infrastructure available. On the small pilot scale it was difficult to recycle the sulfuric acid more than 100 times, but no negative effects could be observed. The problem in the acid recycle tests was that the acid inventory had to be small in order to maximize the number of times the sulfuric acid was recycled, and at the same time have enough material to accommodate the sampling and analysis of the process. In a full-scale MNB plant, the acid cycle time is typically about 5 minutes, so that 100 pilot plant cycles corresponded to only a single plant operating shift.

Surprisingly, no meaningful data on the kinetics of heterogeneous benzene nitration could be found in the literature at the time. In the isothermal MNB process, kinetics had never been of much interest since the nitrator was always "big enough", provided that the required heat-transfer area could be accommodated within the nitrator volume, provided that the acid concentration was such that nitronium ions were present, and provided that the benzene was well dispersed in the acid.

In the pilot plant the kinetics were studied through adiabatic batch nitration experiments, where the extent of nitric acid conversion was established by recording the rise in nitrator temperature as a function of time. Time zero was when the total batch change of benzene was injected into the nitrator at a selected initial nitrator temperature, mixed acid composition, and agitation intensity. All three variables could be examined separately through this technique.

The outcome of the kinetics study – mostly on a 100 ml beaker scale, but also in a nitrator vessel of 25 cm diameter, and even a single run in a 200 liter reactor – was to scale up the nitrators on the basis of maintaining a constant power input per unit volume. To the surprise of the research engineers and chemists, and of the first commercial users of this technology, the nitration rates in the full-scale plants were about two times faster than anticipated. None of the common stirred-tank scaling rules could explain the high nitration rates. Evidently something else was having a significant effect on the nitration rate.

Sometime after the completion of the adiabatic pilot plant work, a few studies on the kinetics of nitration reactions were presented by a number of researchers at the 169th Meeting of the American Chemical Society in 1975 (*5*). The findings

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of these studies were useful for comparing relative nitration rates of different aromatic compounds, but they could not be used to size the adiabatic nitrators.

Following the successful commissioning of the first two adiabatic plants, and benefiting from the experience obtained during the start-ups, five more adiabatic plants were built using the stirred nitrators as described in reference (*4*).

US Patents were granted to the American Cyanamid Company for the adiabatic process in 1977 (*6*) and 1978 (*7*). In the course of a review of prior art technology it was found that the DuPont Company had actually patented an adiabatic batch process in 1941 (*8*).

The DuPont Company also recognized the potential of MDI growth in the 1970’s, and developed an alternative adiabatic process, called the azeotropic process, where the heat of nitration was removed through the boiling of benzene and water. Patents were granted for this process in 1975 (*9*) and 1976 (*10*).

With a number of adiabatic MNB plants having come on stream, and in view of the rapid capacity growth, the Stanford Research Institute published a report on the economics of the isothermal and adiabatic technologies in 1986 (*11*). The isothermal MNB technology was still widely used at that time.

In 1990 a chapter on “Nitrobenzene and Nitrotoluene” was published in John McKetta’s Encyclopedia of Chemical Processing and Design (*12*), where the technical merits of the isothermal and adiabatic processes were compared.

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Second-Generation Adiabatic MNB Technology

In the late 1980’s some of the engineers who played lead roles in the development of the first-generation adiabatic MNB plants came together again to see if anything could be done to improve the process. A motivating factor was to answer the nagging question of why, in the first-generation plants, the plant-scale nitrators gave twice the nitration rates compared to those obtained in the pilot plant. It was then postulated that the benzene was not optimally dispersed in the pilot nitrator, as had tacitly been assumed. Could it be that the data generated in the kinetic studies were nothing more than the results of a transient dispersion phenomenon? To test this hypothesis, some beaker-scale experiments were carried out where benzene was pre-dispersed in sulfuric acid for some time, and where the nitration reaction was initiated by “dumping in” the stoichiometric amount of nitric acid. This addition sequence differed from that used in the earlier kinetic studies, where benzene was injected into mixed acid. As speculated, different nitration rates were observed, depending on the length of time of benzene pre-dispersion. It was also noted that, when stopping the agitator part-way through a run, the reaction would stop within seconds and that the ensuing phase separation was very rapid, even though the benzene and nitrobenzene droplets were very small.

It became apparent that the initial dispersion of benzene and the degree of benzene-sulfuric acid coalescence do have significant effects on the nitration rate. These effects are very difficult to quantify when scaling stirred-tank nitrators.

From these observations a concept for a new type of nitration reactor was developed. Benzene would be uniformly added through a special inlet manifold, which would disperse the benzene over the cross section of the mixed acid

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inlet pipe. The dispersion would then pass through jet-impingement plates that were spaced and sized to meet specific mixing requirements as the reacting mixture passed through the plug-flow nitration train. It was soon recognized that the nitration rate-controlling mechanisms changed as the reacting mixture passed through the nitration train. A timely opportunity then offered itself to demonstrate the jet impingement nitrator in a commercial first-generation plant, and to subsequently retrofit and expand this plant.

In the early 1990’s the first grass-roots second-generation plant was commissioned, and since that time 15 plants have been built, or are in the process of being built, using this technology, with a combined capacity of about 5 million MTPY. Details of the technology were publicized by the author of this paper in a presentation given at the 209th National Meeting of the American Chemical Society in 1995 (*13*).

The second-generation adiabatic process, which forms the basis of the modern MNB plant, incorporates a number of important features which distinguish it from the first-generation process. It uses lower nitric acid concentrations in the mixed acid, which lowers the temperature rise through the nitration train, allowing the MNB/Acid decanter to operate under a nitrogen blanket at atmospheric pressure. This enhances the safety of the process in that the chance of developing secondary exotherms, which are known to occur through a reaction between MNB and sulfuric acid at temperatures above 180 °C in a pressurized nitrator, is greatly reduced. In the first-generation process, the MNB/Acid decanter had to be pressurized to prevent benzene flashing, and an emergency quench tank had to be provided. The second generation process also uses a type of plug-flow nitrator rather than the first-generation back-mixed nitrators in series (i.e., series of CSTRs). This feature, together with the lower operating temperatures, results in a 50% reduction of the nitrophenol generation rate. Several specific aspects of the new process were patented (*14*, *15*).

Operational Issues

In addition to energy efficiency and capital savings in the nitration train and acid concentrators, there are many other important aspects which play a role in MNB production economics, including plant reliability, safety, MNB purity, waste treatment and disposal, and the impact on the environment.

Reliability

With reference to plant reliability, it has to be recognized that the MNB plant represents just one step in the multi-step synthesis of MDI. The total investment for a world-scale MDI complex is of the order of several hundred million dollars, of which the MNB plant accounts for less than a quarter. Since it is not desirable to hold large inventories of intermediates, the MNB plant reliability and the on-stream factor are of great economic importance. Current second-generation adiabatic MNB plants achieve on-stream factors of over 99%.

The oldest first-generation MNB plant has now been in operation for 34 years, and has similarly achieved very high on-stream factors.

Safety

A number of key safety aspects always have to be kept in mind during design of an MNB plant, but also in the course of its long-term operation. These aspects can be classified under the following headings:

Exotherms in the Nitration Train

It has been found that significant exotherms occur in the nitration train if the sulfuric acid/MNB mix reaches temperatures of about 180 °C in a pressurized nitrator (*16*). The reactions between acid and MNB result in the formation of tar and unknown gaseous by-products, which can cause overpressure in the nitration train.

Exotherms in MNB Distillation

Several incidents have been reported where explosions occurred in the sump of MNB distillation columns. The culprits have been leaky steam valves in the reboiler during shut-downs leading to the slow concentration of unstable impurities in the sump of the columns, or the accumulation of unstable sodium salts of nitrophenols in the heat transfer area of the reboiler (*17*).

Nitric Acid/MNB

An explosion caused by a reaction between nitric acid and MNB leveled an MNB plant in 1960 with a number of fatalities (*18*). It has been shown that nitric acid/MNB mixtures can detonate (*19*).

Ammonium Nitrite

In some plants ammonia is used in MNB washing to remove nitrophenols from the crude MNB. More commonly, a caustic solution is used for this purpose. Introducing ammonia to a plant where NO_X is produced as a by-product always has to be viewed with concern. Unstable solid ammonium nitrite can form through gas-phase reactions and settle in unexpected places (for example in "dead" vent pockets), or can deposit in the casing of benzene pumps handling the benzene recycle stream. Violent decompositions are known by the author to have occurred in a number of installations.

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Benzene Handling

The major imported feedstock in an MNB plant is benzene, which is classified as a carcinogen. Nitric acid is often produced on site. While methods for bulk shipment and handling of benzene from refinery sources are well developed, the disposal of the small benzene waste stream, which can be contaminated with trace amounts of aliphatic compounds that were initially present in the benzene feedstock, is of concern. This purge stream is commonly sent off-site for disposal. Due consideration has to be given to handling this waste stream in an environmentally safe manner. An aliphatics purge process which greatly reduces benzene purge losses has been recently developed by NORAM.

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Crude MNB Purification

Crude MNB from a nitration train contains nitrophenols (NPh's), dissolved or entrained sulfuric acid, dinitrobenzene (DNB), dissolved nitric oxide (NO), and excess benzene. The NPh's and acid are commonly neutralized in an aqueous washing system to form water-soluble salts. The adiabatic process operates with a stoichiometric excess of benzene to ensure that essentially complete nitric acid conversion is obtained in the nitration train. Excess benzene is removed by steam stripping or vacuum distillation, and is then recycled back to the process. Aliphatic impurities coming in with the benzene partially oxidize to carboxylic acids, but also accumulate in the benzene recycle stream. NO_X is stripped in the benzene recovery process and in the sulfuric acid concentrator, and is further treated in the NO_X abatement area of the MNB plant. Some gas phase aniline processes require very low concentrations of DNB (dinitrobenzene, <10ppm) in the feed MNB to minimize catalyst poisoning. Therefore, MNB purification via distillation may be required in some cases.

Waste Treatment

A number of liquid waste streams are generated in an MNB plant, including wash water containing nitrophenolic compounds, an aliphatics-containing benzene purge stream, a possible sulfuric acid purge, and a dinitrobenzene containing purge stream. The following is a brief review of the status of current waste treatment technologies.

Treatment of Nitrophenols

Nitrophenolic waste treatment was simple in the first two adiabatic plants; one plant was permitted to use an existing "deep well" injection site, and the other had available very large site-wide activated carbon beds. Nitrophenols are toxic to the micro-organisms in biological treatment plants, even at low concentrations. Treating nitrophenols in biological water treatment plants would require massive dilution water volumes for a world-scale MNB plant, which is usually not practical. Even then, there is doubt that some of the nitrophenolic isomers are actually degraded. A hydrothermal process (*20*) has been developed whereby nitrophenol in waste water is thermally degraded at high temperature and pressure under slightly subcritical conditions. The effluent from this thermal degradation process can be handled in biological treatment plants. NORAM has built a dedicated biological treatment plant for nitrogen and BOD removal in the effluent from an adiabatic MNB plant, using the thermal degradation process for the pre-treatment of the nitrophenol-containing wash-water.

An alternative approach to dealing with nitrophenol wash-water is incineration.

Aliphatics Purge

Various aliphatic compounds occur in trace quantities in nitration grade benzene and are partially degraded through oxidation in the nitrators, but some of the aliphatic species can also build up in the benzene recycle loop to a point where they may have to be purged. As the purge contains both aliphatics and a stoichiometric excess of benzene, as well as some MNB, this purge results in benzene losses. If good quality benzene is available, a purge is usually not required. However, benzene from certain supplies can contain stable species that can build up in recycle streams, even if they are present at very low levels.

Sulfuric Acid Purge

In a typical world-scale plant, the sulphuric acid inventory in the nitration train corresponds approximately to the hourly intake of nitric acid. Contaminants present in the nitric acid will build up in the sulfuric acid loop, typically by a factor of several hundred, until the contaminants reach a steady state concentration in the process. Typically, this steady state is reached through purge from acid entrained in the crude MNB, and acid spray entrainment in the vapor stream leaving the sulfuric acid concentrator. Additional sulfuric acid purge for process reasons is normally not required unless the feed nitric acid contains unusually high concentrations of non-volatiles such as iron, calcium and lead. Sulfuric acid-containing wash-water could possibly be recycled to the nitration train in order to reduce sulfate concentrations in the aqueous plant effluent.

NO_X Recovery

A patent (*21*) has been issued for a process operating at elevated pressure to capture NO_X generated in the nitration train for recycle as nitric acid. The benefit is a slight improvement in the nitric acid yield, but more importantly, this process substantially reduces the concentration of nitrites and nitrates in the effluent water, and thus reduces water treatment costs.

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Dinitrobenzene Purge

In plants where MNB is distilled to remove heavy fractions and DNB, the residue has to be purged from the still bottoms. This purge is typically incinerated off-site.

Environmental

The total residual NO_X and benzene vent rates from an MNB plant can be kept below 1 kg/h, even in a world-scale plant, through conventional scrubbing systems. This is, however, no longer sufficient. In new MNB plants the vent from the plant is normally sent to a plant-wide thermal oxidizer.

Patents and Technology Advancement

It is inevitable that a chemical having a long, steady and rapid growth profile, such as MDI and its precursor MNB, will be of increasing commercial significance to producers, and will, therefore, become the focus of dedicated R&D efforts. In the case of MNB this is reflected in numerous patent applications (*22*, *23*) which have been filed over the past 40 years. Nowadays MNB technology is advanced in small steps, through the know-how accumulated over the past 35 years by plant designers and through the day-by-day experience of the plant operators. Something new is learned from every project, and each new plant incorporates incremental improvements.

Summary

- The world's MNB plant capacity has grown almost 10-fold between 1974 and 2012, from less than one million MTPY to a capacity approaching 10 million MTPY, representing a growth rate of about 8% per year.
- Virtually all new MNB capacity has come from two generations of adiabatic MNB processes. The first process, having been developed in 1974, uses stirred nitrators in series under pressure, while the second-generation technology, developed in 1988, uses plug flow nitrators operating against an atmospheric back-pressure. Most of the old isothermal plants have been shut down and scrapped.
- The driver for MNB growth has been the growth in MDI-based urethanes, which were first commercialized in the 1960's.
- Within the next few years China will account for about 50% of world MNB production.
- The enormous size of world-scale MNB plants, some with capacities in excess of 500 thousand MTPY (1600 MTPD), has necessitated the refinement and optimization of MNB purification technologies, and development of technologies to deal with by-products in an environmentally sound manner.
- Benzene yields in the adiabatic process exceed 99.9% and nitric acid yields exceed 99.7%.

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- Economic technologies exist to degrade biotoxic nitrophenols such that the aqueous effluents from an MNB plant can be treated in biological treatment plants.
- Nitrite and sulfate concentrations in the effluent can be controlled to meet site-specific regulations.
- In most plants there is typically only one aqueous effluent stream to be dealt with, and a single plant vent, which normally is routed to a site-wide thermal oxidizer.

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Chapter 2

Effect of Reaction Conditions on the Formation of Byproducts in the Adiabatic Mononitration of Benzene into Mononitrobenzene (MNB)

Sergio Berretta*,[1] and Brian Louie[2]

[1]NORAM Engineering and Constructors, Ltd., 200 Granville Street,
Suite 1800, Vancouver, B.C., V6C 1S4 Canada
[2]BC Research, Inc., 200 Granville Street,
Suite 1800, Vancouver, B.C., V6C 1S4 Canada
***E-mail: sberretta@noram-eng.com**

Two main impurities are made in the industrial production of MNB. These impurities are nitrophenols and dinitrobenzene (DNB). The formation rates of these impurities are significantly affected by the initial reaction conditions. Understanding these effects is an important first step in the continuous on-going research aimed towards reducing the formation of these impurities. However, very limited work has been published on this subject. This paper presents the findings of a study done by the authors, conducted in a laboratory setting, examining the effect of relevant industrial operating conditions on the formation rates of nitrophenols and DNB. The selected operating conditions, which can usually be manipulated in most industrial production MNB facilities, are: initial sulfuric acid concentration, average reaction temperature, and nitric acid concentration in the mixed acid feed.

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Introduction

Mononitrobenzene is produced industrially using a number of adiabatic nitration technologies. The concept of adiabatic nitration was first introduced by Castner (*1*) in the 1940s. However, it was not until the 1970's when Alexanderson (*2*, *3*) proposed a new set of process conditions for the adiabatic technology that Castner's adiabatic nitration ideas finally led to a new commercial process.

Today, a few small industrial mononitrobenzene production facilities are still built using the conditions proposed by Alexanderson. However, the majority of new industrial mononitrobenzene adiabatic plants are now built based on the process conditions proposed by Guenkel (*4*, *5*) in the 1990's. The main advantage of Guenkel's nitration process is a substantial reduction in the formation of oxidation by-products, specifically nitrophenols, in the case of the nitration of benzene. Since this last significant development, researchers at NORAM Engineering have been working at further reducing the formation of these by-products. As part of this challenge, and within the umbrella of a very large research program, the authors ran a short test program with the aim of further understanding how the process conditions described by the Guenkel process (*4*) affect by-product formation. The findings from that work are the focus of this paper.

Process Overview

Current "adiabatic" commercial processes for the manufacture of MNB typically consist of a continuous addition of benzene to a mixture of sulfuric acid and nitric acid, commonly called "mixed acid". The sulfuric acid acts as a catalyst disassociating the nitric acid into the reacting nitronium ion. It also acts as a heat sink for the significant heat released in the formation of nitrobenzene. In addition, it absorbs the water produced in the reaction. Following separation of the organic and acid phases, the heat of reaction, which is mainly contained in the large volume of sulfuric acid, is used to aid in the re-concentration of the sulfuric acid in a flash evaporator.

Commercially, the nitration reaction of benzene follows Alexanderson's or Guenkel's proposed operating conditions. Alexanderson proposed that MNB should be commercially made most efficiently when the nitric acid concentration in the mixed acid is 3 to 7.5 wt%, sulfuric acid concentration is 58.5 to 66.5 wt% with the balance as water. He also specifies that the temperature of the initial mixed acid must be in the range of 80 °C to 120 °C (*3*). Compared to the "isothermal" technologies of the day (i.e., prior art at the time), Alexanderson's conditions led to a significant reduction in the formation of the by-product DNB, to within less than 500 ppm. However, these conditions still lead to significant nitrophenol by-product formation. On the other hand, Guenkel proposed a set of operating conditions using a nitric acid / sulfuric acid / water tertiary diagram with the following limits: 82 wt% sulfuric acid and 18 wt% nitric acid, 55 wt% sulfuric acid and 45 wt% water, and 100 wt% sulfuric acid, and with the additional constraint that the initial mixed acid temperature must be in the range of 97 °C to 120 °C (*4*). Guenkel's invention, which led to a significant

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reduction in nitrophenol formation, is believed to be characterized by a mixed acid composition in which nitric acid is more fully dissociated to nitronium ion leading to an increase in the reaction rate. As shown by Guenkel (*4*), the formation of by-product nitrophenol, for the conditions proposed, is in the range of 1700 ppm.

Description of the Test Program

Based on the referenced works (*3*, *4*) and the objectives of the broader research program, it was decided to focus the test program on the effect of the following three process variables in the formation of nitrophenols and DNB by-products in the production of MNB:

- Sulfuric Acid Concentration
- Nitric Acid to Sulfuric Acid Ratio (i.e., concentration of nitric acid in mixed acid)
- Reaction Average Temperature

The aim of this work was to manipulate these process variables through a set of experiments and measuring their effects on the formation of by-products. To minimize the number of experiments, the study was done based on a factorial style analysis.

A typical factorial designed experiment includes experimental runs for all combinations of settings, both high and low, of the variables to be studied. The minimum number of experiments to complete a study is then defined as 2^N where N is the number of variables to be studied. Since there were three variables of interest included in the test program, then the minimum number of required experiments was 8.

Based on objectives of the broader research program, it was decided that changes on the process variables of interest would be limited to the following ranges:

- Sulfuric Acid Concentration: 62 to 72 wt%
- Nitric Acid to Sulfuric Acid Ratio (mass basis): 0.022 to 0.033
- Reaction Average Temperature: 70 to 100 °C

The selected experimental conditions are graphically shown in Figure 1.

Overall, eight experiments were required to cover the “factorial cube”. However, it was arbitrarily decided to add an additional two experiments to better define trends, taking the total number of experiments to ten. The experiments were repeated twice to check the reproducibility of the results, for a total of twenty experiments.

All reactions were performed using an 8% molar excess of benzene, relative to the nitric acid.

Table I summarizes the targeted operating conditions for each experiment.

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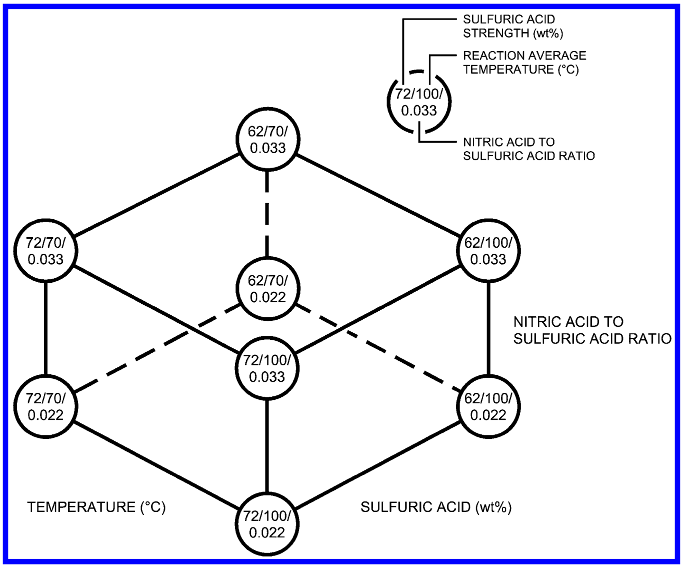

Figure 1. Experimental Conditions. (Courtesy of Sergio Berretta).

Table I. Proposed Experimental Conditions for Each Run

Experiment No.	*Nitric Acid to Sulfuric Acid Ratio (mass basis)*	*Sulfuric Acid Concentration (wt%)*	*Reaction Average Temperature (°C)*
1	0.022	62	70
2	0.022	62	70
3	0.022	62	100
4	0.022	62	100
5	0.022	72	70
6	0.022	72	70
7	0.022	72	100
8	0.022	72	100
9	0.022	67	85
10	0.022	67	85
11	0.033	62	70
12	0.033	62	70
13	0.033	62	100
14	0.033	62	100
15	0.033	72	70
16	0.033	72	70

Continued on next page.

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Table I. (Continued). Proposed Experimental Conditions for Each Run

Experiment No.	*Nitric Acid to Sulfuric Acid Ratio (mass basis)*	*Sulfuric Acid Concentration (wt%)*	*Reaction Average Temperature (°C)*
17	0.033	72	100
18	0.033	72	100
19	0.033	67	85
20	0.033	67	85

Experimental Set Up

All experiments were performed in the pressurized glass reactor (PGR) shown in Figure 2.

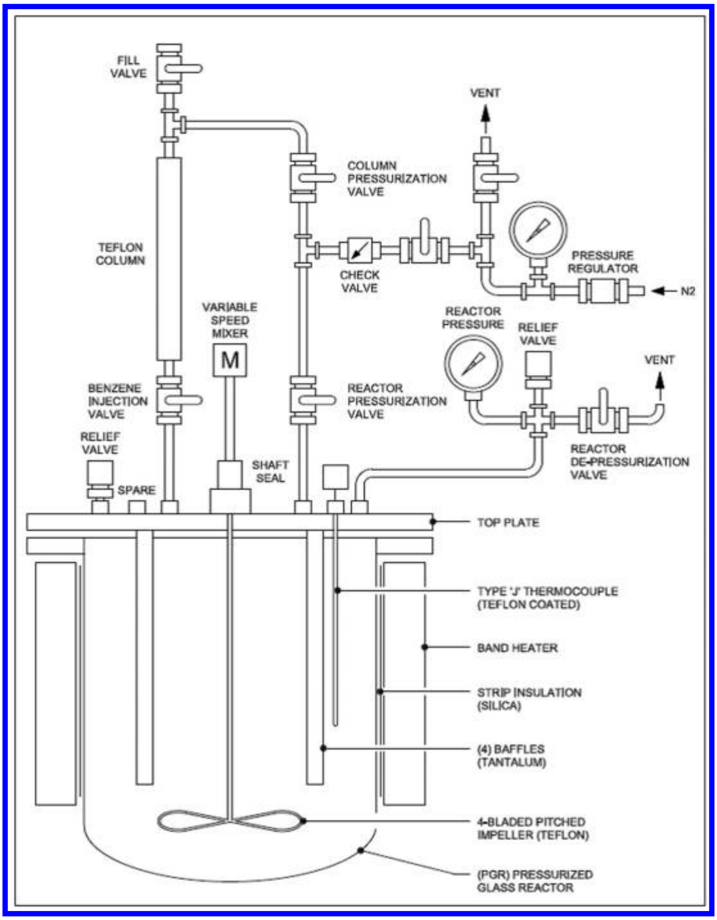

Figure 2. Experimental Apparatus. (Courtesy of Sergio Berretta).

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The PGR consists of a 3” I.D., 450 ml, hemispherical bottomed glass reactor clamped underneath a ¼” thick stainless steel plate. A gasket ensures a tight seal between the reactor and the metal plate. Reactor contents are mixed using a 4-bladed Teflon® impeller that is connected with a shaft seal to an overhead variable speed mixer. Tantalum baffles attached to the top plate improve mixing while a Teflon® covered Type J thermocouple was used to measure the temperature of the solution. Nitrogen gas was used to pressurize the reactor and prevent benzene boiling and also to inject liquids into the reactor from the overhead reservoirs. The initial heat input was via a manually- controlled heating band.

Experimental Procedure

In a typical nitration experiment the sulfuric acid and the nitric acid were charged to the PGR., The reactor was then attached to the top plate. An overhead feed reservoir was then filled with benzene. The acid mixture was pressurized to 40 psig, then mixed and heated to the required initial temperature. The mixer was then started. Benzene was injected at a predetermined rate from the feed reservoir through a ¼” Teflon® dip tube into the high intensity mixing zone of the reactor.

Once the reaction was deemed to be complete, as assessed by the temperature rise of the mixture, the reactor was depressurized and the contents poured into a Pyrex® bottle. A portion of the organic layer, which quickly forms a layer on top of the acid, was removed with a pipette into a separate vial for analysis. Then a sample of the acid was also removed with a pipette into a separate vial and also sent out for analysis. The samples were maintained in a refrigerator at 4 °C until their time of analysis. To avoid possible contamination, the experimental apparatus was rinsed thoroughly and dried before the next experiment.

Each of the two samples per experiment (i.e., MNB and acid samples) was analyzed for:

- Picric acid concentration
- 2,4 dinitrophenol concentration
- 2,6 dinitrophenol concentration
- 2-mononitrophenol concentration
- 4-mononitrophenol concentration
- dinitrobenzene (all isomers)

Each sample was analyzed twice to check the reproducibility of the results.

Results and Discussion

The actual observed reaction conditions for each experiment varied somewhat from the “targeted” conditions (Table I). Specifically, the “reaction average temperature” variable proved hard to control. Table II presents the actual observed experimental reaction conditions for each test.

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Table II. Actual Reaction Conditions for Each Run

Experiment No.	*Nitric Acid to Sulfuric Acid Ratio (mass basis)*	*Sulfuric Acid Concentration (wt%)*	*Reaction Average Temperature (°C)*
1	0.022	62	70
2	0.022	62	68
3	0.022	62	102
4	0.022	62	98
5	0.022	72	72
6	0.022	72	72
7	0.022	72	102
8	0.022	72	102
9	0.022	67	86
10	0.022	67	86
11	0.033	62	61
12	0.033	62	61
13	0.033	62	95
14	0.033	62	95
15	0.033	72	70
16	0.033	72	70
17	0.033	72	99
18	0.033	72	100
19	0.033	67	83
20	0.033	67	83

The test results are summarized on Figures 3 and 4. The figures show the average analytical result for each combination of operating conditions.

Let us first analyze the experimental results with respect to nitrophenol formation. The data in Figure 3 was introduced into Microsoft Excel and its multivariable regression analysis tool was used to develop a correlation between nitrophenol formation and the process variables: reaction average temperature, sulfuric acid concentration, and nitric acid to sulfuric acid ratio. Equation 1 is the output from the analysis. For convenience in the following equations 1 and 2, the units for nitric acid to sulfuric acid ratio were changed to concentration of nitric acid in the sulfuric acid in wt%.

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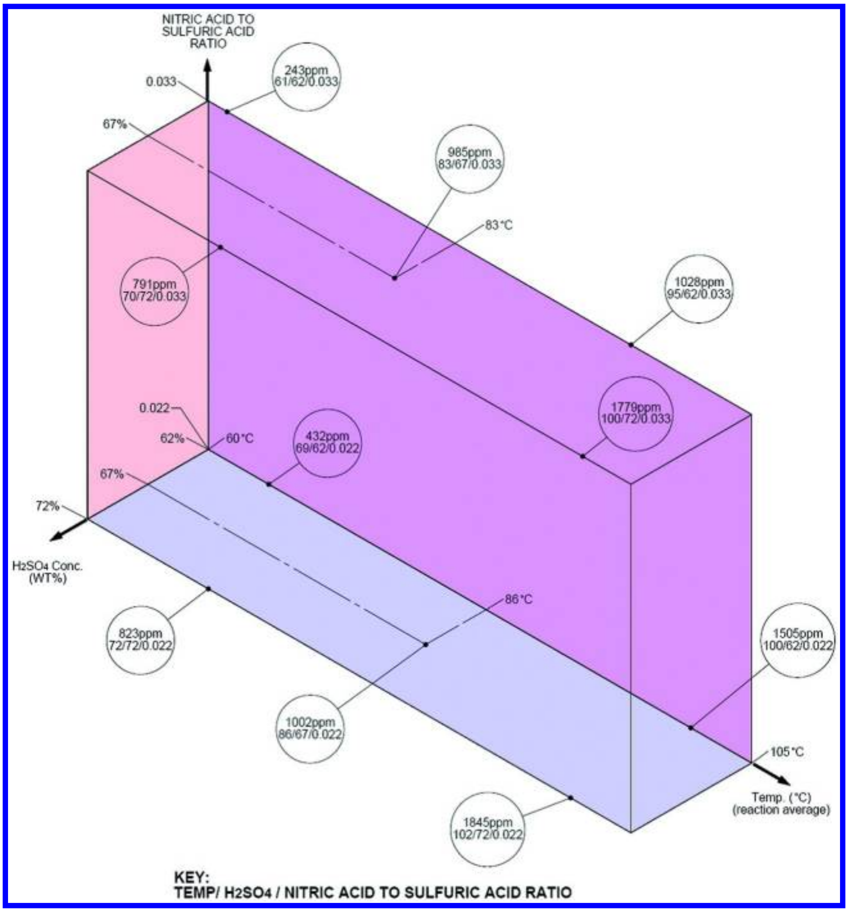

Figure 3. Effect of Reaction Average Temperature, Sulfuric Acid Concentration, and Nitric Acid to Sulfuric Acid Ratio on Nitrophenol Formation. (Courtesy of Sergio Berretta). (see color insert)

$$Y = -3900 + 31.72 \times T + 32.67 \times S + 39.07 \times R \qquad (1)$$

where Y: concentration of nitrophenol in produced MNB, ppm
T: reaction average temperature, °C
S: sulfuric acid concentration, wt%
R: nitric acid concentration in mixed acid, wt%

The validity of equation 1 is bounded within the variable limits presented under the heading “Description of Test Program”. The statistical errors on equation 1 are presented in Table III. The *produced MNB* under Y is defined as the total MNB produced in the reaction which is the addition of both MNB in the organic phase and dissolved MNB in the acid phase.

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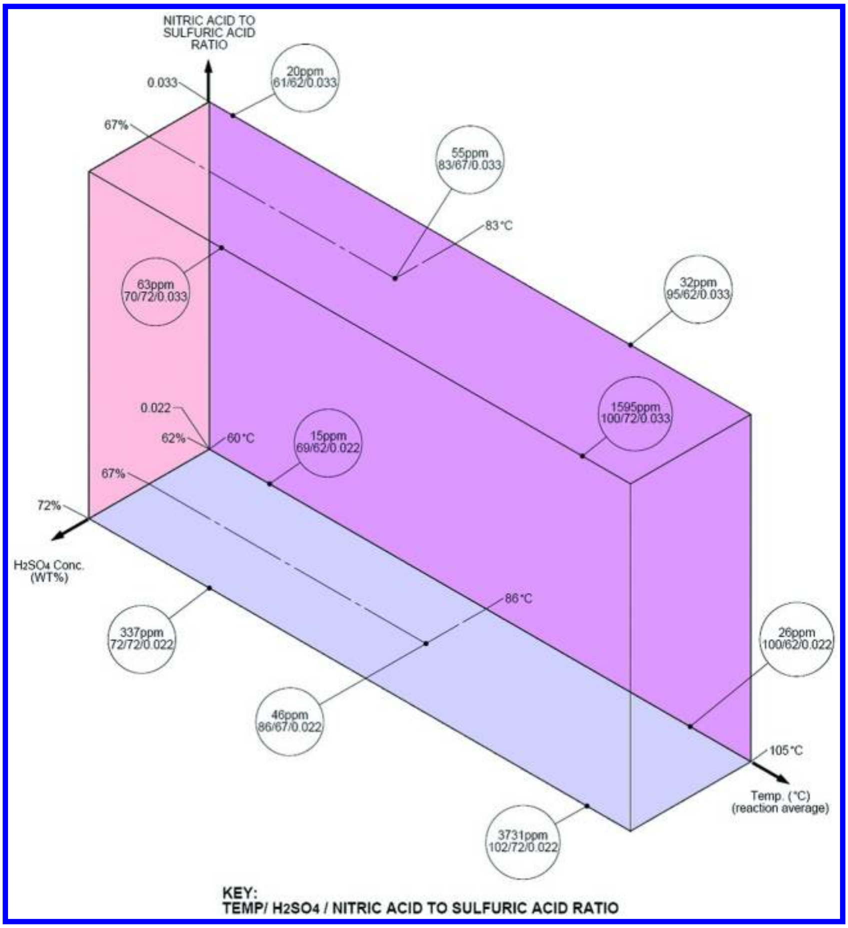

Figure 4. Effect of Reaction Average Temperature, Sulfuric Acid Concentration, and Nitric Acid to Sulfuric Acid Ratio on DNB Formation. (Courtesy of Sergio Berretta). (see color insert)

Table III. Statistical Errors of Equation 1

	Coefficient	***Standard Error***
Intercept	-3900	485
T	31.72	2.42
S	32.67	8.13
R	39.07	50.69

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Equation 1 indicates that for every 1 °C change on reaction average temperature, nitrophenol formation changes proportionally by 32 ppm. The standard error of 2.42 on the coefficient of 31.72 suggests that the correlation matches the experimental data very closely, as graphically shown in Figure 5.

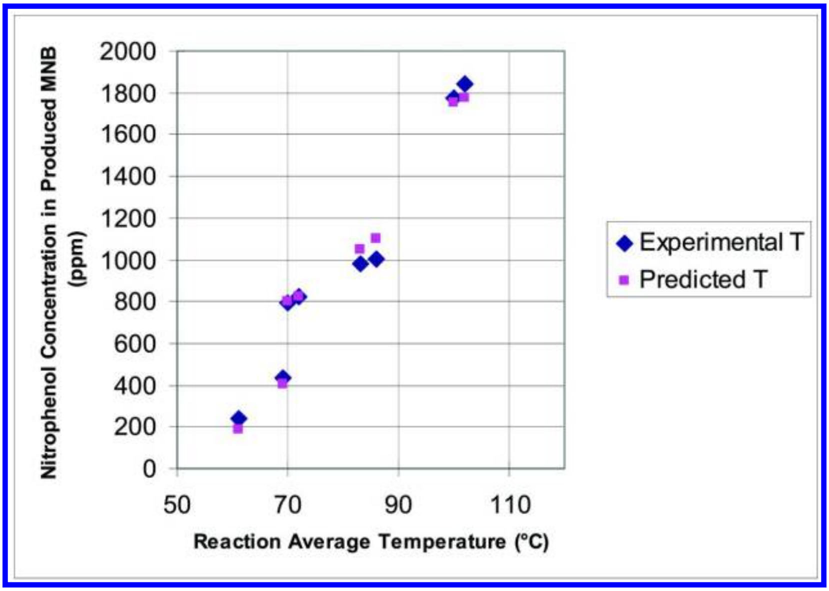

Figure 5. Effect of Reaction Average Temperature on Nitrophenol Formation. (Courtesy of Sergio Berretta). (see color insert)

Similarly, Equation 1 indicates that for every 1 wt% change in sulfuric acid concentration, nitrophenol formation changes proportionally by 33 ppm. The standard error of 8.13 on the coefficient of 32.67 suggests that the correlation matches the experimental data very closely, as graphically shown in Figure 6.

For the effect of nitric acid / sulfuric acid ratio on nitrophenol formation, equation 1 provides a poor fit relative to the experimental data (i.e., standard error of 50.69 on the coefficient of 39.07). In fact, the magnitude of the standard error can lead to either a positive or negative coefficient as the multiplier of this variable, meaning that it cannot be concluded whether the nitric acid / sulfuric acid ratio has a proportional, inversely proportional, or any effect at all, on nitrophenol formation.

Let us now analyze the experimental results in regards to effects on DNB formation. The data in Figure 4 was introduced into Microsoft Excel and its multivariable regression analysis tool was used to develop a correlation between DNB formation and the process variables: reaction average temperature, sulfuric acid concentration and nitric acid to sulfuric acid ratio. Equation 2 is the output from the analysis.

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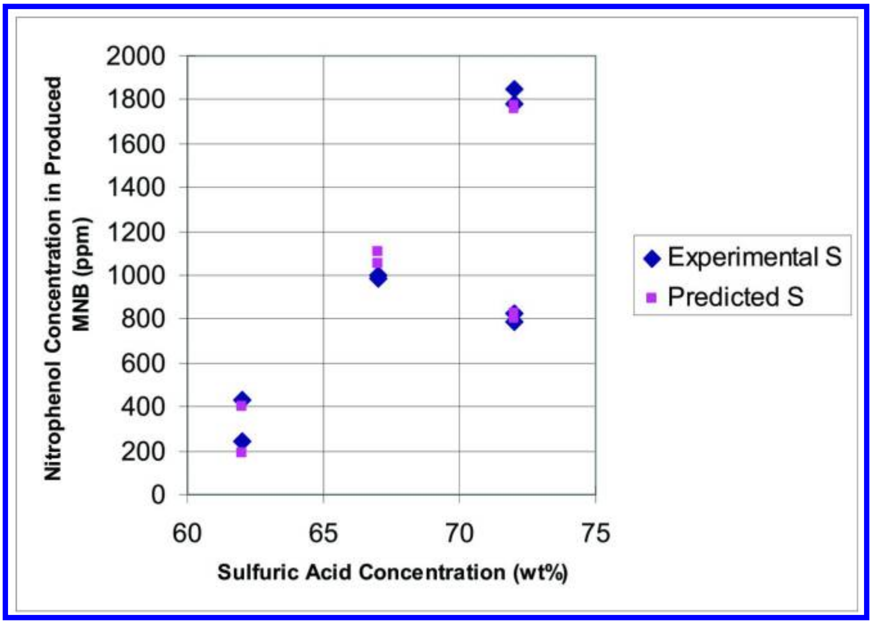

Figure 6. Effect of Sulfuric Acid Concentration on Nitrophenol Formation. (Courtesy of Sergio Berretta). (see color insert)

$$Z = -9878 + 35.98 \times T + 123.73 \times S - 303.71 \times R \qquad (2)$$

where Z: concentration of DNB in produced MNB, ppm
T: reaction average temperature, °C
S: sulfuric acid concentration, wt%
R: nitric acid concentration in mixed acid, wt%

The validity of equation 2 is bounded within the variable limits presented under the heading "Description of Test Program". The statistical errors on equation 2 are presented in Table IV.

Table IV. Statistical Errors of Equation 2

	Coefficient	*Standard Error*
Intercept	-9878	5193
T	35.98	22.52
S	123.73	71.49
R	-303.71	580.59

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Equation 2 indicates that for every 1 °C change on reaction average temperature, DNB formation changes directly proportional by 36 ppm. However, the standard error is significant (i.e., 22.52), indicating that the effect on DNB formation may in reality be either mild or significant, but directly proportional nevertheless. The poor fit is graphically shown in Figure 7.

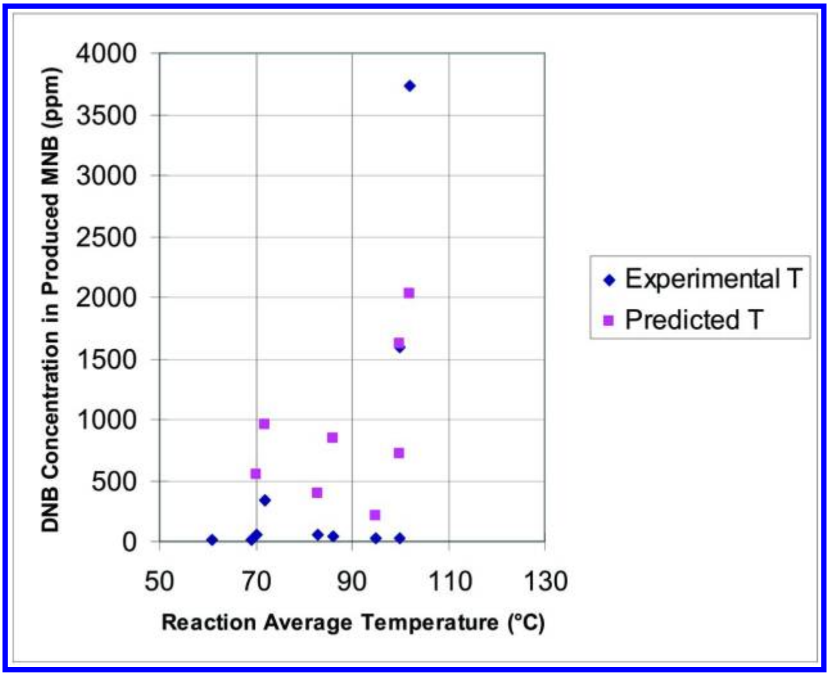

Figure 7. Effect of Reaction Average Temperature on DNB Formation. (Courtesy of Sergio Berretta). (see color insert)

Similarly, Equation 2 indicates that for every 1 wt% change on sulfuric acid concentration, DNB formation changes proportionally by 124 ppm. However, the standard error is significant at 71.49. Regardless, the effect of sulfuric acid concentration on DNB formation is significant overall, and directly proportional. Figure 8 shows the fit of the correlation relative to the experimental data.

For the effect of nitric acid / sulfuric acid ratio on DNB formation, equation 2 provides a poor fit relative to the experimental data (i.e., standard error of 580.59 on the coefficient of -303.71). In fact, the magnitude of the standard error can lead to either a positive or negative coefficient as the multiplier of this variable, meaning that it cannot be concluded whether nitric acid concentration in the sulfuric acid has a proportional, inversely proportional, or any effect at all, on DNB formation.

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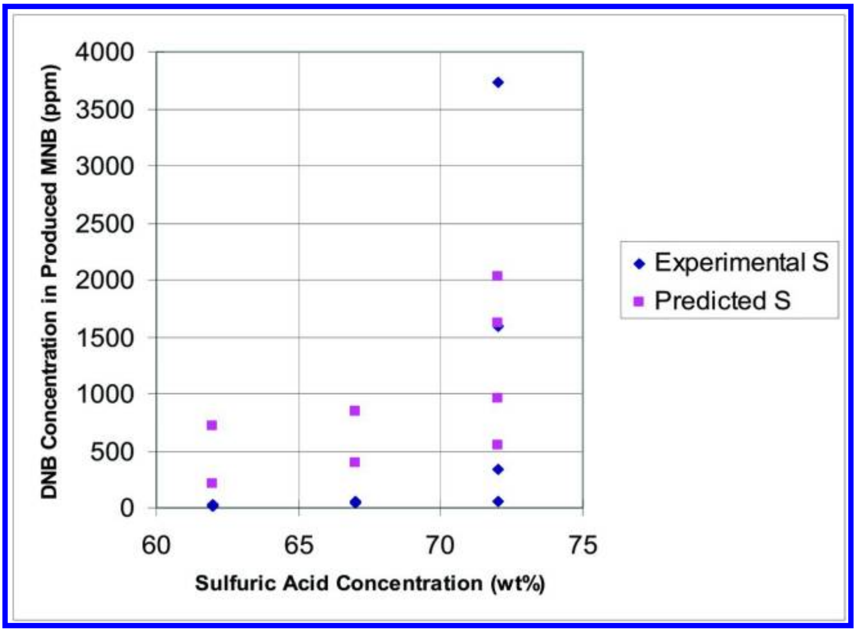

Figure 8. Effect of Sulfuric Acid Concentration on DNB Formation. (Courtesy of Sergio Berretta). (see color insert)

Conclusions

The results from the experimental work show that both average reaction temperature and sulfuric acid concentration affect the reaction rates of both nitrophenol and DNB formations. However, these two process variables also affect the reaction rate of MNB production. It is known that increasing the reaction temperature or sulfuric acid concentration increases the reaction rate of MNB formation (*6*).

At a high level, the findings from this work suggest that in the industrial production of MNB a substantial reduction in by-product formation, relative to current levels, is possible, by reducing the reaction average temperature and/or sulfuric acid concentration. However, this benefit must be weighed against the drop in the reaction rate of MNB production.

The expected change in nitrophenol and DNB formations due to manipulation of temperature and sulfuric acid concentration can be approximately predicted through equations 1 and 2 respectively.

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Chapter 3

Adiabatic Nitration for Mononitrotoluene (MNT) Production

M. Gattrell*,1 and B. Louie2

1NORAM Engineering and Constructors, Ltd., Vancouver, B.C., Canada
2B.C. Research Institute, Burnaby, B.C., Canada
***E-mail: mgattrell@noram-eng.com**

Adiabatic nitration has revolutionized mononitrobenzene (MNB) production, but has not similarly impacted the production of other nitro-aromatics. The issues related to changing to adiabatic nitration are discussed by comparing the nitration of toluene versus benzene using literature data and adiabatic stirred reactor nitration tests. The topics discussed include nitration rates, isomer distribution, and by-product formation. The homogeneous chemical reaction rate for the nitration of toluene is faster than benzene, but the overall rate for interphase mass transport and reaction is found to be fairly similar. The MNT isomer distribution is found to be a function of sulfuric acid strength, temperature, and nitric acid strength. The easier oxidation of toluene versus benzene results in a greatly increased number of oxidation by-products. This presents analytical difficulties in quantifying total by-products. Deeply colored, oxidized by-products can also accumulate in the recycled spent acid producing so called "black acid". However, once understood, the issues related to implementing adiabatic MNT production appear manageable.

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Introduction

Interest in continuous adiabatic nitration versus continuous isothermal nitration is due to the large energy savings possible by using the exothermic heat of the nitration reaction for the re-concentration of the spent sulfuric acid. The differences between the two processes can be seen by comparing the process flow diagrams for the production of MNT from toluene in Figure 1.

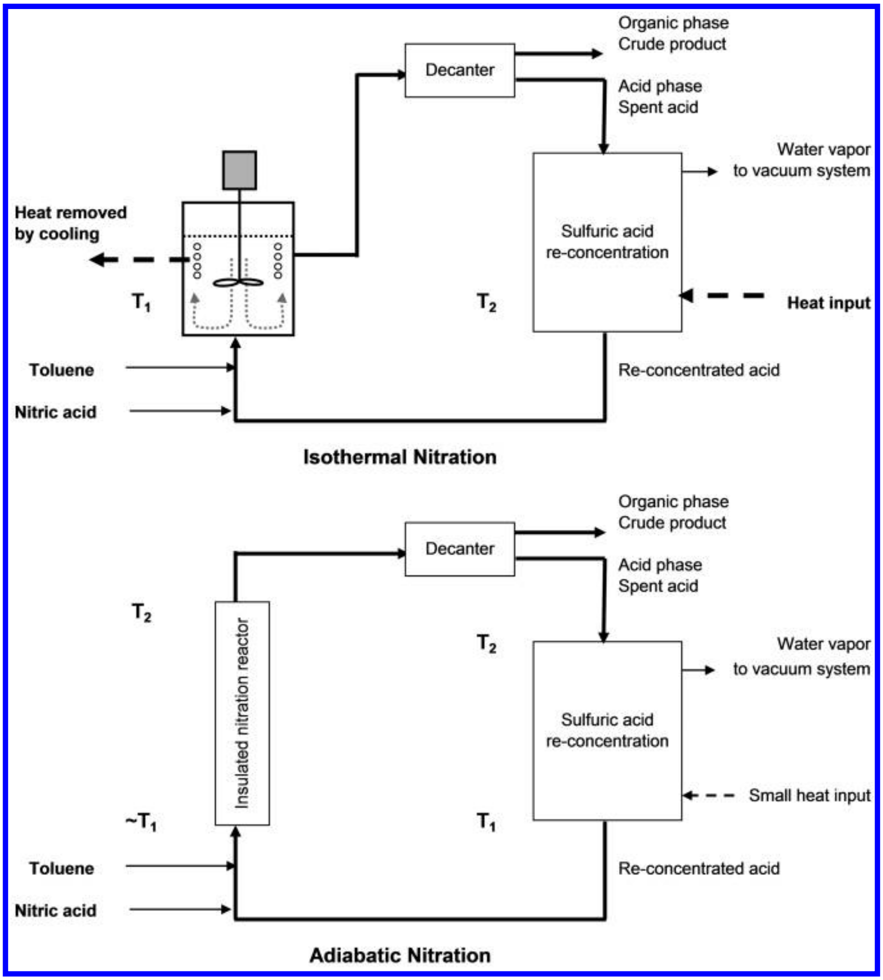

Figure 1. Simplified flow diagrams for the nitration of toluene to produce MNT via the commercial isothermal process and a potential adiabatic process.

In the isothermal process (*1–4*), re-concentrated sulfuric acid is combined with feed nitric acid to generate "mixed acid" or "nitrating acid". This nitrating acid is mixed with toluene in a series of cooled, stirred reactors to create a two-phase liquid-liquid dispersion. Good mixing is required in the reactors both to create a large interfacial area between the two phases for the reaction to occur and to provide good heat transfer between the reaction mass and the reactor's cooling coils. Ample, reliable cooling is critical to remove the heat of reaction to avoid a potentially catastrophic thermal runaway (*5*). After the reaction has completed, the two-phase mixture is fed to a decanter where the phases are allowed to separate into a crude organic product stream and a “spent acid” stream. The spent acid phase consists of the starting sulfuric acid diluted by water generated in the nitration reaction and water that enters with the nitric acid feed. This spent acid is heated and the water is evaporated under vacuum to re-concentrate the acid. The high temperature involved in this re-concentration step (~130-180 °C) also helps to decompose or strip out organic contaminants that may build-up in the acid. One advantage of this approach is that the nitration temperature and the acid re-concentration temperature can be independently optimized. Two disadvantages are the danger of thermal runaway if the reactor cooling malfunctions and the large energy input required to re-concentrate the spent sulfuric acid.

For an adiabatic process (*6*), the toluene would also be mixed with the nitrating acid, but the heat of reaction would not be allowed to dissipate. The reactor(s) can either be a series of stirred tank reactors or a plug flow reactor with static mixing elements. The temperature of the reaction mixture will then rise due to the heat of reaction, with the temperature rise controlled to a safe limit by controlling the amount of nitric acid and organic reactant added to the recirculating sulfuric acid. The hot two-phase mixture exits the reactor(s) and continues to the decanter where it is allowed to separate into a crude organic product stream and a “spent acid” stream. For the adiabatic process this resulting hot spent acid is then flashed under vacuum to re-concentrate the sulfuric acid. Most of the energy for this flash re-concentration comes from the heat contained in the hot spent acid, with very little external energy required compared to the isothermal process. In this way adiabatic nitration uses the heat of the nitration reaction to provide the majority of the energy for the sulfuric acid re-concentration.

A drawback of the adiabatic approach is that it links the nitrator starting temperature to the acid re-concentration temperature which results can result in a higher nitration reactor temperature and a lower acid re-concentration temperature than in an isothermal process. A higher nitration temperature can cause increased by-products. A lower acid re-concentration temperature decreases the destruction and stripping of contaminants from the spent acid. Together these effects raise concerns about the build-up of contaminants in the acid recycling loop over time.

When adiabatic nitration of benzene to MNB was implemented, these problems were not found to be significant. While the adiabatic benzene nitration reaction was carried out at higher temperatures which should increase by-products, the higher temperature also led to lower reaction times. Further, limitations on the safe temperature rise (i.e. the safe maximum acid loop temperature) combined with a much lower cost for acid recycling drove a shift to reaction conditions using less total reaction per pass (i.e. with lower concentrations of nitric acid and benzene in the nitrator feed). These new conditions (*7–9*) allowed for adiabatic operation with little increase in by-products. The shorter reaction times and the lack of need for cooling coils with adiabatic operation also allowed a shift to plug flow type reactors with static mixing elements, resulting in improved volumetric efficiency. Overall, these factors have resulted in the adiabatic route now dominating commercial MNB production (*10*).

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However, while it should be possible to adiabatically nitrate many compounds, so far the technology is not widely used beyond MNB. To understand some of the issues, this paper will investigate the example of toluene nitration to MNT.

Experimental

The adiabatic toluene and benzene nitration tests were carried out in a batch manner using the 500 mL pressurized, insulated, stirred glass reactor shown in Figure 2. During operation the reactor was kept pressurized with nitrogen gas at ~3 barg to prevent boiling of the toluene or benzene. In the tests about 400 g of a mixture of sulfuric and nitric acids in water was first put in the reactor and a heating rate chosen to bring it to the target starting temperature. To begin the experiment, room temperature toluene or benzene was then injected into the stirred reactor using nitrogen pressure (over ~1-2 s). The reaction was followed by monitoring the reactor temperature with time, with an example curve shown in Figure 3. In Figure 3, the acid temperature started at 90 °C. Room temperature toluene was then injected at time 0 causing cooling, but this was followed by a rapid temperature increase due to the exothermic nitration reaction. At 3.5 minutes, the temperature rise leveled off indicating that the reaction was essentially over, though the reactor was run until 5-6 minutes to ensure complete reaction. Note, that the measured temperature rise is less than the theoretical value due to the thermal mass of the glass reactor and some heat losses. After the reaction was finished the reactor contents were emptied into a graduated cylinder and left to separate into organic and acid phases at room temperature.

The organic phase was analyzed for residual reactant and products by gas chromatography using a flame ionization detector (GC-FID). The organic phase was also extracted with 0.1 M aqueous NaOH to recover acidic oxidation by-products. This extract was analyzed using high performance liquid chromatography (HPLC) using a C-18 column at 35 °C. The mobile phase was pumped at 0.4 mL/min and gradient elution was used starting from a 1 wt% acetic acid-sodium acetate buffer (pH ~4.5) and changing to acetonitrile over 12 minutes. Detection used a UV absorption detector using a range of wavelengths (270, 320, 360 and 450 nm) to give the best signal to noise for the individual compounds (example chromatograms are presented later in the paper).

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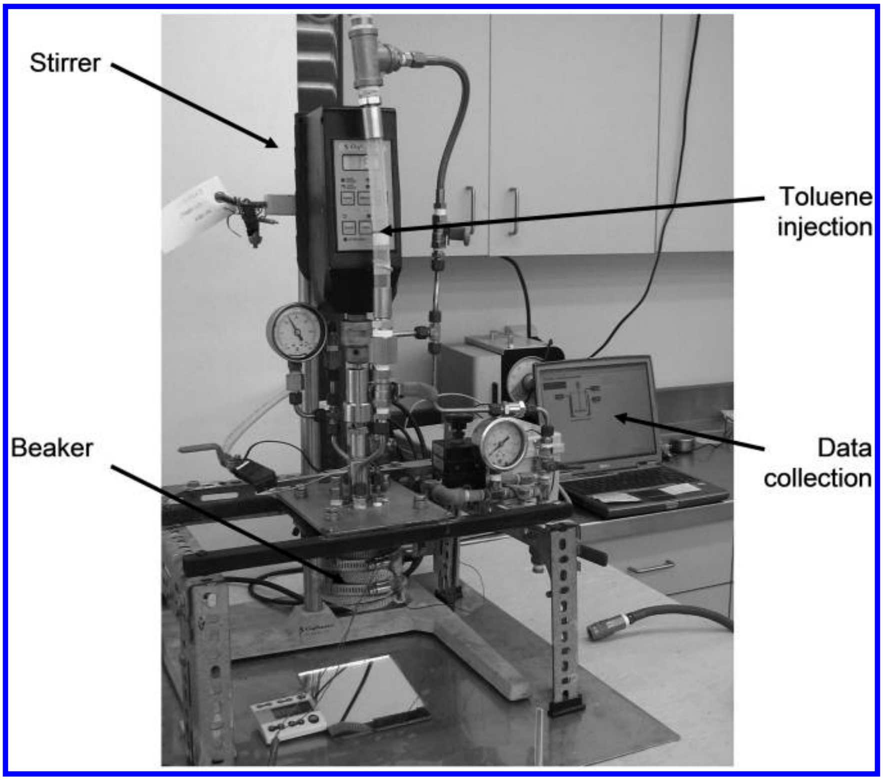

Figure 2. Batch type, stirred, insulated, pressurized glass reactor used for the adiabatic nitration screening tests presented in this paper.

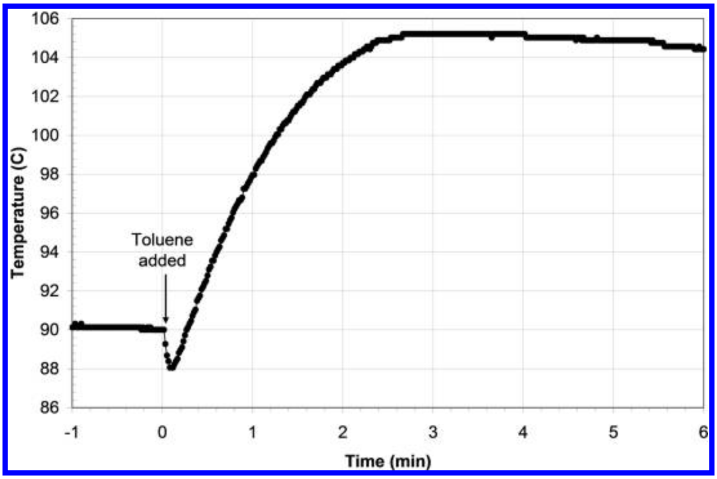

Figure 3. An example temperature-time curve obtained with the reactor shown in Figure 2. Example is for: 64.6 wt% H_2SO_4, 3.0 wt% HNO_3, 1.10 mole toluene/mole nitric acid, and stirring at 1200 rpm (~16 watts/liter, W/L). The starting acid temperature was 90 °C and the injected toluene was at room temperature.

Results and Discussion

Reaction Rate

The toluene nitration rates observed from the temperature rise data were not much different from those for benzene nitration. This might be considered to be surprising since the reported chemical reaction rate constants for toluene nitration at room temperature in 63 to 73 wt% sulfuric acid are from 11 to 18 times higher than those for benzene (*11*). However, under normal industrial conditions the nitration of toluene can be described as a fast 2 phase reaction (*12–14*) with the overall reaction rate controlled both by mass transport and chemical reaction kinetics. Figure 4 shows a diagram of the expected shape of the toluene concentration profile in the acid phase adjacent to a drop of the organic phase. Toluene is assumed to dissolve in the acid phase at the interface at a concentration roughly determined by its pure component solubility in the acid phase and its mole fraction in the organic phase. Under fast kinetic conditions this toluene then reacts while it diffuses into the acid phase, becoming essentially completely reacted before reaching the bulk acid phase (i.e. within the mass transfer boundary layer). If it is assumed that the small amount of dissolved toluene does not significantly perturb the nitric acid concentration profile, then the overall reaction rate can be written as given in equation 1.

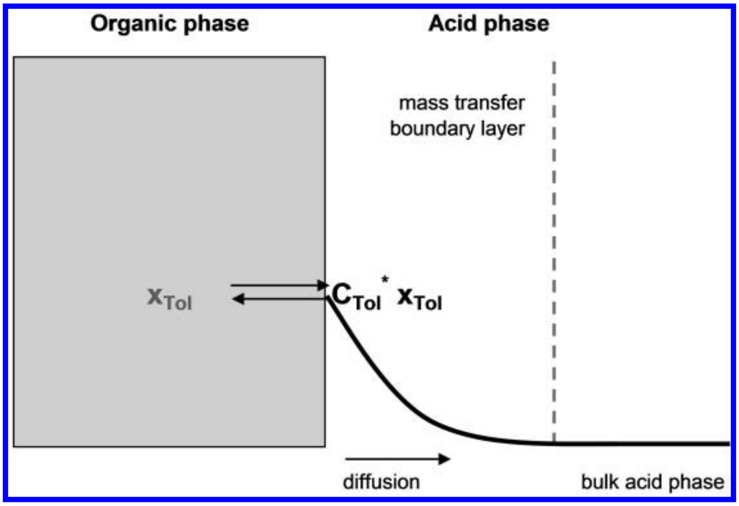

Figure 4. The expected concentration profile shape for the fast 2 phase reaction of toluene as it diffuses into the mixed acid phase (13, 14).

$$nitration\ \ rate = aC_{Tol}^{*}x_{Tol}\sqrt{k_C C_{HNO3} D_{Tol}} \qquad [1]$$

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Where:

a is the organic phase–acid phase interfacial area, which is influenced by factors such as: mixing intensity, interfacial tension, coalescence rate and organic phase volume fraction.

C_{Tol}* is the solubility of pure toluene in the mixed acid. This is influenced by temperature and the mixed acid composition.

x_{Tol} is the mole fraction of toluene in the organic phase, which will change as the reaction proceeds.

k_C is the apparent nitration chemical reaction rate constant (i.e. in terms of nitric acid), which is influenced by temperature and sulfuric acid (catalyst) strength.

C_{HNO3} is the concentration of nitric acid in the mixed acid.

D_{Tol} is the diffusion coefficient of toluene in the mixed acid, which is a function of temperature and the mixed acid composition.

It can be seen from equation 1 that an increase in the chemical reaction rate constant (k_C) by 11 to 18 times will only increase the observed overall rate in the fast two-phase reaction by the square root of these values and so a factor of 3.3 to 4.2. In addition, the room temperature solubility of toluene in 70 to 76 wt% sulfuric acid (C_{Tol}*) is about 3.1 to 4.1 times lower than for benzene (*15*) which, based on equation 1, will essentially cancel the reaction rate increase. The diffusion coefficient for toluene is also slightly lower than for benzene (*14*). The exact balance of these different factors will vary with temperature and sulfuric acid strength, but the resulting effect is that the overall toluene nitration rate is not greatly different than that for benzene nitration. Thus, for adiabatic MNT production, a nitrator with a similar size and mixing intensity (pressure drop) to those used for MNB production could be used.

Isomer Distribution

When nitrating toluene, three isomers are produced as shown in Figure 5. If MNT is the desired end nitration product, the different isomers can be separated and sold, with different isomers having different market values. However, the bulk of MNT production is for further nitration to dinitrotoluene (DNT), which is used for the production of toluene diisocyanate (TDI) based polyurethanes (*1*). For polyurethane production, vicinal DNT isomers (2,3 and 3,4 DNT) must first be removed from the DNT mixture. Thus for DNT production, forming 3-MNT during toluene nitration not only represents a waste of starting chemicals, but also adds costs for by-product removal and disposal. The 3-MNT is also undesirable for the production of trinitrotoluene (TNT) (*16*). Unfortunately, the yield of 3-MNT increases with temperature, and adiabatic nitration would operate at higher temperatures than isothermal nitration.

Figure 6 shows a compilation of mononitrotoluene isomer distribution data under different conditions from our adiabatic nitration work reported here, as well as literature adiabatic (*17*) and isothermal nitrations (*18*, *19*). (Note that for the adiabatic tests, average temperatures were plotted.) In spite of differences in the reaction conditions, the yield of 3-MNT can be seen to clearly increase

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with temperature showing that it is a dominate factor. As well as temperature, the isomer distribution is also influenced by the make-up of the toluene hydration sphere (i.e. the arrangement of the molecules around the toluene when it dissolves in the acid phase) and so the acid phase composition will have some effect. Multi-variable regression was therefore used to correlate all the data in Figure 6 with temperature, sulfuric acid concentration and nitric acid concentration. Example plots of the multi-variable fits for 4-MNT are shown in Figure 7, and the ranges over which the variables were correlated can also be seen. The results of the correlations are given in equations 2 to 5.

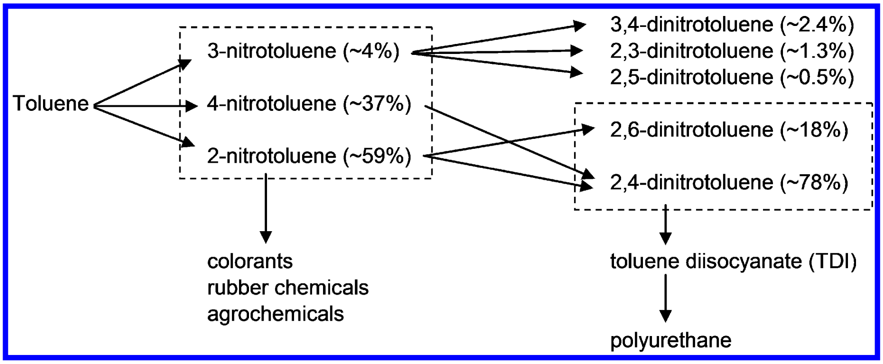

Figure 5. Different isomers produced by toluene nitration to MNT and the main paths for further nitration of MNT to DNT. (Percentages are typical values for isothermal nitration (1)).

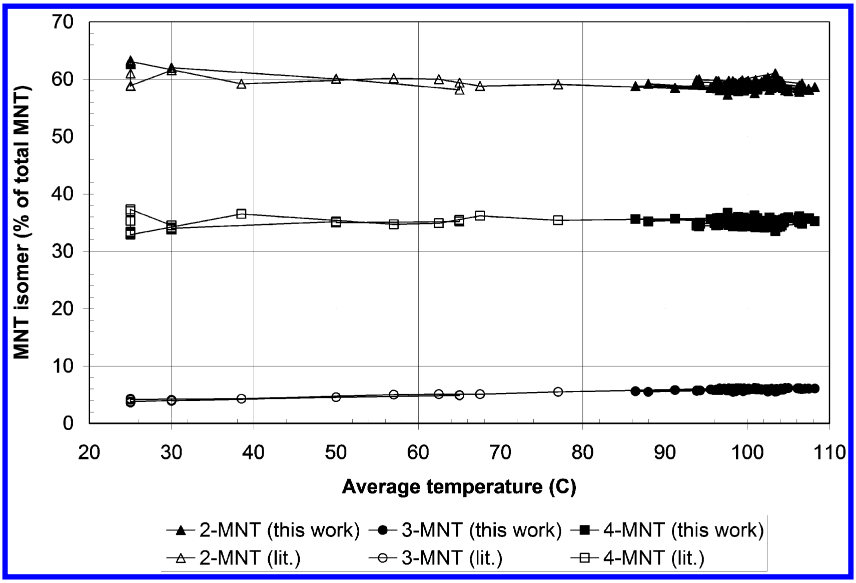

Figure 6. Data for the isomer distribution of toluene nitration versus temperature. Filled symbols: this work, open symbols literature (17–19).

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2-MNT=

$$(76.3 \pm 1.9) - (0.197 \pm 0.026)S - (0.033 \pm 0.004)T - (0.350 \pm 0.096)N \quad [2]$$

3-MNT=

$$(3.33 \pm 0.39) - (0.0002 \pm 0.0054)S + (0.024 \pm 0.001)T + (0.055 \pm 0.020)N \quad [3]$$

4-MNT=

$$(21.2 \pm 1.7) + (0.184 \pm 0.023)S + (0.008 \pm 0.004)T + (0.345 \pm 0.084)N \quad [4]$$

2-MNT/4-MNT=

$$(2.87 \pm 0.13) - (0.0148 \pm 0.0019)S - (0.0014 \pm 0.0003)T - (0.027 \pm 0.007)N \quad [5]$$

Where:

S = starting sulfuric acid (wt%), T = average temperature (°C) and N = starting nitric acid (wt%), with the fitted ranges shown in Figure 7.

From the coefficients of the fitted equations 2 to 4, it can be seen that increased sulfuric acid strength decreases the percent of 2-MNT while increasing the percent of 4-MNT, with little clear effect on the percent of 3-MNT. Increased temperature decreases the percent of 2-MNT and increases the percent of 3-MNT, with a smaller increase in the percent of 4-MNT. Increased nitric acid strength decreases the percent of 2-MNT, increases the percent of 3-MNT and increases the percent of 4-MNT. Though, the high relative uncertainty on the fitting coefficient for 3-MNT with nitric acid strength suggests that further work would be required to refine this result. Other correlations are available in the literature which report partial fits for only one isomer or only the 2-MNT/4-MNT ratio, but give similar trends (*16*, *20*). Data is also available at higher and lower sulfuric acid strengths (*18*, *21*), however this was not included because when looking at a wider set of conditions it appears that non-linear fits would be required (see for example Barnett et. al Figure 3 (*18*)).

Based on these results, changing from an isothermal to an adiabatic nitration process, resulting in a higher nitration reaction temperature, will cause an increase in 3-MNT. This would detract from the value of the energy savings possible with adiabatic production of MNT if DNT was the desired final product. Thus, the operation of such an adiabatic MNT process would need to be designed to operate with as low a temperature as possible, essentially requiring as low a vacuum as possible in the acid re-concentration stage to produce a satisfactory strength of sulfuric acid at lower temperatures. From the correlation the use of a minimal amount of nitric acid might also be helpful to minimize 3-MNT. Another option might be to replace the sulfuric acid with a different type of acid. It has been reported that use of phosphoric acid (*21*) or acetic acid (*16*) changes the isomer distribution. However, most other acids would be less practical than sulfuric acid for an industrial nitration process.

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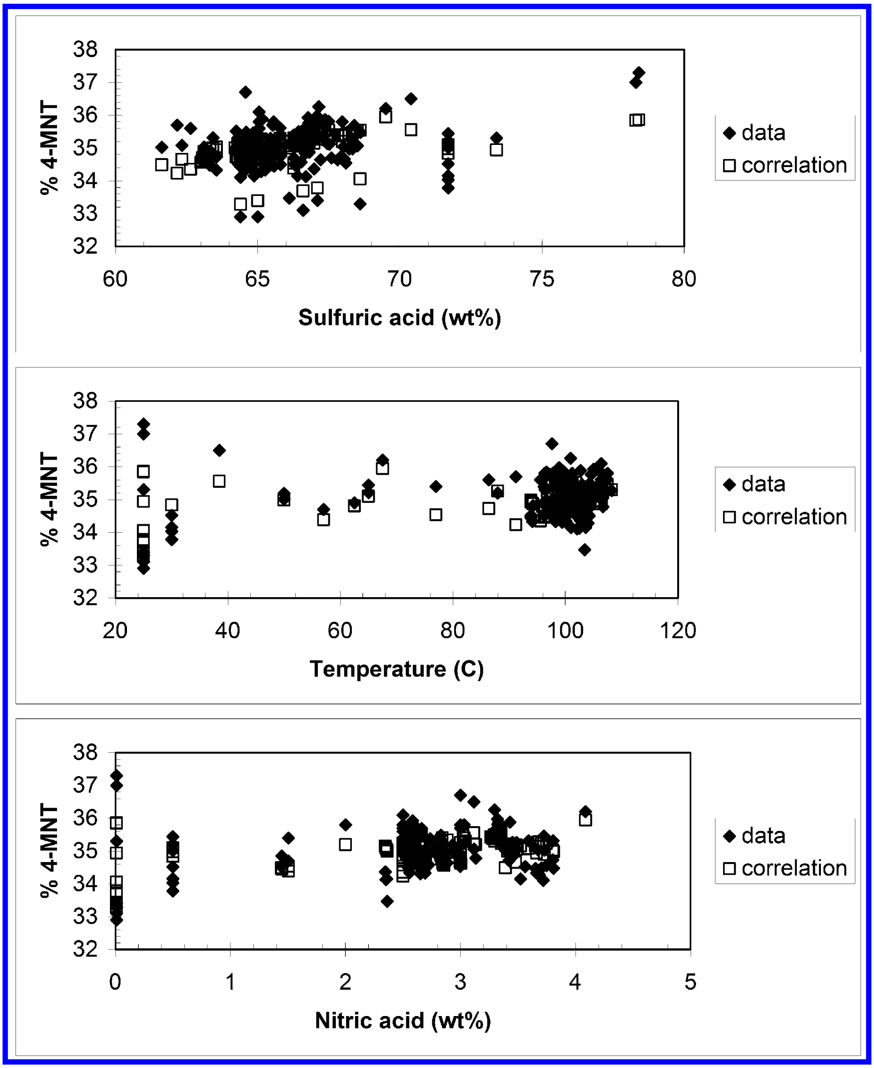

Figure 7. Correlation plots for fitting 4-MNT as a linear function of sulfuric acid, temperature and nitric acid over the indicated ranges.

Toluene Nitration By-Products

For toluene, the presence of the methyl group on the benzene ring makes the ring easier to oxidize. In DNT production, it is reported that the isothermal toluene to MNT stage can generate on average about 0.72 wt% nitrocresols (*4*) as compared to about 0.2 wt% nitrophenols for MNB production (*10*). Further, the methyl group itself can be oxidized leading to benzoic acid products. This is an important difference because this makes MNT less stable towards oxidation than MNB. This is a factor that needs to be considered in the design of the nitration reactor system. Some of the reaction routes and oxidation by-products from the nitration of toluene are shown in Figure 8. These compounds can be further oxidized and different isomers of these compounds will also be produced. Quantification of such a large number of oxidation by-products is a considerable analytical challenge. These oxidized, more water soluble by-products will also tend to partition into the spent acid phase during the product decanting. The large amount of such by-products generated during toluene nitration therefore raises issues about the build-up of such by-products in the acid loop with repeated acid recycling.

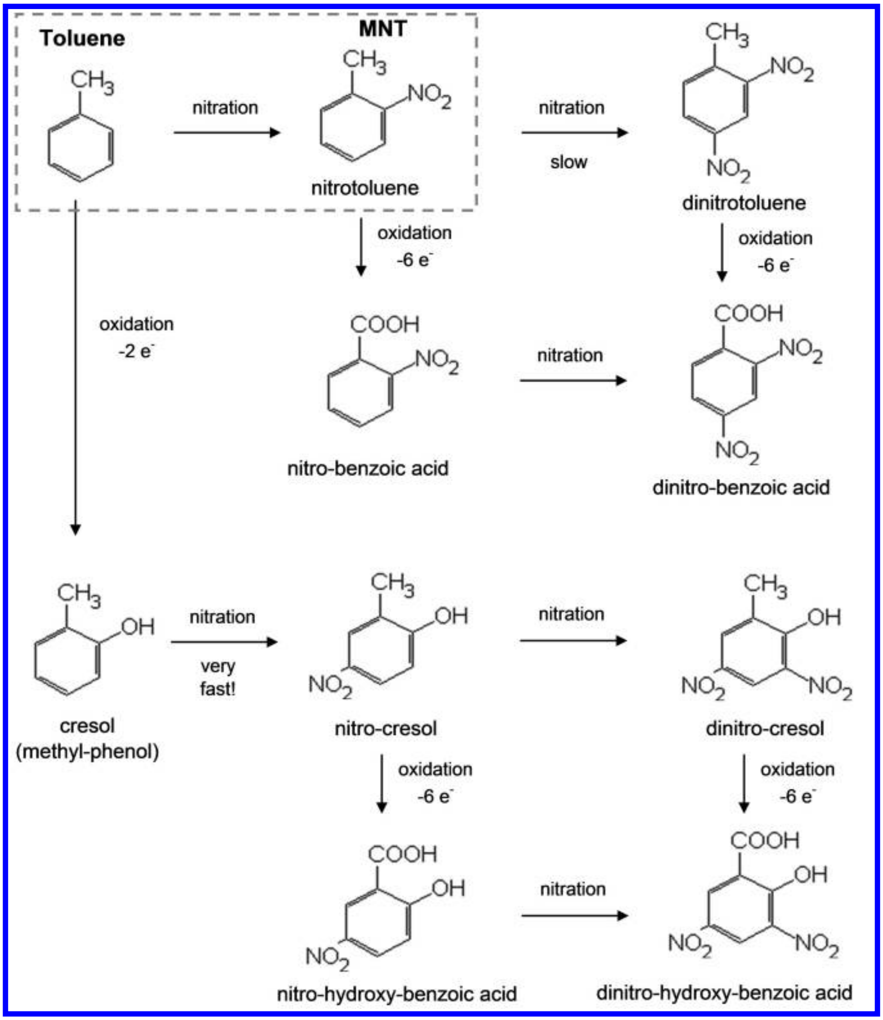

Figure 8. Diagram showing some toluene oxidation by-products. Further oxidation of these by-products will lead to more possible compounds. Also, other isomers will be produced.

Quantification of the by-products from benzene nitration is commonly done by HPLC. The organic phase can be extracted with caustic solution to recover oxidation by-products for analysis and the spent acid phase can be neutralized

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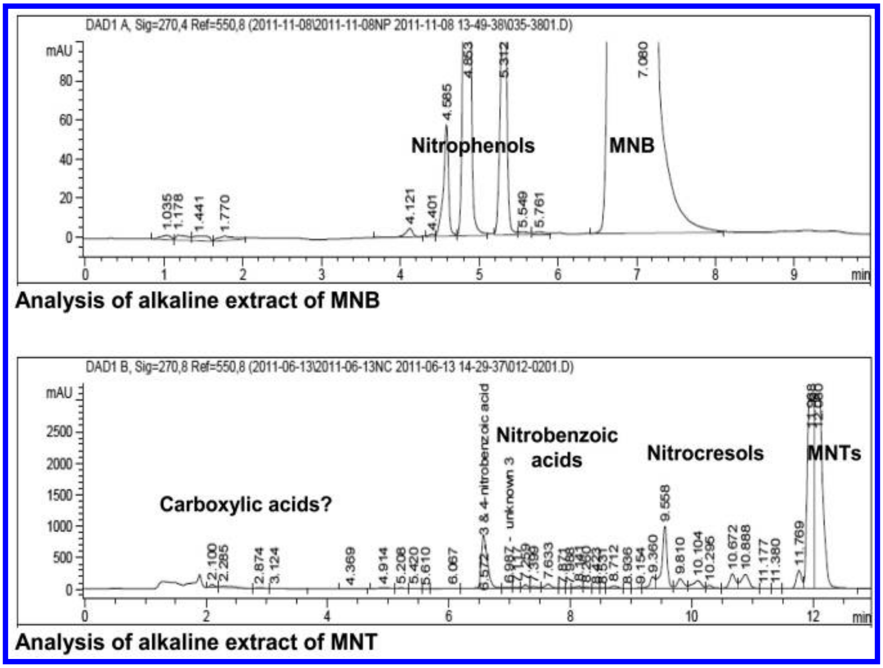
and analyzed directly. A typical MNB extract chromatogram is shown in Figure 9 where the main mono-, di- and tri- nitrophenols can be separated and quantified. The much larger variety of oxidation by-products for toluene nitration is apparent in the lower chromatogram in Figure 9. A limited number of the expected oxidation by-product compounds resulting from the nitration of toluene can be obtained and used to prepare standards to identify and quantify some peaks. Using these available standards to track different families of possible by-products can provide a "window" into the oxidation reactions, but falls short of properly quantifying the total amount of oxidation occurring.



Analysis of alkaline extract of MNB

Analysis of alkaline extract of MNT

Figure 9. Chromatograms showing the increased complexity of monitoring by-products for toluene versus benzene nitration. (UV detection at 270 nm shown in these plots).

The importance of measuring the total amount of oxidation occurring can be seen when comparing results from our 500 mL reactor done with different starting temperatures. As the nitration temperature is increased from 80 to 100 °C, the resulting organic and spent acid phases become progressively darker indicating a likely increase in oxidation by-products. However, simply measuring some of the cresols and benzoic acids shows a peak production at 90 °C (see Figure 10, peaks in the 6 to 11 minute range). However, one can see a steady increase in unresolved peaks of more water soluble compounds in the 1 to 4 minute range. Thus, it appears that for the test starting at 100 °C, the rate of decomposition of cresols has increased faster than their rate of formation. This would result in a decrease in the cresol concentrations being tracked by the HPLC, but not because of decreased cresol formation.

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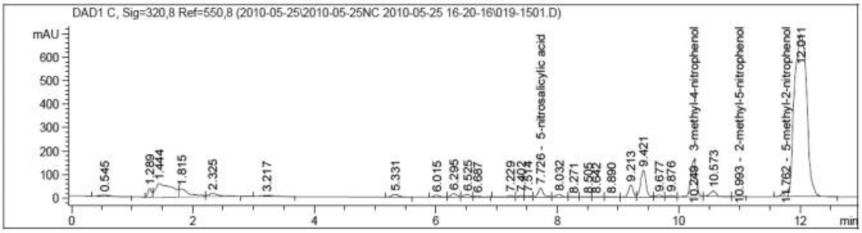
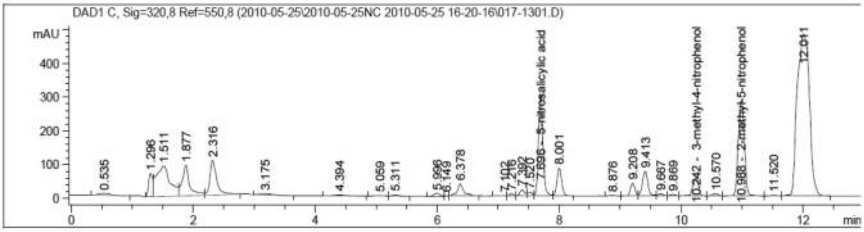
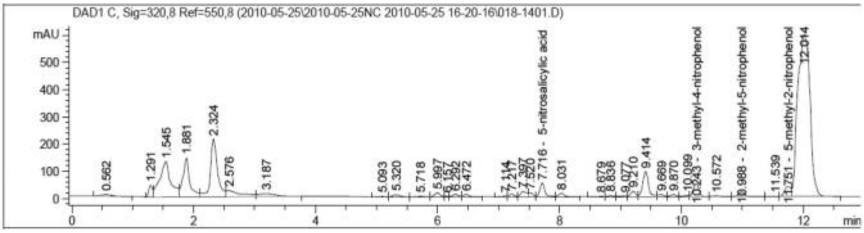


Initial temperature 80 C



Initial temperature 90 C



Initial temperature 100 C

Figure 10. Chromatograms from the analysis of the alkaline extract of the crude MNT product for various nitration starting temperatures. (UV detection at 320 nm shown in these plots).

One approach that has been used to measure the total amount of the oxidative side reactions is to measure the production of nitrous acid (*22*), which is generated from the nitric acid by the oxidation reactions. An alternative method evaluated in our work was to titrate the crude MNT product with caustic. This involved placing the crude MNT sample in a beaker with an equal volume of water and vigorously mixing to create a well dispersed two-phase solution. This was then slowly titrated with an aqueous NaOH solution, allowing the two phases to equilibrate after each addition of caustic. This results in a titration curve as shown in Figure 11. From such a curve one can measure the total amount of water soluble acid compounds and different classes of compounds can be crudely quantified. The approach is shown in Figure 11 where the shallow plateaus in the titration curve have been assigned to certain classes of oxidation products. The assignments are based on the pK_a's of the different families of oxidation by-products, and because this is an extractive titration, the plateau positions also include approximate corrections for the compound's acid form partition coefficient (~1 pH unit for the nitrobenzoic acids and ~2 pH units for the nitrocresols). Note, however, that the large number

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of possible isomers will give a range of pK_a values and extraction coefficients for each family of compounds, and so the identification of the by-products by this method is only approximate. However, it does provide a useful cross-check and compliment to the HPLC analysis.

Black Acid

A second issue with toluene nitration is the possibility of producing a dark colored spent acid referred to as "black acid" (*4*, *23*, *24*). Black spent acid can cause foaming in the acid re-concentrator, when the re-concentrated acid is re-used it can cause emulsions in the decanter and, eventually, after repeated re-use can cause tar deposits in the acid loop. In isothermal MNT production, black acid is formed if excess toluene occurs (i.e. the moles of toluene present are sufficiently greater than the moles of nitric acid so that the nitric acid is essentially consumed). This is one reason why isothermal MNT production typically uses excess nitric acid (*1*, *3*, *4*). Though, even with excess nitric acid nitration, a follow-up toluene solvent extraction of the spent acid is sometimes used to recover dissolved MNT and some of the unreacted nitric acid, which if not carefully operated can lead to an excess toluene situation and black acid. This is different from benzene nitration. In modern adiabatic benzene nitration, the nitration reactor is run with excess benzene in order to react essentially all the nitric acid. The unreacted excess benzene can be easily recovered and recycled, resulting in very good utilization of the feed chemicals, and no problems with black acid occur (*2*, *10*).

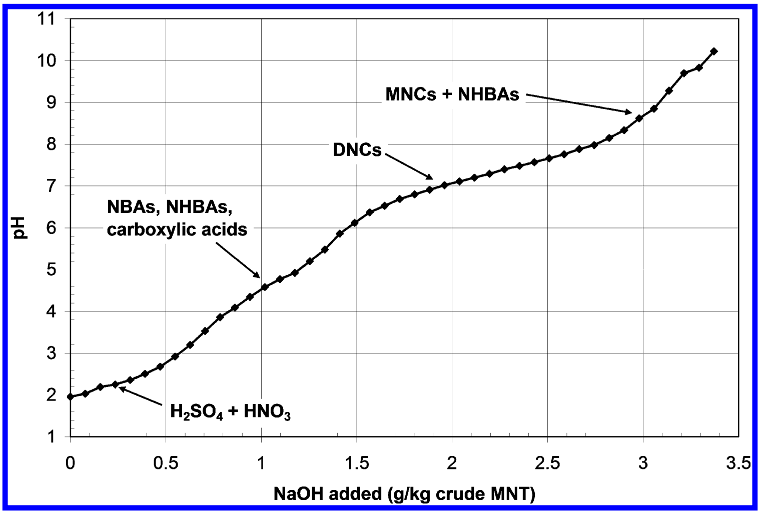

Figure 11. Example titration curve for crude MNT product with plateaus tentatively labeled. The plateau pH depends on the compound's pK_a and its partition coefficient between MNT and water. The plateau width depends on the compound's concentration. NBAs = nitrobenzoic acids, NHBAs = nitrohydroxybenzoic acids, DNCs = dinitrocresols and MNCs = mononitrocresols.

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The formation of black acid is believed to be related to reactions of nitrous acid with organic material. Black acid formation can be avoided by the removal of nitrous acid from the spent acid (*23*). Black acid is also suppressed in the presence of nitric acid (*24*). In considering the possible reactions of nitrous acid, a key intermediate is likely the nitrosonium ion-toluene complex. This is one of a family of dark orange to deep red colored complexes that are formed on mixing aromatic compounds with nitrosonium ion (*25*, *26*). In our testing, mixing benzene or toluene with 0.5 mM $NaNO_2$ in 70 wt% sulfuric acid immediately produces a dark orange-red color. If nitric acid is also present, the solution initially turns orange but then lightens to a yellow color over a few minutes. It is thought that the nitrosonium ion-aromatic compound complex can be oxidized by nitric acid to a nitronium ion-aromatic compound, that then would react to form a nitroaromatic (*25*, *26*). Under excess organic conditions, where the nitric acid is fully consumed, the nitrosonium ion-aromatic compound complex can presumably react via other pathways leading to the highly polar, sulfuric acid soluble, surface active, deeply colored compounds that are characteristic of black acid. One such route would be the oxidation of the aromatic compound by the nitrosonium ion which would lead to nitric oxide and oxidized by-products such as cresols. A second reaction route may be via the formation of nitrosotoluene (*27*). In the absence of nitric acid the nitrosotoluene might react further through disproportionation reactions or through redox reactions with easily oxidized organic compounds to produce a variety of compounds such as hydroxyl amines and azo compounds (*28*). As azo compounds tend to be highly colored compounds their formation, if it occurred, would be consistent with the highly colored nature of black acid. These possible reactions are diagrammed in Figure 12.

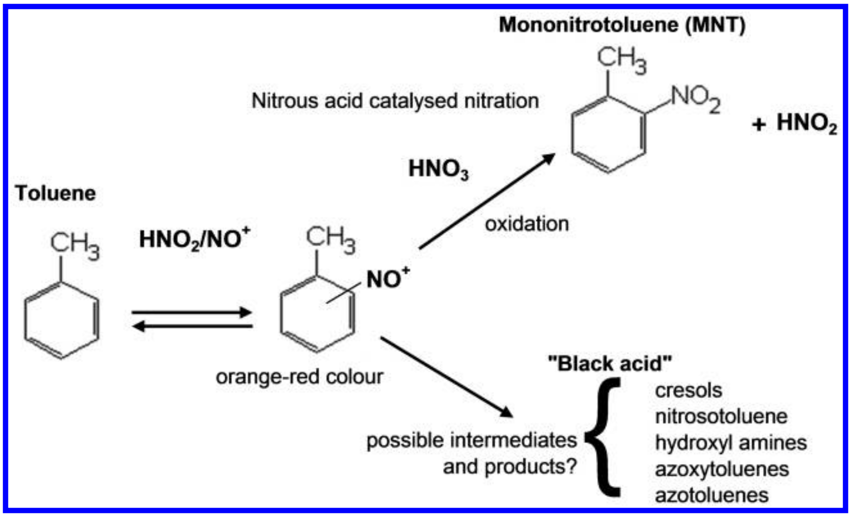

Figure 12. Possible products formed via the nitrosonium ion-toluene complex with and without nitric acid present.

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In our adiabatic nitration tests, when using excess toluene it was observed that the initial cloudy white reaction mixture produced when the toluene was injected turned to a pale yellow within one minute of toluene addition. The solution then became progressively more orange between 2 to 4 minutes and finally turned red between 4 to 5 minutes. (Conditions: a mixture of 2.5-3.0 wt% nitric acid and 64-68 wt% sulfuric acid in water with a starting temperature of 80-100 °C and a molar ratio of toluene to nitric acid of 1.0-1.1). However, if the reaction was run with excess nitric acid (moles nitric acid to moles toluene of 1.05-1.2) the pale yellow color also appeared after 1 minute but then no further color change occurred. While black acid was not formed in any of the tests, the appearance of a red color near the end of the excess toluene reaction (where the last traces of nitric acid would have been completely reacted away), and no red color when excess nitric acid was present, seems consistent with the observed results for mixing toluene with nitrous acid without nitric acid present (which produced a dark orange-red color) and with nitric acid present (which resulted in a light yellow color).

The toluene results, however, contrast with the results for benzene nitration. Using excess benzene with similar nitration conditions, the mixed reaction solution went from a cloudy white when the benzene was introduced to a greenish-yellow after 1 to 2 minutes with no further color change after that time. Excess nitric acid tests produced the same result. This is, of course, consistent with the ability to run excess benzene in commercial adiabatic MNB production without any issues with spent acid quality. A key reason for this difference is likely related to the much lower amount of oxidation by-products with benzene nitration and so a corresponding lower concentration of nitrous acid in the spent acid. A second reason may be the greater resistance to oxidation of benzene versus toluene which could act to slow the rates of black acid formation reactions and in doing so lower the amount of nitric acid required to suppress them (assuming competitive reactions as speculated in Figure 12). The appearance of red spent acid in these excess toluene adiabatic nitration tests as opposed to black acid reported for industrial isothermal toluene nitration may then be due to the lower amount of reaction using 2.5-3.0 wt% nitric acid in these tests versus 17-32 wt% nitric acid for typical isothermal toluene nitration (*1*). This would result in less total reaction and so less total oxidation by-products and less nitrous acid in the spent acid. The lower total reaction per pass typical of adiabatic nitration may therefore be the reason that only "red acid" rather than "black acid" is observed for our experiments that ran with excess toluene.

Acid Recycling

If adiabatic nitration using excess toluene conditions still produces black acid type compounds, but simply fewer of them because less total reaction is carried out, this raises the question of what happens when the spent acid in such a process is repeatedly re-concentrated and re-used. A series of four tests was carried out where the spent acid from each nitration test was re-concentrated under vacuum at about 80 °C at 20 mbar, and then re-used for the subsequent nitration. The experiments used a mixture of 65.1 wt% H_2SO_4 and 2.5 wt% HNO_3 in water, 1.10 mole toluene/mole nitric acid, stirring at 1200 rpm (a mixing power of ~16 W/L) and a starting

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acid temperature of 90 °C. After each test the spent acid was progressively darker and HPLC analysis showed cresols in the organic phase increased from 6400 ppm to 8900 ppm, with the cresol concentrations in the acid phase showing a similar trend (see Figure 13).

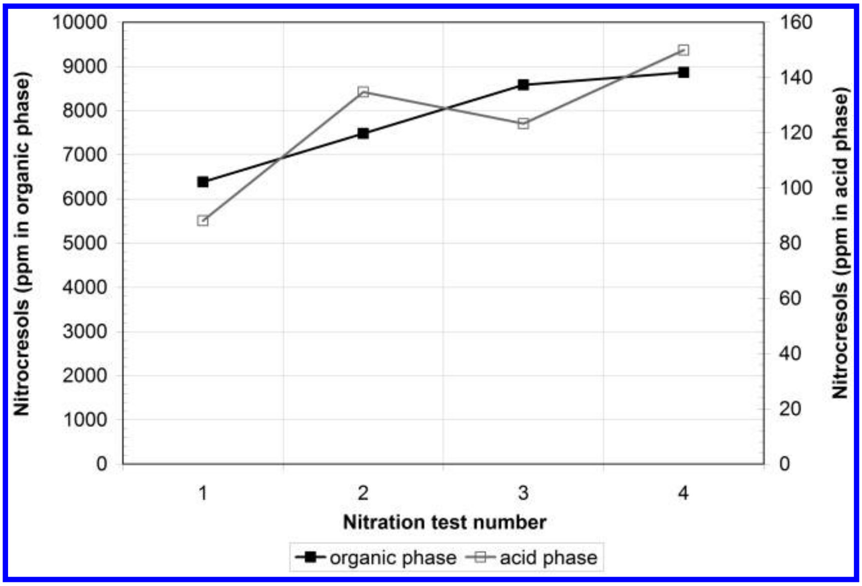

Figure 13. The increase in HPLC measured cresols with repeated re-use of the sulfuric acid. (Test 1 used fresh acid and the acid was then re-concentrated and re-used for each additional test).

This build-up of by-products in the re-used acid may reach a steady state over time. If not, some method to control the build-up of contaminants may be required such as bleeding off some acid, extracting or stripping the acid, or running the process with excess nitric (with a resultant slight loss in chemical utilization). In isothermal nitration (with 15 to 25 wt% nitric acid in the starting mixed acid), it has been reported that toluene nitration with excess toluene can be successfully carried out without black acid causing problems through the use of steam stripping of the spent acid at around 160-180 °C integrated with the acid re-concentration (*29*). This same patent also provides an example showing problems found with the build-up of organic compounds when recycling sulfuric acid during adiabatic toluene nitration under excess toluene conditions where the acid was being re-concentrated using flash evaporation at 90 °C at 60 mbar. Thus, to properly develop a usable adiabatic toluene nitration process, testing must consider the effect of the nitration conditions on the quality of the resulting re-concentrated acid. This means that testing must include the full acid recycle loop rather than a single nitration reaction in isolation.

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A design for a small laboratory scale acid loop test system to perform such experiments is shown in Figure 14 with a photo of the completed system in Figure 15. This system incorporates the key process components to allow testing with continuous acid recycling. One difference from a full scale adiabatic acid recycle loop (as diagrammed in Figure 1) is the use of air stripping for re-concentrating the acid. In this case a metered flow of warm, dry air is used to remove water vapor from the sulfuric acid re-concentration vessel (i.e. to lower the water vapor pressure) as opposed to using a vacuum system. This avoided the need for vacuum rated equipment and allowed for a compact system that could fit in a fume hood (see Figure 15). The small size (production rate of ~1 kg MNT/h) also minimizes chemical consumption and waste generation. This design of experimental equipment therefore provides a simple system to assemble and operate for the proper testing of adiabatic nitration in a way that considers the full acid loop and the impact of acid recycling, which is key to a successful adiabatic nitration process.

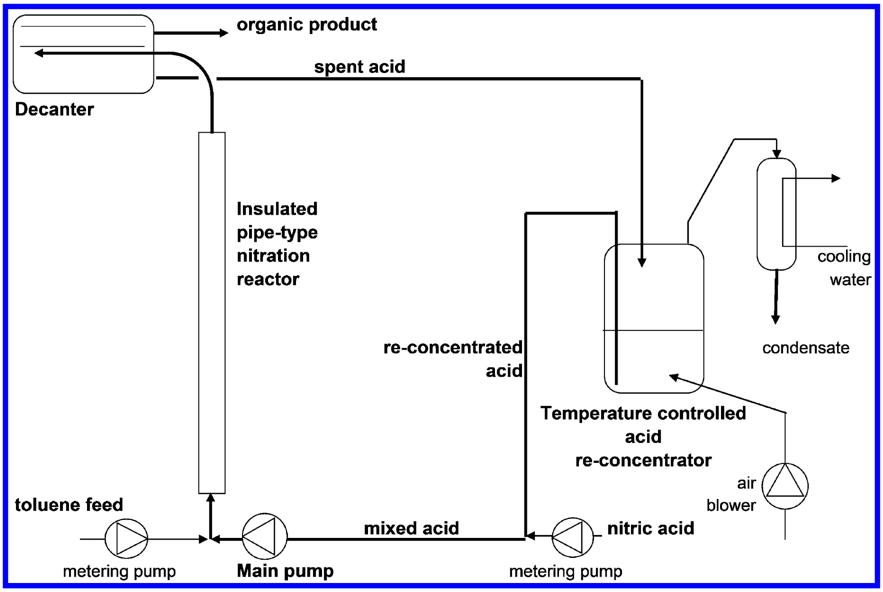

Figure 14. Diagram of a nitration acid loop test system.

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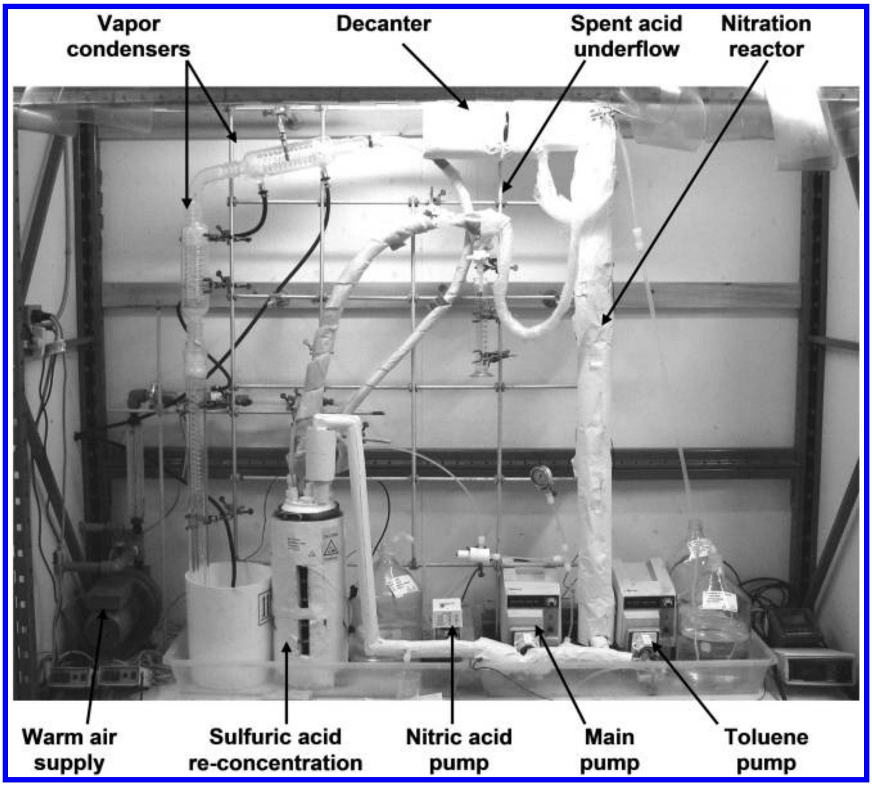

Figure 15. Photo of the nitration acid loop test system.

Conclusions

As has been demonstrated in MNB production, adiabatic nitration has the potential for significant energy savings versus isothermal nitration and so it would be desirable to use adiabatic nitration for a wider variety of compounds. One potential candidate compound for adiabatic nitration is toluene.

The effective reaction rate for toluene nitration under industrial conditions is similar to that for benzene nitration and so nitrator designs for adiabatic MNT would likely be similar to those used for MNB. However, the higher temperatures encountered with adiabatic nitration leads to a shift in the product isomer distribution, with a clear correlation between increased average nitration temperature and increased 3-MNT. This is an issue if adiabatic toluene nitration was to be used as a first step in the production of DNT for polyurethane manufacture. In such a case, the adiabatic process should be designed so as to minimize the average nitration temperature and possibly also to minimize the amount of nitric acid in the nitrator feed.

Toluene is more easily oxidized than benzene and results in a greater variety and a larger total amount of oxidation by-products. This makes the complete identification and full quantification of these by-products by HPLC impractical. It is therefore suggested that while HPLC can be used to track key representative

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compounds, it should be combined with some other method to quantify the total oxidation by-products. One possible method is a base titration of the organic product which gives a quantitative measure of the total number of acid groups present, and from the pH of their neutralization, a possible indication of the family of compounds present.

Black acid did not immediately form with excess toluene adiabatic nitration, possibly due to the much lower amounts of nitric acid used for adiabatic nitration resulting in lower amounts of nitrous acid in the spent acid. However, significant amounts of acid-phase soluble colored by-products are formed, which may build up in the acid loop with continuous acid re-use. This issue highlights the need for any study of adiabatic toluene nitration to include within its scope the full acid recycle loop. The equipment to do such a study is not overly complex and a design has been presented that can be made small enough to fit within a fume hood.

Overall, some of the key issues related to implementing adiabatic nitration of toluene have been identified. These issues may result in some compromise in the product quality in moving from isothermal to adiabatic nitration, or possibly some additional process steps (for example for acid clean-up), however none of the issues appear to completely prevent adiabatic toluene nitration. Further, while additional costs would be associated with these issues, this must be balanced against the large energy savings possible with adiabatic nitration. Future work using a full adiabatic nitration loop test system will hopefully provide clear answers to some of these questions.

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Chapter 4

Nitrophenolic By-Products Quantification in the Continuous Benzene Nitration Process

Tiago J. G. Costa,[1] Anabela G. Nogueira,[1,2] Dulce C. M. Silva,[2]
Alejandro F. G. Ribeiro,[2] and Cristina M. S. G. Baptista*,[1]

[1]Department of Chemical Engineering, University of Coimbra,
Pólo II, Rua Sílvio Lima, 3030-790 Coimbra, Portugal
[2]CUF - Químicos Industriais, Quinta da Indústria,
Beduído, 3860-680 Estarreja, Portugal
***E-mail: cristina@eq.uc.pt**

The High Pressure Liquid Chromatography (HPLC) method for nitrophenols measurement in the benzene nitration process has been improved. A new eluent mixture was studied using two different compositions and the 30/70 (%v/%v) ratio of acetonitrile and aqueous potassium dihydrogen phosphate solution proved sufficient in accurately quantifying every nitrophenolic compound. The influence of the pH upon peak resolution was assessed and pH 7.0 provided the best results. Once the chromatography parameters were set a reproducibility study was carried out confirming the accuracy of the method.

Introduction

The nitration of benzene yields mononitrobenzene (MNB), a precursor to aniline. Aniline is used in the manufacture of pharmaceuticals, dyes, pigments, 4,4′-methylenedianiline, and solvents. The nitration is usually carried out in mixed acid media composed of sulfuric acid, nitric acid and water (*1–3*) via an electrophilic substitution reaction (*4–6*). The reaction is accomplished in a two-phase system: the aqueous acid phase and the organic phase. Of interest to technologists involved in the manufacture of MNB via the mixed acid liquid-liquid exothermic reaction are the challenges of mass transfer and reaction kinetics (*1–3*, *7–11*). The benzene nitration has a well-established mechanism (*5*), accepted by

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many experts in the field, where it is believed that mononitrobenzene formation takes place in the aqueous phase. Industrially, the yield of MNB is high, but significant side reactions occur during nitration. Benzene nitration by-products mainly consist of dinitrated and nitrophenolic compounds. Several authors (*7*, *12*) posit that the dinitrated compounds are formed through a consecutive reaction after the mononitration of benzene while nitrophenolic by-products are formed via a reaction parallel to the main reaction route. The nitrophenols (NPs) produced are mono-, di- and tri-nitrophenol (MNP, DNP and TNP, respectively).

By-product formation is a concern in most industrial processes. In the particular case of nitrophenols, mononitrobenzene producers are dealing with toxic compounds requiring well designed remediation processes that are heavily regulated. For these reasons minimization of their formation is desired. A considerable amount of work has been dedicated to understanding and reducing by-products formation (*12*, *13*). This effort is challenging, mainly due to the lack of extensive knowledge of by-product formation mechanisms and adequate kinetic and mass transfer data.

Most research in this field has been carried out at the lab scale (*5*, *6*, *10*, *11*) using operating conditions that do not always match those of the industrial adiabatic process, and only traces of nitrophenols are produced. The amount of literature concerning their formation is sparse. Mass transfer limitations between the organic and acid phase are pointed out by Burns and Ramshaw (*12*) as partly responsible for nitrophenol formation. It has been suggested that the benzene oxidation agent is undissociated nitric acid that dissolves in the organic phase resulting in the formation of phenol, the precursor of the nitrophenolic compounds (*12*). The rate of phenol transfer to the acid phase is very fast (*3*), and a sequence of sulfonation and nitration reactions (*14*) leads to the nitrophenolic by-products. Once formed, the nitrophenolics (NPs) partition back to the organic phase. An increased interfacial area between the two reacting phases is thought by many to promote benzene mass transfer to the aqueous phase where nitrobenzene is formed, increasing process selectivity and yield, and the design of the reactors has for many years been driven by this principle. In the first patent on the adiabatic nitration process (*15*), the dispersion of the organic phase is achieved by means of continuous stirring of the reacting mixture. In the 1990s a new and different configuration has been patented (*16*) and this makes use of newly designed impingement elements which provide finely dispersed benzene drops improving interfacial area. A different strategy that employs microreactors to improve the contact between the two phases has been tested more recently (*7*, *17*).

Interfacial area is one of the operating parameters influencing process selectivity and it is known that mixed acid composition (*3*), feed flow ratio between benzene and nitric acid and reaction temperature (*13*) are also relevant. Nevertheless, the information currently in the literature is insufficient to predict levels of nitrophenols production in industrial processes. To gather the desired data, studies can be run in an actual industrial process. Operating factors that govern nitrophenol production are chosen, and then changed in the process to determine their impact on the formation of the impurities. Frequently however, the degree of change in each factor is limited so as to not impact the rate of production of the product.

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The success of such a plant study is highly dependent on the ability to sample process streams and analytically determine the impurity profile with accuracy and precision. Although most of the nitrophenolic impurities can be quantified by gas chromatography (GC), trinitrophenol cannot, as it is not easily volatilized and can be adsorbed on the GC column due to its polarity. A literature survey (*18–21*) confirmed HPLC as the best analytical technique for quantifying phenol and its nitrated derivatives. Several HPLC methods have been developed and studied, many for identifying and quantifying phenols in waste water (*18*, *21*). Another related analytical study concerned a medical application (*23*).

In previous studies on nitration (*9*, *13*) HPLC was used to measure NPs, and the methods employed proved to be robust for quantifying the predominant by-products. The literature survey summarized above showed that the current methods could be improved to afford better quantification of additional by-products. The subject of this paper is the optimization of analytical methods to quantify the nitrophenolic by-products resulting from the nitration of benzene.

Experimental

Materials

The chemicals used to prepare samples, analytical standards, and HPLC eluents were purchased from different suppliers.

The 1M sodium hydroxide solution (analytical reagent grade) and HPLC grade acetonitrile were supplied by Scharlau Chemie S.A.. Phosphoric acid (85% w/w) and potassium dihydrogen phosphate (analytical-reagent grade) were purchased from Panreac.

Standard solutions, used for HPLC calibration, were prepared with: 4-mononitrophenol (98% w/w, where w/w is taken to mean the weight of 4-nitrophenol divided by the total weight of material) and 2,4-dinitrophenol (97% w/w) purchased from Aldrich, 2-mononitrophenol (98% w/w) was provided by Fluka, 2,6-dinitrophenol (98% w/w) was supplied by TCI and 2,4,6-trinitrophenol (99% w/w) was purchased from BDH.

Water used in this study was obtained from a Milli-Q purification system from Millipore.

Preparation of Standard Solutions

Standard solutions were prepared by adding known quantities of each analyte to ultra-pure water. The nitrophenols were first mixed with approximately half of the volume of water required, then about 1 g of sodium hydroxide (1 M) was added to promote the complete dissolution of the analytes at room temperature. To complete the preparation, ultra-pure water was added until the final desired concentration of analyte was obtained. As a result of this study, the pH of the final standard solution was adjusted to 7.0 by adding a small amount of aqueous solution of phosphoric acid (1M). Each standard solution contained the five nitrophenols used in this study at different concentrations which ranged from 2 – 10 ppm by

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weight for 2- and 4-mononitrophenol and 2,6-dinitrophenol, and 11-160 ppm by weight for both 2,4-dinitrophenol and 2,4,6-trinitrophenol.

Sampling Procedure

The plant samples analyzed were collected in different locations in the nitration train at a CUF-QI nitrobenzene plant. The chemical compounds used in the benzene nitration process are known to be hazardous, requiring particular sampling procedures ensuring operator safety. Moreover, in the particular continuous process studied the operating temperature was greater than 100 ºC, and in order to stop the reaction, the samples were cooled as soon as collected from the reactor. Benzene nitration is a heterogeneous liquid-liquid reaction. The samples are allowed to stand and cool, where upon the phases separated. Due to the different matrices, different analytical procedures were used to measure the composition of each phase. This work focuses on the organic phase and, in particular, on measuring the nitrophenols in that phase.

Nitrophenols Identification

Nitration samples were collected from the plant and allowed to separate. A portion of the organic phase was treated with calcium carbonate to neutralize and remove any trace acid present. The sample was filtered and then analyzed by GCMS. A GC-MS from Agilent, models GC-7890A and MS-5975C, with a HP-5MS column (30 m x 0.25 mm x 0.25 µm), was used for identifying the nitrophenols present in the organic phase collected from the nitrobenzene plant. The volume of sample injected onto the GCMS was 1 µL, oven conditions were: 40 ºC (1 min), to 100 ºC (15 ºC/min), 20 ºC/min to 240 ºC, and 10 ºC/min to 310 ºC, using helium as carrier gas at constant flow (30 mL/min). The main objective of this work was to better quantify the compounds identified by GCMC by HPLC.

Sample Preparation for HPLC Analysis

The sampled organic phase is less dense and usually darker than the aqueous phase, enabling for an easy identification of each separated phase after a short settling time. The literature indicated that the nitration reactions leading to nitrophenols occur in the acid phase, and these by-products transfer into the organic phase. The samples injected onto the HPLC were aqueous based. Therefore, the nitrophenols must be extracted from the organic phase. This is performed by adding 1 mL of the organic phase to 2 mL of sodium hydroxide solution (1 M), shaking this mixture vigorously and then separating the two phases in a centrifuge. The extraction yield was found to be 94% and the efficiency of the process can be confirmed by the change in color of organic and aqueous phases. The aqueous extract, containing the extracted NPs, was diluted (*13*) and pH adjusted. This was performed by adding 20 mL of ultra-pure water to 1 mL of the extracted aqueous phase, followed by a careful addition of phosphoric acid (1 M) until a pH of 7 was obtained.

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HPLC Conditions and Instrumentation

The reversed-phase HPLC system consisted of a HPLC pump model K-1001 and an ultraviolet detector model K-2501, both from Knauer. Quantification was done at 360 nm, and a UV spectrum of each analyte could also be obtained in the 'stop flow' mode. Data processing employed chromatographic software from DataApex.

The literature was surveyed to choose the HPLC columns best suited for this study. The Mediterranean Sea 18, 5 μm, 250 mm x 4 mm column, reference TR-010038 from Teknokroma packed with C18 silica matched the features mentioned by Belloli *et al.* (*19*) as suitable for obtaining the separation of all the NPs in the samples. The column was placed in an ELDEX oven at 30 ºC. The flow-rate was 1 mL/min, and the isocratic mobile phase consisted of a mixture of acetonitrile and an aqueous solution of KH_2PO_4 (50 mmol), as buffer (*18*). Two eluent compositions were prepared for study. The first eluent was a 50%/50% (v/v) mixture of acetonitrile and the aqueous KH_2PO_4, and the second was a 30%/70% (v/v) acetonitrile and aqueous KH_2PO_4. Before use, the solutions were filtered through a 0.45 *μm* nylon membrane and degassed. The volume of sample injected was 10 μL.

Results

The first stage of the study consisted in identifying the nitrophenols present in organic phase in the samples collected from the plant. The goal was the quantification of the predominant nitrophenols as well as the trace by-products. We wanted to confirm the presence and amounts of each nitrophenol reported in the literature. GCMS was used to determine the nitrophenols present in the samples, which were identified according to the chromatographic retention times of authentic material, Table I (see the Experimental Section for details of the analysis).

A separate standard of each analyte was injected onto the HPLC to determine retention times. Preliminary work suggested an adequate isocratic solvent system to start with was 30% volume acetonitrile and 70% volume aqueous solution of KH_2PO_4 (50 mmol), at pH 7.0 at a 1 mL/min flow rate. A chromatogram of a sample containing the 5 nitrophenolic compounds is shown in Figure 1.

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Table I. Nitrophenols present in the organic phase of the samples – GC-MS information

Abbreviation	*Compound*	*CAS Number*	*Retention time (min)*
2 MNP	2 Mononitrophenol	88-75-5	5:07
4 MNP	4 Mononitrophenol	100-02-7	6:13
2,6 DNP	2,6 Dinitrophenol	573-56-8	10:51
2,4 DNP	2,4 Dinitrophenol	51-28-5	12:31
TNP	Trinitrophenol	88-89-1	21:05

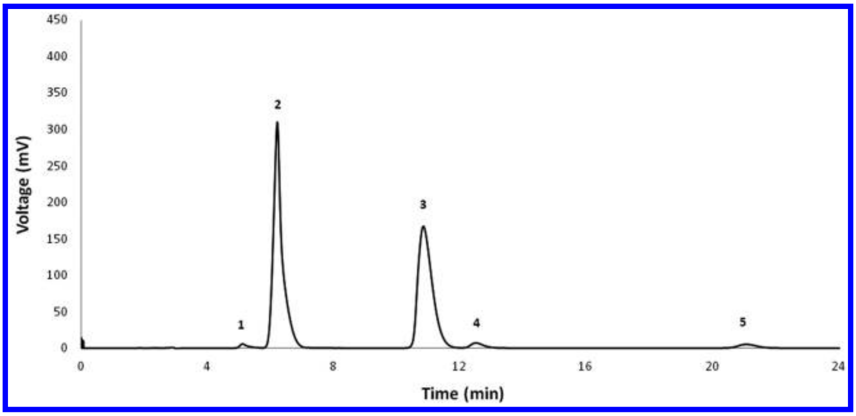

Figure 1. HPLC run with reference compounds: 2,6 DNP (1), 2,4 DNP (2), TNP (3), 4 MNP (4) and 2 MNP (5).

Eluent Composition

It is known (*21*, *23*) that eluent composition is one of the parameters influencing the separation of the analytes. The eluent used was a solution composed of acetonitrile (*21*, *24*) and aqueous KH_2PO_4 (50 mmol); two volumetric ratios of these two components were assessed in this study: 50/50 (%v/%v, acetonitrile/aqu) according to Alber *et al.* (*18*), and 30/70 (%v/%v, acetonitrile/aqu) with the hope of improving peak separation as suggested by Preiss *et al.* (*21*). The pH of the two eluents assessed was 7.0. Figure 2 shows the overlay of the two chromatograms obtained using the two eluent systems.

An increase in the aqueous component of the eluent resulted in longer retention times and better separation of the analytes. The hydrophobic analytes interact with the C18 more as the percentage of the aqueous component of the

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eluent is increased, resulting in the longer retention times and better overall separation. Moreover, this improved separation enabled quantification of the five nitrophenols in the sample, while only three components were detected with the 50/50 acetonitrile/aqueous eluent (peaks 1 and 5 do not show in the 50/50 (%v/%v) chromatogram). The 2- and 4-mononitrophenol and 2,6-dinitrophenol amounts in the standard were low, thus the small peak height in the chromatogram.

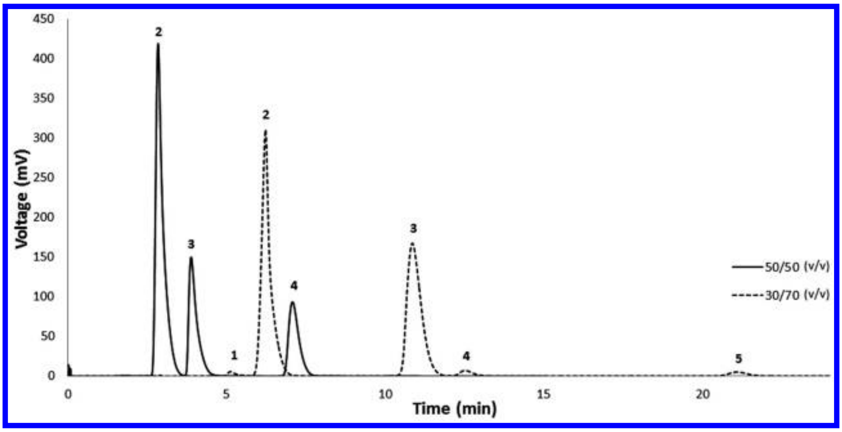

Figure 2. Chromatograms using different volumetric ratios of acetonitrile and aqueous potassium dihydrogen phosphate as mobile phase: 2,6 DNP (1), 2,4 DNP (2), TNP (3), 4 MNP (4) and 2 MNP (5).

The chromatograms in Figure 2 were further assessed by calculating R_S, a parameter that expresses the degree of separation of the peaks. According to Pombeiro (*25*), the R_S should be greater than 1.5 for complete separation of two neighboring peaks. Other important chromatographic calculations (*24*, *25*) were done to access the efficiency of the separation of the analytes, namely determining the retention factor (k′), the selectivity α and the plate number (N). The chromatographic data was analyzed using the Clarity chromatographic Station Software to provide the chromatographic efficiency parameters listed in Table II for the two eluent compositions studied.

The optimal range for retention the factor k′ is 1 to 10 (*25*); higher values do little to improve resolution of the peaks and only results in longer analysis time. Selectivity values (α) in Table II are greater than 1.0, as expected, as they refer to retention factors of neighboring peaks. The magnitude α does not indicate the advantage of one eluent system over the other. As shown in Table II, the HPLC separation parameters with the 30/70 (%v/%v) eluent composition led to an improvement of the resolution, R_S, for each analyte. The use of 30/70 (%v%/v) acetonitrile/aqueous-buffer gave superior peaks separation and resolution.

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Table II. HPLC separation efficiency parameters for two mobile phase compositions

<table>
<tr><th><i>Nitrophenols</i></th><th colspan="2"><i>2,6DNP</i></th><th colspan="2"><i>2,4DNP</i></th><th colspan="2"><i>TNP</i></th><th colspan="2"><i>4MNP</i></th><th colspan="2"><i>2MNP</i></th></tr>
<tr><td>Eluent – acetonitrile/ Aqu KH_2PO_4 (50 mmol)</td><td colspan="10">50/50 (%v/%v)</td></tr>
<tr><td>k′</td><td colspan="2">* nd</td><td colspan="2">4.3</td><td colspan="2">5.9</td><td colspan="2">11.6</td><td colspan="2">* nd</td></tr>
<tr><td>α</td><td colspan="3">-</td><td colspan="2">1.4</td><td colspan="2">1.9</td><td colspan="3">-</td></tr>
<tr><td>N</td><td colspan="2">* nd</td><td colspan="2">665</td><td colspan="2">1658</td><td colspan="2">3242</td><td colspan="2">* nd</td></tr>
<tr><td>R_s</td><td colspan="3">-</td><td colspan="2">2.0</td><td colspan="2">5.4</td><td colspan="3">-</td></tr>
<tr><td>Eluent – acetonitrile/ Aqu KH_2PO_4 (50 mmol)</td><td colspan="10">30/70 (%v/%v)</td></tr>
<tr><td>k′</td><td colspan="2">0.9</td><td colspan="2">1.3</td><td colspan="2">3.1</td><td colspan="2">3.7</td><td colspan="2">7.0</td></tr>
<tr><td>α</td><td colspan="3">1.5</td><td colspan="2">2.4</td><td colspan="2">1.2</td><td colspan="3">1.9</td></tr>
<tr><td>N</td><td colspan="2">3088</td><td colspan="2">3324</td><td colspan="2">3114</td><td colspan="2">6670</td><td colspan="2">8606</td></tr>
<tr><td>R_s</td><td colspan="3">2.3</td><td colspan="2">5.7</td><td colspan="2">2.4</td><td colspan="3">8.7</td></tr>
</table>

***nd- not detected**

Adjustment of pH

The pH of the samples, standard solutions and eluent is an important factor that influences both accuracy and the precision of the method (*22*). To assess the influence of the pH of the sample on the separation, the pH of the samples were varied from 1.0 to 12.0. Figure 3 shows over-layed chromatograms for samples with a pH of 1, 7, and 12 adjusted with phosphoric acid (1M). It can be seen that the retention times and peak shapes of the analytes, and the ability to detect 4-MNP and 2-MNP are significantly impacted by the pH of the sample. This is most likely due to the degree of ionization of the nitrophenols in solution (*22*). The pH of the sample dictates the extent of ionization of the nitrophenols in the sample, as does the pH of the eluent. The UV absorbance value at the wavelength used for quantification will also be affected by the extent of ionization.

The study of sample pH impact on the HPLC chromatography used a standard that contained the nitrophenols at the targeted concentrations shown in Table III. The pH of the nitrophenolic mixture standard was adjusted with phosphoric acid (1M) to provide samples with pHs of 1, 5, 7, 10, and 12. The pH adjusted samples were then analyzed to determine the best sample pH for the optimization of analysis time and accuracy of the quantification of each analyte. These results are summarized in Table III, and it is clear that a sample pH of 7 gave the best quantification result. Recall that the pH of the eluent was 7. Varying the pH of the eluent was not a subject of this study.

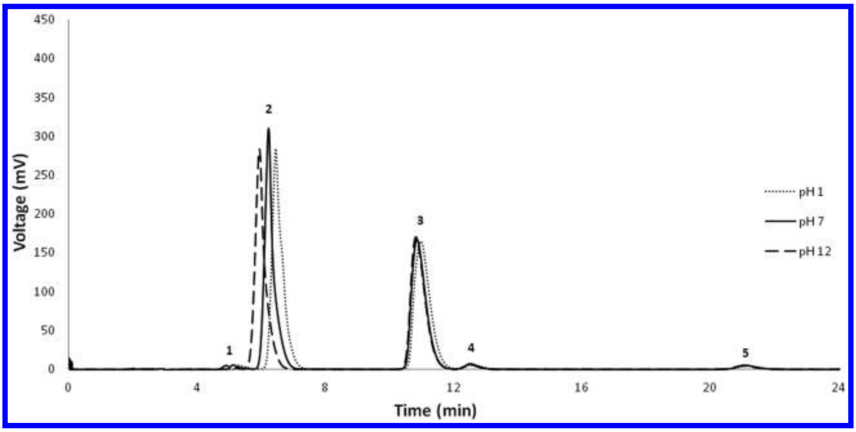

Figure 3. Influence of pH of the sample upon the chromatograms obtained from the same sample with 2,6 DNP (1), 2,4 DNP (2), TNP (3), 4 MNP (4) and 2 MNP (5). The eluent composition was 30/70 (%v/%v) and the eluent flow rate 1 mL/min.

Table III. Influence of sample pH upon the quantification of nitrophenols. The eluent composition was 30/70 (%v/%v) and the eluent flow rate 1 mL/min.

	Composition (ppm)				
	2,6 DNP	***2,4 DNP***	***TNP***	***2 MNP***	***4MNP***
Target composition	*7.5*	*81.8*	*65.2*	*7.5*	*8.2*
pH					
1	8.3	87.2	70.6	8.1	8.7
5	12.5	86.8	69.7	8.0	8.9
7	7.4	81.9	64.7	7.2	8.3
10	11.1	86.7	68.1	7.9	8.7
12	8.8	84.4	66.5	7.6	8.4

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Standard Curves

Having established the best operating conditions for the HPLC analysis, calibration curves were determined. Five standard solutions with different concentrations of each of the five nitrophenols were prepared. Two concentration ranges were considered: 11-160 ppm by weight for the predominant analytes (2,4-dinitrophenol and trinitrophenol) and 2-10 ppm by weight for 2- and 4-mononitrophenol and 2,6-dinitrophenol. These standard solutions were injected on the HPLC and results used to determine calibration curves for each nitrophenol. The equations of the regression lines for each analyte had an R^2 (coefficient of determination) of 0.99, Table IV. This study demonstrated the precision of the method within the concentration range of interest.

Table IV. Validation range of the linear response for each solute

Compound	*Validation range (ppm)*	*Equation of line* [a] *(slope and intercept; R^2)*
2 Mononitrophenol	2-10	$y = 27.137x - 2.5873$; $R^2 = 0.9997$
4 Mononitrophenol	2-10	$y = 24.307x + 5.4361$; $R^2 = 0.9999$
2,6 Dinitrophenol	2-10	$y = 13.43x - 3.2565$; $R^2 = 0.9964$
2,4 Dinitrophenol	11-160	$y = 73.377x + 5.9492$; $R^2 = 0.9999$
Trinitrophenol	11-160	$y = 81.13x + 11.402$; $R^2 = 1$

[a] x= concentration of solute (ppm) and y=Peak area (mV.s)

Reproducibility of the Analytical Method

Ten replicate injections were made for each standard solution used in this study. The coefficient of variation (CV) was calculated to assess intra-assay precision. The calibration was carried out for five consecutive days using the five standard solutions and the CV calculated to assess inter-day assay variation. The results of this study for one of the standard solutions are presented in Table V. The mean value ($\overline{x}$) the standard deviation (σ), CV, and the percent error were calculated. The error was consistently below 10% and the lower errors (0.71 and 1.18 %) correspond to the predominant by-products confirming the adequacy of the method. Inter-assay precision was shown to be less than 4%.

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Table V. Reproducibility parameters for a standard solution

Compound	$\bar{x}$ *ppm*	*σ ppm*	*CV (%)*	*Error (%)*
2,4 DNP	80.9	0.37	0.46	1.18
TNP	78.3	0.21	0.27	0.71
2,6 DNP	8.1	0.27	3.38	9.27
2 MNP	8.3	0.06	0.68	2.33
4 MNP	8.7	0.07	0.82	2.18

Conclusion

The main goal of this study was to improve the HPLC method used to quantify the nitrophenolic by-products produced in the nitration of benzene. The challenge included measuring the mononitrophenol isomers and 2,6-dinitrophenol, at low concentrations levels, where quantification has been difficult in the past. The work carried out began with the selection of the HPLC column and optimization of the mobile phase. The composition of the new mobile phase, acetonitrile and aqueous potassium dihydrogen phosphate solution dramatically impacted the chromatography. Two eluent compositions were assessed: 50/50 (%v/%v, acetonitrile/aqu) and 30/70 (%v/%v), and the satisfactory identification, separation and quantification of the five nitrophenols in the samples were only achieved with the 30/70 (%v/%v) mixture. The best quantification of the analytes was obtained with a sample pH of 7.0. In spite of the improved performance of this HPLC method, it is important to note that the analysis time is now longer, although less than the 30 minutes, commonly considered as an acceptable limit. The use of an ultra-high pressure liquid chromatograph would undoubtedly result in a much lower analysis time. In addition to the improved chromatography, the new method also allows using a lower oven temperature (30 ºC), and a longer column lifetime is expected, in part due to the change in the eluent.

Acknowledgments

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Chapter 5

Improved Processes for the Recovery of Nitric and Sulfuric Acids from Nitration Plants

Manfred Pertler,[*] Gottfried Dichtl, Ulrich Walter,
Theo Hessenius, and Joachim Korbach

De Dietrich Process Systems GmbH (formerly: QVF Engineering GmbH),
55122 Mainz, Germany
[*]E-mail: MPertler@qvf.de. Web site: www.qvf.com

De Dietrich Process Systems has a long history in the recovery of nitric and sulfuric acids for all different types of nitration processes. Most of these recovery operations are tailor-made designs and provide the most efficient solutions to our customers. We fabricate the equipment needed for these operations from highly corrosion resistant borosilicate glass and glass-lined steel. An improved system to recycle acid in a DNT manufacturing facility is discussed.

Introduction

The QVF® BAT (Best Available Technology) allows the optimized concentration and recovery of combined spent acid recycle streams from a Dinitrotoluene (DNT) facility, specifically the spent DNT sulfuric acid (~70 wt% sulfuric acid), nitric acid (~ 1-2%) and the pre-concentrated acidic yellow water (from the first water wash of the DNT product).

A two distillation column process has been designed for acid recovery. The first column is fed with the combined recycle acid streams, where the nitric acid is almost completely separated from the spent sulfuric acid, to afford an overheads product of nitric acid of up to 99 wt% (weight percent). In the second column the remaining organics present in the spent sulfuric acid, such as MNT/DNT,

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are recovered by a highly efficient stripping process using live stream injection. The organics are steamed distilled overhead. The remaining sulfuric acid bottoms product (~83 wt% sulfuric acid) from this stripping column has a content of less than 10 ppm organics. This pre-concentrated sulfuric acid is concentrated up to 89 wt% or even above 97 wt%, in subsequent sulfuric acid concentration (S.A.C.) units and then re-used for nitration.

With this combined QVF® process, we tremendously reduce the operating energy costs (almost 30% less), lower cooling water consumption, and achieve lower investment costs, while also reducing fugitive emissions.

History of De Dietrich / QVF®

A pictorial history of the company is shown in Figure 1.

Figure 1. Since 1684 De Dietrich has designed industrial systems and products. (Courtesy of Manfred Pertler). (see color insert)

In 2000 De Dietrich acquired QVF Engineering GmbH including all the existing QVF® and SCHOTT® acid plant technologies. All former glass and process systems activities from Quickfit, QVF Corning, EIVS, SCHOTT Engineering and QVF Glastechnik are now concentrated in the De Dietrich Process Systems Group.

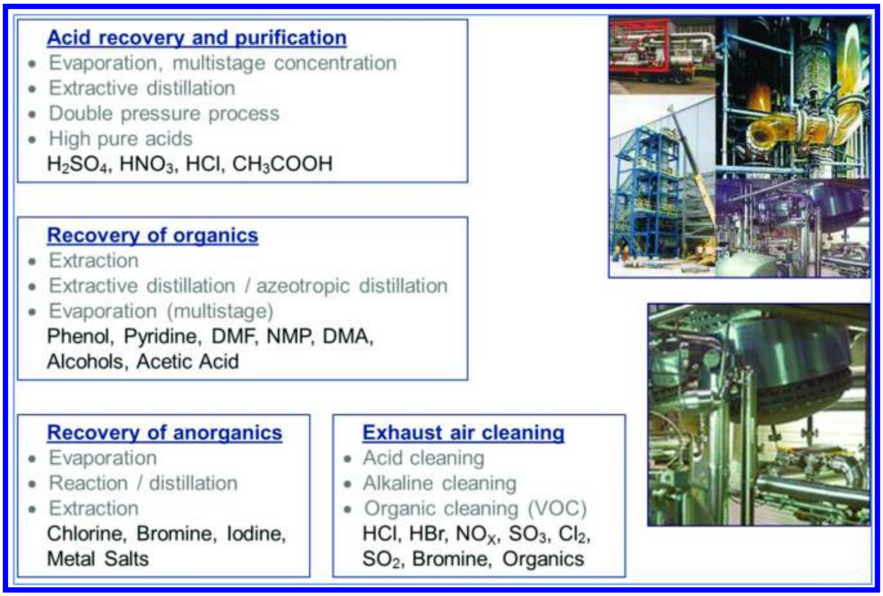
The photos shown in Figure 2 include De Dietrich® glass-lined equipment, Rosenmund® filter dryers, and a QVF® borosilicate glass column packed with the structured DURAPACK. These systems are used world-wide in highly corrosive applications. De Dietrich also provides service when called upon. In 2009, the year De Dietrich celebrated its 325th anniversary, all the De Dietrich subsidiaries worldwide, changed their names to De Dietrich Process Systems. Hence, QVF® has been established as a brand of De Dietrich Process Systems. De Dietrich Process Systems GmbH, Germany, has two main tasks worldwide: Borosilicate Glass and Process Systems design.

Figure 2. De Dietrich Process Systems Group. (Courtesy of Manfred Pertler). (see color insert)

Process Systems Expertise includes:

- development of in-house technology,
- reliance of De Dietrich patented technology,
- access to a comprehensive experience base in the industry,
- lastly, fabrication of equipment that is designed in-house, marrying the expertise of process design and materials of construction (Figure 3).

For the development and optimization of different process systems we use our own experimental facility, providing a full range of service from the feasibility study to commissioning of equipment, to after-market maintenance, on a global basis.



Acid recovery and purification
- Evaporation, multistage concentration
- Extractive distillation
- Double pressure process
- High pure acids

H_2SO_4, HNO_3, HCl, CH_3COOH

Recovery of organics
- Extraction
- Extractive distillation / azeotropic distillation
- Evaporation (multistage)

Phenol, Pyridine, DMF, NMP, DMA, Alcohols, Acetic Acid

Recovery of anorganics
- Evaporation
- Reaction / distillation
- Extraction

Chlorine, Bromine, Iodine, Metal Salts

Exhaust air cleaning
- Acid cleaning
- Alkaline cleaning
- Organic cleaning (VOC)

HCl, HBr, NO_X, SO_3, Cl_2, SO_2, Bromine, Organics

Figure 3. Process Systems Design and Process Expertise. (Courtesy of Manfred Pertler). (see color insert)

Recovery of Acids in a DNT Nitration Facility

The author assumes that the reader is familiar with DNT manufacture (*1*). The 1st generation process to treat weak spent sulfuric acid from DNT manufacture is shown in Figure 4.

This simplified flow sheet shows only the main units of operation of the process, namely the denitrification (DENI) column C1 and the nitric acid – pre-concentration (NA-PC) column C2. Both columns operate at atmospheric pressure. The subsequent S.A.C. stages as well as a NOx absorption unit, which are usually included in the full scope of the plant design, are not shown in Figure 4. The weak spent sulfuric acid (~70 wt%), containing nitric acid and according to the solubility a DNT content of 0.5 wt%, is fed into the denitrification column C1. Heat to the column is provided by a steam heated horizontal evaporator E1. DNT and nitric acid are taken off over-head of C1 and the sulfuric acid, now at 72 to 75 wt% H_2SO_4, leaves the evaporator and contains between 0.1 and 0.4 wt% DNT. The overheads are condensed in a condenser. The bulk of the condensed DNT is separated and recovered in a horizontal separator. The aqueous phase collected in the separator is then mixed with the acidic yellow wash water from the first water wash of the DNT product, containing 10-20 wt% nitric acid, 5-12 wt% sulphuric acid and < 0.5 wt% DNT. This mixture is fed to the NA-PC column C2. An energy penalty is paid for the condensation of the overheads to recover the DNT, as the nitric acid must be re-evaporated in the NA-PC (C2). The nitric acid and DNT are taken overhead of C2 and condensed. The condensate containing ~1 wt% nitric acid and less than 0.15 wt% of DNT is fed to an additional phase

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separator (not shown in Figure 4) before it is forwarded to waste water treatment or is reused as wash water.

This 1st generation technology only provided for about 80% recovery of the DNT in the feed to C1, complicating the operation of C2 and subsequent S.A.C. units. The bulk of the DNT is not stripped in C1 and remains in the effluent of the horizontal evaporator (E1).

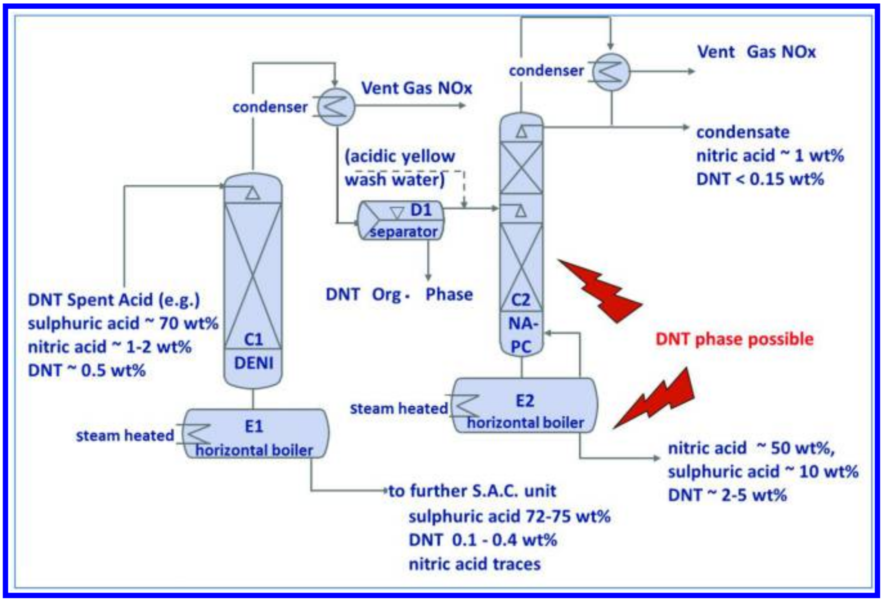

Figure 4. DENI / NA-PC: 1st Generation Acid Recovery Process Design for a DNT Manufacturing Facility. (Courtesy of Manfred Pertler). (see color insert)

The subsequent S.A.C. units concentrate the 72 to 75 wt% sulfuric acid from C1 (from E1) up to 89 or even above 97 wt%. These additional S.A.C.s are run under vacuum using cooled condensers. DNT can foul or even block the condensers. One way to overcome these issues is to add MNT to the S.A.C. overheads to keep the DNT from fouling the condensers.

There is almost no organic stripping inside of the NA-PC Column C2, so that the soluble DNT in the C2 feed, that does not leave the C2 overhead, leaves via the horizontal boiler E2 at the bottom of the C2. The concentration of DNT in the E2 effluent is between 2 and 5 wt%, together with ~50 wt% nitric acid, and ~ 10% sulfuric acid. The continuous increase of the DNT concentration inside of the C2 increases the risk that a second DNT phase or at least some small aggregated droplets of DNT could be established at the bottom of C2 or in the horizontal boiler E2. Under normal operating conditions, the temperature in the bottom of C2 and of E2 can be as high as 130 °C, especially if the sulfuric acid concentrations increase above 10 wt%. This is a temperature at which DNT can decompose, the consequences of which can be severe.

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The disadvantages of the 1st generation acid recovery process can be summarized as follows:

- inefficient stripping of DNT in C1 (only 80% of the DNT in the feed to C1 is taken overhead),
- risks with a DNT phase in the NA-PC C2, which can decompose,
- an additive (e.g. MNT) is needed to avoid fouling in the condensers in the S.A.C. units.

A first improvement to this system was made decade ago, which yielded to the 2nd generation acid recovery process, Figure 5.

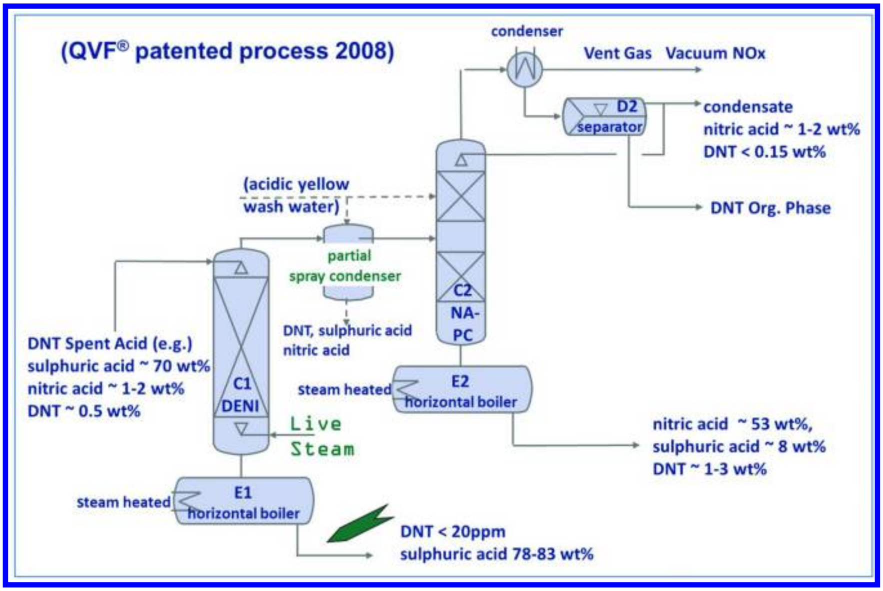

Figure 5. 2nd Generation Acid Recovery Unit for a DNT Nitration Process (Patent No. DE 10356499B3). (Courtesy of Manfred Pertler). (see color insert)

The main advantage of the 2nd generation process is that the vast majority of the DNT is stripped under vacuum conditions (380 mbar) out of the spent sulfuric acid using live steam injection in the first column C1 (Figure 5). Heat is provided to C1 with a steam heated horizontal heat exchanger (E1). The acid leaving E1 contains less that 20 ppm DNT. Since the acid leaving E1 (78 to 83 wt% H2SO4) is virtually devoid of DNT, there are no operational issues with the condensers in subsequent S.A.C. units and MNT does not need employed to prevent fouling by DNT deposits in condensers.

The partial spray condenser on top of C1 is fed with acidic yellow wash water to effect the partial condensation of a mixture of DNT, sulfuric acid and nitric acid. This aqueous condensate recovered from the condenser is sent back to the nitration, via a storage tank. The nitric acid and DNT that is not condensed then

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feeds the NA-PC column, C2. The DNT that is fed to C2 is partially removed over-head. The overheads product is composed of 1 to 2 wt% nitric acid and a small amount of DNT ~ 0.15 wt%. Since the NA-PC column C2 is also operated under the same vacuum conditions (~ 380 mbar), the temperature of the effluent of E2 is below 100 °C. The composition of the effluent is ~ 52 wt% nitric acid, ~ 8 wt% sulfuric acid, and 1-3 wt% DNT. The cooler temperature of the E2 effluent and the lower amounts of DNT in the effluent of E2 reduces the potential for the formation of a separate DNT phase and for the decomposition DNT, both of which are safety concerns.

The recovery of DNT in the acid recovery system is >95%, since the recovered sulfuric acid only contains less than 20 ppm DNT, and the condensate from C2 contains little DNT (1500ppm, water saturated with DNT).

To summarize the 2nd generation acid recovery system:

- high efficiency of DNT stripping is achieved,
- low operational cost since cooling water and steam consumption has been reduced,
- lower investment costs are achieved.

The best available acid recovery technology is the 3rd generation of QVF® DENI-S.A.C. process, where separate units for the recovery of nitric acid, sulfuric acid and condensate have been designed (Figure 6).

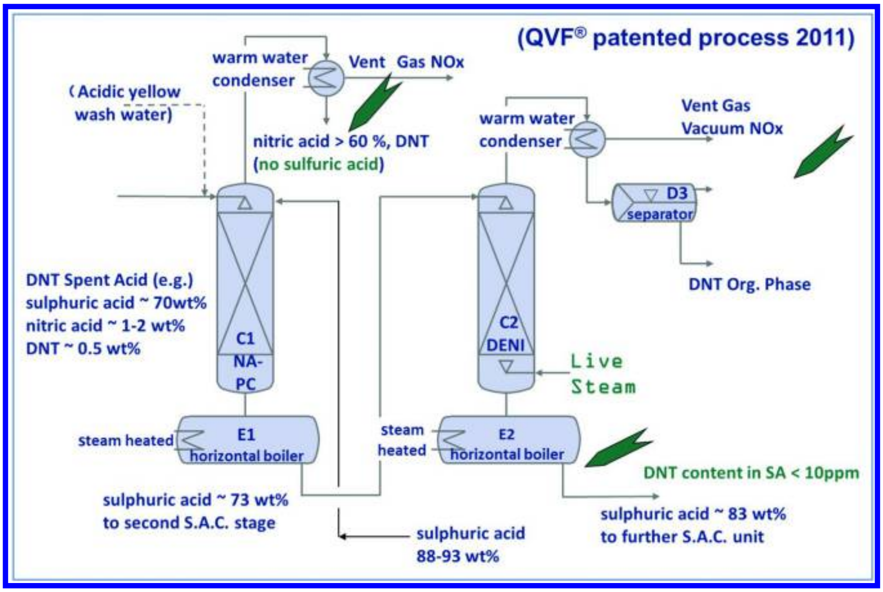

Figure 6. 3rd Generation Acid Recovery System (Best Available Technology) for a DNT Manufacturing Facility provided by QVF® (EP2295375A1; US Patent Application No. 13/395810). (Courtesy of Manfred Pertler). (see color insert)

C1 is fed with a mixture of spent sulphuric acid (~70 wt%), containing nitric acid (1-2 wt%), and DNT (< 0.5 wt%) and acidic yellow washing water. It is also fed 88 to 93 wt% H_2SO_4, so that more concentrated nitric acid can be obtained as an overheads product. The purpose of C1 is to strip-off all of nitric acid, and HNO_2, as well as a portion of the DNT that is present in the feed. This packed stripping column is operated at ambient pressure and is designed as a combined stripping and concentration unit operation. The overheads of C1 are condensed. The condenser is cooled with 55 °C water to avoid fouling of the condenser with solid DNT. The condensate is about 60 wt% nitric acid containing a small amount of DNT. This nitric acid can be used back in the nitration process.

The 60 wt% nitric acid collected overhead of C1 can be concentrated further in a N.A.C./S.A.C. (nitric acid concentrator/sulphuric acid concentrator) if desired.

The effluent of C1 still contains considerable amounts of DNT. It is composed of ~73 wt% H2SO4, traces of nitrogen species, and up to 4000 ppm DNT. This stream is fed to the C2, the denitrification column, run at 380 mbar. Live steam is injected into C2 to facilitate the removal of the DNT from the C2 feed. The flow of the live steam must be strictly controlled to strip the DNT and any MNT from the feed without overly diluting the system with water, resulting in a more dilute effluent from the bottom of C2. Heat is supplied to C2 with a steam heated horizontal evaporator (E2). The overheads of C2 is condensed in a condenser cooled with 55 °C cooling water, to protect against DNT fouling of the condenser. Condensate from the condenser of C2 is fed by gravimetric flow to liquid/liquid separator vessel D3 for separating organics from aqueous condensate. The organic rich phase is fed to a receiver vessel outside the battery limits for re-use in customer's nitration processes. The acidic aqueous phase from D3 is discharged to customer's waste water treatment system.

The effluent of E2 contains <10 ppm DNT and a maximum of 83 wt% H2SO4. This acid is fed to a third stage S.A.C. for further concentration (up to ~97 wt%). The low amounts of DNT in the E2 effluent protect down-stream equipment from fouling and the associated safety issues.

Technical Improvements of the Equipment

The equipment used in the 3rd generation acid recovery process utilizes the De Dietrich patented distributer and packing support CORE Tray® (Figure 7), and the optimized porous-free and highly corrosion-resistant structured DURAPACK® packing made from borosilicate glass (Figure 8).

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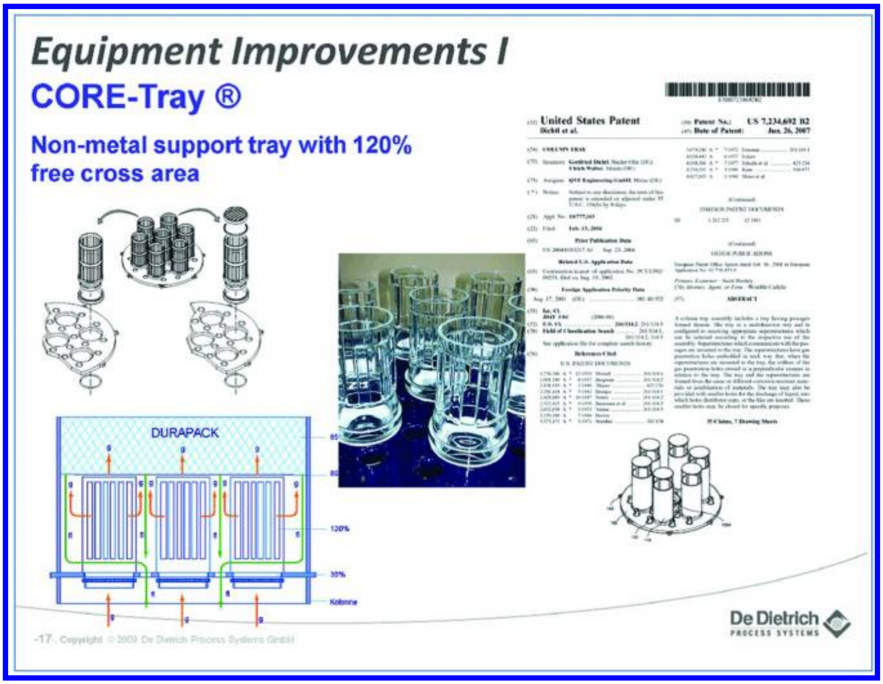

Equipment Improvements I

CORE-Tray ®

Non-metal support tray with 120% free cross area

United States Patent
Dichtl et al.
Patent No.: US 7,234,692 B2
Date of Patent: Jun. 26, 2007

Figure 7. Corrosion Resistant Tray (Patent No. US 7234692B2). (Courtesy of Manfred Pertler). (see color insert)

Equipment Improvement: DURAPACK

United States Patent
Dichtl et al.

Corrosion resistant structured packing made from Borosilicate Glass

300 m²/m³, fire polished, smooth surface

Figure 8. Corrosion-resistant Structured Packing (Patent No. US 6726188B2). (Courtesy of Manfred Pertler). (see color insert)

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Summary

Benefits of the 3rd generation of the QVF® acid recovery system are:

- efficient stripping of DNT from the recycle sulfuric acid to lower than 10 ppm,
- no separate nitric acid concentration unit requirement,
- nitric acid concentration up to 99% is possible if desired,
- minimal nitrogen containing species in the condensate of C2, simplifying water treatment,
- no sulfuric acid in the nitric acid overheads of C1,
- optimized design for capital and operation costs.

Plants with a capacity of up to 150 MT/hr (metric ton per hour) feed rates have been demonstrated by the De Dietrich Group. The entire process, from design engineering, equipment fabrication, and service can be offered from a single entity.

References

1. For the reader that is not familiar with the manufacture of DNT in mixed acid media, see Hermann, H.; Gebauer, J.; Konieczny, P. Industrial Nitration of Toluene to Dinitrotoluene: Requirements of a Modern Facility for the Production of Dinitrotoluene. In *Nitration: Recent Laboratory and Industrial Developments*; Albright, L. F., Carr, R. V. C., Schmitt, R. J., Eds.; ACS Symposium Series 623; American Chemical Society, Washington, DC, 1996; pp 234−249.

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Chapter 6

Nitration Technology for Aromatics As Described in the Patent Literature

Johannes Duehr*

Am Holzbruch 19, 47802 Krefeld, Germany
***E-mail: johannes.duehr@t-online.de**

Several trends in nitration technology have emerged as ascertained by examination of the patent literature. The adiabatic process has become state of the art for benzene nitration. Nitration waste water treatment has moved from extraction processes to thermal processes (for safety reasons). Though many patents claim adiabatic toluene nitration, analogous to the adiabatic nitration of benzene, most new dinitrotoluene plants continue to use isothermal processes; this is most likely to control isomer ratios and to avoid high temperatures for safety concerns. Several patents focus on the improvement of the washing area to isolate the byproducts as well as to recover nitric acid. The field of gas-phase nitration is active; however this process is not competitive with liquid-phase processes using sulfuric acid. The challenge remains to find an efficient catalyst for the gas-phase nitrations.

Introduction

The nitration of organic molecules has been practiced for almost 200 years. For example, the first nitration of the benzene molecule to mononitrobenzene (MNB) was recorded by Mitcherlich in 1834. Today MNB, mononitrotoluene (MNT), and dinitrotoluene (DNT) have become versatile precursors to many other commodity chemicals such as aniline which is used to produce dyes, rubber chemicals, and polyurethanes.

The production of these nitrated species continues to increase to meet market needs. There has been a continuous effort to improve the nitration processes during

In Chemistry, Process Design, and Safety for the Nitration Industry; Guggenheim, T.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2013.

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the periods of growth. The process development has focused on safety concerns, economical aspects (costs), and environmental challenges.

The number of patents in the field of nitration is large. The most relevant were selected to review here, and in particular the industrially relevant patents related to MNB and MNT/DNT technologies will be emphasized. This paper discusses how these patents have shaped the current MNB and MNT/DNT industries, and what they suggest for future process trends. These are very high volume products and are mostly feed materials for the production of polyurethanes.

Process Overview and Trend Areas for MNB and MNT/DNT

The methods to manufacture these materials are comprised essentially of the same major process steps, as shown in Figure 1.

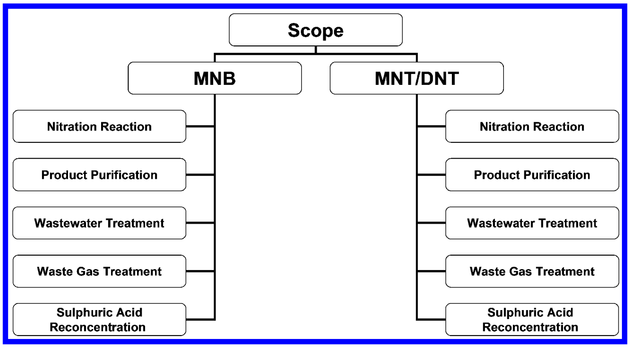

Figure 1. Scope and Definition of the Trend Areas.

The first step is the nitration reaction, which provides the crude product. The reaction is followed by a product purification process, which involves a liquid-liquid extraction step of the organic product phase with a water or basic aqueous wash. The aqueous extract must be treated before discharge to the environment; the quality of the discharged water must meet strict purity specifications as mandated by governmental agencies. Similarly, the vent gases from the plant have to be treated. In most cases, where a mixture of sulfuric acid and nitric acid are used as the nitrating media, the spent acid is diluted by the water created in the reaction, and must be reconcentrated before being fed back to the nitration step.

The author has assumed that the reader is familiar with the basic chemistry and process engineering for the mixed acid nitration of benzene and toluene to afford nitrobenzene and MNT/DNT, respectively (*1*).

Patents

The patents reviewed tend to focus in a particular key area. Some focus on heat integration, using the reaction enthalpy to supply the energy demand for reconcentrating spent sulfuric acid. Other patents focus on lowering by-product formation, such as nitrophenols, nitrocresols, dinitrobenzene (DNB), and in some cases DNT. Some patents show methods of maximizing favorable ratios of desired isomeric products. There are also patents concerning the reduction of emissions, and there are others which describe gas-phase nitration technology.

Summary of Patents Related to the Nitration of Benzene

A review of the patent literature for MNB production suggests that the adiabatic nitration process has almost completely replaced the isothermal process, making the adiabatic reaction the state of the art. The first full-scale plants for adiabatic mixed acid (sulphuric acid and nitric acid) nitration of benzene to produce MNB were constructed in the U.S. in the late 1970's and were equipped with cascades of stirred reactor vessels. The flow of the reaction media in the reactors was upwards so that the discharge from the reactors was under lower pressure. The nitration vessels were pressurized with nitrogen to avoid evaporation of residual benzene at the higher temperatures present at the tail end of the reaction vessel train.

The concept of the continuous MNB process was first presented by Castner (*2*) and further refined by Alexanderson et al. (*3*, *4*). The reaction rate of nitration of benzene with nitric acid is limited by mass transfer. The reaction itself occurs at the surface of the organic (benzene) droplets as nitric acid reaches the interface between the mixed acid phase and the organic phase. The surface area, over which the reaction takes place, is maximized by creating an emulsion between the mixed acid continuous phase and the organic (benzene) dispersed phase as small droplets.

A design of a mixing device for a plug flow reactor was described by Evans (*5*), with the intention to increase the interfacial surface area between the mixed acid and organic phases using high shear forces and turbulence. An aromatic substrate and/or mixed acid can be forced through an annulus to form fine droplets of each phase when the substrate and mixed acid are contacted with one another in a reaction chamber.

Guenkel et al. (*6*) claim a nitration feed condition, for the concentration of nitric acid in the mixed acid, which is outside the operating range previously mentioned in the literature. Maintaining the nitric acid concentration below 3% favours the complete dissociation of nitric acid to nitronium ions and thus accelerates the reaction rate. Mixing elements are used to generate a fine emulsion of organic droplets in the mixed acid. Thus the mass transfer is enhanced and the overall reaction rate increases. A significant benefit of the rate increase was that the desired nitration reaction was favoured and the production of impurities was minimized. An additional advantage of these operating conditions was improved safety due to lower operating temperatures and lower nitric acid concentrations. The reactor type was a plug flow reactor.

The invention of Larbig (*7*) relates to a process for treating the basic aqueous extracts from the nitrated product washing step that contains nitrophenolic compounds. The nitrophenolics are dissolved in the water as their corresponding phenate salts. These salts are bactericides and cannot be released untreated into a conventional biological plant. Larbig claimed a process to treat the effluent water under pressure at temperatures above 170 °C resulting in the decomposition of

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the nitrophenolics to carboxylic acids, which can then be successfully treated in a subsequent biological wastewater treatment plant. The treatment is done in a liquid filled system without the addition of air.

Lailach et al. (*8*) published a patent for a SAC (sulfuric acid concentration) plant in an isothermal nitration plant, using a horizontal evaporator using a steam heated exchanger constructed with tantalum. The evaporator is operated under vacuum conditions.

Rae et al. (*9*) introduced a plug flow reactor with built-in devices to form and regenerate the organic droplets in an emulsion from mixed acid and organics. The reactor has been called the jet impingement reactor, because of the formation of jet streams which impinge at a wall to afford fine droplets of the dispersed phase.

McCall (*10*) describes another technology to use the heat of the nitration reaction in the process. Benzene was vaporized and fed to the nitration reactor along with the mixed acid, where the reaction takes place in the liquid phase at a temperature of about 120 – 160 °C. The heat of reaction is used to evaporate the water formed in the reaction as well as the excess benzene as an azeotropic vapour phase. The reaction resembles an adiabatic process. The vapour leaving the reactor is condensed. The condensate forms 2 phases, a lighter benzene phase and a water phase.

Gas-phase Nitration is the subject of the patent of Sato et al. (*11*). It is only one example of numerous patents describing a gas-phase nitration. The motivation to switch to gas-phase nitration is to avoid the large quantities of waste sulfuric acid generated in a mixed acid nitration. The nitrating agents are nitrogen oxides NO_2 or N_2O_4. The reaction occurs in the presence of a solid catalyst comprised of acidic mixed oxides such as WO_3, MO_3, TiO_2 and optionally SiO_2 or ZnO. Other patents of Sato mention catalysts comprised of acidic clay minerals ion exchanged with polyvalent metals. The process has been tested on a laboratory scale.

Brereton et al. (*12*) integrated the vent gas treatment with the nitration plant. He describes a pressurised absorption column for NOx gases to produce a weak nitric acid which is recycled to the reactor as a separate feed. Thus the yield of nitric acid can be improved. The NOx content remaining in the vent gas is small, and in some instances can be discharged without further treatment. If organic is present in the gas stream off the adsorption column, then the stream can be sent to a volatile organic oxidizer before being discharged to the atmosphere.

Hermann et al. (*13*) describe a mixing apparatus used to mix nitric acid, sulphuric acid and an aromatic organic to achieve a rotating main flow in a central mixing tube at the entrance region of the reactor to form an emulsion.

Gillis et al. (*14*) present a tubular plug flow reactor for nitration having built-in static mixing elements separated by coalescing zones. The mixing elements provide for efficient nitration in a two-phase system (organic and mixed acid) due to the formation of small droplets in the mixing zones. It is claimed that lower levels of impurities result in this process configuration.

Knauf et al. (*15*) claim the use of an electrophoresis device to facilitate the separation of organics from the wash water. The washed organic phase is passed through an electric field created by the electrophoresis device. The organics still contain small droplets of conductive water which are electrically charged and migrate to charged metal plates where they coagulate and can be separated. The

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purity of the organic product can be improved. This is an electrostatic coalesce of sorts.

Boyd (*16*) describes a method to treat waste water from mixed acid nitration. A concentrated alkaline aqueous extract of the organic product, containing dissolved sodium nitrophenates is treated in a process involving supercritical water oxidation.

Eiermann et al. (*17*) describes a liquid phase nitration of an aromatic hydrocarbon using NOx and oxygen gas in the presence of a heterogeneous oxide catalyst, in the presence of at least 0.1 mol% water (with respect to the aromatic hydrocarbon). Use of the catalyst in the liquid phase reaction avoids the corrosive medium of hot sulfuric acid.

Berretta (*18*) defines other process conditions for the adiabatic reaction to form MNB in mixed acid media. A process is claimed wherein the nitric acid concentrations is kept as low as reasonably possible (less than 3% in the mixed acid), and to start the reaction at a low temperature (60°C – 96°C). The temperature rise in the reactor is limited to about 20°C. Limiting the temperature was the main factor identified that limited the formation of the typical by-products (<1200 ppm of nitrophenolics, < 80 ppm dinitrobenzene).

Berretta (*19*) describes a process to reduce the amount of dinitrobenzene formed in the adiabatic nitration of benzene in a plug flow reactor. Sulfuric acid and benzene are fed to the front end of the tubular reactor. The nitric acid is fed into the reactor at multiple points. Some of the nitric acid is combined with the incoming sulphuric acid, and the balance of the nitric acid is fed a one, two, or more points further down the reactor. Splitting the nitric acid feed in this manner results in less DNB formation.

Gattrell (*20*) describes a wet air oxidation method to treat wastewater generated in the manufacture of nitrated aromatic hydrocarbons in mixed acid media. Wastewater containing nitrophenolic by-products containing at least three equivalents of sodium hydroxide with respect to the total amount of nitrophenolic compounds was heated in a reactor at 300 °C at ~450 psig for 90 minutes to provide a water effluent that was amenable to convention biological wastewater treatment.

Berretta (*21*) teaches a method to treat a nitrobenzene product, that has already been washed with water and with alkaline water, with an acidic wash water with a pH of <6. The acid used to acidify the water is typically nitric acid, but other acids are described. The washed product is then fed to a stripper column or distillation column to remove the volatile acid, the starting organic reactant, and some of the neutralized by-products, to ultimately afford a more pure product.

Summary of Patents Related to the Nitration of Toluene

The major difference between the mixed acid nitration of toluene and the mixed nitration of benzene is that the process to nitrate toluene, to produce mono and dinitrated products, is commercially practiced using isothermal reaction systems. Adiabatic systems, however, are described in the patent literature.

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Hoek (*22*) describes a process for the manufacture of trinitrotoluene (TNT), executing the reaction in 3 steps (from toluene to MNT, MNT to DNT, DNT to TNT). The reactions were done in a batch mode, but a continuous system is also described.

Rowland (*23*) patented improvements for the continuous nitration process for the production of MNT in a first step, and DNT from MNT in a second step. Thus he could influence the isomer ratio in the product in favour of the 2,4-DNT isomer.

Samuelsen (*24*) patented a continuous isothermal nitration process of toluene using an arrangement of several stirred tank reactors by feeding toluene in a counter-current fashion with a nitrating agent (typically a mixed acid system of sulfuric acid and nitric acid). NOx recovery was integrated into the process by conveying NOx streams back to the reactors.

Milligan et al. (*25*) describe an improved method to purify the spent acid from the manufacture of DNT in three steps. The first step involves treating the acid that had been separated from the product with an oxidizing agent (such as hydrogen peroxide) to convert nitrous acid to nitric acid. Nitrous acid content in the recycled sulfuric acid was linked to the color of the DNT product. The treated sulfuric acid was then extracted with the toluene feed to remove the nitric acid. Finally, the sulfuric acid was again treated with an oxidizing agent to destroy residual organics present in the acid.

Gerken et al. (*26*) describe a fully-integrated SAC unit for the isothermal two-step nitration of toluene to form MNT and DNT. The sulfuric acid is fed to the process in a counter current manner, from the DNT stage to the MNT stage. The acid leaving the MNT nitration section of the plant is then fed to a horizontal evaporator, equipped with a steam-heated reboiler (tube and shell). The evaporator is run under vacuum (40 to 100 mbar) at 170 to 185 °C. The overheads of the evaporator contain mostly water, MNT and DNT. The oveerheads is condensed. Because of the low temperature of the coolant on the condenser, the 2,4-DNT can crystallize in the condenser, impairing the heat transfer or even plugging the equipment. This can be avoided by injecting MNT or a mixture of MNT/DNT, preferably from the mono nitration step, into the evaporator or directly into the vapour off the evaporator prior to the condenser. The DNT is kept in solution at the condensation temperature.

Adams (*27*) et al. claim a solvent extraction method to recover nitrophenolic by-products from the wash water. This is accomplised by adjusting the pH of the waste water according to the distribution coefficients of the by-products so that extraction can be done selectively. For example, the basic wash water from a nitrobenzene facility contains trace nitrobenzene and polynitrated phenolics, such as dinitro- and tri-nitrophenol. The basic wash water is extracted with a hydrocarbon solvent to remove nitrobenzene. The pH of the basic water can be adjusted to 2 to 3 with sulfuric acid, and then extracted with ethylbenzene to recover high purity marketable dinitrophenol, after removal of the ethylbenzene. The aqueous phase can then further be acidified with sulfuric acid to a pH of 0.8 to 1.2, and again extracted with a hydrocarbon solvent. The hydrocarbon solvent is removed to afford picric acid with a purity of 99%.

Quakenbush (*28*) described the reaction between toluene and nitric acid in the liquid phase, and in the presence of a selected hydrated nitrate metal

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salt. Sulfuric acid is not used. The molar ratio of toluene:HNO_3:metal salt was approximately 1.0:20.0:0.9. An example of the hydrated nitrate system was a mixture of $Mg(NO_3)_2$ and $Zn(NO_3)_2$. Nitration in the presence of the metal salt reduced the shock sensitivity of the product reaction mixture. The reactor had to be cooled to control the heat of reaction. The process used a large excess of nitric acid (20 moles HNO_3 per mole of toluene). The formation of phenolic by-products was minimized in this process, and was less than 350 ppm in total.

Mason (*29*) describes a process for producing DNT in the liquid phase using anhydrous nitric acid and toluene at low reaction temperatures but without using the hydrated nitrate salts. The product is free from nitrocresols.

Schieb et al. (*30*) propose one single adiabatic step to produce DNT where the reaction heat is used to reconcentrate the spent acid.

Schieb's invention was elaborated by Klingler et al. (*31*). Toluene is nitrated in mixed acid media using weak nitric acid in sulfuric acid to afford MNT in an adiabatic process. The acid and MNT are separated in a decanter. The acid is sent to a flash unit to remove a portion of water. Strong nitric acid is then added to the effluent acid from the flash vessel. This mixed acid is then contacted with the MNT product from the first stage nitration in a second nitration reaction vessel. The reaction mixture from the second stage nitrator is sent to a decanter. The acid phase from the decanter is sent to another flash unit and a portion of water is removed overhead and condensed. The overheads contain DNT. MNT is added to the vapour stream to avoid fouling of the condenser off the second flash unit.

Hermann et al. (*32*) optimize the recovery of acids in the washing area of DNT manufacture. He describes a counter current flow of diluted aqueous solution containing nitric, sulfuric, and nitrous acid against the flow of crude DNT product. The resulting aqueous extract can be fed directly back to the nitration vessel, or concentrated first and then returned to the nitration vessel.

Zhang et al. (*33*) describe the manufacture of DNT in a nitric only process. Toluene is fed to a loop reactor along with 65 to 75 wt% nitric acid at 35 to 65 °C, with a short contact period to afford a solution of MNT in nitric acid. The ratio of acid to organic is 20:1 to 30:1. The solution is cooled in a separator to <30 °C to provide an organic product phase and an acid phase. The acid phase is recycled back to the loop reactor with fresh acid. The MNT phase is then fed to a second continuously stirred tank reactor (CSTR) loop reactor along with ~94 wt% nitric acid at 30 to 65 °C. The second nitration reaction mixture is then treated with an alkali metal nitrate to effect phase separation of the product from the acid phase (see Mason, R.W., US Patent 5,001,272). The product phase is then purified in the conventional manner.

The Klingler et al. (*34*, *35*) patented aspects of the adiabatic mononitration/dinitration of toluene in mixed acid media. In one example toluene is nitrated in a continuous single nitration step to afford DNT that contains residual MNT. The molar ratio of HNO_3:toluene is about 1.9:1.0. The heat of nitration and optionally additional heat is used to distill a porton of the water present from the reaction mixture. The presence of MNT in the overheads prevents fouling of the condenser. Additional nitric acid can then be added to the reaction mass, to convert any residual MNT to DNT, before separation of the organic product phase from the acid phase in a separation vessel.

Münnig et al. (*36*, *37*) combine the alkaline and the acidic water streams resulting from the washing of a nitrated aromatic, along with the aqueous condensate from the SAC. The pH of the combined stream is adjusted to 5. The organic present in the combined aqueous solution is allowed to settle as a separate phase and removed. This combined aqueous stream is then extracted with toluene. The toluene extracts nitrophenolics, MNT, and DNT. The toluene phase is then fed to the first nitration reactor.

Hermann et al. (*38*) describe a process to remove and to recover all acids and NOx from a crude nitrated aromatic product by means of a continuous extraction process using a cross current washing process coupled with a counter current multistage extraction process. Simplistically, the nitration mixture is allowed to phase separate to provide an organic product phase and an acid phase (composed of sulfuric acid, residual nitric acid, dissolved to produce concentrated sulfuric acid, which is sent back to nitration. The organic phase is then washed with water in a cross current process in a stirred tank and the resulting emulsion is sent to a settler. The organic phase from the settler is washed again with water in a cross current manner in another stirred tank. The emulsion from this stirred tank is sent to another settler where the organic and aqueous phases separate. The wash waters from the settlers can either feed the SAC unit or be sent directly back to nitration. The organic product from the last settler is then washed in a conventional counter current manner. Vent gases from the wash vessels is sent to a NOx scrubbing unit to recover the NOx as dilute nitric acid, which can then be sent back to nitration.

Fritz et al. (*39*) describes an electrolytic cell to treat the alkaline waste water from washing a nitrated aromatic product. In one example, the anode compartment of an electrolytic cell was charged batch-wise with the 100 mL of brown basic water from washing of a nitrated product that was composed of 1.5 g/L of $NaNO_2$, 20 g/L of Na_2CO_3, 10 mg/L of MNT, 1 g/L of DNT, and 0.5 g/L of picric acid, with a chemical oxygen demand of 6500 mg/L. The cathode compartment was charged with 1M sodium hydroxide. Current was passed through the cell for 4 hours at 60 °C. The majority of the organic material was electrochemically oxidized to afford a clear aqueous phase, the chemical oxygen demand of which was 150 mg/L.

Bae et al. (*40*) claim mixing the alkaline and acidic water washes produced during the purification of MNB or DNT with the condensate from a SAC unit. The resulting solution is pH adjusted to <5 and cooled to <50 °C. Any nitroaromatic that phase separates from the cooled aqueous phase is recovered. The water phase is then concentrated by vacuum distillation, and the bottoms product is incinerated.

Denissen et al. (*41*) describe methods for continuously preparing a mononitrated aromatic, such as MNB, in an adiabatic process. A plug flow reactor design is described that employs internal mixing elements.

Mackenroth et al. (*42*) describe the nitration of aromatic hydrocarbons (toluene and benzene) using aqueous metal nitrates as the nitrating media at ~100 °C, wherein the metal is in the +3 oxidation state, $M(NO_2)_3$. The molar ratio of water to metal nitrate salt is on the order of 4:1 to 9:1. Sulfuric acid is not used in the process. Nitric acid can also be added to the metal nitrate media to effect the desired nitration reaction.

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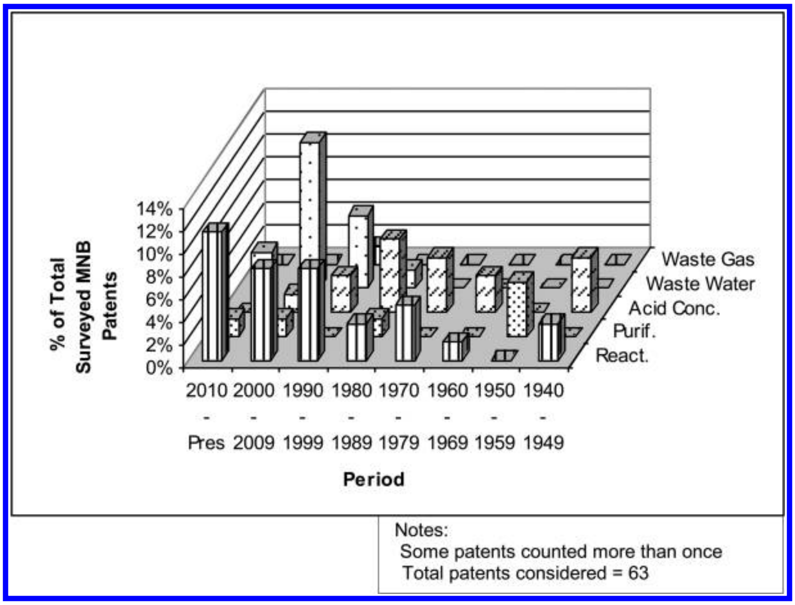
The patents reviewed above are a selection of a large number of published patents. The author selected the patents above to review, taking into account their novelty and relevance to the nitration industry.

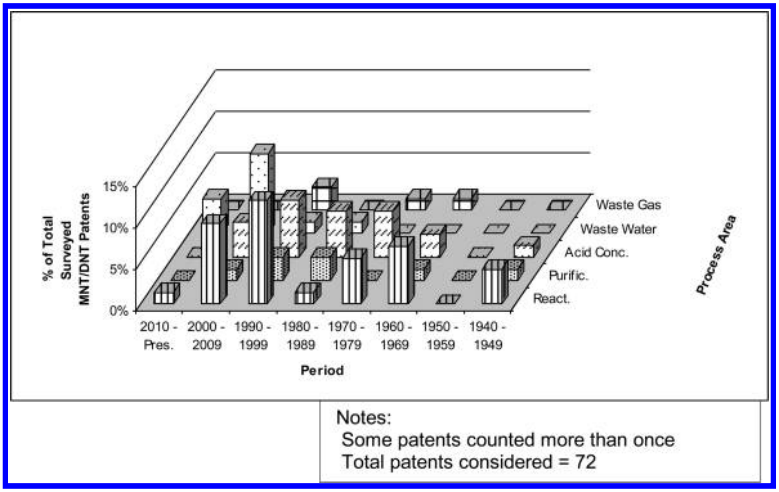
Trends

The histograms in Figure 2 (benzene nitration) and in Figure 3 (toluene nitration) give the patent frequency over the years by assigned process areas.



Notes:
Some patents counted more than once
Total patents considered = 63

Figure 2. Patent Frequency by Area - Nitration of Benzene.



Notes:
Some patents counted more than once
Total patents considered = 72

Figure 3. Patent Frequency by Area - Nitration of Toluene.

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Analysis

There is a recent spike in patent activity for the nitration of benzene. Gas phase reaction technology has been a relatively active area of study since the 1940's, peaking around the 70's to 80's, and declining since. This decline may be due to the emergence of adiabatic processes. SAC technology patents are numerous in the 70's to 80's. Waste water treatment patents peaked between 2000 and 2009. Reaction patents are numerous in the last 3 decades, following the trend to conduct the reactions adiabatically.

There are a few waste gas treatment related patents. This could potentially change, as more strict NOx regulations are on the horizon globally.

The patents surveyed concern the manufacture of MNB, MNT/DNT or both. Most patents are from companies that have been making these products for many years. There are few patents from small independent companies.

Summary

Following the historic development of the nitration technology over time as described in the patent literature, one can state the following:

- The adiabatic process has become state of the art for benzene nitration.
- Waste water treatment technologies are moving from extraction processes to thermal processes (for safety reasons).
- There are many patents claiming adiabatic processes for the nitration of toluene. However, to the author's knowledge, new plants are still designed using isothermal processes. The reason may be in the shift of isomer ratios or because of safety concerns that come with higher operating temperatures.
- Some patents focus on improvement of the washing area to isolate the by-products as well as to recover nitric acid.
- The field of gas-phase nitration has some activity, but to date is not competitive with the liquid-phase process using sulfuric acid. It is still a challenge to find a convenient catalyst to assist in gas-phase nitration.

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Chapter 7

Advances in Water Treatment of Effluents fromMononitrobenzene (MNB) Production Facilities

Steven Buchi,*,[1] Sergio Berretta,[2] and Tony Boyd[1]

[1]NORAM Engineering and Constructors Ltd., Vancouver, B.C., Canada
[2]B.C. Research Institute, Burnaby, B.C., Canada
***E-mail: sbuchi@noram-eng.com**

Nitrophenolic compounds are formed as by-products in the industrial production of MNB. Normally, these by-products must be removed from the product MNB and end up in the water effluent of industrial facilities. These compounds are bio-toxic and must be treated before the effluent is discharged to a biological treatment facility or the environment. A short list of treatment options includes the following proven technologies, representing current industrial best practices: thermal destruction, wet oxidation, ozonation, solvent extraction, and incineration. Biological treatment is a secondary treatment step for further purification of aqueous waste streams. The above technologies are used by different MNB manufacturers, but no comparative analysis of these technologies is available in the open literature. In this paper, the authors try to fill this void by presenting a comparison of these treatment options, using public literature, with reference to three main criteria: ability to meet current environmental standards, economic targets, and process robustness.

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Introduction

In the production of Mononitrobenzene (MNB), as with many other nitrations of aromatic compounds, nitrophenolic species are formed as a by-product of the nitration reaction. In the case of industrial MNB production these are predominantly di-nitrophenols but the mono- and tri- (more commonly known as picric acid) nitrophenol isomeric species are also formed to some degree.

Typically, these nitrophenolic by-products need to be removed prior to the MNB being processed in the downstream processes. This is achieved by contacting the crude MNB with an alkaline water stream in a multi-stage counter-current washing system. The nitrophenols, which are organic acids, are neutralized and extracted into the alkaline water phase. This nitrophenol rich water effluent stream is generally known as “strong effluent” or “red water”.

In most MNB plants, caustic soda is used as the washing base to provide the required alkalinity, although ammonia is also used. The drawbacks to using ammonia are that it is a weaker base than caustic and as such results in an inferior washing efficiency. Also ammonia introduces the possibility of forming unstable ammonium nitrate/nitrite salts which require experience and careful system design to ensure a safe and reliable plant. However, ammonia is preferred as the washing base if incineration is chosen as the strong effluent treatment option, which is discussed later.

Nitrophenols are bio-toxic and therefore this effluent stream normally necessitates pre-treatment to reduce its toxicity before it can be discharged to a biological treatment facility or to the environment.

There are several different strong effluent treatment technologies currently available and practiced industrially, with the preferred treatment technology often dictated by site-specific conditions and clients’ preference. The objective of this paper is to provide a comparative analysis of the different effluent treatment technologies with regards to capability to meet current environmental standards, economic targets, and process robustness.

Background

Thermal Destruction

Thermal destruction (*1*) is the process whereby the aromatic ring of the nitrophenol molecule is thermally cracked at elevated temperature and pressure in the absence of oxygen. The process operates at sub-critical conditions with a temperature of approximately 540 °F to 640 °F (280 °C to 340 °C) and at a sufficient pressure to ensure that the water effluent remains in the liquid state. Under these conditions, and given sufficient residence time, the nitrophenols are broken down into short chain hydrocarbons, mostly comprised of organic acids. Nitrogen bound to the nitrophenols is typically converted to ammonia (NH_3) as well as some amount of nitrate/nitrite (NO_3^-/NO_2^-). Figure 1 below is a graphical representation of the process.

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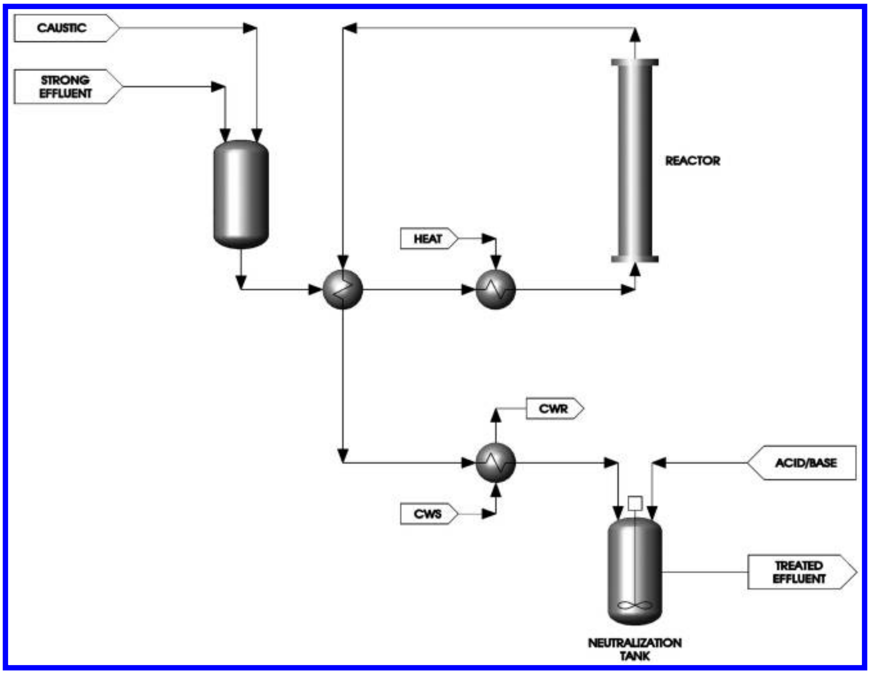

Figure 1. Simplified Schematic of the Thermal Destruction Process.

In general, the use of thermal destruction in the treatment of strong effluent does not lead to an effluent suitable for discharge into the environment. However, it sufficiently destroys the nitrophenols, reducing the bio-toxicity to a level that the effluent can subsequently be treated in a biological treatment facility. It should be noted that even though this technology reduces the toxicity of the effluent, the Chemical Oxygen Demand (COD) and total nitrogen (TN) of the effluent remains largely unchanged. Depending on the allowable discharge limits of nitrogen species and the capability of the downstream biological treatment plant a denitrification step may be required.

Two companies have developed and offer competing thermal destruction technologies. These two technologies are in operation in several nitration plants with proven safety records. With the many years of cumulative operating time (>100 years), there has only been one safety incident that has been reported involving a Thermal Destruction process. The design of the involved thermal destruction technology has subsequently been improved to increase the layers of protection against the process upset that led to the event.

Operating costs of thermal destruction units are relatively low as heat integration allows for almost complete energy recovery.

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Wet Oxidation

In Wet Oxidation (*2*), the strong effluent is oxidized by the addition of air or oxygen under sub-critical conditions. The process operates under conditions similar to Thermal Destruction; that is, at high temperatures (between 540 °F and 640 °F) and at a pressure to ensure the effluent remains in liquid state. The addition of an oxidant helps to oxidize the higher molecular weight compounds into lower molecular weight molecules and thereby reduces the COD of the treated effluent. Also, due to the oxidizing environment, the nitrogen bound to the nitrophenols is expected to form mostly nitrate/nitrite (NO_3^-/NO_2^-).

Following the Wet Oxidation Reactor the treated liquid is sent to a flash drum where the excess air/oxygen is separated from the liquid effluent. The resulting off-gas typically requires further treatment with the normal method being a thermal oxidizer or flare. Figure 2 below is a graphical representation of the process.

This technology should in principle produce an effluent which does not need further treatment for denitrification and COD reduction. However, in practice the COD reduction is generally lower than 80%. Therefore, further biological treatment is usually required, although the loading will be much smaller than that of the effluent treated by the Thermal Destruction process.

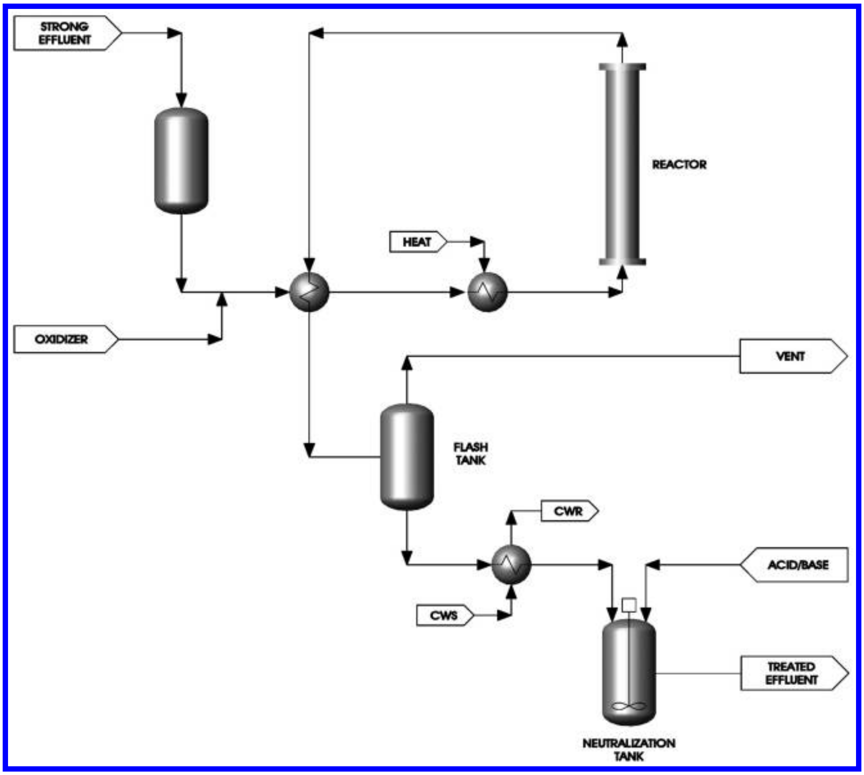

Figure 2. Simplified Schematic of the Wet Oxidation Process.

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As opposed to Thermal Destruction, the Wet Oxidation process is normally carried out under fairly acidic conditions. Therefore, the use of expensive materials of construction is required, which results in a relatively high capital cost.

Wet Oxidation is currently being used to treat strong effluent from at least one nitration plant in Europe. This process has similar safety concerns as with Thermal Destruction. An additional potential operating problem experienced with this technology is the formation of scaling due to precipitation of inorganic salts.

Partial Wet Oxidation (*3*), a variation to full Wet Oxidation, is a new technology which has been piloted in the treatment of strong effluent, but has yet to be commercialized. This technology attempts to gain some of the benefit of reducing COD with air/oxygen addition while minimizing the aggressive operating conditions such that less expensive materials of construction can be used.

Solvent Extraction

Solvent Extraction (*4*) involves first acidifying the strong effluent to precipitate the dissolved nitrophenolate salts in the strong effluent as their conjugate organic acids. The free organic nitrophenols are then extracted by contacting the aqueous effluent stream with an organic solvent, typically toluene, which has a very low solubility in water. The aqueous effluent and organic solvent streams are then separated. The water stream, saturated with the extracting solvent, is then stripped to remove and return the solvent back to the extraction step. The resulting effluent stream still contains significant amounts of COD, mainly as toluene, such that direct discharge to the environment is not possible and additional treatment in the form of a biological system or activated carbon beds is required.

The extracting solvent, laden with nitrophenols, is sent to an evaporator where the majority of the solvent is recovered. Complete solvent recovery is not practical as nitrophenols will reach the solubility limit, precipitate and solidify which causes operational and safety concerns. This concentrated nitrophenol stream is considered a fuel and as such it is incinerated with negligible energy disposal costs. Figure 3 below is a graphical representation of the process.

Solvent Extraction is known to be currently used to treat strong effluent from at least two nitration plants on the US Gulf Coast.

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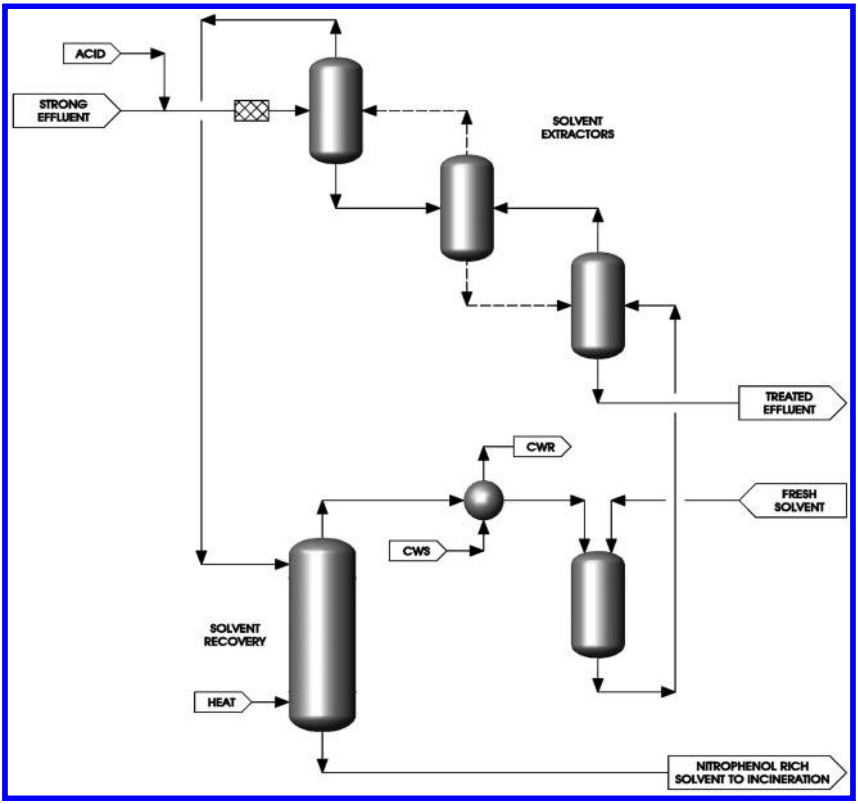

Figure 3. Simplified Schematic of the Solvent Extraction Process.

Ozonation

Ozonation (*5*) is a process where the strong nitrophenol effluent is contacted with ozone to oxidize and degrade organic compounds. The resulting effluent contains significant levels of carbonate (CO_3^{-2}), nitrate (NO_3^-) and nitrite (NO_2^-). The process operates at a temperature of approximately 140 °F (60 °C). The COD of the stream is low and aromatic compounds are decomposed to very low levels. However, depending on allowable nitrogen limits, the effluent may require a denitrification step downstream of the ozonation unit.

Gas generated in the process contains small quantities of ozone and therefore needs further treatment prior to being vented to the atmosphere. A thermal oxidizer or flare to handle this small gas stream is the preferred treatment option.

Due to the relatively rapid decomposition of ozone, it is typically necessary to generate the ozone at site using ozonators. Either dry air or oxygen can be used as a feed to the ozonators with oxygen increasing the efficiency of the generator. Figure 4 below is a graphical representation of the process.

Ozonation is known to be currently practiced in at least two nitration plants on the US Gulf Coast.

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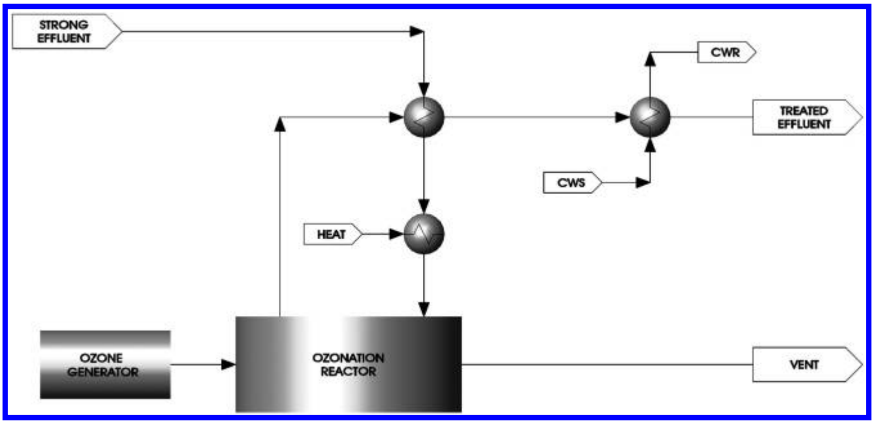

Figure 4. Simplified Schematic of the Ozonation Process.

Incineration

Incineration (*6*) is a well-established process and is capable of treating many industrial wastes including solids, liquids, sludges and gaseous waste streams. In general, incinerators are considered off-the-shelf equipment with designs ranging from a simple one stage incinerator to more complex arrangements including recovery boilers to achieve better energy efficiency and flue gas scrubbers to remove acid gases prior to discharge to atmosphere.

Chemicals within the waste streams are thermally decomposed to their primary combustion products of carbon dioxide, water and ash. At temperatures of 1300 °F (700 °C), most chemicals are broken down into lower molecular weight compounds, and at temperatures of 1800 °F (1000 °C), nearly all wastes are fully oxidized.

Nitrogen containing species should, in theory, be reduced to form N_2; however, in practice small amounts of NOx gases are present. However, the NOx concentration should be below most regulatory emission levels. Sulfur compounds in the strong effluent, such as sulfate, produce sulfur oxides (SOx) in the incinerator. As a result, an acidic wash of the crude MNB can be done prior to extracting the nitrophenols into the strong effluent to reduce sulfates and thus give low SOx concentrations in the incinerator flue gas. Figure 5 below shows a graphical representation of the process.

In general, inorganic salts produce ash in the incinerator and require an ash removal and collection system, thereby complicating the design of the incinerator. This is why ammonia is preferred over caustic as the washing base to extract nitrophenols into the strong effluent, since ammonia is reduced to nitrogen (N_2) in the thermal oxidizer, whereas the ash left by the sodium greatly complicates the oxidizer design and operation.

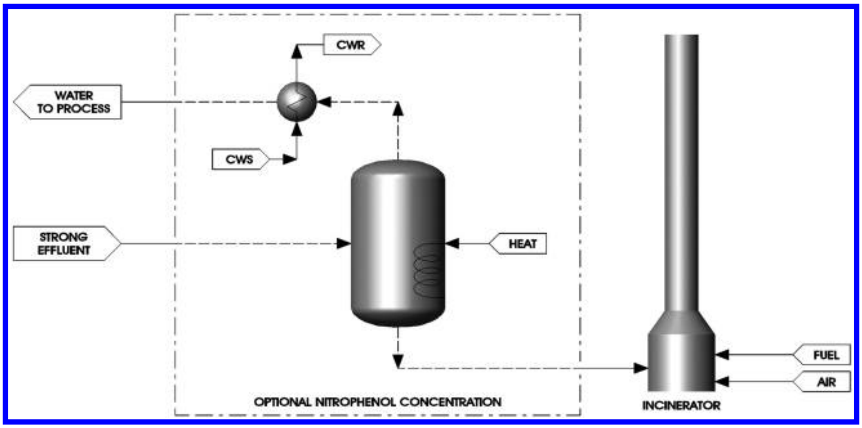

Figure 5. Simplified Schematic of the Incineration Process.

Incineration of strong nitrophenol waste effluent streams is known to have been practiced in at least two adiabatic MNB plants in Europe with one of them still operating. Both of these plants used ammonia-based washing to avoid residual soda ash thereby simplifying the incinerator design and operation.

Operating costs of incineration are relatively high due to the large amount of water that must be vaporized. However, energy efficiency can be increased with the addition of a recovery boiler. Alternatively, the strong effluent stream can be concentrated prior to incineration to minimize the amount of water required to be evaporated as well as reducing the size of the thermal oxidizer. An additional benefit to incineration is that no further treatment, such as biological treatment, is required.

Deepwell/Biotreatment

There are other possible treatment options that have been used to treat the raw strong effluent and are currently in operation, such as deepwelling and biological treatment. These options either require strict environmental permitting and/or large amounts of dilution water. As a result, these technologies are generally viewed as not being available or practical and are not further discussed in this paper.

Results and Discussion

The economics and performance of the treatment options considered above were investigated as follows. Calculations were done for a 300,000 MTPY MNB plant with a strong effluent stream given in Table I below.

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Table I. Strong Effluent Flow and Composition

Flow rate	6000	kg/h
Temperature	50	°C
Nitrophenolates	1.5%	wt%
MNB	10	ppm
Nitrates/Nitrites (as $NO3^-$)	200	ppm
Sulfates (as $SO4^{-2}$)	100	ppm
COD	12500	ppm

For each option the post-treated effluent quality was estimated based on the available information provided in the references and is presented in Table II.

Table II. Expected Effluent Quality

	Thermal Destruction (ppm)	*Wet Oxidation (ppm)*	*Solvent Extraction (ppm)*	*Ozonation (ppm)*	*Incineration (ppm)*
Residual Aromatics (e.g. Nitrophenols, MNB, Toluene)	≤10	≤10	600	≤1	N/A
Total Nitrogen (as NO3-)	9000	9000	200	9000	N/A
Sulfates (as SO4--)	100	100	100	100	N/A
COD	9300	2400	1700	low	N/A

In general, Thermal Destruction only removes the bio-toxicity, whereas the other technologies produce a more polished effluent with varying degrees of COD reduction with Incineration producing little to no liquid effluent. Additionally, Solvent Extraction is the only considered technology where the nitrogen species are extracted, reducing the total nitrogen of the effluent.

Both operating and installed capital costs were also approximated for each treatment option with the following basis for calculations. The results are shown in Figure 6.

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Basis of Operating Cost Estimates

Direct operating costs for the various treatment options were estimated using utility and chemical costs given in Table III. No allowance was made for additional maintenance costs, extra operating staff, environmental permitting or extra lab charges for effluent monitoring.

Table III. Utility and Chemical Costs

Description	*Cost (USD)*	*Basis*
Steam	20	US$/tonne
Cooling Water	0.028	US$/tonne
Power	0.06	US$/kWh
Natural Gas	0.3	US$/m3 NG
Caustic Soda	400	US$/tonne (100% Basis)
Sulfuric Acid	100	US$/tonne (100% Basis)
Toluene	1100	US$/tonne
Ammonia	450	US$/tonne (100% Basis)
Liquid Oxygen (LOX)	290	US$/tonne

Basis of Capital Cost Estimates

Equipment costs were estimated by pricing only the main equipment items (pumps, heat exchangers, tanks, vessels, columns, internals, etc.) for the given treatment technology. Auxiliary components such as piping items, instrumentation and additional infrastructure are not included. The equipment cost was then scaled using a Lang factor of 3 to obtain a total installed cost of the technology.

The additional costs for treatment technologies that require a thermal oxidizer or flare for off-gas, denitrification stage to handle nitrate/nitrites and/or biological treatment to further reduce COD, were not calculated. In many cases there will be a site-wide biological treatment plant or a thermal oxidizer and the additional loading will have a negligible effect on their size and operating costs.

Additionally fixed charges such as depreciation, taxes and technology licenses were not taken into account.

Thermal Destruction is seen to have the smallest operating costs out of all the considered technologies but has a relatively high capital cost. Whereas Incineration with concentration has the smallest capital cost but has a relatively high operating cost and requires significant time and cost to permit.

When comparing the installed cost plus 3 years of operating costs the most economical treatment technologies appear to be Thermal Destruction, Solvent Extraction and Incineration with concentration. Wet Oxidation should also be considered.

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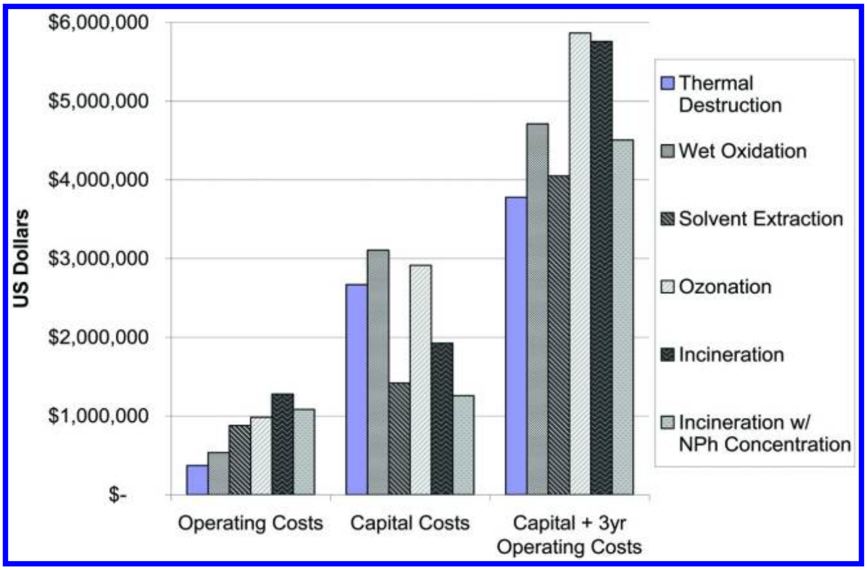

Figure 6. Expected Operating and Capital costs for different treatment options for a 300,000 MTPY MNB plant. (see color insert)

It should also be mentioned that the economics of Incineration is largely dependent on the fuel costs of the region, which can vary widely. This could lead to Incineration becoming more favorable in locations where fuel is relatively inexpensive.

Conclusion

All the technologies discussed have proven track records and can be used to treat strong effluent from a MNB plant. In most jurisdictions, Incineration is currently the only technology which meets environmental discharge limits without requiring addition treatment steps such as denitrification and/or biological treatment.

If the site has biological treatment, Thermal Destruction is the preferred choice. In fact most of the latest built MNB plants around the world have opted for this option to treat their strong effluent.

In all cases selection of the chosen technology to treat strong effluent is dependent upon the local facilities and conditions as well as environmental permit requirements.

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Chapter 8

Incorporation of Oxidation Enhancement through Hydrogen Peroxide Addition into a Tested Mass Transfer/Reaction Model for an Industrial NOx Absorption Process

Kyle G. Loutet,[*,1] Andres Mahecha-Botero,[1,2] Tony Boyd,[1]
Steven Buchi,[1] and Clive M. H. Brereton[1]

[1]NORAM Engineering and Constructors Ltd., 200 Granville Street,
Suite 1800, Vancouver, BC, Canada V6C 1S4
[2]Department of Chemical and Biological Engineering,
University of British Columbia, 2360 East Mall, Vancouver, BC,
Canada V6T 1Z3
[*]E-mail: kloutet@noram-eng.com

A comprehensive mass transfer/reaction model was developed in the process simulator Aspen Plus to simulate an industrial NOx absorption process. The model, recently published by the authors, was tested by comparison with data collected at the world-scale Wilton mononitrobenzene plant in Redcar, UK, and the model was found to accurately predict NOx removal. In the current study, an advanced NOx absorption technique, namely the addition of hydrogen peroxide as an oxidizer to an absorption process, was incorporated into the model in an attempt to quantify improvements in NOx absorption. The use of hydrogen peroxide to enhance NOx absorption processes has been studied in the past, with specific focus on the ability of hydrogen peroxide to oxidize nitric oxide (NO) to nitrogen dioxide (NO_2) and to oxidize nitrous acid (HNO_2) to nitric acid (HNO_3). The current study, which focuses on the latter oxidation, finds that the enhanced oxidation of HNO_2 shows significant potential for improving NOx absorption.

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Introduction

Industrial NOx absorption, utilized in the manufacture of nitric acid and in the treatment of waste gases from the nitration and other industries, is a complex absorption operation involving numerous gas- and liquid-phase chemical reactions and mass and heat transfer phenomena. Designing NOx columns for the purpose of pollution abatement, both air and water, is of particular interest as industrialized and developing nations become increasingly conscious of their environmental footprints. A reliable and accurate model of NOx absorption operations represents a useful tool to improve designs and ultimately meet and exceed environmental targets for both air and water.

In a past study, a rate-based model (i.e. a model that accounts for reaction and mass transfer kinetics) was developed in the process simulator Aspen Plus and tested using data gathered at the world-scale Wilton mononitrobenzene plant in England (*1*). This model focused on the pressurized, counter-current absorption of NOx into water, resulting in the production of dilute (<20 wt%) nitric acid as a liquid product. In the current study, an alternative configuration is studied wherein hydrogen peroxide is added to the system to enhance NOx absorption.

NOx Formation and Capture in Industrial Nitration Processes

The formation of NOx as a byproduct in nitration processes is an industry-wide problem. In NORAM Engineering's patented benzene nitration process (*2*), in which nitrobenzene is continuously and adiabatically produced in a mixed acid medium, the amount of NOx generated is predictable, based on knowledge of the factors that control its formation. Two pathways to NOx formation are presented below.

(a) Nitrous acid contained in the feed nitric acid decomposes to form nitric oxide (NO)

$$\mathbf{3\ HNO_{2(l)}} \rightarrow HNO_{3(l)} + H_2O_{(l)} + \mathbf{2\ NO_{(g)}} \quad (1)$$

(b) Nitrous acid produced in side reaction (2) decomposes to NO via reaction (1)

$$C_6H_{6(l)} + 4\ HNO_{3(l)} \rightarrow C_6H_2(NO_2)_3OH_{(l)} + 3\ H_2O_{(l)} + \mathbf{HNO_{2(l)}} \quad (2)$$

The byproduct NOx gases produced in the nitration step are separated from the liquid products in a three phase separator and sent to a NOx absorption column. In the NOx column, the gases and air are fed to the bottom of the column and contacted with demineralized water under pressure. The nitric acid produced in the NOx column is collected and recycled to the nitration step, reducing the need for more fresh nitric acid feed, lowering the NOx in the plant vent, and reducing the nitrate/nitrite levels in the plant effluent (*3*). A portion of the liquid outlet is typically cooled and circulated to the top and/or to an intermediate point in the column. The column can contain packed or trayed sections or a combination of both. Figure 1 shows a simplified version of the NOx absorption process. Also shown in Figure 1 is a point where hydrogen peroxide might be introduced into a NOx absorption system, that is, at the bottom of the column.

In order to understand the need for cooling and pressure in the NOx absorption column, an understanding of the chemical reactions in both the gas and liquid phases is required. The simplified reactions shown in Table 1 are adopted from the literature.

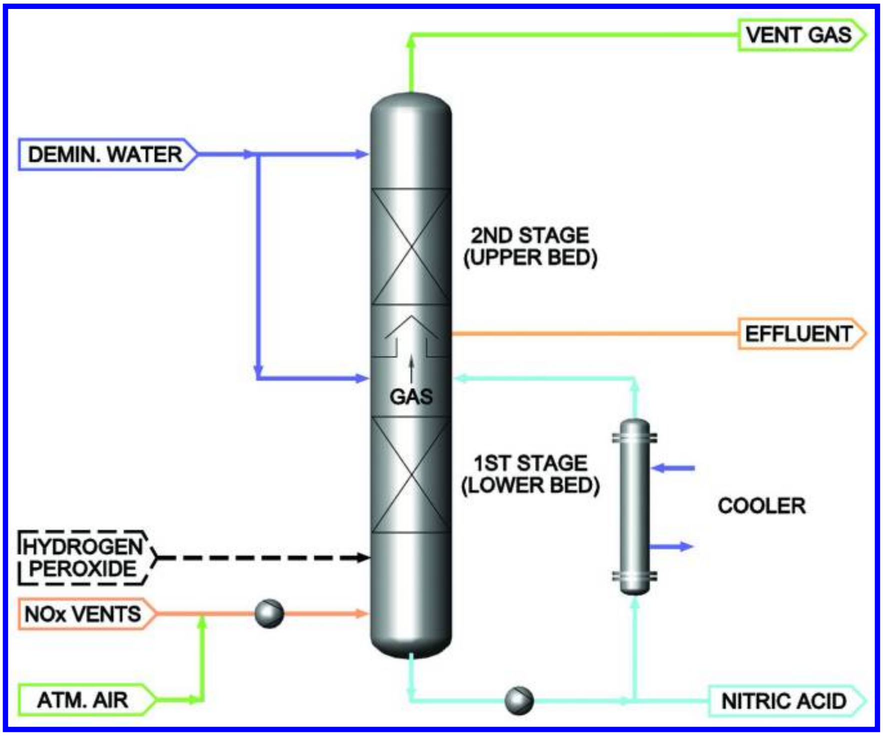

Figure 1. Schematic of industrial NOx absorption process with possible hydrogen peroxide injection point identified. (see color insert)

The near-completion of reaction R1 is crucial to NOx absorption as NO is marginally soluble in the liquid phase (*6*). Air is therefore added upstream of the NOx column to initiate the oxidation of NO to NO_2. Reaction R1 is unusual in that it is kinetically favored by *low* temperature. A low temperature column is therefore favorable for NO oxidation to NO_2 and it has the added benefit of increasing the solubility of NOx species in the liquid phase. Hence the need for a cooler as shown in Figure 1. R1 is also third order in pressure and NOx absorption systems are pressurized largely for this reason (*6*). Pressure has the added benefits of forcing equilibrium reactions R2 and R3 to the product side and reducing the equilibrium gas-phase concentrations of N_2O_3 and N_2O_4, which are known to be the primary species that are absorbed from the gas phase to the liquid phase where they react to form nitric and nitrous acid.

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Table 1. Salient gaseous NOx and aqueous phase reactions

Reaction	*Stoichiometry*	*Phase*	*Reference*
R1	$2\ NO + O_2 \rightarrow 2\ NO_2$	Gas	(*4*)
R2	$2\ NO_2 \leftrightarrow N_2O_4$	Gas	(*4*)
R3	$NO + NO_2 \leftrightarrow N_2O_3$	Gas	(*4*)
R4	$N_2O_3 + H_2O \leftrightarrow 2\ HNO_2$	Gas	(*4*)
R5	$N_2O_4 + H_2O \leftrightarrow HNO_3 + HNO_2$	Gas	(*4*)
R6	$2\ NO_2 + H_2O \rightarrow HNO_2 + HNO_3$	Liquid	(*5*)
R7	$N_2O_3 + H_2O \rightarrow 2\ HNO_2$	Liquid	(*5*)
R8	$N_2O_4 + H_2O \rightarrow HNO_3 + HNO_2$	Liquid	(*5*)
R9	$3\ HNO_2 \rightarrow HNO_3 + H_2O + 2\ NO$	Liquid	(*5*)

Once into the liquid phase, N_2O_3 and N_2O_4 react with water via reactions R7 and R8, respectively, both of which produce HNO_2. Nitrous acid in turn decomposes via R9, producing NO which desorbs to the gas phase, bringing the NOx absorption process full circle. The suppression of reaction R9 is the focus of many NOx absorption enhancement systems, including enhancement by hydrogen peroxide addition.

NOx Absorption Enhancement by Hydrogen Peroxide Addition

The suppression of reaction R9 has the potential to significantly improve the NOx absorption process. Traditional designs have utilized bases such as caustic soda to remove HNO_2 as sodium nitrite. Although effective at reducing NOx emissions, this method produces a liquid effluent containing sodium nitrites and nitrates which must be treated and which cannot by recycled to the nitration plant. The use of hydrogen peroxide to remove HNO_2 represents an elegant solution to this problem as the reaction products are nitric acid and water (R10):

$$HNO_{2(l)} + H_2O_{2(l)} \rightarrow HNO_{3(l)} + H_2O_{(l)} \qquad R10$$

The liquid waste from a peroxide-enhanced absorption process thereby avoids costly effluent treatment and can potentially be recycled to nitration.

Hydrogen peroxide can also enhance NOx absorption by assisting the oxidation of NO to NO_2 on the gas side (R11). This would, however, require the vaporization and gas phase injection of hydrogen peroxide into the system. The enhancement of NO oxidation is not studied here, the reasons for which are given in the following section.

$$NO_{(g)} + H_2O_{2(g)} \rightarrow NO_{2(g)} + H_2O_{(g)} \qquad R11$$

The use of hydrogen peroxide to enhance NOx absorption has been studied in the past (*7–11*) and results have shown that significant potential for improvements in NOx absorption are achievable. Of particular interest is the observation that

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NOx absorption *increases* with increasing nitric acid concentration when hydrogen peroxide is present (*8*). In nitric acid solutions free of additives such as caustic or peroxide, NOx absorption has been shown to decrease with increasing nitric acid concentration (*12*). The ability to achieve higher nitric acid concentrations translates to decreased water usage. If the nitric acid is to be returned to the nitration reaction step, then increased energy efficiency is achieved since any water added to nitration must ultimately be boiled off.

From a practical standpoint, the retrofit of an existing NOx absorption system to allow for hydrogen peroxide introduction should be relatively simple. The materials of construction that are commonly employed for NOx absorption columns, such as 304 and 316 grades of stainless steel, are also compatible with solutions of hydrogen peroxide. The number of peroxide-enhanced NOx absorption units currently installed industrially is not known but a review of the patent literature suggests that it has seen extensive application. One patent (*13*) describes the use of hydrogen peroxide to scrub NOx from the off-gas from a metal dissolution process while another patent (*14*) describes the use peroxide to treat off-gas from a nitric acid etching step. The construction of a pilot-scale, peroxide-enhanced NOx absorption column is also described in the literature (*7*).

Experimental Methods and Model Development

In the previous study (*1*), data from an operating NOx absorption system were collected and analyzed. A rate-based model was developed in Aspen Plus (utilizing the *RateSep* add-on) in an attempt to simulate plant conditions. Model results were compared with plant data and the model was found to accurately predict NOx removal. Details on the collection and analysis of plant data, development of the model, including but not limited to reaction kinetics, vapor-liquid equilibria, and selection of mass transfer correlations can be found in the previous study (*1*). A schematic of the NOx absorption process is shown in Figure 1.

In the current study, no additional plant data were collected. The modeling results from the previous study are compared to the modeling results from the current study, which now includes hydrogen peroxide addition to the absorption system. All data presented herein represent modeling results.

Addition of Hydrogen Peroxide to the Rate-Based Model

Hydrogen peroxide is incorporated into the rate-based model in the liquid phase via reaction R10. Although hydrogen peroxide can also enhance NOx absorption in the gas phase via reaction R11, this is not accounted for in the model. The reaction of NO with HNO_2 in the gas phase is a complex reaction mechanism involving free radicals and its incorporation into the model will require an additional study.

It should also be noted that from an operability standpoint, the authors feel that peroxide injection into the liquid phase is the more appealing option. Whereas peroxide injection into the gas phase necessitates a vaporizer and potentially

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increases the load on the compression system, injection to the liquid phase is straightforward. The peroxide can simply be added to the absorber sump on flow control.

The oxidation of HNO_2 to HNO_3 by H_2O_2 in the liquid phase is fast and the rate expression shown below has been developed (*11*).

$$\frac{-d[HNO_2]}{dt} = k[H_3O^+][H_2O_2][HNO_2]$$

where $k = 3012\ L^2\ mol^{-2}\ s^{-1}$

A number of simulations are presented in the Results and Discussion section. The previous study (*1*) documented 17 experimental plant trials. Although the original intention was to test different process conditions in each trial, the experimenters were constrained due to plant limitations with regard to safety, production, and process control. Details about the 17 trials can be found in the published study (*1*).

Results and Discussion

Under normal conditions in the NOx absorption process, NOx gas enters the column at a concentration on the order of 8-10% by volume. The gas passes through a lower section of packing which operates with a large circulating flow of liquid and the concentration drops to about 10,000 ppmv. Finally, the gas passes through an upper packed bed in which demineralized water passes “once through” and wherein the NOx concentration drops to about 300-400 ppmv in the vent gas. In the previous study, model predictions were found to match plant data to within about 3%. Under normal operation, the NOx column is operated at approximately 2.7 bar(g). Note that in Figure 1 an effluent liquid stream is shown as a side draw from the middle of the column. The side draw is in place to allow the column’s upper section to be operated with caustic solution rather than demineralized water. When the column upper section is run with demineralized water, the effluent stream is simply combined with the nitric acid solution off the column bottoms. When operated with caustic solution to the upper bed, the effluent side draw becomes laden in sodium nitrate/nitrite, which then requires separate treatment in a biological treatment system. Avoiding this biological treatment is the key driver to operating the upper column section with demineralized water rather than caustic solution.

Under conditions of NOx absorption with peroxide addition, the predicted improvements in NOx capture efficiency are significant. Table II shows the model-predicted NOx concentrations from the lower packed bed under normal conditions and under conditions of peroxide addition. Model convergence issues were encountered for Trials 13 and 14 and have hence been omitted from the study. Results are represented graphically in Figure 2.

Some interesting observations are noted from these results. Firstly, the lower bed performance with peroxide addition approaches the total column performance for normal conditions. Specifically, gas exiting the lower bed has a NOx concentration on the order of 300-400 ppmv, whereas without peroxide addition, the NOx concentration does not reach the 300-400 ppmv range until after the upper bed. This implies that less packing material and a shorter column might be feasible when peroxide addition is utilized.

It is also interesting to note that the simulations were re-run at atmospheric pressure with peroxide addition, whereas normal conditions in the column are 2.7 bar(g) and no peroxide addition. These results, too, are shown in Table II. What is interesting is that at atmospheric pressure with peroxide addition, the predicted NOx composition leaving the lower bed is similar to the predictions at the normal (i.e. pressurized) conditions *without* peroxide addition. In systems where a final NOx concentration of 5000-10000 ppmv is acceptable, operation of the NOx absorption column at or slightly above atmospheric pressure with peroxide addition could mean significant capital and operating cost savings (compared to pressurized without peroxide) as it would eliminate or reduce the size of the compressor, and potentially lower the mechanical design pressure of the column and cooler. As will be demonstrated in Figure 3, however, achieving 300-400 ppmv at atmospheric pressure with peroxide addition remains a challenge.

The upper packed bed was also studied and results are shown in Table III and represented graphically in Figure 3. Here, NOx concentrations refer to the gases exiting the top of the column. The improvement in performance is not nearly as pronounced as in the lower packed bed. This is in large part due to how peroxide is added to the system. Under the proposed arrangement, peroxide is added to the bottom of the column and is therefore only exposed to the bottom bed. The suppression of the nitrous acid decomposition reaction is therefore not achieved in the upper packed bed. Although the results are not presented herein, suppression of R9 (i.e. nitrous acid conversion to water, nitric acid and NO) in the upper packed bed is not nearly as effective as in the lower bed and the results are only marginally better than those shown in Table III. One hypothesis to explain this is that nitrous levels in the upper bed are much lower than in the lower bed since the bulk of the NOx gas has been absorbed in the lower bed. The nitrous decomposition reaction (R9) is therefore less prevalent in the upper bed and so its suppression has a less marked effect on NOx absorption

The other obvious difference for the upper packed bed is the performance at atmospheric pressure with peroxide addition. Performance at atmospheric pressure with peroxide is significantly lower than at normal conditions (i.e. pressurized without peroxide). This is likely due to the fact that the gas leaving the lower bed contains significant quantities of nitric oxide (NO) and the kinetics of the oxidation of NO to NO_2 are third order in pressure. At atmospheric pressure, very little of the NO escaping the lower bed is oxidized to NO_2 and since NO is sparingly soluble in the liquid phase, the overall absorption of NOx is significantly reduced.

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Table II. Lower packed bed performance with and without peroxide addition

	NOx Outlet Concentration from Lower Packed Bed		
Trial	*Normal Conditions (ppmv)*	*With Peroxide Addition to the column bottom (ppmv)*	*With Peroxide Addition at Atmospheric Pressure (ppmv)*
1	6385	343	5015
2	6301	329	4245
3	7088	354	3869
4	6952	452	3575
5	9762	771	9174
6	14888	1537	12852
7	7265	395	4606
8	6875	333	4539
9	4307	433	6146
10	7997	544	6806
11	7870	500	5500
12	10423	808	6553
15	6088	397	5620
16	6236	409	5998
17	6451	425	5966

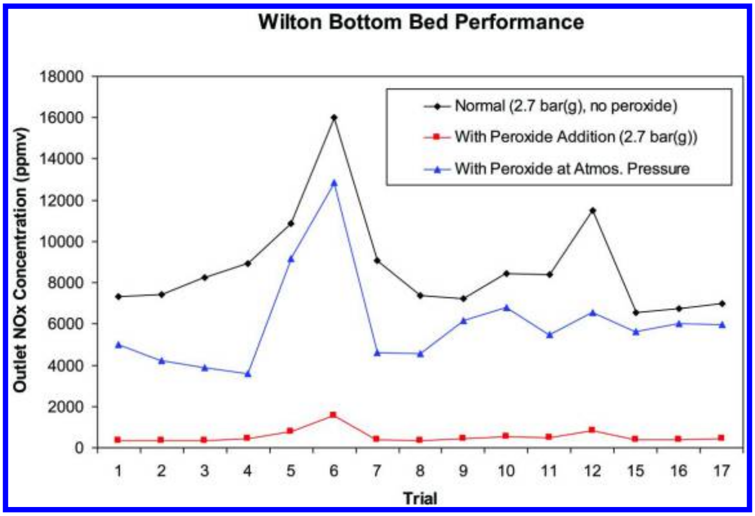

Figure 2. Graphical representation of lower packed bed performance with and without peroxide addition. (see color insert)

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Table III. Upper packed bed performance with and without peroxide addition

	NOx Outlet Concentration from Upper Packed Bed		
Trial	*Normal Conditions (ppmv)*	*With Peroxide Addition to the column bottom (ppmv)*	*With Peroxide Addition at Atmospheric Pressure (ppmv)*
1	1322	230	4280
2	423	164	3148
3	396	157	1804
4	329	147	2671
5	474	224	5209
6	501	267	3888
7	397	163	3227
8	426	165	3312
9	712	248	4781
10	556	223	4089
11	466	216	3595
12	932	356	3897
15	393	160	3512
16	395	164	3679
17	406	168	3713

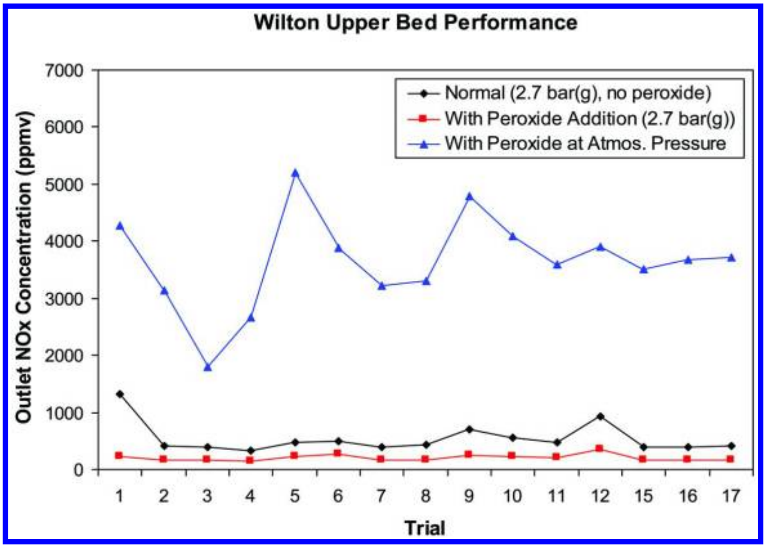

Figure 3. Graphical representation of upper packed bed performance with and without peroxide addition. (see color insert)

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Conclusions and Recommendations

As regulations on NOx emissions to the atmosphere and nitrite/nitrate level in effluents become more stringent, scientists and engineers will need to devise and implement new NOx abatement technologies. These new technologies must be energy efficient. The addition of a chemical agent such as hydrogen peroxide appears to have great potential to reduce NOx emissions without producing nitrite/nitrate-laden effluents. In certain applications, such as when final NOx concentrations of 5000-10000 ppmv can be tolerated, its use may also allow for lower pressure NOx absorption systems to be adopted, meaning decreased energy consumption and increased safety. The viability of atmospheric pressure NOx absorption will greatly depend on the target outlet NOx concentration from the column. It has been shown that achieving low NOx concentrations at atmospheric pressure is challenging, even with the addition of peroxide.

The economics of incorporating hydrogen peroxide addition to the liquid phase of an existing NOx absorption are not expected to be prohibitive. Since the materials of construction often used in NOx absorption columns are typically compatible with peroxide solutions, a significant retrofit will likely be unnecessary. Rather, the retrofit could be as simple as adding a system to deliver peroxide, along with the requisite provisions for flow control. Additional equipment, such as storage tanks and offloading stations, might be required at sites not already using hydrogen peroxide, which could significantly increase the capital cost of the retrofit. From a variable cost standpoint, a typical price point for 50 wt% industrial grade hydrogen peroxide is about US$750 per metric tonne. For the Wilton plant investigated herein, the peroxide consumption is predicted to be about 240 tonnes/year for an annual cost of US$180,000. This would have to be compared to the variable cost of a competing technology, such as selective catalytic reduction (SCR). Note that fixed costs associated with the addition of an SCR would likely be much higher than those with the peroxide retrofit.

In the NOx absorption system shown in Figure 1, the compressor typically makes up in excess of 50% of the bare equipment cost for world-scale plants such as Wilton, and typically consumes between 75 and 150 kWe. Depending on the cost of electricity, the variable cost for the pressurized system could be very comparable to that of the peroxide system, which combined with the potential 50% reduction in fixed cost, could make an atmospheric pressure, peroxide system economically attractive.

The drawbacks of adding hydrogen peroxide would include increased chemical consumption, the challenges that come along with introducing a new chemical into an established chemical process (especially at existing plants) and the increased absorption system complexity.

Additional work is required before a peroxide-enhanced system is implemented on the industrial scale in a mononitrobenzene plant. Perhaps most importantly, the implication of recycling nitric acid containing excess peroxide to nitration needs to be carefully studied. The excess peroxide will likely oxidize benzene to phenol which will ultimately be nitrated and lead to higher nitrophenol content in the effluent. Similarly in non-nitration applications, and depending on the use of the nitric acid produced in the NOx absorption operation, the implications of having excess peroxide in the nitric acid would have to be considered. Also, the optimization of how peroxide is added to the absorption system is required. Finally, experimental tests are required to assess the validity of the simulation results.

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Chapter 9

Bench-Scale and Pilot Plant Nitration Experiments – Practical Considerations

Evan Hobenshield[*]

BC Research Institute, Burnaby, British Columbia, Canada
[*]E-mail: ehobenshield@bcri.ca

The development of new nitration processes usually starts at the bench or pilot plant scales. The path of development is very specific to the particular nitration process to be investigated. Some nitration processes can be particularly hazardous; others can be hard to scale up or control. Many of these challenges can be difficult to manage, especially when considering a new nitration process, or new operating conditions for a known process, where little or no published data is formerly available. Researchers at BC Research have found through over 20 years of nitration research that a well-designed experimental methodology can ease many of these challenges. This paper presents a well-established nitration reaction research methodology. In particular, experimental design, apparatus design, safety evaluation, scales up issues, and sampling and analytical techniques are discussed.

Overview

The first nitration to be reported was that of benzene itself. Mitscherlich in 1834 prepared nitrobenzene by treating benzene with fuming nitric acid (*1*). Since then, nitration has been the subject of continuous study. Many means have been used through the years to effect the nitration of organic substrates. For example, nitronium salts in solution in inert organic solvents have been used to nitrate a wide range of aromatic compounds (*2*). Benzene and its derivatives have been reacted with solutions of mercuric nitrate in concentrated nitric acid to give nitrophenols. Today, most high volume nitrations are done in mixed acid media (sulfuric acid and

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nitric acid). Nitrobenzene, nitrotoluene, dinitrotoluene, and nitrochlorobenzene are all manufactured by nitrating an aromatic starting material in mixed acid.

Though nitration technology is a mature industry, specific nitrations still require development, especially that involving high production volume. For example, the nitration of benzene over solid acid catalyst (*3*, *4*) is an active area of research. The nitration of benzene in mixed acid media continues to be optimized (*5–7*).

In general, nitration reactions are exothermic, and resulting nitration mixtures can generate a large amount of energy upon decomposition. Nitrations are potentially dangerous even on the gram scale. In addition, by-products are typical in the nitration of aromatic substrates, which creates challenges in plant design and operation. The corrosive nature of the mixed acid must be carefully considered at the lab, pilot and industrial scale. In a research laboratory, these are some of the many challenges that the researcher must consider.

Introduction

Through the years, BC Research has conducted numerous nitration studies, and in the process has developed a practical methodology for undertaking nitration research programs. The methodology includes the consideration of the following steps:

(1) setting clear objectives,
(2) performing a thorough literature search,
(3) designing the appropriate experimental plan,
(4) designing the experimental set-up,
(5) conducting a safety audit,
(6) developing a sampling and analysis plan,
(7) and having a chemical spill cleanup plan and a chemical disposal plan.

There are many aspects of experimental design to consider in each of these steps, and careful planning will spare the researcher of delays, of chemical releases and of more serious accidents.

Defining the Program Objectives

A research program typically originates from a specific product or process need. Research objectives must be defined. Frequently this effort is not given enough consideration. Research programs should start with defined objectives that are concise and limited in scope. Most importantly, they should be within the constraint of available physical and financial resources. The process of defining the objectives should follow an established method, and requires the up-front involvement of all technology functions, management (client), and researchers. As an example, the following established iterative procedure has been successfully used by BC Research through many projects (Figure 1)

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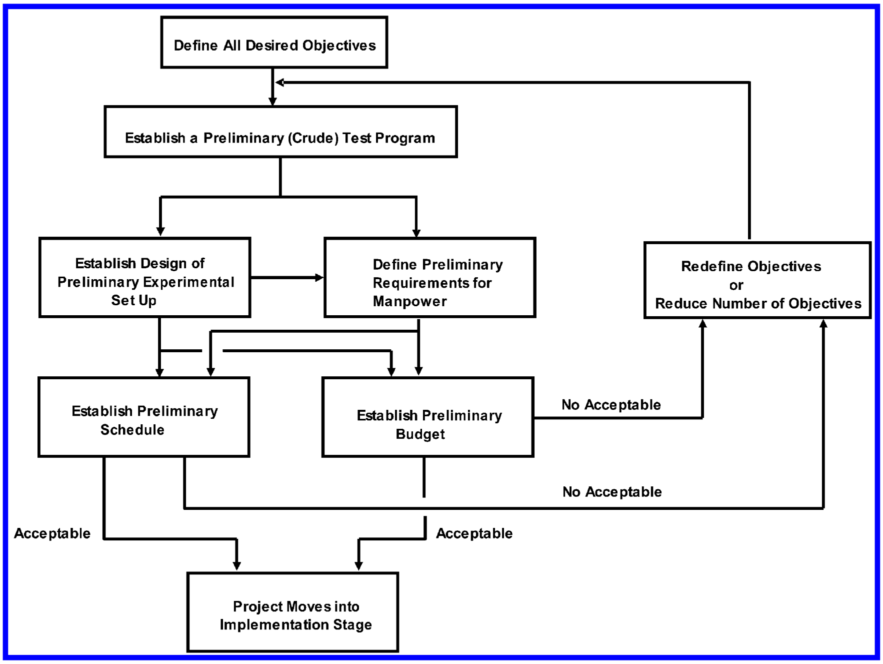

Figure 1. Research Program Planning.

Research programs with well-defined objectives typically lead to better test programs with lower R&D costs, shorter schedules, and better results.

Programs with a number of poorly defined objectives typically result in overly complicated experimental designs and laboratory equipment. On the experimental side, the number of experiments increases substantially to cover all boundaries of the poorly defined objectives. Experimentally, vessels and auxiliary equipment is configured for maximum flexibility to meet all objectives, which usually means that the system is not an optimal design for a specific objective, leading to compromised results.

Literature Search

A thorough literature search is required, bounded by the defined objectives of the research program. A proper literature search usually helps steer the project in the right direction from the onset, and potentially saves time and resources. There is considerable literature concerning nitration reactions, and it is not unusual that some of the research objectives are simply met by finding the appropriate literature source.

A literature search, bounded by a nitration research program, should have three main objectives:

- to find relevant data and information concerning objectives,
- to collect relevant physical properties, thermodynamic data, and kinetic data for the nitration system to be studied,

- to collect all relevant hazardous information, and health and safety data,
- to gather of relevant information on appropriate experimental set-ups,
- and to gather information on appropriate analytical techniques.

A typical search would include sources such as academic journals, handbooks, patents and the internet. In general, this is a very broad set of sources, so where should one start? A good starting point is provided with the following sources:

- Nitration and Aromatic Reactivity - J.G. Hoggett
- Aromatic Chemistry - John D. Hepworth
- Handbook of Reactive Chemical Hazards - Bretherick
- Benzene and Its Industrial Derivatives - E.G. Hancock
- Unit Processes in Organic Synthesis - P.H. Groggings
- Handbook of Organic Chemistry - Beilstein
- Handbook of Industrial Chemistry - Riegel's
- A Comprehensive Treatise on Organic and Theoretical Chemistry - Mellor
- Gmelin Handbooks
- Landolt-Börnstein
- Kirk-Othmer
- Ullmann's Handbook
- CRC Handbooks
- Solubilities of Inorganic and Organic Compounds - Seidell & Linke
- International Critical Tables
- Journal of Physical and Chemical Reference Data
- Journal of Chemical and Engineering Data
- NIST Database
- Patent Databases

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Experimental Design Plan

Once the research program objectives are determined and the literature search is completed, it is time to define the experiments required to meet the objectives (the experimental design stage). Experimental design deals with the science of collecting the maximum amount of relevant data or information with a minimum amount of time and resources (i.e., minimum number of experiments). An experiment is a system composed of independent input variables (factors) and dependent output variables (results).

The methodologies used to define the experimental plan typical follow one of two approaches: the traditional (classical) experimental method or the statistical design method.

In the classical experimental method the factors affecting the result are identified, and then experiments are designed to investigate each relevant factor, one at the time. The factor investigated is manipulated while all other factors are held constant. To better understand the effect on the result, three values of a given factor are chosen (i.e., low and high end values of the range of interest, and a value in the middle of the range). With this approach the number of experiments

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to complete the study is particularly large. For instance, if the effect of three factors is to be tested, the minimum number of experiments to complete the work is estimated as 3^3, or 27. Of course, the number doubles when repeating experiments to assess the reproducibility of the results.

In general, running a test program according to the classical scientific method requires thoroughness and time. An important "weakness" of the classical experimental method is that it is not possible to single out interaction effects among factors.

The statistical design method, or so-called factorial design method, provides a more efficient experimental design tool. It is less time consuming than the classical method, and more importantly it allows the study of interactions among factors. It provides the means to predict how changing more than one factor simultaneously could affect the result. A factorial design includes experimental runs for all combinations of values for each factor (high and low). It is helpful to visualize the settings of three variables (factors), for example, as the corners of a cube (factorial cube). This is called a 2^3 design. For example, if the three factors of interest are temperature, pressure, and time, the factorial cube representing the experimental conditions of the research program would look as follows (Figure 2).

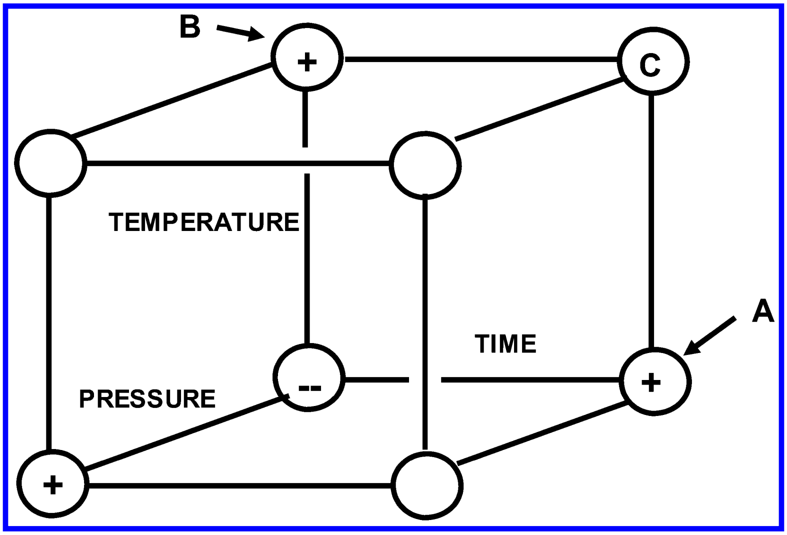

Figure 2. Experimental Design for Three Factors.

On the above factorial cube, effects on the result due to temperature, pressure and time are shown along the Z, X, and Y axes respectively. Starting at the origin of the axes, a change on the "time" factor would take us to corner "A" of the cube. The experimental conditions covered between the origin of the axes and corner "A" would test how "time" affects the result. Similarly, a change on the "temperature" factor would take us from the origin of the axes to corner "B" of the cube. A simultaneous change in the "time" and "temperature" factors would take us to corner "C" of the cube. The experimental conditions of corner "C" would test how the simultaneous change of "time" and "temperature" affects the result, which

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would allow us to understand interactions between the “time” and “temperature” factors on the result.

A concise paper on the details of setting up a factorial experimental plan is provided by Murphy (*8*). A more detailed explanation on the subject of factorial testing is provided by Antony. (*9*).

The first phase of experimental design is to choose the factors to be studied, and the high, medium, and low target value for each factor. This is an important step that, if performed properly, can reduce both the cost and schedule of the program. This step is usually accomplished with a set of screening experiments. To understand the importance of screening experiments, let us look at a test program that investigates the effect of temperature, stoichiometric ratio of the reactants, energy input, catalyst concentration, and system pressure on the reaction kinetics of a particular nitration reaction. In a factorial design study, the minimum number of experiments required to complete the work would be 2^5, or 32. However, a few screening experiments would quickly establish that the “system pressure” and “stoichiometric ratio of reactants” factors have little or no effect on the reaction kinetics, simplifying the program to a 2^3 factorial test (i.e., minimum of eight experiments).

As a starting point, the typical factors significantly affecting the most generic aspects of mixed acid nitration reactions are provided in the following Table I.

Table I. Factors affecting mixed acid nitration reactions

	Reaction Kinetics	*Selectivity*	*Yield*
Temperature	√	√	√
Power Input to Agitator	√	--	--
Sulfuric Acid Concentration	√	√	√
Reactants Stoichiometry	--	√	√
Time	--	--	√

-- Does not significantly affect the variable.

Experimental Apparatus (Configuration of Equipment)

The next step in the research program is the selection and configuration of the laboratory equipment to be used in the study. In the research of nitration reactions, the experimental apparatus design typically revolves around the reactor.

Some idea of the reaction kinetics and heat of reaction must first be understood. The next step is the selection of reactor type and appropriate scale for the study.

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Chemical kinetic studies attempt to determine the rates of pertinent reactions, and understanding factors that affect the rates. The desired kinetic data may already be available in the open literature. Alternatively a few screening beaker tests can be done to gather sufficient data. If screening tests are required, a first step is to define a parameter that can be used to infer the degree of conversion of the reactants. Given that nitration reactions are highly exothermic, this parameter is usually the increase in temperature.

Kinetics looks at the time / conversion relationship. It deals with the determination of how many moles of reactants have been converted to product in a specific time frame, and establishing rate equation. The rate expression can then be used to determine the required reactor residence time for a specific yield. In many reaction systems, the extent of the reaction cannot be inferred by temperature, and therefore laboratory analysis is required. In addition, the extent of the reaction may be highly affected by the thermodynamic equilibrium of the system. Fortunately, mixed acid nitration reactions are classified as “irreversible”. In irreversible reactions, the thermodynamic equilibrium for the reaction highly favors formation of products, and only an extremely small quantity of the limiting reagent remains in the system at equilibrium. If the extent of reaction is not limited by thermodynamic equilibrium constraints, then the limiting reagent is the one that determines the maximum possible value of the extent of reaction. Under these conditions, which apply to mixed acid nitration reactions, temperature is a good measure of the “extent of reaction”, as is conversion of reactant(s) to products.

Researchers should be careful to distinguish between the problem of determining the reaction rate function and the problem of determining the mechanism of the reaction. The latter involves a determination of the exact series of molecular processes involved in the reaction. It is by far the more difficult problem. From the chemical engineer’s viewpoint, who is interested in the design of the scale of the reactor, knowledge of the reaction mechanism is useful, but not essential. The engineer is more concerned with the problem of determining a reaction rate expression for use in design calculations.

Thermodynamics, on the other hand, is concerned with equilibrium systems, systems that are undergoing no net change with time. Thermodynamics of chemical reaction looks at the conditions at which the reactants are converted to product at the same rate as products are converted back to reactants. On reaction systems with strong reversible reactions, total required product throughput and yield would, for example, affect the reactor size and configuration. Reaction systems that are highly reversible generally require recycle loops and are configured differently than for irreversible reactions.

Choice of the nitration vessel is next important step in the program. There are primarily three types of reactors to consider for nitration reactions, the batch reactor, a plug flow reactor (PFR) or a continuous stirred tank reactor (CSTR). Other types of reactor are used for industrial nitrations. Two other types of reactors are a forced convective tube reactor and a high speed mixing reactor (such a nitration inside a pump). These alternative reactors will not be discussed here.

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The batch reactor is the simplest configuration. Reactants are charged to the system and rapidly mixed. Mixing is typically carried out with a mechanical agitator. The reaction rate varies with time but it is always uniform throughout the vessel. The reactor can be configured to perform adiabatic or isothermal reactions. For isothermal reactions, a cooling jacket with a temperature controller is attached to the reactor. Batch reactors are not limited by residence time and therefore provide the highest possible conversion for most reactions, and therefore the highest yield.

The PFR and CSTR are continuous flow reactors, feed enters the inlet of the reactor and product leaves the exit of the reactor. However, these two types of reactors typically behave very differently with respect to conversion and selectivity.

The PFR behaves like a batch reactor. It is usually visualized as a long tube where discrete volumes of reactants enter the reactor at time = 0. Each discrete volume mixes as it moves through the reactor, but it does not mix with other discrete volumes upstream or downstream. Reactants in each volume ‘age’ and react as they flow down the tube. A discrete volume that has been in the reactor for “t” seconds would have the same composition as if it had been in a batch reactor for “t” seconds. The composition of a batch reactor varies with time. The composition of a discrete volume flowing through the PFR varies with time in the same way.

A CSTR is continuously feed regents while the reaction mixture continuously leaves the reactor. The level in the reactor is typically controlled as desired. The reactants are mechanically agitated in the reactor. Mixing is sufficiently fast so that the entering feed quickly disperses throughout the vessel and the composition at any point is approximately the average composition. The concentration of the reactor outlet is the same as the reactor internal composition. A set of CSTR in series models a PFR. In general, both the PFR and CSTR are easier to scale up.

The typical design intent of a reactor is to maximize yields and selectivity (i.e., operating cost of an industrial process) in the smallest possible equipment volume (i.e., capital cost of an industrial reactor). The objective of maximum reaction in a minimum of volume is achieved in a PFR rather than a single CSTR. In a single CSTR the concentrations of reactants in the reactor is equal to the concentrations of reactants in the effluent of the reactor. However, in a PFR the concentrations of reactants change throughout the length of reactor. As the concentrations of reactants decrease, the reaction rate decreases. Therefore a PFR requires a significantly smaller volume than a CSTR for the same extent of reactant conversion.

In industrial mixed acid nitration reactors, a single CSTR is rarely used. If a CSTR is the preferred reactor design, a series of CSTRs is typically employed, which simulates a PFR. In general, a number of CSTRs connected in series are used for isothermal nitration reactions, wherein control of temperature is easily accomplished. PFRs are the preferred choice for adiabatic nitration reactions.

Any mixed acid nitration reaction can be operated adiabatically or isothermally. The selection of an adiabatic or isothermal reaction is dependent upon the reaction’s desired yield, selectivity, design, and safety constraints. In the adiabatic process, the heat generated by the reaction is typically used to re-concentrate the sulfuric acid from the nitration. However, in the adiabatic

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process the reaction temperature is not controlled, and since the reaction temperature has a significant effect on the isomeric distribution of some nitration products, then it follows that it also has an effect on the process selectivity and yield. For example, nitrobenzene is typically produced adiabatically, because nitrobenzene has no isomers. Toluene is nitrated isothermally to control the isomeric distribution of the three isomers of the nitrotoluene product, as well as safety concerns.

In general, batch reactors are better suited to perform the screening experiments for a nitration research program. The scale of the reactor is not very important. However, the size should be minimized (e.g. <500 mL), especially when dealing with new nitration reactions or new conditions of a known reaction. Nitration reactions are very exothermic and can be dangerous. Additionally, some nitration products are thermally unstable.

The selection of a PFR or a series of CSTRs for the experimental study is somewhat dependent on whether the nitration will be conducted adiabatically or isothermally. If the study involves a nitration reaction with a product that has an isomer distribution, then a set of cooling jacketed CSTRs in series should be used for maximum research flexibility. This would be a more expensive set up than a PFR, but it would allow the investigation of both isothermal and adiabatic reaction conditions if the reactors are properly designed.

The scale of the apparatus for any research work is an important consideration. To properly scale the apparatus one must first define the relevant non-dimensional numbers. For example, when considering the importance of work impinging the reaction mixture through mixing, one important factor is the Reynolds number (Re). It can be interpreted as the ratio of the parameters that contribute to turbulent flow to parameters that contribute to laminar flow. Another relevant non-dimensional number is the Weber number (We) which is a measure of the relative importance of the fluid's inertia compared to its surface tension. It is a useful quantity in understanding the formation of droplets.

There are a number of papers and general literature on the subject of reactor scale-up and dimensional analysis (*10*, *11*). Although helpful, the available literature fails to clearly indicate how small an experimental apparatus should be and still provide predictive behavior of a full–scale industrial reactor. However, several research programs at BC Research have shown that a reactor scale-up of 1:100 provides an acceptable experimental reactor size for mixed acid nitration reactions.

Once the kinetic data is in hand, and the selection of the reactor type is made, and the scale factor is defined, the exact reactor design can be addressed. We have learned that two design issues must be carefully considered before completing the reactor design: mixing and the design of the reactant feed system(s).

The "mixed acid" or "nitrating acid" is a mixture of nitric and sulfuric acids with sufficiently strong acidity to generate the nitronium ion, which is the active nitrating species. In general the organic compound to be nitrated (e.g., benzene, toluene, etc.) has a low solubility in the mixed acid and forms a second phase when mixed with the acid media. Because of the low organic solubility in the mixed acid and the rapid rate of the nitration reaction, the reaction is thought to take place in the acid phase close to the interface of the organic phase and

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acid phase (*12*). Therefore reaction vessels are well mixed to generate a large interfacial area between the two phases to facilitate a rapid predictable rate of nitration. However, generating a large interfacial area is not sufficient. The reactants must also be evenly distributed throughout the reactor. For example, in the production of nitrobenzene, unintended locations in reactor systems containing high concentrations of nitric acid relative to the benzene can lead to over-nitrated product (i.e., formation of dinitrobenzene). These unintended areas are typically due to poor mixing or to a poor design for the introduction of materials to the reactor system. The reactants must be introduced in the best possible location within the reactor and at the right flow rate to avoid these macro effects. Poor mixing is also a significant safety concern. Poorly mixed locations that suddenly contact the acid phase with a large amount of organic phase can result in a rapid evolution of heat that cannot be dissipated in a timely manner. This can lead to thermal decomposition, the consequences of which can be severe (*13*).

The target criteria for 'perfect' mixing in a batch reactor or CSTR is that $t_{1/2}$ is at least 8 times greater than t_{mix}. The definition of $t_{1/2}$ is the half-life of the organic substrate (*14*). A practical way to determine t_{mix} for a specific reactor geometry, is to charge the vessel with a weak acid containing an indicator that changes color when the solution is neutralized with a base. A small excess of concentrated base is added quickly to the reactor with mixing. The mixing time, t_{mix}, corresponds to the time the color completely changes throughout the solution.

For a given reactor configuration, the t_{mix} depends primarily on the density, viscosity, and Re number of the reaction mixture, as well as the geometrical configuration of the reactor.

Researchers at BC Research have found that for reactors with reasonable aspect ratios, the mixing required to obtain fast nitration reactions is attained when the power input into the reactor is in the range of 8 to 12 Watts/kg.

How fast the reactants will mix also depends on where and how the reactants are introduced into the reactor. If the reactants are introduced too fast or are added in a low mixing area (e.g., behind a reactor baffle plate), then localized concentration inhomogeneities may lead to non-optimal reaction conditions. In a typical nitration experiment, the nitric acid and sulfuric acid are pre-mixed before the organic phase is charged. In a PFR, the organic phase should be introduced through a manifold that creates even distribution through a cross-sectional region at entrance to the reactor. In a batch reactor or CSTR, the organic phase should be introduced into the suction side of the agitator and close to the high shear point of the impeller (i.e. at the impeller tip). The rate of reactant introduction is also important. The ratio of the mixed feed rate to the substrate feed rate is typically 25:1 to 30:1.

In a PFR or CSTR, the flow of mixed acid to the reactor can be readily measured. However in a batch reactor the mixed acid flow which is established by the recirculation flow within the reactor cannot be easily measured. On the other hand, the internal flow rate can be estimated using the following correlation (*9*),

$$q = n\ D^3\ Nq$$

where:

q: volumetric flow rate, m^3/s

n: rotational speed of the impeller, revolutions/s

D: diameter of impeller, m

Nq: Flow number

Nq numbers for different impeller geometries can easily be found in the literature. Several Nq values are shown below.

Nq = 0.5 , for marine propellers (square pitch)

Nq = 0.87, for a four-blade 45°C turbine

Nq = 1.3, for a disk turbine

Nq = 0.47 for a HE-3 high-efficiency impeller

Lastly, when employing a PFR or CSTR reactor, one must decide whether the sulfuric acid, once separated from the product, will be reconcentrated and fed back to the nitration vessel. Typically, recycling the sulfuric acid more closely mimics the contemplated commercial facility.

A study where the sulfuric acid is not recycled is substantially lower in cost but garners considerably less information about a process that wishes to recycle the acid industrially. The quality of the sulfuric acid can impact experimental results. For example, in a commercial process the recirculated sulfuric acid can contain product and by-products, which can impact diffusion of fresh substrate into the mixed acid media. Further, traces metals can accumulate in the sulfuric acid recycle loop and impact aspects of the chemistry.

Safety Audit

A hazards evaluation of the experimental equipment configuration should be undertaken, along with scrutiny of the operating procedures. The same precautions taken in an industrial nitration facility should be taken in the design of the laboratory or pilot plant equipment used for the study. These precautions include, but are not limited to: knowledge of detonable compositions, knowledge of compositions subject to a run-away exothermic decomposition, elimination of low points where NOx, organics, nitric acid, nitrous acid, and other species can collect, heat removal management, and estimation of energy content of reaction mixtures (compared to TNT). In some cases the energy required to initiate a deflagration or detonation of reaction mixtures should be determined. Management of gas evolution must be taken into account, especially NOx management. The experimental configuration should not allow for the nitration reaction mixture to become isolated in a confined area, such as being double blocked in a transfer line. The mixing of the organic substrate with mixed acid must be efficient to eliminate the possibility of local concentration inhomogeneities in the reactors. The ratio of HNO3:H2SO4:H2O:organic must strictly be controlled throughout the system to avoid unintended reactive mixtures. Any friction point in the process should be evaluated in terms of the amount of energy that can impinge on process streams (e.g., valves, pumps, agitator foot-bearings). Materials of construction must be compatible with strong acids.

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Studies may use indirect materials in the process, such as oils, greases, protective devices, etc. The compatibility of these material with the acids and reaction mixtures must be assessed. Material safety data sheets of all reagents are reviewed.

Emergency shut-down procedures are reviewed. Personal protective equipment such as clothing, gloves, and respirator are chosen. Plans and procedures are developed to address chemical spills and waste disposal.

If the chemical stability of a compound is in question, and no reliable data is available, further work is required before proceeding with the experimental work. Stability of nitration compounds can be assessed using differential scanning calorimetry (DSC) and accelerated rate calorimetry (ARC).

Other safety related items to consider are vent gas composition (presence of carbon monoxide, N_2O), shutdown and startup modes of operation (many accidents happen at these times for various reasons), no flow situations, reverse flow (nitration up stream of the nitrators), presence of organic impurities that lower the onset temperature of decomposition, failure to properly separate acid and organic phases, clean out procedures, unintended nitration in uncooled areas within a process, and impact of fire.

Sampling and Analysis

Part of the experimental plan should include a well-defined sampling and analysis strategy. Mixed acid nitrations are fast reactions, making analysis of unreacted starting material a challenge. Partition coefficients of products and by-products between organic and aqueous acid phases add to the complexity of sampling.

Samples taken at the exit of the experimental reactor, or from the reactor, must always be assumed to have unconverted reactants. Such samples must be quenched to stop the nitration so that the starting material can be quantified. Quenching can be done by rapidly cooling the sample, or by dilution of the sample with cold water. A cooled sample loop can also be employed.

Once samples are taken, the organic and acid phases should be quickly separated, even if the sulfuric acid has been cooled and diluted. Any residual reactant, especially nitric acid, will keep reacting if the phases are not separated. Refrigeration of samples that have been prepared for analysis should be kept refrigerated until performing the analysis.

Typically, both the acid phase and organic phase are analyzed for products and by-products. It is common that several isomers of a particular species are present, and each may require quantification.

Sample preparations that require extraction steps need to be validated with known concentrations of by-products to establish the recovery for each analyte from the compositional matrices to be analyzed.

The analysis of organic components that are present as free acids are typically done via gas chromatography (GC). Neutralized organic compounds (e.g., sodium nitrophenols or sodium cresols) are typically analyzed via liquid chromatography (HPLC). Finally, to assess the completion of reaction where nitric acid is the limiting reactant, residual nitric acid in the spent mixed acid is measured. This is done by measuring the nitrate & nitrite in the acid phase using ion chromatography.

Analytical standards made with volatile solvents are refrigerated to reduce evaporation, and should be prepared in the same compositional matrix as the sample. For example analytical results are improved for dinitrobenzene analyses in mononitrobenzene when the dinitrobenzene standards are prepared in nitrobenzene rather than in dichloromethane.

Conclusion

The experimental methodology and recommendations presented in this paper are based on the know-how gathered by BC Research over the course of 20 years of experimental nitration work. However, the reader should understand that this summary is by no means a comprehensive methodology to use when conducting nitration experiments. Rather it provides a number of practical considerations for those about to undertake a nitration research program.

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Chapter 10

Assessment of Chemical Reactivity Hazards for Nitration Reactions and Decomposition of Nitro-Compounds

Robert W. Trebilcock*,[1] and Seshu Dharmavaram[2]

[1]E.I. du Pont de Nemours & Co., Building K-37, Chambers Works,
Deepwater, New Jersey 08023
[2]E.I. du Pont de Nemours & Co., 1007 Market St.,
Wilmington, Delaware 19898
***E-mail: Robert.W.Trebilcock@dupont.com**

Nitro-compounds made from the nitration of organic molecules are highly reactive chemicals used for producing a variety of commercial products throughout the world. However, the potential for over-nitration and the inadvertent or unexpected decomposition can lead to very high chemical reactivity hazards with dangerous consequences. Such reactions are exothermic leading to generation of heat that can accelerate the reaction causing a rapid temperature and pressure increase in a vessel. A detailed chemical reactivity hazard assessment should include the estimation and/or measurement of several parameters such as the heat of reaction, adiabatic temperature rise, maximum self-heat rate, exothermal onset temperature and oxygen balance.

Introduction

Nitro-compounds made from nitration of organic molecules are chemicals used for producing a variety of commercial products throughout the world. Nitration reactions are also done in the laboratory to synthesize new chemical compounds of interest. Whether done in commercial plants or in the laboratory, nitro-compounds can be highly reactive and a hazards assessment needs to be done to evaluate the potential for over-nitration and inadvertent or unexpected decomposition, which can lead to very high chemical reactivity hazards with

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dangerous consequences. Nitration and decomposition reactions are exothermic leading to generation of heat that can accelerate the reaction causing a rapid temperature and pressure increase in a vessel. In addition to heat released, gas generation can also occur that leads to significant pressure increases.

A detailed chemical reactivity hazard assessment should include the estimation and/or measurement of several parameters such as the heat of reaction, decomposition energy, oxygen balance, adiabatic temperature rise, maximum self-heat rate, and exothermal onset temperature. Once a hazards assessment is completed, for a specific situation or system, then the consequences of a catastrophic event can be analyzed to illustrate the potential impact, which in turn can then drive good risk reduction decisions. The hazards assessment needs to define the expected reaction for the process being evaluated considering reactants, products, byproducts and impurities. It needs to consider both standard operating conditions and unusual conditions.

Moving outside of safe operating conditions has resulted in many accidents both in the laboratory and in commercial plants. The consequences of incidents involving nitro-compounds or nitration can include fires, decomposition, deflagrations, detonations and toxic gas generation.

Over the years there have been many accidents in commercial plants and laboratories involving nitro-compounds and nitration including several in the past few years. As an example, a deflagration occurred on May 19, 1967 in a batch plant making dinitrobenzene at DuPont's Chambers Works plant in Deepwater, NJ (*1*). In normal operation, nitrobenzene would be slowly fed into the sulfuric/nitric acid mixture in the agitated reactor while cooling water was used to remove the heat generated by the nitration reaction. However in this case, it was determined that the nitrobenzene was fed to the batch nitrator without sufficient agitation. The agitator was restarted and the unreacted ingredients reacted suddenly resulting in a temperature rise above 200 °C. The heat of reaction exceeded the cooling capacity of the reactor causing thermal runaway and the material in the reactor deflagrated resulting in a fireball of 20-40 ft in diameter. Extensive damage occurred to the plant. Fortunately, there were no serious injuries from this accident.

This example illustrates just one of the many ways that energy can be released when using nitro-compounds or performing nitration reactions. An accident such as this could occur both in commercial units and in the laboratory.

Chemical Reactivity Hazards Assessment

The first step in completing a hazards assessment for existing or potential process is to define the expected reaction and process. The evaluation needs to consider the reactants, products, byproducts (including gases) and impurities that could be generated by the process. Consideration needs to be made for both planned operating conditions and for potentially unusual conditions.

For handling of nitro-chemicals or for nitration processes some initial hazard screening tools include calculation of the heat of nitration reaction, decomposition energy of nitro-compounds, and oxygen balance of the compounds or mixtures. Some of this information can be found in the literature or calculated from

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the expected reactions or process. Depending on the results of the screening, additional calorimetric testing may be needed.

Heat of Nitration Reaction

Many incidents involving nitro-chemicals or nitration ultimately result from the unexpected generation of heat and generation of gas. One source of heat can be the heat of reaction since most nitration reactions are exothermic. High exothermic heat of reaction is a potential measure of the chemical reactivity hazard, since heat generation can lead to decomposition, deflagration or detonation if not removed by the process equipment.

The heat of reaction can be determined theoretically by using known heats of formation if the overall chemical reactions are known. Testing in calorimeters can also be used to determine the heat of reaction.

Typical heats of reaction for nitration are exothermic. As an example, the heats of reaction for nitration of toluene are listed below in Table I. The high exothermic heats of reaction are typical for nitration reactions and contribute to the high chemical reactivity hazards.

Table I. Heats of Reaction for Toluene Nitration

Reaction	*Heat of Reaction*
Toluene → Nitrotoluene	-185 cal/g
Nitrotoluene → Dinitrotoluene (DNT)	-163 cal/g

Many nitration processes can generate gases and other sources of heat in addition to the heat of reaction from desired products. These need to be considered and included in the design of the process equipment. Nitration reactor design will need to consider heat generation from the following sources:

- Heat of reaction for the main reactions
- Heat of reaction for byproduct and impurity reactions
- Heat of dilution of acids
- Heat of mixing of acids

Heat generated by side reactions, dilution of acids and mixing of acids can be significant depending on the chemistry practiced. The actual heat generated in the reactor can be much higher than the heat generated solely by the desired main reaction. Failure to consider all heat generation in the reactor could result in insufficient cooling capacity in the reactor and increase the potential for thermal runaway.

Once the total heat generated by the reaction is known this can be used to calculate the adiabatic temperature rise in the reactor. In many cases this adiabatic temperature rise can be quite large and can approach or exceed temperatures in which the materials in the reactor begin to decompose.

In the incident described at the beginning of the chapter, the heat generated in the reactor was typically controlled by slow addition of nitrobenzene to the acid in the cooled and agitated reactor. However in the incident, there was insufficient agitation and the unreacted feed materials began to react at once instead of over time when the agitator was started. This caused the temperature in the reactor to rise much faster than the cooling available, resulting in thermal runaway in the reactor. The temperatures in the reactor reached the point where decomposition reactions began to occur.

Some factors to consider in designing the nitration reactors are listed below:

- What is the adiabatic temperature rise on loss of cooling?

  The closer the normal reactor operating conditions are to the decomposition temperatures of the reactor mass, the greater the possibility of having an incident due to high temperature in the reactor. In some cases backup cooling systems may be needed.

- How will the heat of reaction be removed from the reactor?

  Many nitration reactors have internal cooling coils or jackets to remove the heat of reaction. Others are designed with external cooling loops to remove the heat generated. If the materials are thermally stable it may be possible to evaporate some of the reactor mass to cool the reactor.

- How will the rate of heat generation be controlled?

  Normally the rate of heat generation is controlled by limiting one or more of the ingredients being fed to the reactor. The selection of which ingredients to limit can influence decomposition temperatures and the potential energy released if decomposition would occur.

  Sometimes the rate of reaction is limited by mass transfer between phases or limited by the reaction rate kinetics. In these cases, changes in agitation or temperature can have a large effect on the reaction rate.

- How do changes in reactor temperature affect the reaction kinetics?

  Increasing the reactor temperature will in most cases increase the reaction rate. The reaction rate may increase exponentially with increased temperature, while the heat removal capacity of the reactor will only increase linearly with temperature. This can result in thermal runaway if the reactor temperature is allowed to rise above normal operating conditions. Increasing plant capacity without changing the reactor could cause the reactor to approach limits in its cooling capacity, especially during unusual conditions.

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- What conditions in the reactor can cause upsets in the reactor that could lead to thermal runaway or thermal decomposition?

  Unsteady operation can change the rate of reaction or cooling required causing upsets in the reactor that could lead to thermal runaway or thermal decomposition. Some factors to consider are:

  - ✓ Wrong type or amount of material fed to the reactor
  - ✓ Incorrect time, order or rate of addition of materials to the reactor
  - ✓ Accumulation of reactants in the reactor
  - ✓ Contamination in the reactor
  - ✓ Operation at wrong temperature
  - ✓ Unsteady agitation (none, too little, too much, variable)
  - ✓ Loss of cooling (plugged tubes, loss of cooling water, fouling)
  - ✓ Excessive heating (control failure, initial heating on startup, self or overheating on shutdowns, insufficient heating, heating from external sources such as tracing, friction, mechanical energy, fire)
  - ✓ Incorrect amounts of catalysts, inhibitors, sulfuric acid or water
  - ✓ Inadvertent addition of water to the system (heat of dilution)

Nitro-Compounds' Decomposition Energy

Many nitro-compounds will decompose with a significant release of energy if heated to the point where decomposition begins. Understanding the temperatures, energy released and outcomes (decomposition, deflagration, detonation) of thermal events is an important consideration in the design of commercial plants or laboratory testing plans.

Decomposition energy is usually exothermic for nitro-compounds and can generate gases. The decomposition energy can be significantly higher than the heat of reaction generated by the expected process chemistry. Decomposition energy of pure compounds or mixtures can be estimated using various thermodynamic modeling programs. One of the programs that can be used to develop the reaction thermochemistry is ASTM CHETAH® (Chemical Thermodynamic and Heat [Energy] Release Program) developed by the American Society for Testing and Materials (ASTM). The thermodynamic calculations described in this chapter were done using HT-65, a DuPont high temperature thermodynamics estimation program developed in the 1960's for the formulation of explosives. HT-65 estimates enthalpy and decomposition products using a Gibbs free energy minimization method.

An illustration of the potential heat released from a decomposition reaction and also combustion of dinitrotoluene is listed below in Table II.

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Table II. Heat Released from Reactions of DNT

Reaction	***Heat Released***
Decomposition Energy (DNT)	-900 cal/g
Heat of combustion (DNT)	-4,000 cal/g

The heat generated by the expected reaction of toluene to DNT (shown in Table I) is about half the energy that could be released if DNT were to decompose. The decomposition energy of DNT is for pure DNT. This energy is based on the oxygen available in the DNT molecule. If pure DNT were to decompose, this is the amount of heat that would be expected to be released. How DNT decomposes (decomposition, deflagration or detonation) is determined by the conditions under which the decomposition occurs such as rate of heating and confinement. DNT is not completely oxygen balanced, but if extra oxygen is available during the decomposition then the heat released could approach the heat of combustion.

High exothermic decomposition energy is a measure of the chemical reactivity hazard of nitrochemicals since unexpected heat sources can lead to decomposition, deflagration or detonation. Since most nitro-compounds will release heat upon decomposition it is important to understand at what temperature the decomposition begins. The closer the normal operation is to the decomposition temperature the greater the risk. Impurities or mixtures could lower the decomposition temperature of pure materials.

It is important to understand the decomposition properties of the chemical and mixtures early in the development process to avoid the potential for unexpected reactions both in laboratory development tests and in the actual commercial facility. High calculated heat of reaction or decomposition energy increases the need for actual calorimeter testing to determine parameters such as:

- Potential for thermal decomposition
- Adiabatic temperature rise
- Quantity and rate of heat release
- Gas evolution
- Decomposition rates vs. temperature
- Initial decomposition onset temperature

Many testing methods are available to determine the decomposition temperature of nitrochemicals or mixtures of nitro-compounds. Only two will be discussed in this chapter.

A quick screening method for determining heat of reaction or the onset temperature of decomposition is Differential Scanning Calorimeter (DSC). The advantages of using a DSC to develop decomposition temperatures is that the test can be run very quickly and needs only a very small sample. The small sample size and speed of the test is also a disadvantage since some thermal events can be missed by the instrument.

Figure 1 shows a diagram of a DSC. A small sample is placed in the sample cell and the sample is heated. The calorimeter compares the temperature in the

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sample cell with the temperature in the reference cell and creates a plot showing exothermic or endothermic reactions as a function of temperature. A typical DSC output curve is shown in Figure 2.

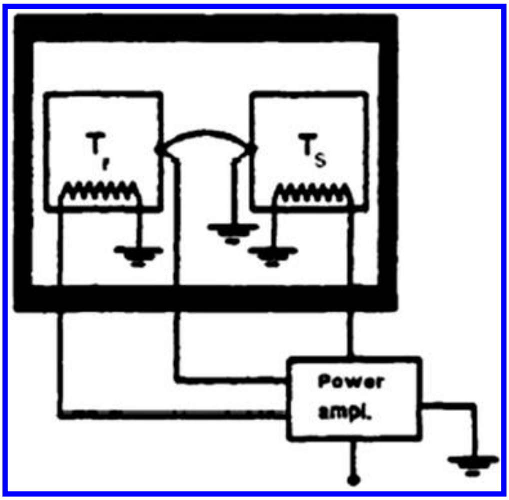

Figure 1. Differential Scanning Calorimeter (DSC).

Another calorimeter is the Accelerating Rate Calorimeter (ARC). This calorimeter uses a larger sample size (1-50 ml). The sample size is large enough that mixtures can be evaluated, the sample can be mixed during the test and materials can be sampled after the test is complete. The ARC is a good instrument for developing process data and evaluation of runaway reactions.

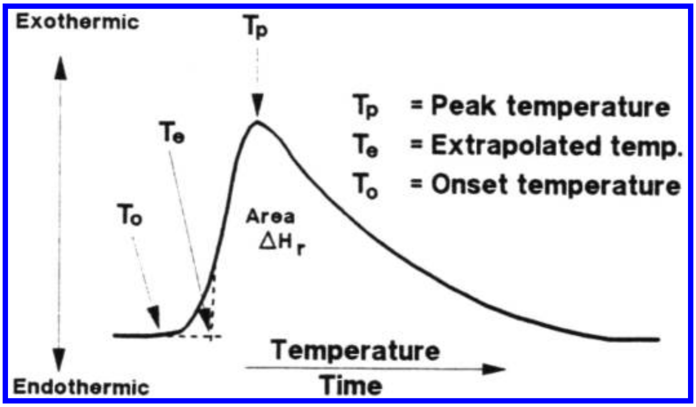

Figure 2. Typical Differential Scanning Calorimeter (DSC) Curve.

Figure 3 shows a schematic of a typical Accelerating Rate Calorimeter. The sample is placed in the spherical bomb and the sample is heated in a heat-wait-search mode to determine exothermic behavior in the calorimeter. Differences in the heat input and the observed heat output are recorded. Pressure buildup in the

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bomb is also recorded. The sample in the bomb can be agitated. One disadvantage of the ARC testing is longer run times. Also the sample size is still fairly small and can limit the accuracy of some of the measurements.

The ARC test can be used to develop the following information:

- Heat of reaction
- Onset temperature for decomposition reactions
- Adiabatic temperature rise
- Rate of change in pressure and temperature vs. time
- Self-accelerating decomposition temperature
- Detailed kinetics
- Post test sampling of gas evolution or reaction products is possible

An example of an ARC run is shown in Figure 4. The sample run in the ARC test shown in Figure 4 is a mixture of two phases. The organic phase consists primarily of nitrobenzene (80%) and dinitrobenzene (20%). The organic phase also contains some reaction byproducts such as picric acid (0.5%). The second phase is an acid phase consisting of 78% sulfuric acid. Excess nitric acid was added to the acid phase to simulate an over-nitration condition. The acid phase also contains some reaction byproducts such as nitrosylsulfuric acid. The two phases were mixed in the ARC during the testing.

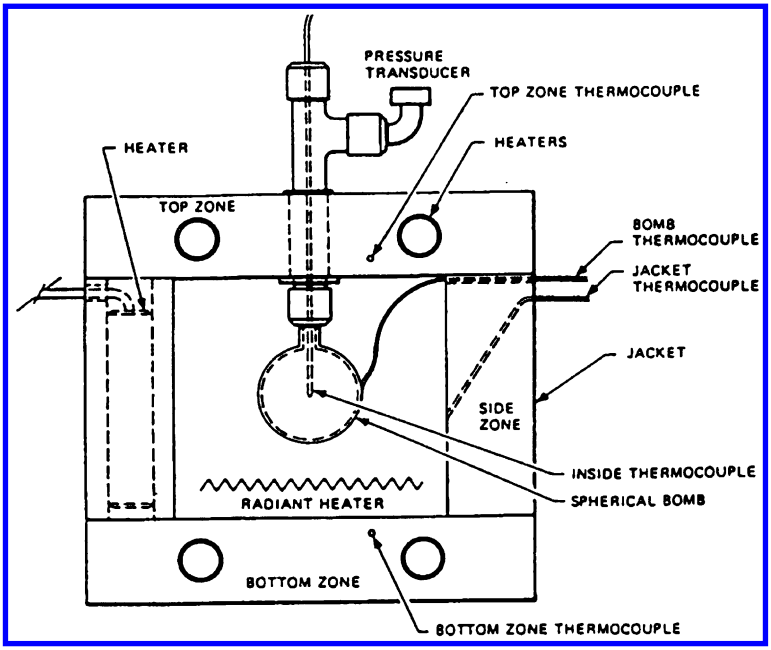

Figure 3. Accelerating Rate Calorimeter (ARC).

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The ARC test results shown in Figure 4 illustrates the advantages and importance of performing calorimetric hazards screening of actual mixtures for the collection of decomposition data. Literature values or DCS/ARC testing of pure Nitrobenzene or Dinitrobenzene would have suggested a decomposition temperature of around 300°C. However the ARC test in Figure 4 shows that the under normal reaction conditions, with the presence of impurities in the organic and acid phases, the actual point where decomposition reactions begin can be considerably lower (130 °C). These initial self-heating rates are very low but the rate of decomposition rises very quickly with increasing temperature and significant decomposition could occur below 300°C.

The ARC test shows that actual decomposition safety margins could be significantly lower than what would be predicted based only on testing of pure compounds or literature values. Impurities can lower the decomposition temperature and increase the rate of temperature rise. Some impurities to consider are:

- Nitric Acid, oxidizers and other compounds containing oxygen
- Byproducts such as more highly nitrated impurities
- Impurities such as nitrophenols

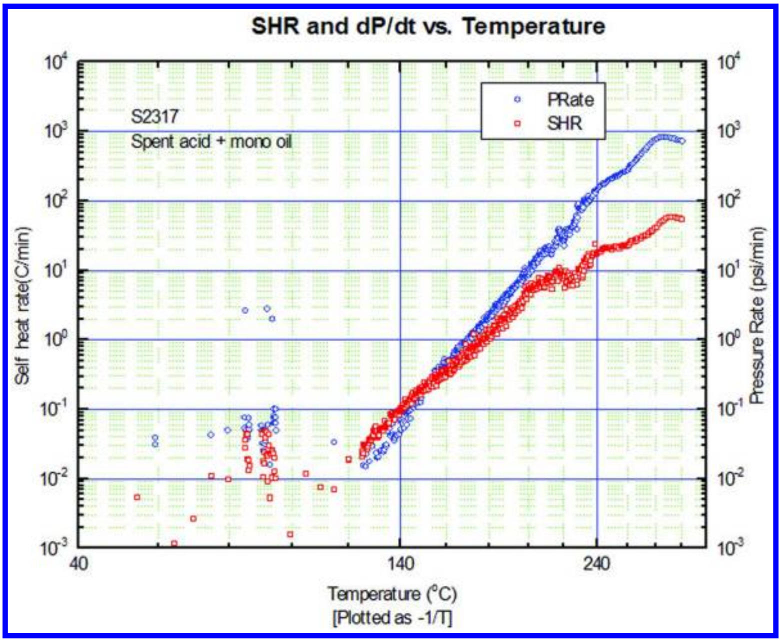

Figure 4. ARC test nitrobenzene, dinitrobenzene and sulfuric acid with impurities. (see color insert)

The ARC test provides information on the onset of self-heating. At the onset of self-heating, the temperature rise may be small, much less than one °C per minute. There may be conditions where reactive materials are held above the onset of self-heating for long periods of time. The slow self-heating could be significant

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if the heat generated by the self-heating is not allowed to be removed. Some of these conditions could occur while the plant is not running. Some examples where slow self-heating could occur and result in thermal runaway over time are listed below:

- Material trapped under insulation can begin to self-heat and the insulation can prevent loss of the heat causing thermal runaway
- Materials can be held under heat in process equipment or piping for long periods of time during shutdowns causing thermal runaway
- Oxidation reactions (exposure to air or other oxidizers) can create decomposition by-products that may have a lower decomposition temperature than normal products
- Self-heating could increase the reaction rates of side reactions that result in formation of impurities with lower decomposition temperature. In some cases the decomposition products can autocatalyze the decomposition reaction (*2*).

Any process upset that results in heat generation that exceeds the rate of cooling can lead to decomposition. Some examples include:

- Unsteady operation
- Wrong ratio of ingredients
- Starting of agitation
- Unexpected leaks into or out of the process
- Backflow of reactor mass or other organics into nitric acid feed lines

The plant design needs to consider other sources of heat that could heat the materials to the point of decomposition. Some potential sources of heat that could lead to decomposition reactions are listed below:

- Heat buildup in deadheaded pumps or centrifuges. Decomposition reactions (decomposition, deflagration or detonation) have occurred when material has been deadheaded in pumps and centrifuges long enough to reach the decomposition temperature. Temperature rise in these conditions can be quite rapid.
- Friction caused by rotating equipment, seals or other mechanical action. There have been cases where material has accumulated in packing of agitator seals and decomposition reactions started when the packing was tightened. Pump seals can also be a source of heat.
- External heat sources such as failure of temperature control in heat exchangers or tracing.
- Impact can be considered a source of heating that can cause decomposition reactions to occur. Need to consider impact due to metal to metal contact, tramp (foreign) material or mechanical failure. Sand or grit can increase impact sensitivity. Impurities (byproducts, nitric acid, and oxygen containing compounds) can increase impact sensitivity.

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Some impurities such as picric and styphnic acid salts are very impact or friction sensitive if isolated and allowed to dry.

- Adiabatic compression can generate very high temperatures if gases are compressed due to pressure changes in the process. The heat from the compressed gas can transfer to reactive materials and begin decomposition reactions.
- Electrical shock, static electricity or electrical arcs could provide sufficient heat to start decomposition reactions.

Oxygen Balance

Another important calculation when working with nitro-compounds is calculation of the oxygen balance (OB) of the reactants, products and mixtures formed in the process equipment.

The oxygen balance of a compound or mixture is a calculation used to indicate if the compound/mixture is deficient in oxygen per the stoichiometric equation below:

$$C_xH_yO_z + (2x + y/2 - z)\, O \rightarrow x\, CO_2 + y/2\, H_2O$$

For calculating the oxygen balance in % oxygen for non-metallic compounds the following formula can be used where MW is the molecular weight of the material. If the molecule contains N, Cl or S atoms, they are ignored in the calculation.

$$\text{Oxygen Balance (in \% oxygen)} = -1600\, [(2x + y/2 - z)/\, MW]$$

The oxygen balance of mixtures can be determined by taking the oxygen balance of each component in the mixture and multiplying by the compounds weight %. For example, see Table III below, the oxygen balance for nitrobenzene is -162.6 and the oxygen balance for nitric acid is +63.5 using the above equation. A mixture of 70 weight % NB and 30 weight % nitric acid would have an oxygen balance of -94.8.

Table III. Example Oxygen Balance Calculation

Ingredient	***Weight %***	***OB of Ingredient***	***Oxygen Balance***
Nitrobenzene	70%	-162.6	-113.8
Nitric Acid	30%	+ 63.5	+ 19.0
		Oxygen balance of Mixture	-94.8

A negative number indicates that the compound or mixture is deficient in oxygen while a positive number indicates a compound/mixture with excess oxygen. Mixtures with an oxygen balance of -120 to + 80 indicate materials that are well oxygen balanced and may have higher potential chemical reactivity hazards.

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Most commercial explosives are formulated to have oxygen balances close to zero. The most energetic and sensitive explosives are oxygen balanced on a molecular level. See Table IV for the oxygen balance for several high explosives.

Table IV. Oxygen Balance for Several High Explosives

High Explosive	***Oxygen Balance***
Pentaerythritol tetranitrate (PETN)	-10
Nitroglycerine (NG)	+4
Picric Acid	+45
Trinitrotoluene (TNT)	-74

When oxygen balanced on a molecular level, all the oxygen needed to balance the decomposition reaction is present without the need for mixing or material transfer to supply additional oxygen. If the material begins to react due to the input of heat (temperature, impact, friction) the decomposition or detonation energy can be released very quickly.

Mixtures of materials containing oxygen deficient materials (fuels) and oxygen rich materials (oxidizers) can result in oxygen balanced mixtures that are more hazardous than the individual ingredients.

A common commercial explosive is an ammonium nitrate/fuel oil mixture (ANFO) which is a mixture of 94% ammonium nitrate and 6% fuel oil. Ammonium nitrate is positively oxygen balanced at +20 and will release energy upon decomposition of 382 cal/g. By adding 6% fuel oil (OB = -343) to the ammonium nitrate, the oxygen balance of the ANFO mixture is -2. By creating an oxygen balanced mixture the energy released by decomposition or detonation is greatly increased to 841 cal/g. In mixtures, the fuel and the oxidizers are not chemically bonded but they are in sufficient proximity that once decomposition occurs, the oxygen is available to react with the fuels, increasing the energy released.

Table V compares the oxygen balance and energy release (detonation with expansion) calculated using HT-65 for various forms of nitrated benzene and compares the results to TNT.

Starting with benzene you have a material that acts as a fuel with a very negative oxygen balance. In the pure form and in the condensed phase, benzene would not be expected to be very reactive. If benzene is allowed to vaporize and mix with oxygen it will release significant energy if exposed to heat (ignition) sources. As more nitro groups are added forming nitrobenzene (NB), dinitrobenzene (DNB) and trinitrobenzene (TNB) the materials become more oxygen balanced and the amount of energy that could be released upon decomposition increases.

As the oxygen balance approaches zero the required oxygen is available within the condensed phase. Unlike benzene, which needed oxygen from the air to be reactive, NB, DNB or TNB already has some oxygen present. If these materials are heated to temperatures sufficient to begin decomposition, then significant energy can be released without the need for additional oxygen from external sources.

Oxygen balance calculations need to be combined with energy calculations and calorimeter testing to get a more complete understanding of the potential energy released on decomposition. As an example, water has an oxygen balance of zero so adding water to a mixture will bring the mixture oxygen balance closer to zero. However, water acts as an inert and the addition of water will reduce the total energy released on decomposition, by virtue of the fact that it can absorb heat upon vaporization.

Table V. HT-65 Heat Released on Detonation with Expansion

Compound	*Oxygen Balance*	*Equilibrium Temperature °K*	*"Q" cal/g*	*"Q" as % of Q_{TNT}*
2,4,6 Trinitrotoluene (TNT)	-74	3536	937	100
Benzene	-308			
Nitrobenzene (NB)	-163	2413	761	81
Dinitrobenzene (DNB)	-95	3307	919	98
Trinitrobenzene (TNB)	-56	4284	1047	112

Figure 5 below shows a HT-65 calculation done at a constant density of 0.5 g/cc for various mixtures of DNB and water. It shows that as water is added to the DNB, the oxygen balance approaches zero but the total energy released also falls. The drop off isn't linear since HT-65 is predicting different equilibrium products from the different mixtures. DNB/water mixtures are not single phase, so the benefit of water addition may not be seen unless the mixture is kept agitated.

While the addition of water is usually a good way to reduce process safety risk there are a few cases where excess water can cause some issues. Nitration is very sensitive to acid strengths and excess water could stop the nitration and result in accumulation of unreacted nitric acid. The unreacted nitric acid could react quickly if the water is brought back to normal levels. Unreacted nitric acid or organics could cause delayed reactions or more vigorous reaction in other vessels. Unreacted organics could cause flashpoint issues if the unreacted organics are more flammable than the final products. Water added to strong acid could generate sufficient heat to start decomposition.

Excess water can also change the characteristics of the nitric acid ions. In most nitration reactions, the reaction is run under conditions where the nitronium ion (NO_2^+) is the reactive species. Depending on the nitric acid or nitric/sulfuric acid mixture used for nitration, the concentration of the nitronium ion can change, significantly changing the nitration kinetics. In some cases the nitronium ion can drop to very low levels and the nitrate ion (NO_3^-) can begin to become more important. The chemistry done by the nitrate ion may be very different than the chemistry done by the nitronium ion, creating different byproducts which may

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change the heat or reaction, thermal stability, decomposition temperature, gas generation and other significant process parameters. The nitrate ion may cause oxidation reactions in place of the expected nitration reactions. A good discussion of ionic species in nitric acid and nitric/sulfuric acid mixtures can be found in the literature (*3*).

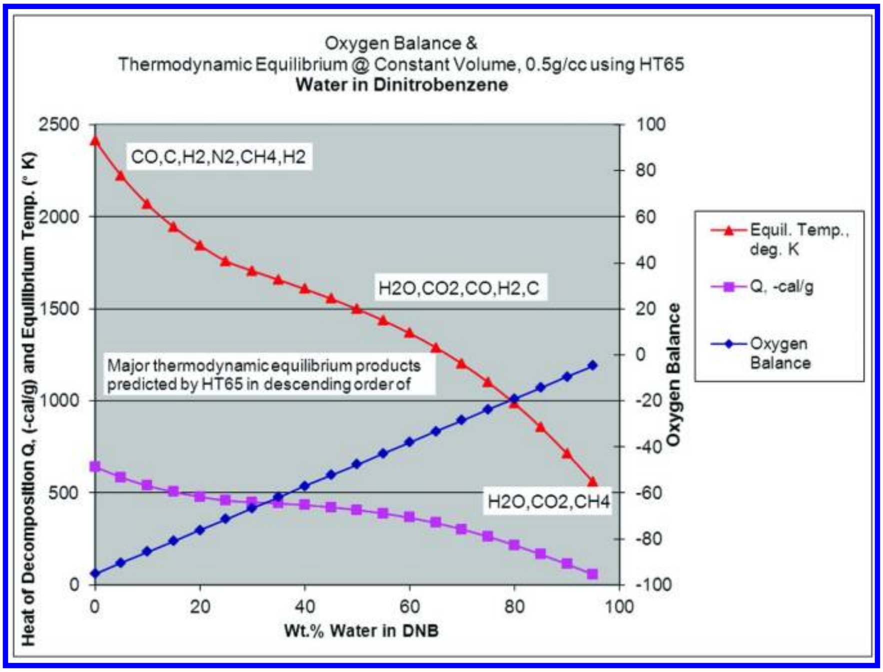

Figure 5. HT-65 calculation for a mixture of DNB and water. (see color insert)

Sulfuric acid is another ingredient that is common in nitration mixtures. Based on HT-65 calculations done at a constant density of 0.5 g/cc shown in Figure 6, the sulfuric acid under equilibrium conditions may supply some oxygen to oxygen deficient organics. Figure 6 shows the predicted oxygen balance and energy released for decompositions of DNB and sulfuric acid mixtures. The equilibrium products suggest that some of the oxygen in the sulfuric acid is available to react with the organics increasing the energy released. The calculated decomposition energy for the DNB/Sulfuric acid mixtures never exceeded the decomposition energy for pure DNB. Sulfuric acid could be a source of oxygen, but it doesn't seem to increase the decomposition energy. Changes in sulfuric acid strength could affect chemical reactivity, since the sulfuric acid strength has a significant impact on reaction rates and the nitronium and nitrate ion concentrations.

Table VI shows the results of some ARC testing for mixtures of DNB and sulfuric acid (90% strength). The DNB and sulfuric acid used in these ARC tests contained typical impurities found in nitration mixtures such as nitrophenols, nitric acid and nitrosylsulfuric acid. ARC test conditions will influence the calculated

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heat of decomposition “Q”. Small sample size may be needed to protect the ARC equipment but will increase the error in the calculated “Q”. Low ARC cutoff temperatures may be needed to protect the ARC equipment but may result in lower calculated “Q” due to the ARC missing part of the decomposition reaction. High self heat rates can exceed the ARC cooling capacity resulting in lower calculated “Q”.

The ARC testing summarized in Table VI below is in general agreement with the HT-65 heat of decomposition calculations shown in Figure 6 for DNB and sulfuric acid mixtures. The ARC testing shows that significant energy can be released from the decompositions of mixtures containing only small amounts of reactive materials like DNB. However, the “Q” values shown in the table cannot be directly used because of the limitations with the ARC testing discussed above.

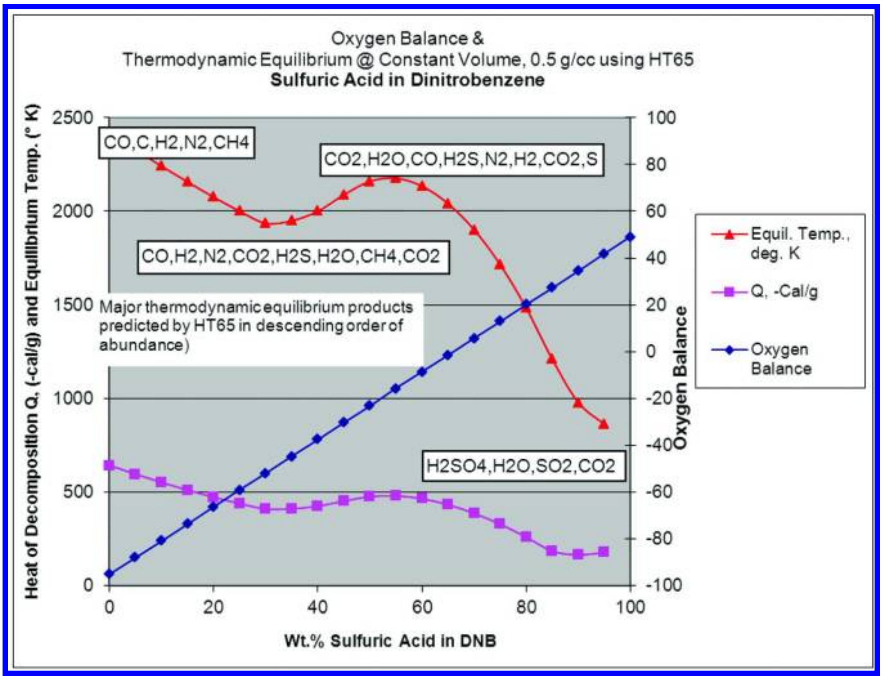

Figure 6. HT-65 calculation for a mixture of DNB and sulfuric acid. (see color insert)

Nitric acid is another ingredient that could become part of nitration mixtures. Since many nitro-compounds are negatively oxygen balanced and nitric acid is positively oxygen balanced (OB= +63) mixtures containing nitric acid will affect the oxygen and energy balances. Figure 7 below shows the HT-65 calculations done at a constant density of 0.5 g/cc for mixtures of NB and nitric acid. Adding extra nitric acid to NB greatly increases the energy released as the oxygen balance approaches zero.

Table VI. ARC Test Results for DNB and Sulfuric Acid (H_2SO_4) Mixtures

Test	*Mixture Composition*	*"Q" cal/g*	*Sample Size g*	*ARC Cutoff Temperature °C*	*Maximum Self Heat Rate °C/min*
1	20% DNB & 80% H_2SO_4	185	4.1	>351	739
2		255	3.0	>393	1000
3	60% DNB & 40% H_2SO_4	399	0.87	>300	
4		305	0.82	307	302
5		385	0.80	350	601
6	100% DNB	528	1.0	>430	>830

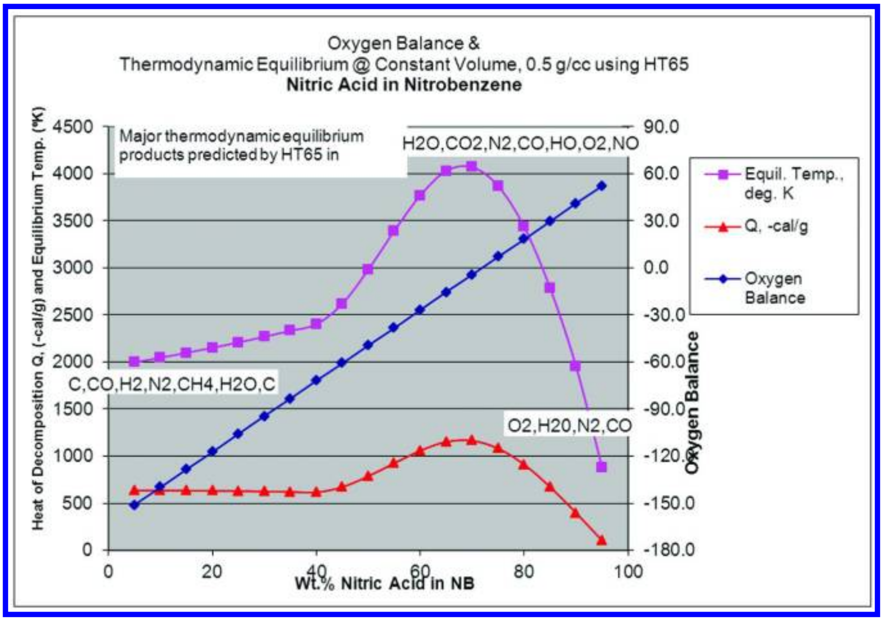

Figure 7. HT-65 calculation for a mixture of NB and nitric acid. (see color insert)

The detonability of nitrobenzene, nitric acid and water systems has been described in the literature (*4*). In one inch diameter steel pipe, pure NB or pure nitric acid was not detonable under the conditions studied. However mixtures of NB containing from about 20% to 90% nitric acid were found to be detonable.

Excess nitric acid is also likely to increase impact and friction sensitivity, lower the decomposition temperature, increase the likelihood of transition from deflagration to detonation and reduce the critical diameter at which detonations can propagate.

Some nitration reactions are done using a large excess of strong nitric acid in the reactor. Reactor mixtures containing large amounts of nitric acid compared to the amount of organics present and also containing very little water are likely to be well oxygen balanced and may be quite reactive.

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When designing processes using nitro-compounds, it is important to consider that abnormal or unsteady feed rates can lead to more oxygen balanced and reactive mixtures. Excess nitric acid could result in overnitration, oxidation reactions, vapor phase nitration, side reactions and acid/base reactions.

Plant design needs to consider places where organics and oxidizers could accumulate. One area to check is in the vent systems. Oxidizers in the vent system could include nitric acid mists, nitrated organics, NOx or ammonium nitrate which if allowed to come in contact with organics or CO could:

- React releasing heat that could cause decomposition
- Oxidize creating new compounds with lower decomposition temperatures
- Form oxygen balanced mixtures that could react if heated by external sources such as fire, steam or electric tracing
- Form flammable mixtures

Thermal stability of nitric acid when mixed with other process materials needs to be considered. This includes not only process ingredients, but also materials such as lubricants, gaskets and other materials used outside the process that could accidentally come in contact with nitric acid.

Process or organic material back flowing into nitric acid feed lines could result in oxygen balanced mixtures and possible reaction without cooling leading to decomposition reactions in the piping.

Impurities or byproducts generated in the process often need to be removed from the final products and in the process can be concentrated. Nitration often generates nitrophenols such as picric and styphnic acids that are very oxygen balanced and are also very impact sensitive when dry. Care must be taken when isolating these compounds. Process leaks containing these compounds can accumulate on equipment or insulation where the water could evaporate leaving behind a impact sensitive residue.

Operations with processes and systems with higher decomposition energies and those that are more oxygen balanced should consider additional testing to determine safe operating conditions. Some of this testing could include:

- ***Critical Diameter:*** Consider running tests to determine the critical diameter of products or mixtures to determine minimum pipe sizes and confinement needed to sustain propagation of a detonation through piping systems.
- ***Impact Sensitivity:*** Consider adding contaminants such as byproducts and impurities. Also consider addition of materials such as sand or grit that may increase the impact sensitivity.
- ***Thermal Stability:*** Consider testing products, byproducts and impurities for thermal stability. Also may want to evaluate reaction mixtures for decomposition onset temperatures.
- ***Card Gap Testing:*** Card gap testing is a way of measuring the sensitivity of materials to propagation of detonation. The more distance between the initiator and the sample the more sensitive the material is to detonation.

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- ***Static Shock Testing:*** Some mixtures can be initiated by static discharges.
- ***Vented Bomb Testing:*** Significant amounts of gases will be generated during decomposition reactions. Depending on the rate of gas generation it may be possible to vent some of this gas and minimize damage to equipment. In some cases, venting can minimize the potential for transition from deflagration to detonation. A typical vented bomb test is the Koenan test, used to classify explosives for shipping.
- ***Cap Sensitivity:*** Mixtures or compounds can be tested for sensitivity to blasting caps. Material detonable by blasting caps is very reactive.

Summary

When evaluating existing process or potential new laboratory programs involving nitro-compounds or nitration a chemical reactivity assessment should be undertaken early in the endeavor and clearly documented.

Heat of reaction data for the expected and unexpected reactions is important to define the cooling systems needed to remove the heat of reaction and to maintain a safe operating distance away from temperatures that begin decomposition reactions or thermal runaway.

Many nitration processes can generate gases and other sources of heat in addition to the heat of nitration reaction in making the desired products. These need to be considered and included in the design of the process equipment. For nitration reactor and design of all other connected process equipment one needs to consider:

- Heat of reaction for the main reactions
- Heat of reaction for byproduct and impurity reactions
- Heat of dilution of acids
- Heat of mixing of acids
- Heat of decomposition for nitro-compounds

The total heat generated in the reactor can be significantly higher than the heat of reaction generated by the desired products. Heats of decomposition of nitro-compounds can be an order of magnitude or more greater than the heats of the nitration production reactions.

Knowledge of the decomposition temperature of reactants, products, byproducts and impurities is important when determining the safe operating temperatures of the process under scrutiny. Thermodynamic programs can be used to predict the energy released if materials or mixtures begin to decompose. Heat release during decomposition for nitro-compounds can be significant and can result in deflagrations or detonations. Estimates can be made of the adiabatic temperature rise and the maximum temperature. Calorimetric testing is likely to be needed to determine key reaction parameters such as the onset temperature and the rate of temperature rise for the decomposition reactions. Actual reactor operating conditions may significantly lower the decomposition onset temperature

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of pure materials since impurities, byproducts or reactants such as nitric acid may be present in the reaction mixture.

The oxygen balance of the compounds and mixtures can be calculated and mixtures with oxygen balances closer to zero are more likely to be reactive. Oxygen balanced mixtures may have higher decomposition energy, have increased impact and friction sensitivity, have lower decomposition onset temperature, have increased potential for transition from deflagration to detonation and have reduced critical diameter at which detonations can propagate.

A thorough chemical reactivity hazards assessment is necessary for safe design and operation of all parts of a process where nitro-compounds are handled and where nitration reactions are conducted.

Acknowledgments

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Chapter 11

Safety Instrumented Systems for Process Safety

Subodh Medhekar[*]

Exponent, Inc., 320 Goddard Way, Suite 200, Irvine, California 92618
[*]E-mail: smedhekar@exponent.com

This paper presents a review of Safety Instrumented Systems based approaches to prevent or mitigate hazardous events by preemptively taking the process to a safe state. Various methods to determine the appropriate Safety Integrity Levels for such system applications are discussed along with a simplified Nitration industry example.

Overview

Safety instrumented systems (SIS) are becoming increasingly popular for safeguarding process plants in the oil/gas, petrochemical, and other process industries. A SIS is a system specifically designed to prevent or mitigate hazardous events by deliberately and preemptively taking a process to a safe state when predetermined process conditions are violated. Safety Interlock Systems, Emergency Shutdown Systems (ESD), and Safety Shutdown Systems (SSD) are common names for such SIS. While the use and application of SIS has grown substantially in the oil/gas, petrochemical, and other process industries over the last decade, for many end users, SIS is still a new concept. SIS systems are now being widely used in nitration plants around the world.

Figures 1 and 2 outline the basic concepts of a SIS. Take the case of a catalyst bed reactor (simplified schematic as shown in Figure 1) whose temperature needs to be controlled to be in a safe state. Normally a basic process control system (BPCS) will monitor the temperature(s) within the reactor and through a variety of ways (including reactant inlet flow control) will attempt to control the temperature within the safe normal temperature bounds (see Figure 2). If for some reason the reactor temperature cannot be controlled (say reactant inlet control valve fails open or sticks open), an alarm may be sounded to alert an operator to take action. However, if the process conditions are such that it is not possible for the operator to respond quickly (or reliably) to avert the subsequent dire conditions (say

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runaway reaction leading to overpressure, reactor damage and fire/explosion), it may be necessary to implement an automated Safety Instrumented System to take an automatic deliberate and pre-emptive action (upon detection of High Temperature) and bring the system to a safe state. In case of this example, upon detection of high temperatures, an automatic Programmable Logic Controller (PLC) can take an action of independently closing the reactant feed stream to the reactor. To be effective this SIS has to be reliable, specific and be independent of the basic process control system.

SIS can be configured in many ways to meet a variety of process goals and performance targets. Each SIS has one or more Safety Instrumented Functions (SIF) with each SIF loop having a combination of logic solver(s), sensor(s), and final element(s).

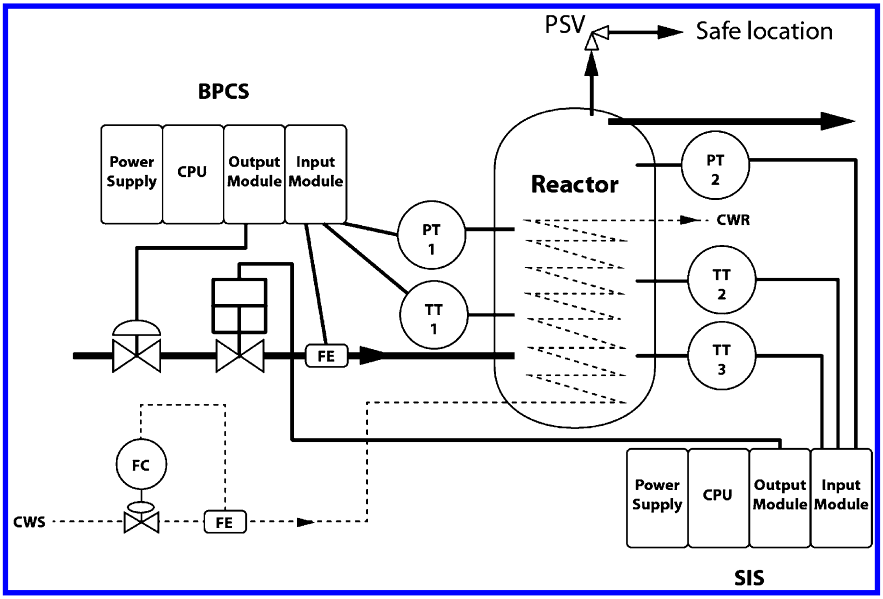

Figure 1. Basic Concepts of SIS and BPCS.

A simple SIS system is shown in Figure 3 and comprises of one sensor, one PLC, and one final element. In this case, upon detection of the process variable being out of bounds the PLC will close the valve (the final element) and bring the system to a safe state.

Figure 4 depicts a more complex system of two sensors (with 2oo2, 2 out of 2 voting logic) and two final control elements. In this configuration, both sensors will have to detect the abnormal process condition and then the PLC will close both of the valves. This configuration is a more complex (and also more expensive) SIS than the one shown in Figure 2 but is also more reliable / effective in reducing the inherent risks and also reducing the likelihood of spurious trips that can be a nuisance to the process operations. A complex and more expensive, which is highly reliable, system may be justified if the dire outcomes are very serious and other means to reduce these risks are not available or are not very reliable.

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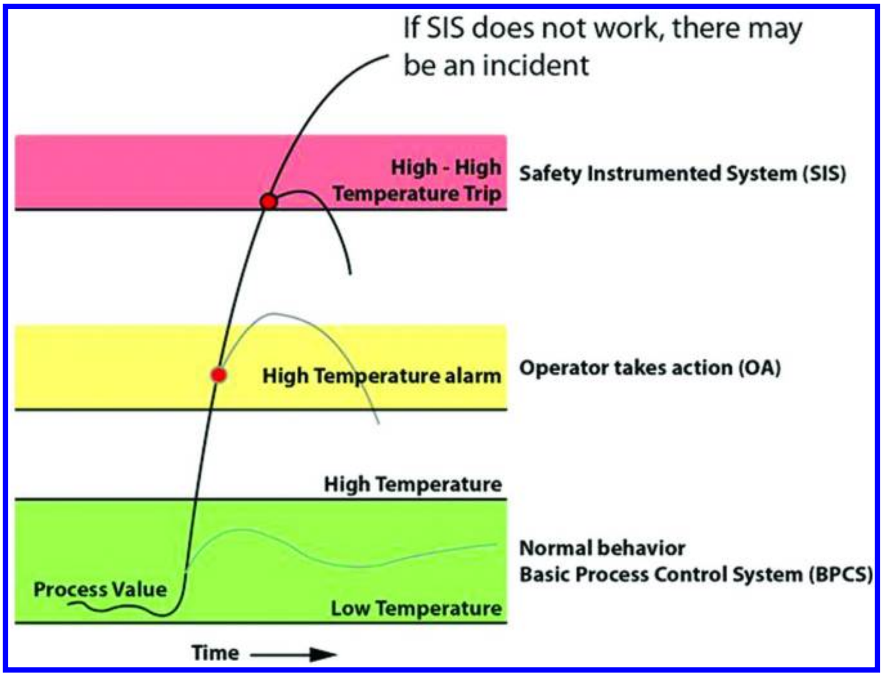

Figure 2. Event Scenario Progression Explaining the SIS Concept. (see color insert)

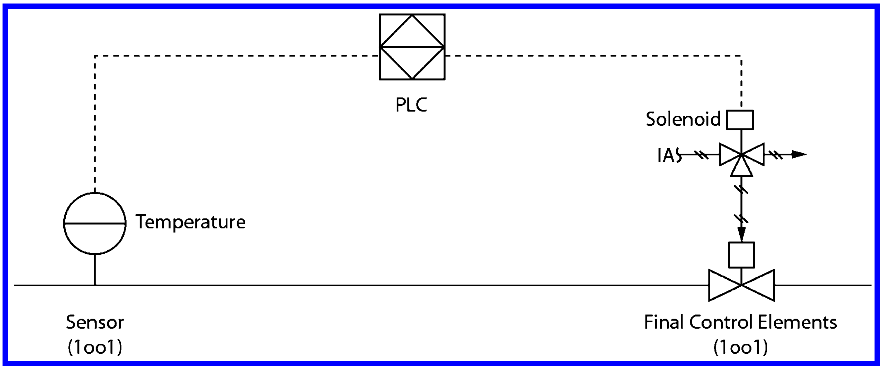

Figure 3. SIF Loop Example (with Single Sensor, Logic Solver, and Single Final Element).

Usually the focus of SIS is to prevent or mitigate dangerous failure consequences. However, in addition to the consideration of dangerous failures, the potential for spurious failures should also be considered when selecting a SIS configuration as a spurious trip can disrupt production and result in significant lost or deferred production costs.

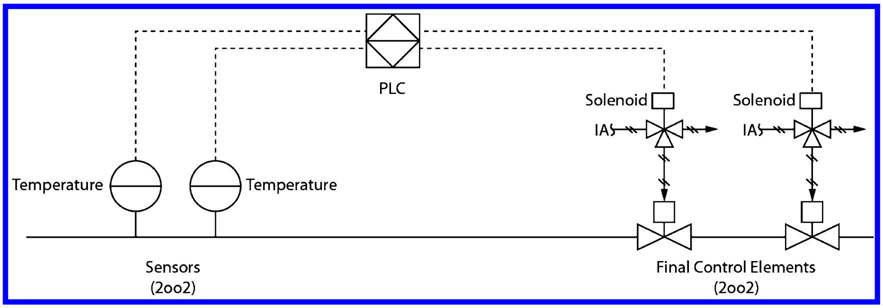

Figure 4. Another Example of SIF Loop (with Two Sensors, Logic Solver and Two Final Elements).

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SIS and Functional Safety Background

Functional safety, as defined by IEC standard 61508, is the safety that control systems provide to an overall process or plant. Increasing use of programmable/ electronic/electric systems to carry out safety functions has raised the desire to design safety systems in such a way as to prevent dangerous failures. The concept of functional safety addresses the growing need for improved confidence in safety systems. Industry experts formalized an approach for reducing risk in the process plant environment through the development of standards IEC 61508, IEC 61511, and ANSI/ISA 84.01.

Functional safety is a term used to describe the safety system that is dependent on the correct functioning of the logic solver, sensors, and final elements to achieve a desired risk reduction level. Functional safety is achieved when every safety function is successfully carried out and the unprotected process risk is reduced to the desired level. A safety instrumented system is designed to prevent or mitigate hazardous events by taking a process to a safe state when predetermined conditions are violated. Other common terms for SISs are safety interlock systems, Emergency Shutdown Systems (ESD), and Safety Shutdown Systems (SSD). Each SIS has one or more Safety Instrumented Functions (SIF).

Typical critical functional safety lifecycle elements include: Hazard / Risk Assessment, Safety Integrity Level or SIL Determination, SIL Verification and Maintenance. SIL1 or SIL2 or SIL3 relate to the levels of Safety Integrity that is determined by the SIL classification analysis. SILa designation means no special SIL requirement. A SIL2 level is more robust and will have a lower Probability of Failure on Demand (PFD) than a SIL1 system. Table 1 defines PFD requirement to meet the various SILs. The Risk Reduction Factor is the inverse of the PFD. Thus, a SIL1 (with a PFD range from 0.1 to 0.01) implies a RRF requirement of 10-100 whereas a SIL3 would imply a RRF requirement of 1000 to 10000.

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Table 1. Relation Between Safety Integrity Levels (SIL) and Required Probability of Failure on Demand (PFD)

Safety Integrity Level (SIL)	***Required PFD***	***Risk Reduction Factor (RRF), 1/PFD***
a	no requirements ($>10e^{-1}$)	< 10
1	$\geq 10e^{-2}$ to $<10e^{-1}$	10 – 100
2	$\geq 10e^{-3}$ to $<10e^{-2}$	100 – 1,000
3	$\geq 10e^{-4}$ to $<10e^{-3}$	1,000 – 10,000
4	$\geq 10e^{-5}$ to $<10e^{-4}$	10,000 – 100,000
X	Intolerable	Intolerable

Hazard/Risk Assessment

Hazard / Risk Assessments are usually performed prior to determination of the SIL levels for the associated SIS. In the process industry, a HAZOP (Hazards and Operability) study is performed to identify potential hazardous scenarios (and their associated consequences and likelihoods). A FMEA (Failure Modes and Effects Analysis), PHA (Process Hazards Analysis) or a HAZID (Hazard Identification Study) are other hazard assessment studies that are also commonly performed.

Before determining the SIL of the SIS, the first step is to conduct a hazard assessment to determine the functional safety needs and identify the tolerable risk level. All mitigation and prevention safety layers (specific to the hazard scenario) must be identified (see Figure 5). After all of the risk reduction and mitigation impacts from the Basic Process Control System (BPCS) and other layers of protection are taken into account, a user must compare the residual risk against their risk tolerance (See Figure 6). If there is still an unacceptably high level of risk, a Risk Reduction Factor (RRF) is determined and a SIS / SIL requirement is calculated. Figure 7 depicts how the unprotected process risk can be incrementally lowered using combinations of non-SIS and SIS layers of protection. If just the non-SIS layers are able to reduce the risk to acceptable levels then a SIS layer may not be needed. However, if despite all non-SIS layers based protection, the risk still remains unacceptably high, then a SIS layer is required. The degree to which this required SIS layer needs to provide additional mitigation protection determines the integrity level of this SIS layer. This required integrity level is assigned during a SIL Determination study. It should be noted that the risk tolerance is subjective and site-specific. Each facility/ organization must determine its own acceptable level of risk to personnel and capital assets based on a variety of factors.

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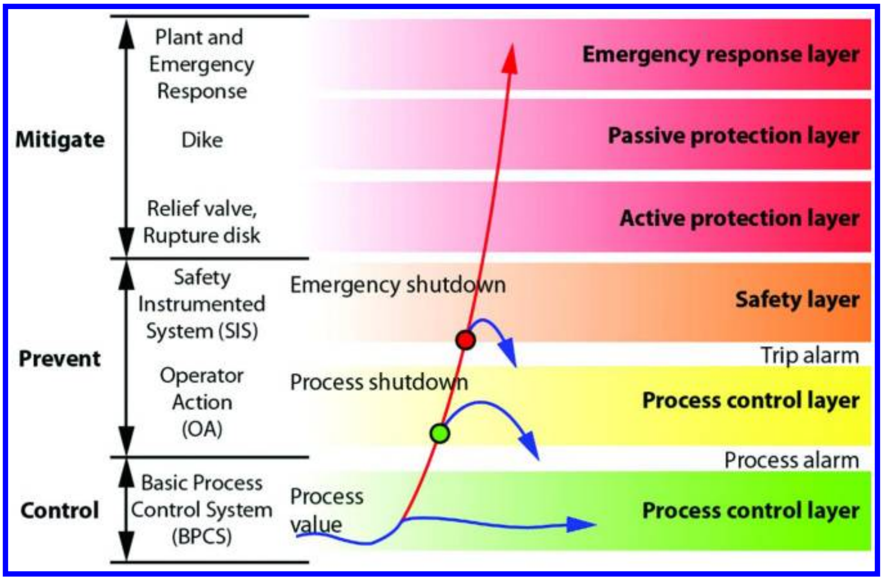

Figure 5. Various Independent Layers of Protection. (see color insert)

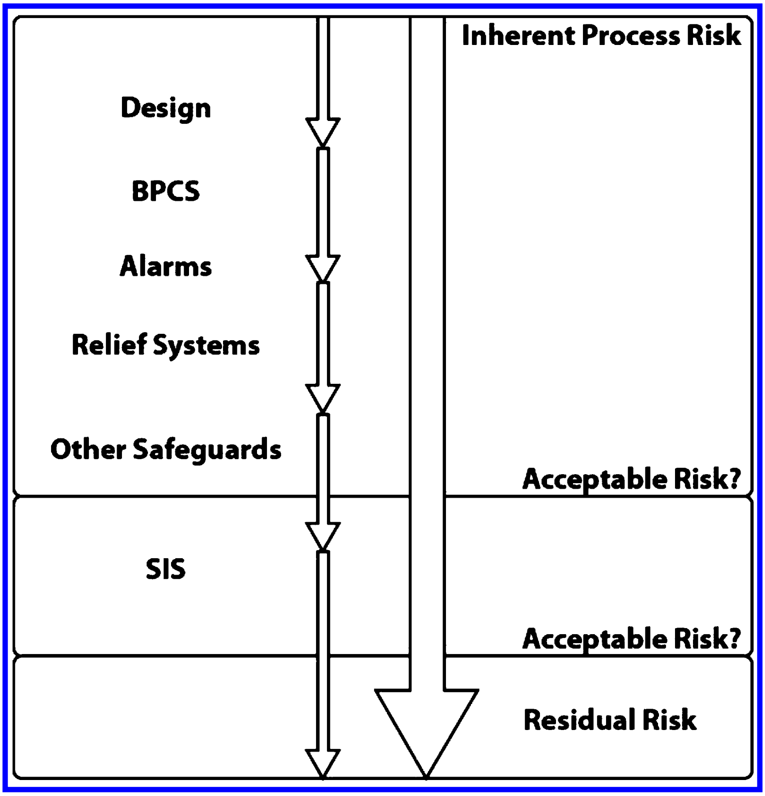

Figure 6. Concepts of Process Risk, SIS and Residual Risk.

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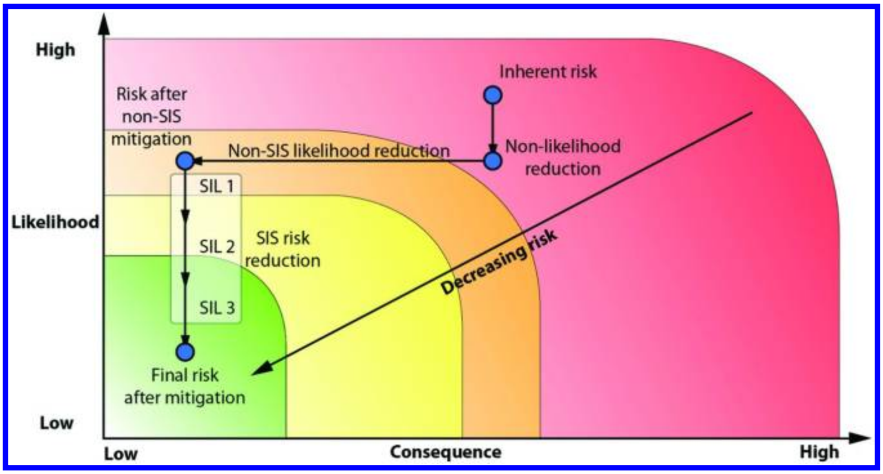

Figure 7. Concepts of Risk Reduction with Various SIS and non-SIL Layers of Protection. (see color insert)

Safety Integrity Level Determination

The classification of Safety Integrity Level (SIL) for a Safety Instrumented Function (SIF) is determined by studying the consequences of failure on demand against the following criteria (impact on reputation is not a criterion for SIL determination):

- Impact of incident on Personnel
- Impact of incident on Environment
- Impact of incident on Asset

The following sections outline two SIL classification/determination approaches: Risk Graph Method and Layer of Protection (LOPA) Method. The risk graph approach is a conservative but a quick method, whereas the LOPA approach tends to be more accurate but requires additional effort. It is possible to use a combination of both methods when evaluating a very large number of SIF loops. In this combination approach, a risk graph approach may be used to classify all loops first and then the LOPA method may be used to re-evaluate/reclassify the SIL 3 (and SIL 2) loops.

The risk graph and LOPA procedures are briefly described below.

Risk Graph Method

The risk graph method is a quick way to determine SIL requirements and is not a detailed method of assessment. Typical SIL requirements for personnel, asset, and environment using risk graph are shown in Tables 2, 3, and 4 respectively. The risk graph method is intentionally conservative, and tends to over-estimate the required risk reduction.

Health and safety consequence ratings, loss consequence ratings, and environmental consequence ratings are rated by the SIL determination team for the various SIFs during the SIL determination study. Each hazard event is ranked through a team consensus judgment by deciding the severity of the event consequences based on its impact to personnel, assets, and environment.

Severity Criteria Based on Avoidance and Exposure

Table 5 shows the mitigation credits assigned to the severity category based on the exposure (to the worker) and the possibility to avert danger. In order to evaluate risk to personnel, a further consideration is given to exposure and probability of avoiding the danger. Depending on these two factors, the severity to personnel as originally evaluated (as per Table 2) can be reduced.

Occupancy at a location (and consequently exposure) is based on time for which personnel are present in the hazardous area. The possibility of avoidance of danger is based on following factors:

1. Operation of a process (supervised or unsupervised)
2. Speed of development of the hazardous event (quick, slow). For example, an explosion is a sudden event
3. Ease of recognition of danger (seen immediately, detected by instrumentation, deduced by operators)
4. Avoidance of hazardous events (escape routes available, engineered protection)
5. Safety experience with similar situations

Probability of avoiding the hazardous event if protection system fails to operate is finite (non-zero) if:

- Systems are provided to alert the operator that the SIS has failed
- The time between operator being alerted and a hazardous event occurring exceeds one hour
- Independent systems are provided to avoid the hazard or the systems are such that they provide enough time for personnel to escape the hazard

Demand Rate

The SIL determination team estimates the demand rate for the scenario(s) being considered using the information presented in Tables 2, 3, and 4. Demand rate is the likelihood of the SIS to be called upon to take protective action. The demand rate is expressed in terms of Mean time between Demands (years). So if a SIL loop is expected to be invoked to provide protection once in 3 years, the Mean time between demands is 3 years and we would use the 1-10 year demand rate category. Where the team is unable to accurately project a demand rate, a conservative estimate is used.

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Process Safety Time

During the SIL classification, the process safety time for each SIF is also determined. The process safety time is a function of the process dynamics and is defined as the period of time that the process can be operated without protection and with a demand present without entering a dangerous condition. The process safety time determines the trip setting and the combined dynamic performance and accuracy requirements for the SIF components, e.g. process measurement delay, time between input state change and output state change in the SIF, and valve stroke time.

Example: A trip is set at process pressure of 150 kPa. The consequences of overpressure will not be realized until the pressure reaches 170 kPa. Given the dynamics of the process and the causes of overpressure, this will take at least 2-minutes. The process safety time therefore is 2-minutes.

Based on the demand rate and consequence severity, a target SIL is assigned.

Table 2. Risk Graph for Personnel

Mean time between demands (Years)	***Health / Safety (Requisite SILs)***					
<1	-	SIL 1	SIL 2	SIL 3	SIL 4	X
1-10	-	SIL 1	SIL 2	SIL 3	SIL 4	SIL 4
10-100	-	SIL a	SIL 1	SIL 2	SIL 3	SIL 3
100-1,000	-	SIL a	SIL a	SIL 1	SIL 2	SIL 2
>1,000	-	-	SIL a	SIL a	SIL 1	SIL 1
Personnel Safety	No injury or health effect	Slight injury or health effect	Minor injury or health effect	Major injury or health effect	Permanent disability or up to 3 fatalities	>3 fatalities
Severity (Numeric)	0	1	2	3	4	5

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Table 3. Risk Graph for Production / Assets (Economic)

Mean time between demands (Years)	***Production Losses / Asset Damage***					
<1	SIL a	SIL a	SIL a	SIL 1	SIL 2	SIL 3
1-10	-	SIL a	SIL a	SIL 1	SIL 2	SIL 3
10-100	-	-	SIL a	SIL a	SIL 1	SIL 2
100-1,000	-	-	-	SIL a	SIL a	SIL 1
>1,000	-	-	-	-	SIL a	SIL a
Personnel Safety	<1K$	1-10K $	10-100K $	100K-1M $	1-10M$	>10M$
Severity (Numeric)	0	1	2	3	4	5

Table 4. Risk Graph for Environment

Mean time between demands (Years)	***Environmental Impact***					
<1	SIL a	SIL a	SIL 1	SIL 2	SIL 3	X
1-10	-	SIL a	SIL 1	SIL 2	SIL 3	SIL 4
10-100	-	SIL a	SIL a	SIL 1	SIL 2	SIL 3
100-1,000	-	-	SIL a	SIL a	SIL 1	SIL 2
>1,000	-	-	-	SIL a	SIL a	SIL 1
Personnel Safety	No effect	Slight effect	Minor Effect	Moderate Effect	Major Effect	Massive Effect
Severity (Numeric)	0	1	2	3	4	5

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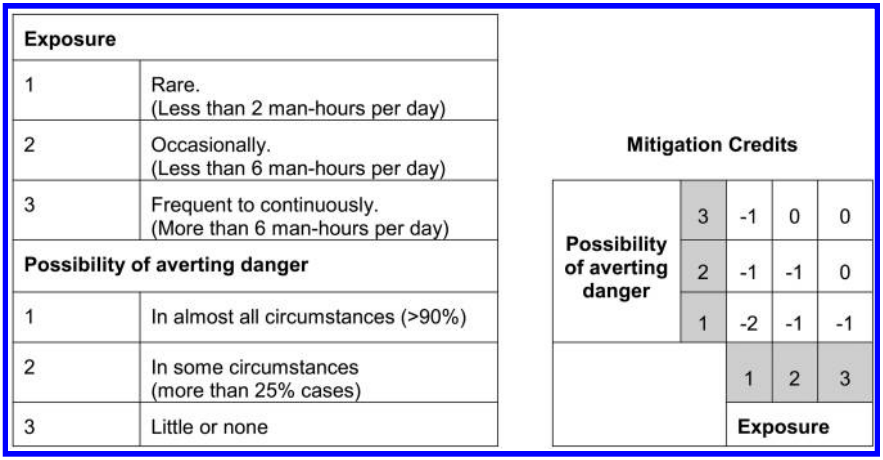
Table 5. Mitigation Credits to Reduce Personnel Severity



Exposure	
1	Rare. (Less than 2 man-hours per day)
2	Occasionally. (Less than 6 man-hours per day)
3	Frequent to continuously. (More than 6 man-hours per day)
Possibility of averting danger	
1	In almost all circumstances (>90%)
2	In some circumstances (more than 25% cases)
3	Little or none

Mitigation Credits

Possibility of averting danger	3	-1	0	0
	2	-1	-1	0
	1	-2	-1	-1
		1	2	3
		Exposure		

In an another version of the Risk Graph approach, instead of using Tables 2-5 listed above, use is made of Risk Graph Figures such as the one shown in Figure 8. Using this approach the analyst simply selects consequence category (C_A, C_B, C_C, or C_D), probability that the exposed area is occupied or not (F_a or F_b), the probability that exposed persons are able to avoid the hazard or not (P_a or P_b) and likelihood/demand category W, indicating the number of times per year that the hazardous event would occur (W_1, W_2, W_3) to determine the SIL level. The SIL determination is usually documented in SIL determination worksheets as shown in Figure 9.

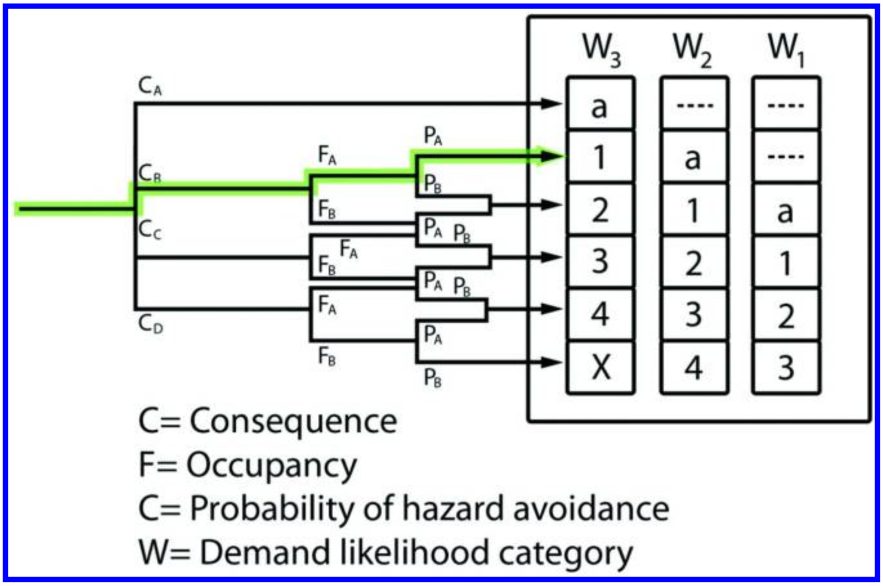


Figure 8. Example Risk Graph for SIL Assignment. (see color insert)

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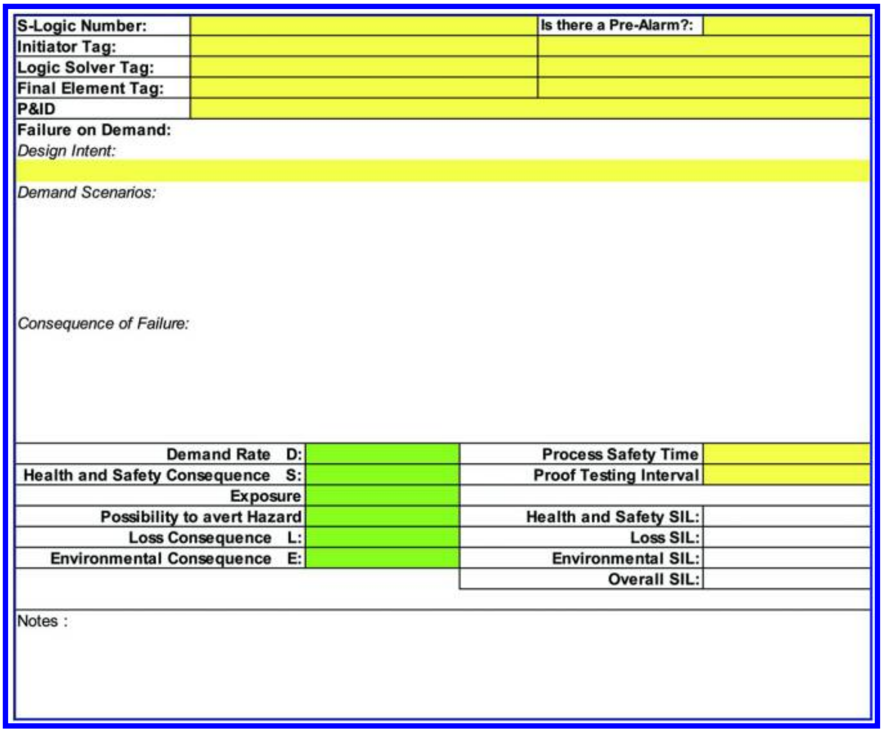

S-Logic Number:		Is there a Pre-Alarm?:	
Initiator Tag:			
Logic Solver Tag:			
Final Element Tag:			
P&ID			

Failure on Demand:

Design Intent:

Demand Scenarios:

Consequence of Failure:

Demand Rate D:		Process Safety Time	
Health and Safety Consequence S:		Proof Testing Interval	
Exposure			
Possibility to avert Hazard		Health and Safety SIL:	
Loss Consequence L:		Loss SIL:	
Environmental Consequence E:		Environmental SIL:	
		Overall SIL:	

Notes :

Figure 9. Example Risk Graph Template. (see color insert)

Layer of Protection Analysis (LOPA)

LOPA is a semi-quantitative method for assessing integrity levels, which enables additional risk mitigation factors, not usually considered by the risk graph method, to be taken into account and, thus, allows a more realistic estimation of the required integrity level. This LOPA approach allows for a more accurate evaluation of risk mitigation from the existing non-SIS layers. If additional risk reduction is required and if it is to be provided in the form of a Safety Instrumented Function (SIF), the LOPA methodology allows for a more accurate and quantitative determination of the appropriate Safety Integrity Level (SIL) for that SIF.

Initiating Event

The LOPA method starts with data developed in the HAZOP (or another other form of Hazard Assessment) study and accounts for each identified hazard by documenting the initiating cause. Each cause is reduced to a discrete failure event. For example, a loss of cooling water to a reactor (as shown in the earlier reactor example, Figure 1) as an initiating cause can be the result of an upstream CW pump failure, a power failure, or a CW control valve failure. The frequency for each type of failure would be different, and the layers of protections can be different for each initiating event.

Once the initiating event occurs, various protective layers can prevent the event from reaching a dire consequence (fire/explosion). The basic process control can take action and shut the process down, the operator can take action to bring the process to a safe state or a PSV can prevent the pressure buildup and relief to a safe location. Figure 10 shows an Event Tree or a simplified LOPA diagram for this example scenario. If these layers are not adequate to reduce the risk to an acceptable level then a SIS can be considered for implementation.

Table 6 provides some generic values that can be selected by the analyst for various typical initiating events encountered during a LOPA study.

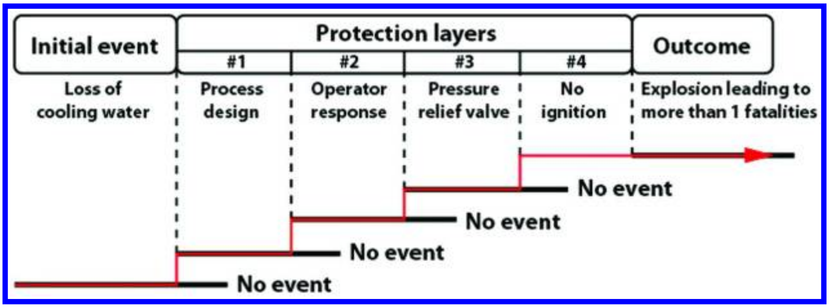

Figure 10. Layers Of Protection Analysis (LOPA diagram)/Event Tree. (see color insert)

Table 6. Generic LOPA Initiating Event Likelihoods

Initiating Event (IE)	***Frequency of Failure, yr^{-1}***
Analyzer failure all types	1e-1
Atmospheric Tankage leak 50 mm hole (acidic contents)	1.0E -03
Atmospheric Tankage leak 50 mm hole (non-acidic contents)	1.0E – 04
Atmospheric Tankage leak rupture (acid contents)	1.0E -04
Atmospheric Tankage rupture (non-acidic contents)	1.0E -06
BPCS instrument loop failure	1.0E -01
Check valve failure external leak	1.0E -03
Compressor failure (10-50 mm leak) axial	1.0E -03
Compressor failure (10-50 mm leak) centrifugal	1.0E -03
Compressor failure (10-50 mm leak) reciprocating	1.0E -04
Compressor rupture all types (>50 mm leak)	1.0E -04
Cooling water failure diverse drivers/redundant pumps	1.0E -01

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Table 6. (Continued). Generic LOPA Initiating Event Likelihoods

Initiating Event (IE)	*Frequency of Failure, yr^{-1}*
Expansion Joint failure large leak	1.0E -02
Expansion Joint failure rupture	1.0E -03
External impact crane load drop	1.0E -04
External impact 3rd party vehicle, backhoe, etc.	1.0E -02
Filter blockage or leak	1.0E -03
Filter rupture	1.0E -05
Flange leak blown gasket or flange separation	1.0E -04
Heat exchanger external leak plate & frame	1.0E -02
Heat exchanger external leak shell & tube	1.0E -02
Heat medium failure	1.0E -01
General Utility Failure	1.0E 01
Instrument connection failure	1.0E -03
Lock Out Tag Out procedure failure	1.0E -03
Loss of power (redundant supplies)	1.0E -01
Operator failure – non routine procedure, stressful, possible fatigue	1.0E -01
Piping – leak 10% section	1.0E -03
Piping – large leak 50mm	1.0E -04
Piping – guillotine fracture	1.0E -05
Pressure vessel <13mm leak in liquid	1.0E -04
Pressure vessel 13mm leak in liquid	1.0E -05
Pressure vessel > catastrophic failure	1.0E -05
Pressure vessel high temp – catastrophic failure	1.0E -05
Pump leak reciprocating	1.0E -01
Pump leak all other types	1.0E -02
Pump catastrophic failure	1.0E -04
Pump fail to run/loose flow	1.0E -02
Single Mechanical seal failure	1.0E -01
Refrigerated tank leak (50mm)	1.0E -03
Refrigerated tank rupture	1.0E -04
Regulator failure	1.0E -01
Relief value opens spuriously	1.0E -02

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Table 6. (Continued). Generic LOPA Initiating Event Likelihoods

Initiating Event (IE)	*Frequency of Failure, yr^{-1}*
Spills	1.0E -01
Turbine/diesel engine speed with casing breach	1.0e -04
Valve failure external leak- motor or air operated valve	1.0E -03
Valve failure external leak – manual valve	1.0E -04
Other initiating events	Develop using experience of personnel

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Layers of Protection

After determining the initiating cause(s) and the consequence, various independent protection layers (IPL) present are analyzed. Each protection layer consists of a grouping of equipment and/or administrative controls that function in concert with the other layers. Protection layers that perform their function with a high degree of reliability may qualify as Independent Protection Layers (IPL). Typical IPLs are alarms, pressure relief devices, etc. that help mitigate the likelihood of an event.

Some mitigation layers may reduce the severity of the impact event but not prevent it from occurring. Examples would be:

- Restricted access
- Deluge systems for fire
- Gas detection alarms
- Fire detection alarms; and
- Emergency evacuation procedures.

The LOPA team evaluates various IPLs present for every scenario and assigns appropriate probability of failure on demands (PFDs).

Table 7 lists the multiple Protection Layers (PLs) that are normally provided in the process industry. The Probability of Failure on Demand (PFD) is the conditional probability of failure of these independent layers of protection. Thus, if one assigns a Basic Process Control System (BPCS) layer in a LOPA study, we can assign a PFD of 1E-01 (or 0.1) which implies that it will work successfully 9 out of 10 times but may fail in1 out of 10 demands.

Conditional probability of ignition (Table 8) is considered for scenarios involving fire/explosion to estimate the likelihood of an event.

Presence of people (Table 9) is considered to modify the likelihood of frequencies that can result in potential fatalities.

Table 7. PFD for Typical IPLs

Independent Protective Layer (IPL)	*Probability of Failure on Demand (PFD)*
Basic process control system	1E-01
Critical Alarm & Human Intervention Simple, well documented action with clear reliable indications that the action is required	1.0E -01
Safety Instrumented Function	
SIL 1 System	1.0E -01
SIL 2 System	1.0E -02
SIL 3 System	1.0E -03
Physical Protection	
Double or tandem seal (leak only)	1.0E -01
Grounding & bonding	1.0E -01
Mechanical stop	1.0E -01
Orifice sized sonic flow	1.0E -01
Manual response to abnormal reading collected regularly on a check list	1.0E -01
Sample collection & analysis to confirm nonhazardous conditions	1.0E -01
Specific design, i.e., self draining lines	1.0E -01
Check valve	1.0E -02
Cylinder dome (during transport)	1.0E -02
Detonation/Flame arrestor	1.0E -02
Deflagration Vents	1.0E -02
Explosion Suppression System	1.0E -02
Fireproofing	1.0E -02
Housekeeping (dust explosion scenario only)	1.0E -02
Open vent	1.0E -02
Relief valve/ Rupture disk	1.0E -02
Rupture pin	1.0E -02
Blast wall	1.0E -03
Bunker	1.0E -03
Event pressure is less than1.0 times MAWP	1.0E -05
Event pressure is between 1.1 and 2.5 timer MAWP	1.0E -03
Event pressure is between 2.5 and 3.5 times MAWP	1.0E -01

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Table 7. (Continued). PFD for Typical IPLs

Independent Protective Layer (IPL)	*Probability of Failure on Demand (PFD)*
Event pressure is over 3.5 times MAWP	1.0E +00
Post release Protection	1.0E -01
Area hydrocarbon detectors	1.0E -01
Concrete Pad with slope	1.0E -01
Deluge System	1.0E -01
Fire Suppression System	1.0E -01
Protective Clothing – specialized	1.0E -01
Restricted Area	1.0E -01
Safety Shower	1.0E -01
Slash Guard	1.0E -01
Bund / Dike	1.0E -02
Foam blanket vapor suppression system	1.0E -02
Underground Drainage System	1.0E -02
Other events	Use experience of personnel

Table 8. Conditional Frequency Modifier – Generic Ignition Probabilities

Conditional Modifiers	*Probability of Ignition*
Vapors containing more than 10% Hydrogen (any quantity)	1.0
Hydrocarbon (M,I. > 0.3mJ) released less than 500kg	0.01
Hydrocarbon (M,I. > 0.3mJ) released between 500kg and 5,000kg	1.0
Hydrocarbon (M,I. > 0.3Mj) released less than 50 kg	0.01
Hydrocarbon (M,I. > 0.3Mj) released between 50 kg and 500 kg	0.1
Hydrocarbon release more than 5,000 kg	1.0
Due to static in closed underground vessel ordinary hydrocarbon	0.1
Release of flammable material due to external collision (crane failure), impact or catastrophic failure	1.0

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ACS Symposium Series; American Chemical Society: Washington, DC, 2013.

Table 9. Conditional Likelihood Modifier- People Present

Occupancy Levels	*Conditional Likelihood Modifier*
People are present all the time	1.0
People are present for less than 12 hours per day	0.5
People are present for less than 1-2 hours per day	0.1

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Target Mitigated Event Likelihood (TMEL)

The likelihood of an event is determined by multiplying the initiating event frequency and PFDs of the various IPLs present. The SIF under consideration is not considered as an IPL. This intermediate event likelihood (initiating event, all IPLs except SIS) is compared with the TMEL to determine the IL requirement for the SIS.

TMEL for various undesirable outcomes (for an example facility) are summarized in Tables 10, 11, and 12.

Figure 11 represents an example LOPA worksheet.

Table 10. Example TMEL Based on Personnel Risk

Severity Level	*Safety Consequence*	*Tolerable TMEL Target, yr^{-1}*
1	Minor injury or First Aid Cases	1×10^{-2}
2	Lost work injuries involving a few days away from work. Restricted work injuries	1×10^{-3}
3	Injury resulting in prolonged absence of work or permanent disability, Minor injuries to three or more workers	1×10^{-4}
4	One or more fatalities and/or permanently disabling injuries	1×10^{-5}
5	Three or more fatalities and/or permanently disabling injuries	1×10^{-6}

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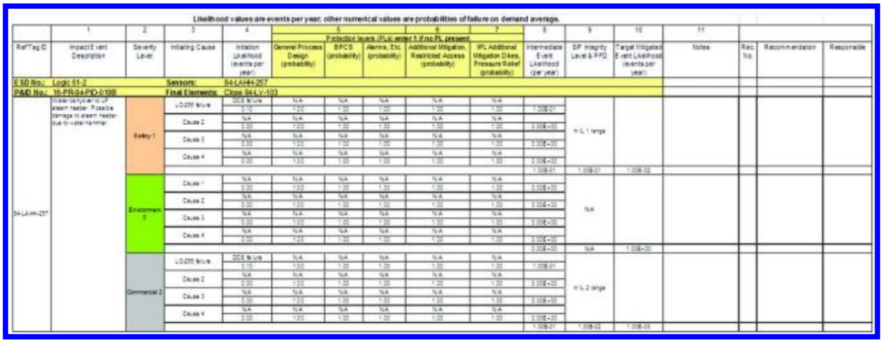
Table 11. Example TMEL Based on Environmental Risk

Severity Level	*Environmental Consequence*	*Tolerable TMEL Target, yr^{-1}*
1	No offsite environmental impact	1×10^{-2}
2	Minor offsite impact with no remediation or costs less than 100,000	1×10^{-3}
3	Moderate offsite environmental impact or remediation costs U$ 100,000 to 1-million	1×10^{-4}
4	Significant offsite environmental impact or remediation costs U$ 1-million to 10-million	1×10^{-5}
5	Extensive off site environmental damage or remediation costs > U$ 10-million	1×10^{-6}

Table 12. Example TMEL Based on Financial Risks

Severity Level	*Financial Consequence*	*Tolerable TMEL Target, yr^{-1}*
1	Less than U$ 100,000	1×10^{-2}
2	Property damage or production loss between U$ 100,000 to 1-million	1×10^{-3}
3	Property damage or production loss between U$ 1-million and 10-million	1×10^{-4}
4	Property damage or production loss between U$ 10-million to 100-million	1×10^{-5}
5	Property damage or production loss greater than U$ 100-million	1×10^{-6}



Likelihood values are events per year; other numerical values are probabilities of failure on demand average.

	1	2	3	4	5	6	7	8	9	10	11			
					Protection layers (PLs) enter 1 if no PL present									
Ref/Tag ID	Impact Event Description	Severity Level	Initiating Cause	Initiation Likelihood (events per year)	General Process Design (probability)	BPCS (probability)	Alarms, Etc. (probability)	Additional Mitigation, Restricted Access (probability)	IPL Additional Mitigation Dikes, Pressure Relief (probability)	Intermediate Event Likelihood (per year)	SIF Integrity Level & PFD	Target Mitigated Event Likelihood (events per year)	Notes	Rec. No.	Recommendation	Responsible

ESD No.: Logic 61-2 Sensors: 94-LAHH-257

P&ID No.: 16-PR-94-PID-0198 Final Elements: Close 94-LY-103

Figure 11. Example LOPA Template/Example. (see color insert)

LOPA Study Example for the Nitration Industry

Let’s consider a common reactor configuration in the Nitration Industry. Figure 12 depicts a continuously stirred reactor in which an organic substrate is reacted with a mixture of H_2SO_4 and HNO_3 acids. The reaction is exothermic and the reactor is cooled using a continuous supply of cooling water (through coils). The reactant and cooling water flow rates are controlled using flow controllers which rely upon individual flow sensors and set point information from the BCPS using the temperature and pressure information from the PI and TI sensors (the BPCS logic is not shown). If the reactor temperature rises for any reason (say loss of cooling water), we could have a runaway reaction leading to overpressures, reactor damage and potential worker injury/fatality due subsequent fire/explosion. Upon the detection of a high temperature the BCPS is programed to close the organic and acid flows to the reactor. We need to determine if the current safety layers are adequate to reduce the risk to acceptable levels. If not, we need to determine what kind of SIS would be required.

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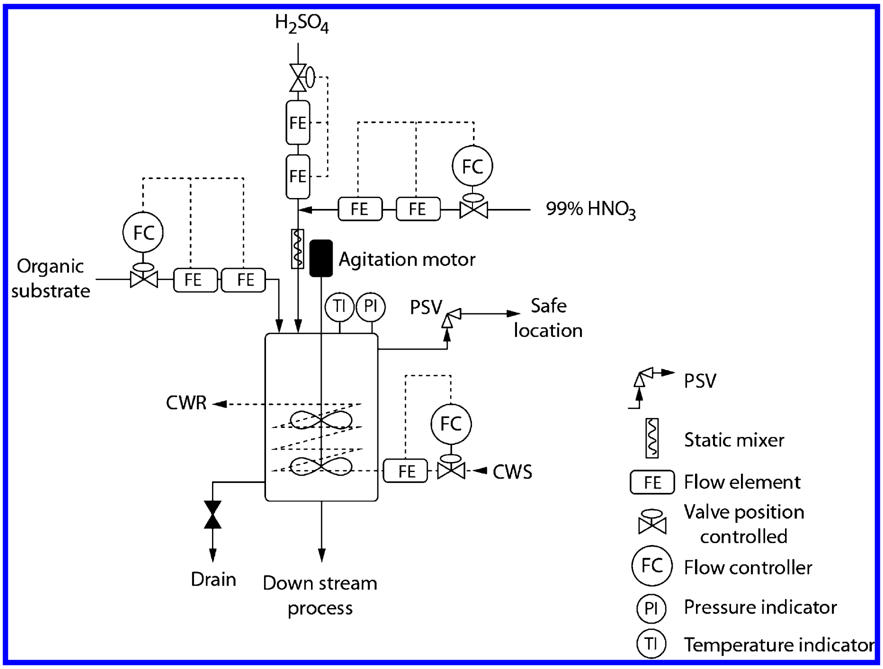

Figure 12. LOPA Example: Nitration Industry Example Reactor.

A simplified Event Tree / LOPA diagram for the system can be constructed as below (Figure 13).

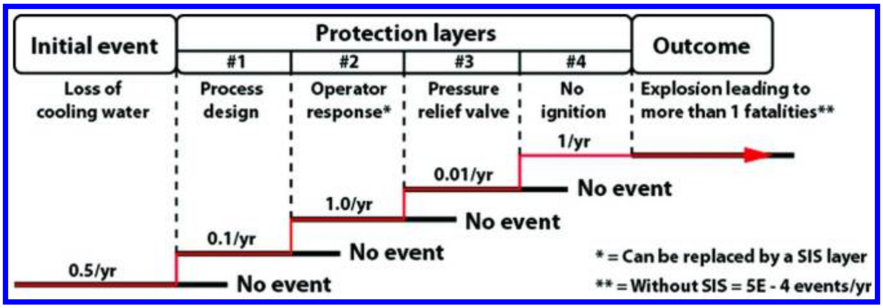

Figure 13. LOPA Tree / Event Tree for the Nitration Industry Example. (see color insert)

We can determine from process operations that loss of cooling water (for various reasons) can be expected once in a couple of years (say once in 2 years or 0.5 times per year) which is our initiating event frequency. We can take credit for the BPCS and assign a PFD of 0.1 (from Table 7). We understand from plant operations, that even though operators are present at the site, they cannot be relied upon to perform emergency action with a short period of time. Thus, we assign the PFD for operator action to be 1.0 (no credit). We assume that the PFD for the relief valve is 0.01 (Table 7) and ignition is guaranteed upon release (PFD=1.0, Table 8). The expected outcome without any additional SIS is 5E-4

Based on continuous operator presence we understand that this explosion event (should it occur) could lead to 1 or more fatalities and, thus, we determine that the TMEL should be 1.0E-5 (Table 10). As the expected outcome without any SIS layer is higher than this TMEL value, there is a need for an additional SIS layer. This SIS layer would need to be configured as a separate independent layer, which could detect the high temperature and take automatic mitigation action.

We calculate that the required RRF for this additional SIS needs to be 5E-4/ 1E-5 = 50. Thus, we need to specify a SIL level of 2 which would have a minimum RRF of 100.

Figure 14 depicts the Reactor Example with an example simple SIS configuration. In this example configuration an independent set of TI sensors can be used along a PLC controller to independently shut off flows of the organic substrate and H_2SO_4 and HNO_3 acids. We can also open the reactor drain valve to divert the reactor contents (if appropriate). The configured SIS would need to meet a specified SIL requirement. The exact configuration with appropriate number of sensors (2oo2, 2 out of 2 voting logic, or 2oo3, 2 out of 3 voting logic), PLC and final element combinations would have to be determined / confirmed during the subsequent verification step to meet this SIL requirement.

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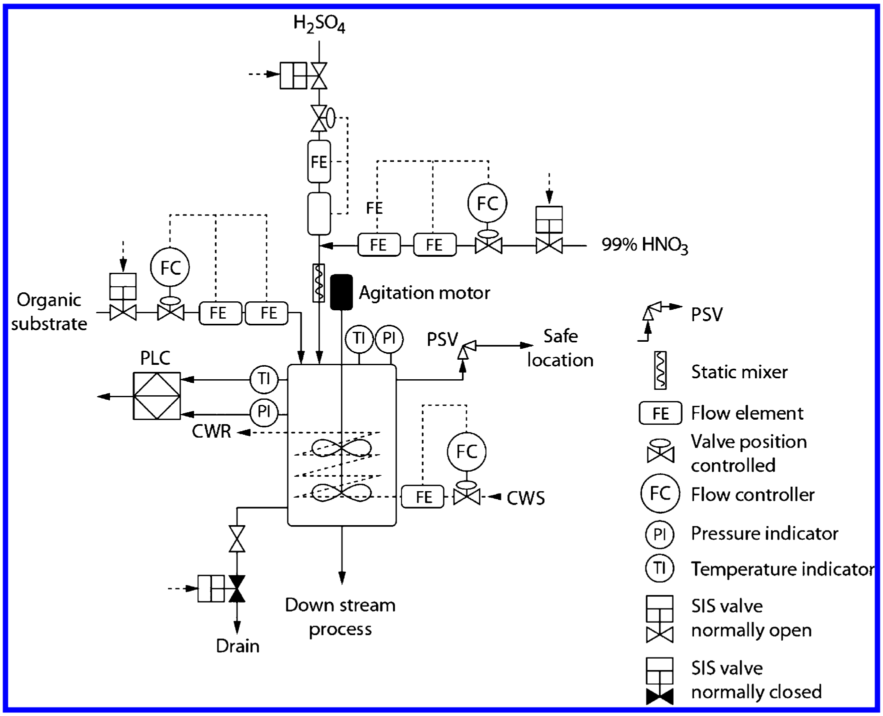

Figure 14. LOPA Example: Nitration Industry Example Reactor with additional SIS.

SIL Verification

The SIL verification study follows the SIL determination study. The objective of the SIL verification is to check if the SIL1 or higher SIF loops (as actually configured) meet the required integrity level (IL) specified during the SIL determination step. The verification is based on the failure rate data of the individual components (initiator, logic solver, final element) of the proposed as-configured SIF loop.

SIL verification is typically performed in accordance with IEC 61511 (*1*). Exponent uses exSILentia (*2*) software available from Exida for SIL verification purposes. Failure data for an element is used to estimate the probability of failure on demand (PFD) for a given time period. PFDavg of sensors, logic solvers and final elements is used to calculate the PFDavg for the SIF. As can be seen from the equation below, the PFDavg value depends on the proof test interval (TI). For the typical studies, a proof test interval of 6-12 months is used.

$$PFDavg_{1oo1} = \lambda^{DD} \text{ x Repair time} + \lambda^{DU} \text{ x } TI/2 \text{ , where}$$

λ – Failure rate (failures per hour)
DD – Dangerous detected
DU – Dangerous undetected
TI – Test Interval for proof testing

The Risk Reduction Factor (RRF) is simply the inverse of the PFDave (RRF = 1/PFDavg). The SIL verification calculation also estimates MTTFS (Mean Time to Fail Spurious) for the SIF.

MTTFS for SIF = 1/Spurious Trip Rate (STR), and

STR for SIF = STR_Sensor + STR_Logic Solver + STR_Final Element

Sample Calculation

	PFDavg	MTTFS	PTI
Sensor	4.48e-04	3460.8	12-months
Logic Solver	6.29e-05	654.85	240-months
Final Element	1.63e-02	250.1	12-months

In this example, since the final element PFD is more than an order of magnitude higher than the other two elements, the PFD for the entire SIF will essentially be the PFD of the final element.

PFDavg for SIF = 1.63e-2

RRF = 1/1.63e-2 = 61.35

Spurious Trip Rate for SIF (/years) = 1/3460.8 + 1/654.85 + 1/250.1 = 0.0058

SIF MTTFS = 1/0.0058 = 172 years

Note, spurious trip rate for an element is 1/MTTFS for that element.

Besides the PFDavg requirement for a given SIL, IEC 61508 (*3*) and IEC 61511 impose architectural constraints on hardware components utilized in a safety function. The architectural constraints represent hardware tolerance (minimum faults that could lead to a loss of the SIF) for a given SIL, and depend upon the hardware's Safe Failure Fraction (SFF).

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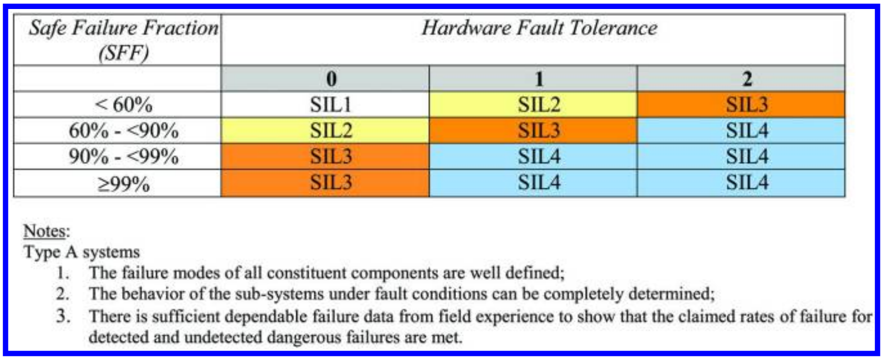
Tables 13 and 14 illustrates hardware fault tolerance for Type A (e.g. valves, relays, switches) and Type B (e.g. transmitters, PLCs) architectures as specified in IEC 61508. A hardware fault tolerance of N implies that N+1 faults could cause a loss of the safety function. For example, a single (1oo1) Type A control valve with a SFF of 58% has a hardware fault tolerance of 0 and is allowed for SIL1 applications; however, for a SIL2 application a redundant, one-out-of-two (1oo2) arrangement, or two valves in series, is required to meet architectural constraints.

Table 13. IEC 61508 Architectural Constraints for Type A Systems (see color insert)



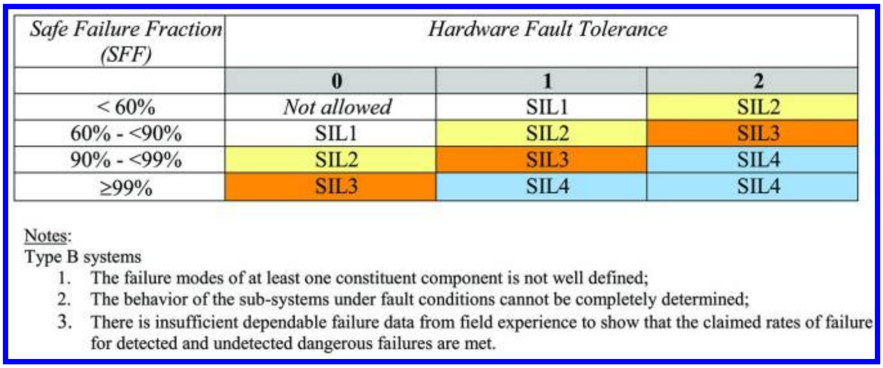
Safe Failure Fraction (SFF)	*Hardware Fault Tolerance*		
	0	**1**	**2**
< 60%	SIL1	SIL2	SIL3
60% - <90%	SIL2	SIL3	SIL4
90% - <99%	SIL3	SIL4	SIL4
≥99%	SIL3	SIL4	SIL4

Notes:

Type A systems

1. The failure modes of all constituent components are well defined;
2. The behavior of the sub-systems under fault conditions can be completely determined;
3. There is sufficient dependable failure data from field experience to show that the claimed rates of failure for detected and undetected dangerous failures are met.

Table 14. IEC 61511 Architectural Constraints for Type B Systems (see color insert)



Safe Failure Fraction (SFF)	*Hardware Fault Tolerance*		
	0	**1**	**2**
< 60%	*Not allowed*	SIL1	SIL2
60% - <90%	SIL1	SIL2	SIL3
90% - <99%	SIL2	SIL3	SIL4
≥99%	SIL3	SIL4	SIL4

Notes:

Type B systems

1. The failure modes of at least one constituent component is not well defined;
2. The behavior of the sub-systems under fault conditions cannot be completely determined;
3. There is insufficient dependable failure data from field experience to show that the claimed rates of failure for detected and undetected dangerous failures are met.

The architectural constraints thus impose additional requirements on the hardware selection and arrangement to achieve a target SIL. The SIL for a safety function presented in this report represents the lower of the two SILs – SIL based on PFDavg and SIL based on architectural constraints.

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Failure Rate Data

The failure rate data used for SIL calculations are typically obtained from a built-in instrument failure rate database (*4*) in the Exida software and from specific failure data provided by the Company. Requests are made from the Company/Vendor for all SIF components' model/make prior to SIL verification. The failure data available for each SIF is summarized and sent to Company/Vendor for review prior to verification. Where specific failure data are not available, generic failure rate data is used.

Figure 15 depicts a typical SIL verification Fault Tree Analysis (FTA) model that is constructed for SIL verification purposes. Figure 16 depicts that example SIL verification model results.

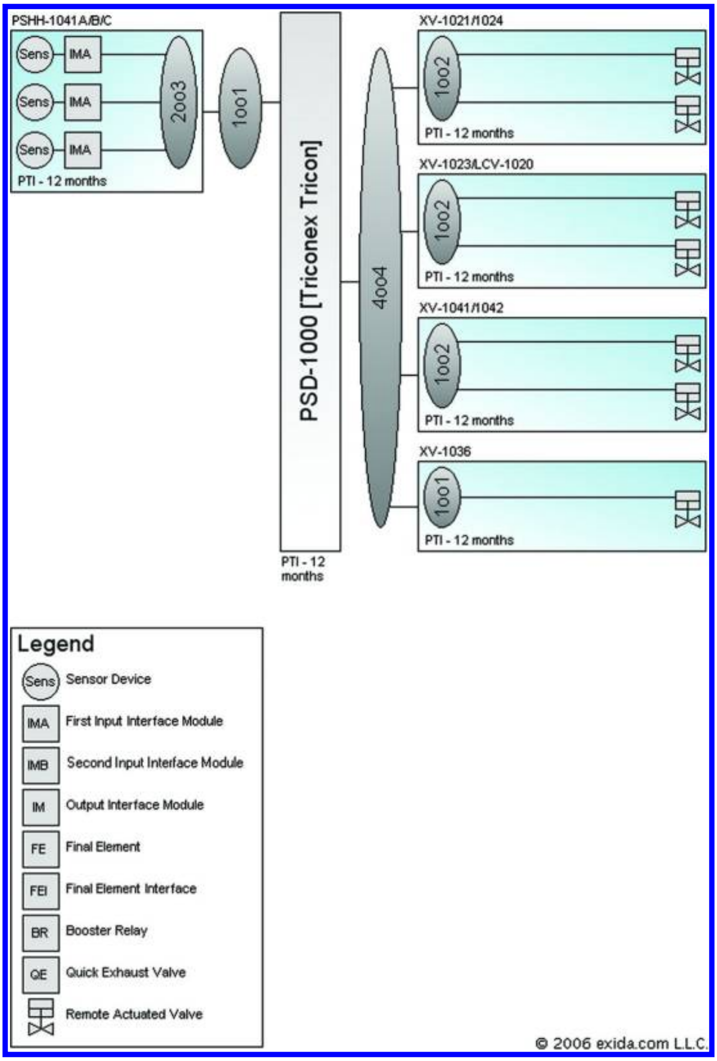

Figure 15. SIL Verification Example FTA Model. (see color insert)

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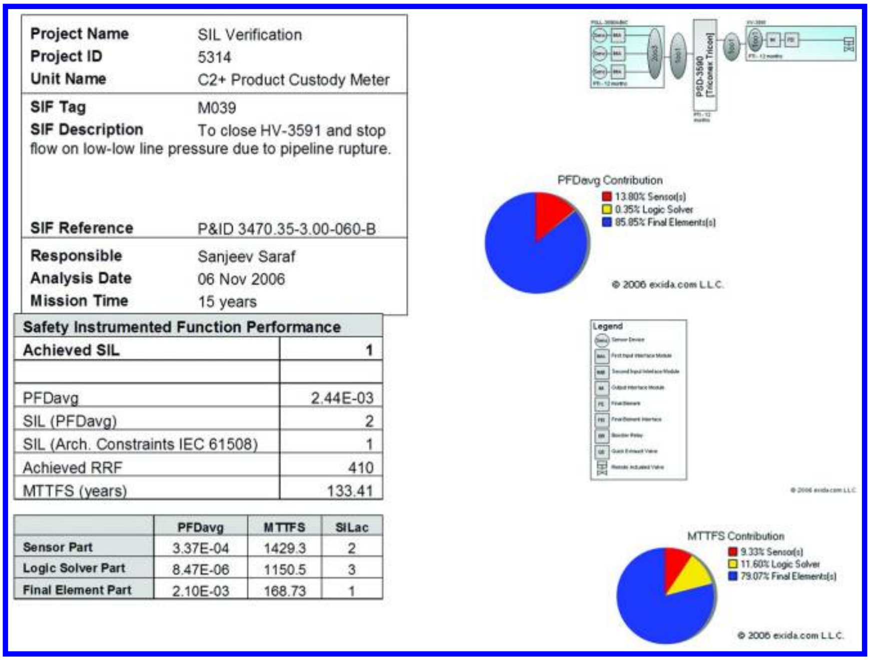

Project Name SIL Verification
Project ID 5314
Unit Name C2+ Product Custody Meter

SIF Tag M039
SIF Description To close HV-3591 and stop flow on low-low line pressure due to pipeline rupture.

SIF Reference P&ID 3470.35-3.00-060-B

Responsible Sanjeev Saraf
Analysis Date 06 Nov 2006
Mission Time 15 years

Safety Instrumented Function Performance	
Achieved SIL	1
PFDavg	2.44E-03
SIL (PFDavg)	2
SIL (Arch. Constraints IEC 61508)	1
Achieved RRF	410
MTTFS (years)	133.41

	PFDavg	**MTTFS**	**SILac**
Sensor Part	3.37E-04	1429.3	2
Logic Solver Part	8.47E-06	1150.5	3
Final Element Part	2.10E-03	168.73	1

Figure 16. Example SIL Verification Model Results. (see color insert)

Maintenance

Proof testing is a requirement of safety instrumented systems to ensure that the SIS is working and performing as expected. Testing must include the verification of the entire system, logic solver, sensors, and final elements. The interval is the period of time that the testing occurs. The testing frequency varies for each SIS and is dependent on the technology, system architecture, and target SIL level. As can be seen in Figure 17, it is possible to achieve higher SIL levels if testing frequency is increased. The proof-test interval is an important component of the probability of failure on demand calculation for the system.

- A typical mission time of 20-years is used based on average lifecycle of most process facilities.
- A proof test interval (PTI) of 6-12 months is assumed for most sensors.
- PTI of 60-months (5-years) is assumed for logic solver.
- PTI of 6-12 months is used for typical final elements (e.g., safety relays involved in final SIF action and valves).
- The proof test coverage (measure of effectiveness of proof test in detecting failures undetected by automatic diagnostics) is usually assumed to be 90% (based on industry accepted values of 80% to 95%).
- A common cause failure Beta of 10% is usually assumed based on industry accepted values of 5% to 10%.

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- Process conditions are assumed to be "clean", i.e. there is no extreme process environment resulting in failure rates higher than reported unless the process conditions indicate otherwise.
- Mean time to Repair (MTTR) is assumed to be 24 hours for sensors, logic solvers and final elements.

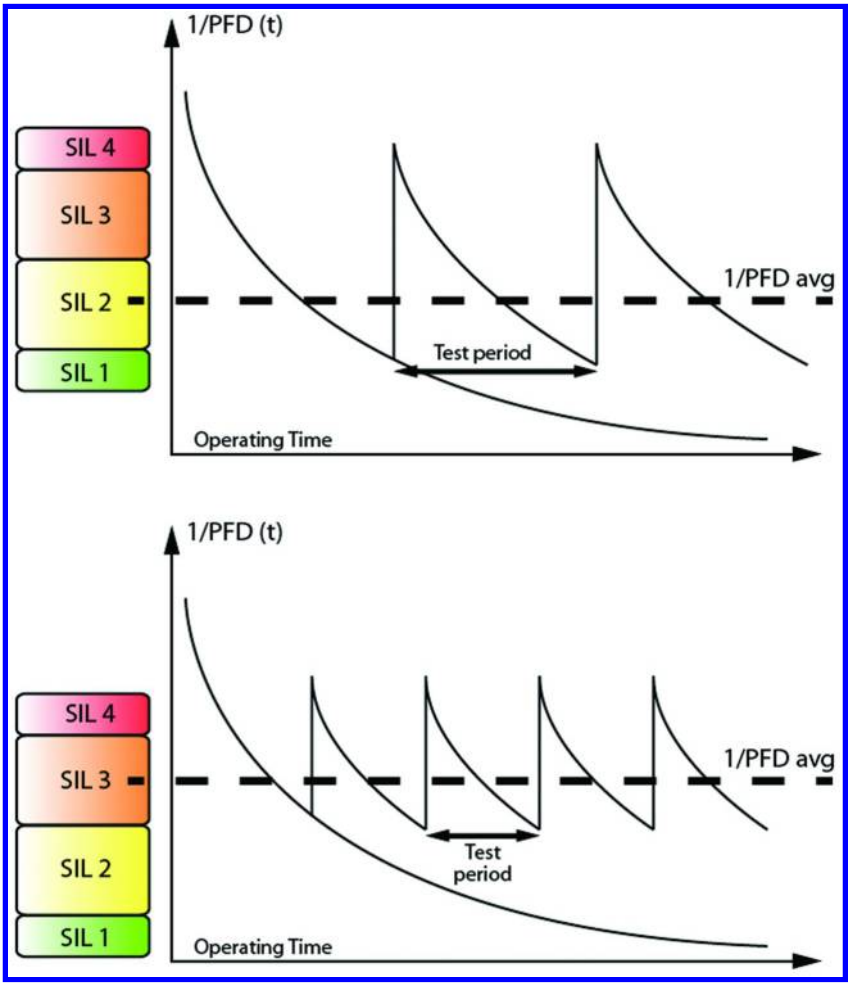

Figure 17. Achieved SIL Based on Testing Frequency. (see color insert)

It is often assumed that (asking for and) getting a higher rated SIS is always beneficial. However, one has to remember that as the SIL level increases, typically the installation and maintenance costs and complexity of the system also increase. Specifically, for the process industries, SIL 4 systems are so complex and costly that they are not economically beneficial to implement. Usually, if process risks are such that a SIL 4 system is required to bring the system to a safe state, then this is usually an indication that the process design needs to be revised.

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SIL based risk reduction is certainly not always the most cost-effective solution for decreasing process risk. Implementing a SIL loop may require increased equipment, which inevitably will require increased maintenance. Higher SIL level will require more frequent proof testing which may ultimately increase the amount of system maintenance. Thus, a SIL based risk reduction is only recommended when process risk cannot be effectively reduced by other methods.

Summary

An overview of Safety Instrumented Systems based approaches was presented. The SIS systems are designed to prevent or mitigate hazardous events by preemptively taking the process to a safe state. Risk Graph and LOPA approaches to determine the appropriate Safety Integrity Levels for SIS applications were presented. An example from the Nitration Industry (Reactor, with Organic substrate & H_2SO_4/HNO_3 reactants) was presented to demonstrate a SIL determination using the LOPA methodology. SIS verification and testing requirements were also discussed. Additional references for SIL determination and verification approaches can be found in References (*5–11*).

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Chapter 12

Lessons Learned from an Explosion in an Ammonium Nitrate Neutralizer

Roland Huet* **and Lawrence E. Eiselstein**

Exponent Failure Analysis Associates, 149 Commonwealth Drive,
Menlo Park, California 94539
***E-mail: huet@exponent.com**

The factors leading up to the large explosion that occurred in an ammonium nitrate neutralizer in Iowa in 1994 will be discussed. Ammonium nitrate (in the form of 83 wt% solution in water) was made in a neutralizer tank by reacting nitric acid with ammonia. At the time of the accident, the neutralizer had been shut down but the contents were kept hot by steam injected through the nitric acid sparger. Several operational factors combined to cause the explosion: the ammonium nitrate was acidified when the nitric acid line was purged into the neutralizer; the neutralizer contents were not being circulated to maintain homogeneity; the neutralizer had been contaminated with chlorides; the prolonged steam heating raised the neutralizer temperature; and the steam bubbles facilitated runaway decomposition.

Ammonium Nitrate Explosions

Ammonium nitrate is widely and safely used as a fertilizer and in many other applications. However, it is well known that under certain circumstances, such as contamination with hydrocarbons or excessive confinement, it can be a powerful explosive. Mixtures of ammonium nitrate and fuel oil (ANFO) are routinely used as explosives. Although the conditions leading to explosions of pure ammonium nitrate are rarely observed in practice there have been a few large accidental explosions of ammonium nitrate. Three such explosions will be briefly reviewed here.

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Texas City, 1947

A large shipment of fertilizer grade ammonium nitrate was loaded and stowed in two cargo ships (the S. S. *Grand Camp* and the S. S. *High Flyer*) in the Texas City harbor in April 1947 for shipment to Europe (*1*) . The ammonium nitrate fertilizer was packaged in paper bags; the fertilizer grains were lightly coated with paraffin (3 wt. %) to avoid caking when exposed to humid conditions (*1–13*).

The S. S. *Grand Camp* was carrying 2200 tons of the wax-coated ammonium nitrate in paper bags when a fire started in one of the ship holds and the crew tried to smother the fire by shutting all hatches and injecting steam into the holds (*1*). The hydrocarbons from the wax and paper, the heat from the fire and the injected steam, and confinement by the closed holds provided conditions necessary for a detonation. After several hours, the *Grand Camp* detonated on April 16, 1947 in the harbor, killing about 600 people in the surrounding dock area and causing over $100 million of property damage (*6*). The fire spread to the S.S. *High Flyer*, which detonated a few hours later on April 17 (*4*). A very similar accident occurred a few months later in Brest, France, one of the European harbors receiving these ammonium nitrate shipments (*1*, *6*).

As a result of these accidents, safer anti-caking agents were developed. Ironically this accidental explosion also led to the development of a new family of industrial explosives, ANFO (*6*).

Port Neal, 1994

An ammonium nitrate fertilizer manufacturing plant located at Port Neal, Iowa, owned by Terra, exploded on December 13, 1994. This explosion killed four Terra employees, injured more than a dozen people, and devastated the plant. This is the incident we will discuss in greater detail below. During a shutdown of the ammonium nitrate production during freezing weather conditions, the ammonium nitrate in the neutralizer vessel was kept hot by steam injection to prevent solidification. In addition, the ammonium nitrate had inadvertently been allowed to become very acidic and contaminated with chlorides; both conditions are known to promote explosive decomposition. After several hours of steam injection, the ammonium nitrate detonated.

Toulouse, France, 2001

An explosion of about 400 tons of ammonium nitrate occurred in Toulouse at the AZF plant (Azote et Fertilisants) on 21 September 2001 (*14–16*). The origin was in a warehouse used to collect ammonium nitrate that did not meet specifications for finished product. The cause of this explosion is unclear, but the leading theory is that a quantity of chlorinated compounds was inadvertently added to the ammonium nitrate pile shortly before the explosion.

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The Accident at Port Neal, Iowa

At 6 am, on the 13th of December 1994, two process vessels (the neutralizer and run-down tank) at Terra International's Port Neal, Iowa ammonium nitrate fertilizer plant detonated, killing four employees, injuring 18 others. All buildings and equipment within a 200-ft radius were leveled (*17–19*). Although there were numerous reasons proposed for this explosion, an independent court appointed expert confirmed that the initial explosion occurred outside the nitric acid sparger. The significance of this and other findings hold valuable lessons for plant operators.

Plant Layout

Terra Industries' Port Neal complex manufactured anhydrous ammonia from methane, water and air. The ammonia was split into four different streams: one for urea manufacture, a second for the manufacture of 55 wt% nitric acid, a third stream was combined with the nitric acid to make ammonium nitrate, and the fourth ammonia stream was for direct sales. Thus the major output products of the site were urea (granules, prill and liquor), ammonium nitrate and ammonia.

Ammonium Nitrate Neutralizer

The ammonium nitrate neutralizer is the vessel in which the ammonium nitrate is made by reaction between ammonia gas and 55 wt% nitric acid. The process is shown in Figure 1 and Figure 2. The neutralizer vessel is about 10 feet in diameter and 15 feet high, it contains a hot 83 wt% solution of ammonium nitrate in water. Ammonia gas is injected at the bottom of the neutralizer through a perforated plate. Nitric acid is injected into the neutralizer through two titanium spargers, which are two tubes 4 inches in diameter bent to form two semi-circles, with two rows of holes to distribute the nitric acid. The ammonia and nitric acid react together to form more ammonium nitrate solution and the heat of reaction keeps the temperature elevated. The neutralizer vessel is not actively cooled; some of the water made during the reaction evaporates naturally to balance the heat of reaction. There is no mechanical stirring; the solution is mixed by the rise of the ammonia bubbles up the center of the tank through a vertical draft tube open at both ends. The vertical draft tube helps set up circulation of the liquid ammonium nitrate, up inside the tube and down outside the tube.

An overflow line on the neutralizer directs the hot ammonium nitrate solution into the rundown tank, from which it is pumped to storage tanks. Vapors in the neutralizer head space, rich in ammonia, are sent to a scrubber where they are neutralized with a weak nitric acid solution (pH above 1.4).

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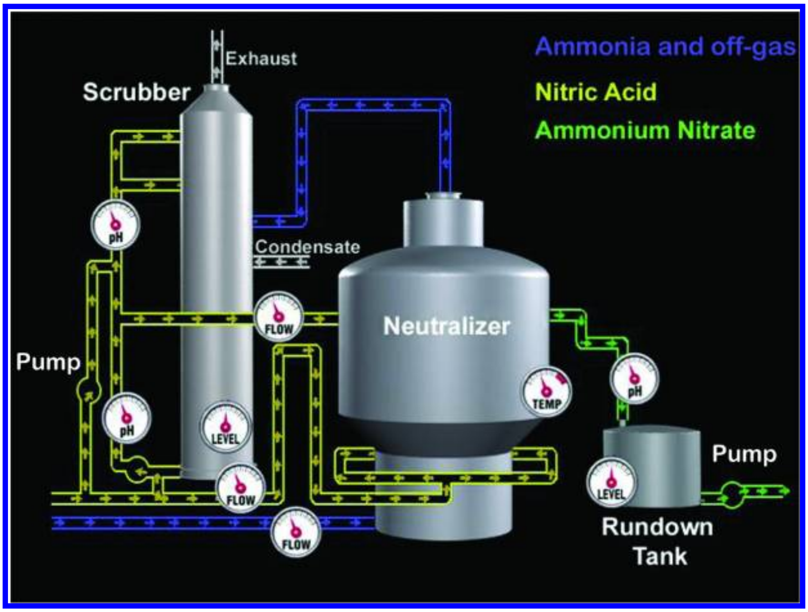

Figure 1. Schematic of the neutralizer process. The ammonium nitrate generated in the neutralizer flows into the rundown tank before being pumped out. The neutralizer off-gas, rich in ammonia, is treated in the scrubber. (Courtesy of Roland Huet). (see color insert)

Figure 2. Interior view of the scrubber, neutralizer and rundown tank. Green indicates the ammonium nitrate solution, blue the ammonia and yellow the nitric acid. The spargers are on the outside of the draft tube. (Courtesy of Roland Huet). (see color insert)

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The Explosion

On December 12, 1994 at approximately 9 pm in the evening, the neutralizer at the Port Neal fertilizer plant was put in hot shutdown. Since there was no longer any heat of reaction to keep the neutralizer hot, and the temperature outside was 10°F (-12°C) the operators were concerned that the ammonium nitrate would salt out and freeze in the neutralizer. To avoid this possibility, they injected 200 psig steam through a hose connected to the nitric acid spargers (*17*). Saturated steam at this pressure is at about 387 °F (197 °C). The steam flow rate was not known nor controlled, and the plant had not set a maximum or minimum temperature for this abnormal operating condition. After about 9 hours of continuous steam injection, conditions in the steam supply system changed, which may have led to superheated steam of unknown temperature being injected into the neutralizer. About 30 minutes later, there was a detonation in the neutralizer and the rundown tank. This resulted in four fatalities, 18 injuries and extensive damage to the plant (*17*, *18*, *20–22*).

Controversy About the Cause of the Explosion

As may be expected in an accident of this magnitude, there was some controversy between the plant operator and the equipment designer about the causes of the explosion. The neutralizer design and the plant operation were the subject of a contentious lawsuit; this fact and the extensive destruction of records caused by the accident were such that many details of the plant layout, process and operation were unclear. We will present the proposed theories, established facts, controversy regarding the root cause, and the conclusions of an independent court appointed expert.

Theories, Established Facts, and Open Questions

During the investigation of this accident, several theories were proposed for the explosion. Some were quickly abandoned because they did not fit with the observed evidence. For instance, there was speculation that some of the pumps shown in Figure 1 may have been the cause of the explosion (*17*, *18*). However, the damage pattern indicated clearly that the first detonation occurred inside the neutralizer (there was no damage to the neutralizer from an outside impact) and none of the pumps that were recovered showed any sign of an internal explosion(*17*).

Two competing theories remained in contention. Terra Industries and its experts asserted that some ammonium nitrate had backed up into the titanium nitric acid spargers and that the first explosion occurred inside this tube because of the severity of the conditions at that location: increased confinement, increased contamination by metal ions, and violent oxidation or burning of the titanium tube that generated enough heat to initiate an explosion (*23*, *24*). On this basis, Terra sued Mississippi Chemical, the designer of the neutralizer, for defective design of the sparger tube. Mississippi Chemical and its experts, including Exponent, countered that poor operating conditions, specifically acidification of the ammonium nitrate, chloride contamination and steam injection for many hours, were the real reason for the explosion (*21*, *25*).

The neutralizer was in hot shutdown at the time of the explosion, and steam had been flowing through the nitric acid spargers for about 9 hours. Evidence strongly suggested that the contents of the neutralizer were very acidic and contaminated with chlorides; two conditions known to promote the explosive decomposition of ammonium nitrate. Numerous tests, such as accelerating rate calorimeter (ARC) tests, confirmed that acidification and chloride contamination increased the rate of decomposition of ammonium nitrate. However, the severity of the contamination was not clearly established, as discussed later, so there was a considerable disagreement between the parties on the conditions inside the neutralizer.

The key question was whether the conditions inside the neutralizer itself (heat, acidity, chlorides and confinement) were enough to lead to a detonation, or if other factors present only inside the sparger tubes were necessary for the detonation to occur. The other factors that could only affect ammonium nitrate inside the spargers were confinement of the ammonium nitrate in a small volume, and reaction of the ammonium nitrate with the titanium walls of the spargers. The controversy thus narrowed to the location of the initial explosion: did it occur in the neutralizer itself due to the heating and contamination of its content, or did it initiate inside a nitric acid sparger, thus implying that confinement and reaction with titanium were necessary for the explosion?

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Independent Assessments

Two independent assessments concluded that the explosion occurred first in the neutralizer itself, thus denying that the spargers played a role in the accident (*17*, *22*).

The first assessment was made by the Environmental Protection Agency (EPA) in their investigation of the explosion (*17*). The main piece of evidence on which they relied was the recorded level in the rundown tank, shown in Figure 3. The liquid level, measured with a pressure transducer, appeared to rise rapidly to 100% (or higher) a few seconds before the explosion. Clearly, this is unlikely to reflect an actual rise of the level in the rundown tank, but is more likely to be an artifact of a change in pressure. Even though the pressure transducer was believed to be a differential pressure transducer and should have been insensitive to changes in the pressure inside the vessel, the only credible explanation for the recorded level rise is a change in pressure inside the vessel (it is possible, for instance, that the upper leg of the level transducer was plugged). This apparent level rise was due to a large-scale decomposition of the ammonium nitrate inside the neutralizer during the last few seconds before the detonation, which rules out an initial detonation inside one of the spargers. If the initial explosion had occurred inside a sparger and triggered a detonation of the entire neutralizer, this detonation would have occurred immediately after the sparger explosion, and there would not have been any pressure rise inside the neutralizer in the few seconds before the detonation.

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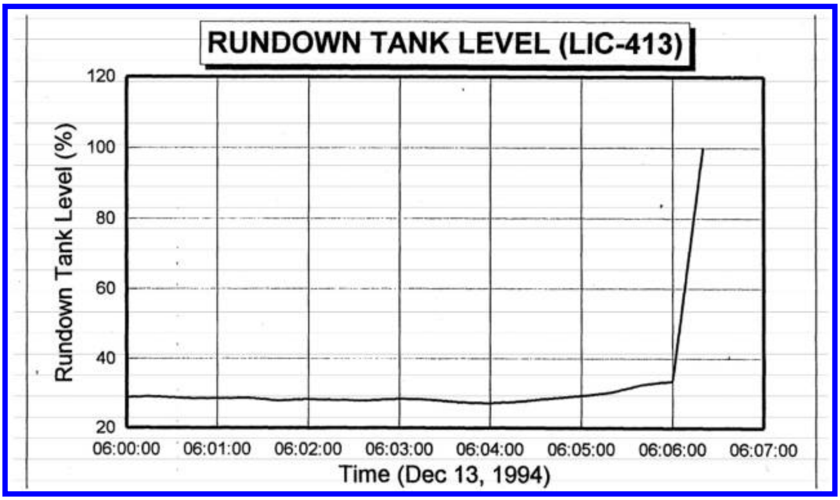

Figure 3. Recorded liquid level in the rundown tank just before the explosion. (Reproduced from ref. (17)).

The second independent assessment was performed by an expert appointed by the court in the trial between the plant operator and the equipment designer. The court-appointed expert examined closely the few recovered fragments of the spargers and determined, through careful analysis of their shape and some computer modeling, that the initial explosion had occurred outside of the spargers, not inside (*22*).

Accident Main Factors

The independent assessments indicated that the conditions inside the neutralizer itself (acidity, chlorides, excessive heat, and confinement) were sufficient to cause the detonation. The reasons for the presence of these four factors are discussed below.

Acidity

Actions of the plant operators prior to and during the hot shutdown caused the ammonium nitrate in the neutralizer to become very acidic, but the operators did not realize it. Low pH is a condition known to promote explosive decomposition of ammonium nitrate (*26–32*).

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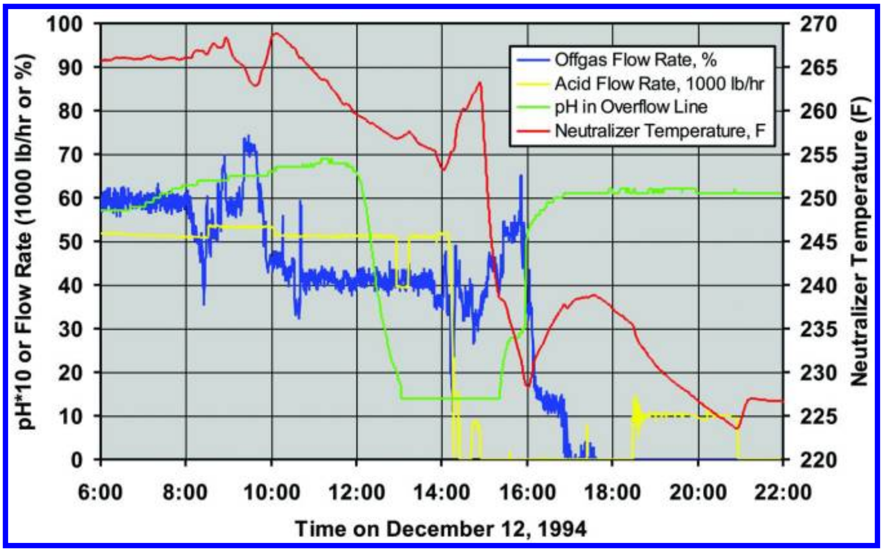

Figure 4. Key neutralizer operating parameters a few hours before the explosion. (Courtesy of Roland Huet). (see color insert)

Figure 4 shows four key operating parameters for the neutralizer a few hours before the explosion, which occurred at about 6 am on December 13, 1994. The neutralizer was operating normally until about 8 am on December 12. At about 10 am, the neutralizer was placed in partial shutdown, with a reduction in the ammonia flow (labeled offgas flow in Figure 4) but no corresponding reduction in the acid flow rate. This led to an acidification of the neutralizer, where the pH plunged to very low values at about 1 pm. The operators apparently became aware of this situation and tried to remedy it starting at about 2 pm: they shut off acid flow but maintained the ammonia flow. The neutralizer appeared to respond and by about 5 pm the recorded pH was back to 6. However, the operators failed to realize that the pH probe was not in the neutralizer itself, but in the overflow line between the neutralizer and the rundown tank (see Figure 1). Since the neutralizer was not in operation, no ammonium nitrate was flowing down this process line and the probe was probably measuring the pH of a small pocket of product in the line. This small quantity of ammonium nitrate was likely neutralized by the ammonia flow into the neutralizer, but there was not enough ammonia injected into the neutralizer to bring its pH back to neutral. Figure 5 shows the pH in the neutralizer computed from the flows of acid and ammonia. The computed pH is in good agreement with the measurement made on a grab sample taken just before the partial shutdown, but becomes very acidic soon after and remains very acidic up to the time of the explosion. The operators did not take any grab samples after the start of the partial shutdown, so they were not aware of the extreme acidity in the neutralizer.

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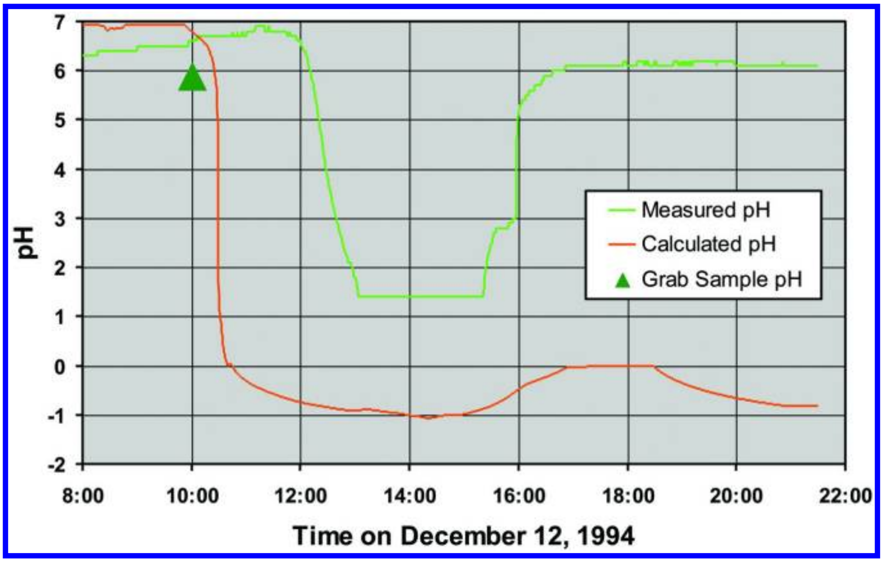

Figure 5. Measured pH in rundown line and calculated pH in neutralizer. (Courtesy of Roland Huet). (see color insert)

Chloride Contamination

The contentious nature of the lawsuit made it difficult to obtain detailed information on the potential sources of chloride contamination. Nonetheless, it appears that the neutralizer was contaminated by chlorides originating from plant cooling water that leaked into the nitric acid manufacturing stream and from there into the AN plant. The chloride levels in the nitric acid were apparently not monitored, even though the nitric acid plant is a logical source of chloride contamination: the EPA report on this incident stated that the level of chloride in the nitric acid at the plant had not been analyzed since 1980 (*17*). Furthermore maintenance records indicated that there was at least one serious cooling water leak into a condenser in the nitric acid production plant, leading to chloride contaminated nitric acid. This leak was recorded on operator logs from December 5-8, and led to a nitric acid plant shutdown on December 8. Increased chloride concentrations are also likely during unstable acid plant operations, such as during startup and shutdown, and the nitric acid plant had been started twice and shut down three times during the week preceding the explosion, for various reasons. Chlorides formed during acid plant operations concentrate in the weak acid trays of the absorption column. Following the emergency shutdown of the nitric acid plant on December 12, contents of the absorption column were pumped to the nitric acid storage tank, introducing chlorides into the ammonium nitrate (AN) process.

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The EPA investigation team concluded that chlorides were present in the nitric acid used in the AN plant. Analytical data provided by Terra indicated chloride concentrations in the west AN storage tank were 168 parts per million, and 557 parts per million in the nitric acid absorption column and the EPA investigation team concluded that chlorides were present in the neutralizer, rundown tank, and west AN storage tank at the time of the explosion.

At about 6 pm on December 12, the nitric acid absorption columns in another part of the plant were drained for repairs. The drained nitric acid was highly contaminated with up to 557 ppm of chlorides. Chlorides are another contaminant well known for accelerating the explosive decomposition of ammonium nitrate (*14*, *33–42*), and action levels based on chloride concentrations range from 1 part per million to 80 parts per million (*17*). The operators meant to send the contaminated nitric acid back to the nitric acid storage tank, but some contaminated nitric acid was pumped into the neutralizer by mistake, as shown in Figure 4: the nitric acid flowmeter recorded a fluid flowing into the neutralizer between about 6:30 pm and 9 pm, Dec 12th, a time when operators denied adding any acid into the vessel. A likely explanation for this recorded flow is that the operators intended to send the contaminated nitric acid from the absorption towers to the nitric acid storage tank, but they used for this operation a pump meant to bring nitric acid into the neutralizer. Whether through improper positioning of valves or misunderstanding of the flow characteristics of the various lines used, some of the chloride-contaminated nitric acid was inadvertently sent to the neutralizer, as shown in Figure 4 . However, the amount of flow into the neutralizer, hence the chloride contamination level in the neutralizer, is not known precisely. Apparently, the operators were not aware of the dangerous effects of chlorides on ammonium nitrate stability.

Excessive Heat

With the neutralizer in shut-down, the operators were concerned about keeping its contents hot during the freezing cold December night in Iowa. The neutralizer was equipped with heating coils near its bottom, designed for this purpose, but they could not be used because of disrepair. The operators instead used a flexible hose to send steam at 200 °C (about 400 °F) directly into the nitric acid sparger, to keep the neutralizer hot and preventing salting out of solid ammonium nitrate. This steam injection lasted for about 9 hours, until the explosion. Further, it is likely that the steam pressure and temperature were increased about one hour before the explosion, in anticipation of a significant steam demand to restart another part of the plant. The steam provided the heat required for the explosive decomposition of the ammonium nitrate.

The temperature distribution inside the neutralizer before the explosion is not known precisely. The neutralizer temperature trend is shown in Figure 4 up to 10 pm on December 12, about 8 hours before the explosion. The recorded temperature remained approximately constant until the explosion. It is likely that the recorded temperature did not capture some local heating within the neutralizer, which was no longer effectively stirred: experiments showed that the steam bubbles collapsed within a few inches of leaving the sparger. As opposed to ammonia bubbles, which

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provided strong mixing in the neutralizer during normal service, the collapsing steam bubbles did not provide any significant mixing of the ammonium nitrate in the neutralizer, so the heat brought in by the steam may not have been evenly distributed in the solution; therefore, the neutralizer thermocouple located away from the titanium sparger may not have registered the highest temperature in the neutralizer.

Confinement

Confinement refers to the situation where gases and other decomposition products are not able to expand freely, thus increasing the pressure in the reaction zone. In the case of ammonium nitrate, this increased pressure tends to favor the rapid explosive decomposition path, which may lead to an explosion (*16*, *43–45*). In the Terra plant, the neutralizer itself was able to provide some confinement for the ammonium nitrate: the neutralizer was an enclosed space, gases generated at a sufficiently rapid rate cannot escape and therefore the pressure will rise. Further, the large volume of the ammonium nitrate solution will also provide pressurization and confinement through hydrostatic and inertial effects.

Conclusions

At its roots, the Port Neal explosion was due to insufficient monitoring during abnormal plant conditions (hot shutdown), because of a lack of operator training and awareness of process hazards. It was not clear that a proper and effective process hazard analysis had been done at the plant, or that the potential hazards that could lead to accelerated decomposition of ammonium nitrate had been identified. As a result, the operators did not realize that the pH measurements were not reliable when the neutralizer was not in production and did not take grab samples during the shutdown. In addition, they were not aware that chlorides would accelerate the explosive decomposition of ammonium nitrate and did not realize that they had sent contaminated nitric acid from the absorption columns to the neutralizer, instead of sending this nitric acid to a storage tank. Finally, they were not aware of the danger of “cooking” the neutralizer with high-temperature steam for 9 hours. All these conditions combined to cause this deadly explosion.

Acknowledgments

The authors would like to acknowledge that the finding regarding the Terra/Mississippi Chemical incident were the result of many investigators from both the government and various companies. The investigation that was performed at Exponent involved many different consulting experts; however we would specifically like to mention the efforts and contributions of Drs. C. A. Rau, Jr., B. Ross and Mr. B. McGoran.

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Chapter 13

Process Design and Operational Controls To Safeguard Strong Nitric Acid Recovery Systems

Thomas L. Guggenheim,[*] Roy R. Odle, and John Pace

SABIC Innovative Plastics, 1 Lexan Lane, Mt. Vernon, Indiana 47620
[*]E-mail: thomas.guggenheim@sabic-ip.com

A nitric acid concentrator-sulfuric acid concentrator (NAC/SAC) is a manufacturing process that produces strong nitric acid, strong nitric being defined as >98 weight percent (wt%). Operating procedures, compositional control, and design of the system are all necessary to ensure a safe process. Typically, 80 to 90 wt% sulfuric acid and 65 to 80 wt% nitric acid are fed to a packed column to provide condensed strong nitric acid overhead and 60 to 70 wt% sulfuric acid as a bottoms stream. The mass balance of constituents across the column during normal, startup, and shutdown conditions must be controlled to allow for the proper operation of the system. This paper will describe the operational and design changes made to a NAC/SAC system after an event in which the strong nitric acid condenser failed. The authors conclude that the condenser failure, which occurred after unusual operating conditions, was most likely caused by rapid gas formation, resulting from the fast decomposition of a thermally unstable condensed phase that had collected in low spots in the NAC overheads system, which led to over-pressurization of the condenser.

Introduction

The Innovative Plastics business unit of SABIC operates a nitration facility in Mt. Vernon, Indiana. The facility nitrates an N-alkylphthalimide (**1**) derivative in 99 wt% nitric acid to afford primarily an isomeric mixture of nitro-N-alkylphthalimides (**2**), used in the manufacture of an engineering thermoplastic (equation 1) (*1*). A by-product of the nitration reaction is

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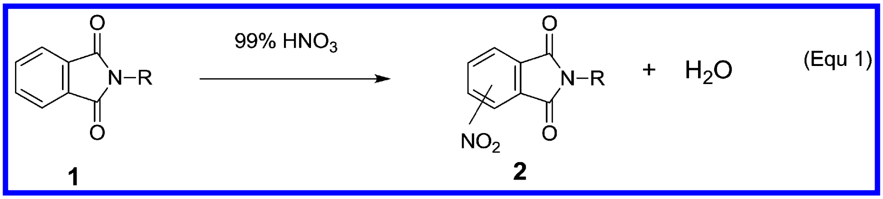
tetranitromethane (**3**, abbreviated as **TNM**, bpt 126 °C). The majority of the strong nitric acid (>97 wt% HNO_3) is removed from the product by evaporation under slightly reduced pressure, and condensed.



$C(NO_2)_4$

3

The recovered nitric acid contains the majority of the TNM produced in the process. The recovered strong acid is combined with weak nitric acid process streams and clean commercial grade 69 wt% nitric acid to afford ~75 wt% nitric acid (*2*). This combined weak nitric acid, stored in the 'weak nitric acid tank', must be concentrated back to >99 wt% HNO_3 for the efficient nitration of the N-alkylphthalimide.

Production of 99 wt% nitric acid is accomplished by continuously feeding the ~75 wt% HNO_3 from the weak nitric acid tank to a packed column (called a nitric acid concentrator, **NAC**) along with ~85 wt% sulfuric acid (balance being water) under slight vacuum. Strong nitric acid (99 wt% HNO_3) is taken overhead of the column and condensed in a water cooled condenser, while weak sulfuric acid (~65 wt%) is taken off the bottom of the NAC.

The exact concentrations of the NAC feed can vary. The sulfuric acid can be 80 to 90 wt%, and the nitric acid can be 65 to 80 wt%. Approximate concentrations of acid streams in wt% are used throughout this paper, as the exact strengths are not critical aspects of the discussion and conclusions.

While shutting down the nitration facility, the overheads condenser on the nitric acid concentrator over-pressurized and failed. Fortunately, there were no injuries resulting from the failure. The subject of this paper explains (i) the investigation of the of the condenser failure, (ii) how the most likely cause of the failure was determined, and (iii) the redesign of the condenser.

Brief Description of the NAC Equipment and Operation

A simplified process flow diagram of the NAC is shown in Figure 1 (*3*). It is a glass column packed with structured glass packing. The ~85 wt% H_2SO_4 and ~70 wt% HNO_3 are continuously fed to the NAC. The sulfuric acid's strong affinity for water effectively 'breaks' the maximum boiling azeotrope of HNO_3/water (~68 wt% nitric acid), allowing for the distillation of >99 wt% nitric acid overhead of the NAC and the collection of weak sulfuric acid (~65 wt%) off the bottom of the

NAC. A steam-heated reboiler provides heat to the NAC, and the 99 wt% HNO_3 is taken overhead at about 660 mm pressure (b.pt. 80 to 81 °C). The 99 wt% nitric acid is condensed in a horizontal condenser, and collected in a storage tank. The two other significant species present in the overheads product are TNM (~0.5 wt%) and dissolved oxides of nitrogen (NOx, 3-5 wt%). Some of the condensed 99 wt% HNO_3 is returned to the top of the column, through a flow control (FC) valve, which controls the composition of the NAC overheads product and the overall production efficiency of the NAC.

The material exiting the bottom of the NAC is primarily composed of ~65% sulfuric acid containing some oxides of nitrogen, nitric acid, and nitrosyl sulfuric acid. This bottom product of the NAC enters a glass denitrification tower (**DEN**), where it is contacted with live steam. The steam hydrolyzes the nitrosyl sulfuric acid to nitrous acid (HNO_2), H_2SO_4, and NOx, some of which is oxidized to nitric acid by the air present in the process. The nitric acid vapor, along with the oxides of nitrogen present in the DEN, is 'chased' by air that is also fed to the DEN back into the body of the NAC, and eventually overhead of the NAC. Finally, the temperature of the vapor exiting the horizontal condenser to the vent system is controlled by the flow rate of cooling water (CWS) through the U-tube bundle inside the condenser. The ~65 wt% sulfuric acid from the bottom of the DEN is concentrated back to 80 to 90 wt% sulfuric acid by simple evaporation of water. The ~85 wt% sulfuric acid is eventually recirculated back to the NAC.

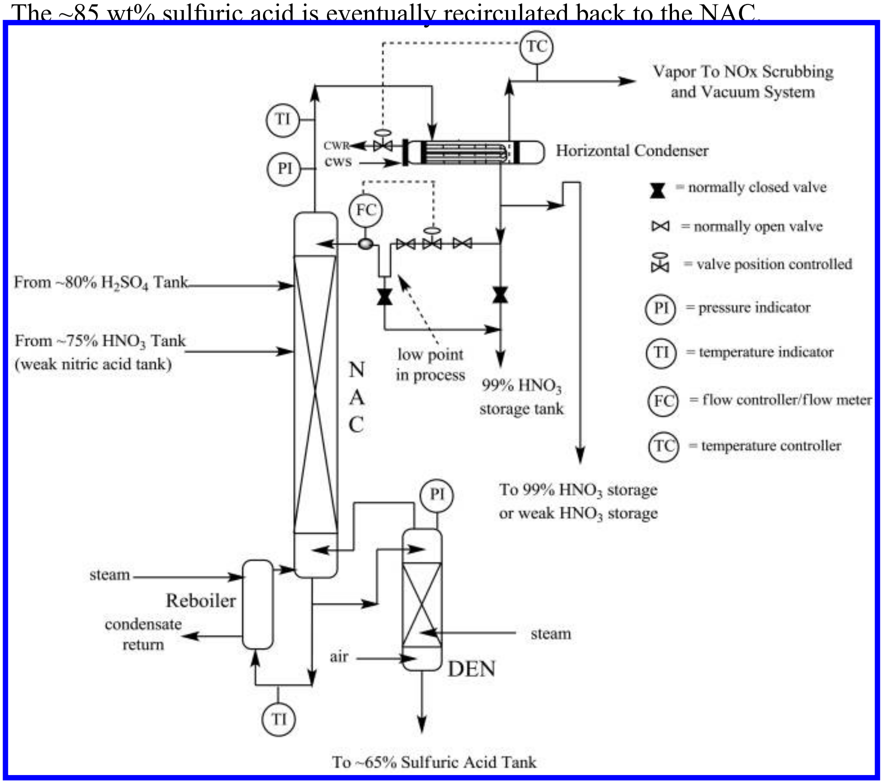
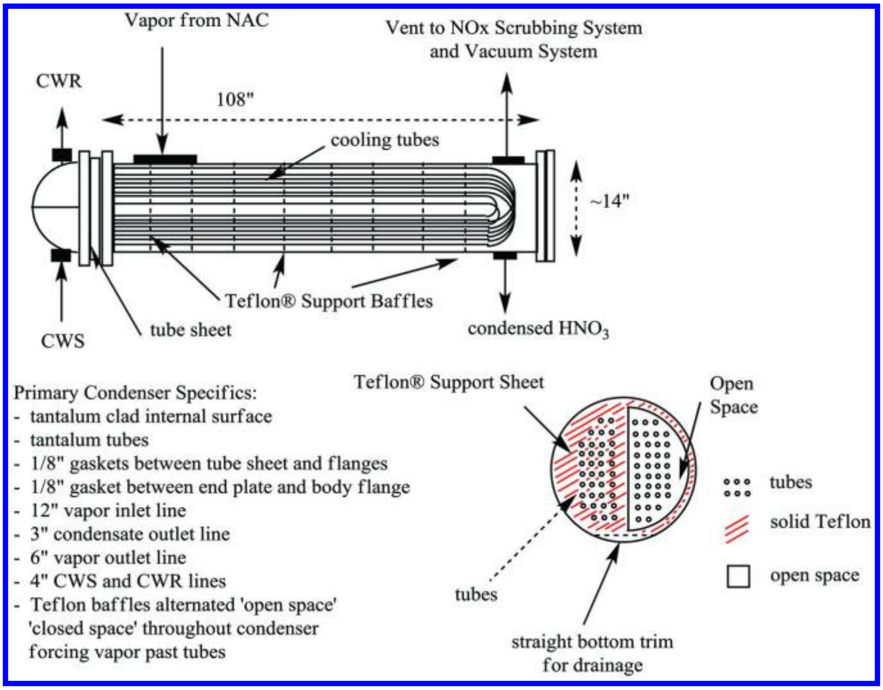


Figure 1. Simplified Schematic of the NAC.

A simplified schematic of the NAC overhead condenser is shown in Figure 2. The overhead vapor line from the top of the NAC enters the top of the condenser. The condenser is constructed with an internal U-tube bundle which is supported by a plurality of evenly spaced Teflon® baffles. The metallurgy of construction of the condenser was compatible with the chemical compositions that were potentially present in the system.



Primary Condenser Specifics:
- tantalum clad internal surface
- tantalum tubes
- 1/8" gaskets between tube sheet and flanges
- 1/8" gasket between end plate and body flange
- 12" vapor inlet line
- 3" condensate outlet line
- 6" vapor outlet line
- 4" CWS and CWR lines
- Teflon baffles alternated 'open space' 'closed space' throughout condenser forcing vapor past tubes

Figure 2. Simplified Schematic of the NAC Condenser. (see color insert)

One half of each Teflon® support is cut out to afford an open space. The open spaces are alternated to the other side for each successive support. This construction forces the vapor off the NAC to contact the tubes evenly throughout the length of the condenser, increasing the heat transfer efficiency. The bottom of each support is trimmed to allow the drainage of the condensate off the bottom of the condenser.

Failure of the NAC Condenser and Damage Assessment

During a shutdown of the nitration facility, the NAC was running in normal mode. The 99 wt% nitric acid and N-alkylphthalimide that feeds to the nitrators had been ceased and the nitric acid was being recovered from the nitrated imide product and stored in the weak nitric acid tank. For brevity, only the salient events leading up to the condenser failure are detailed below.

At 9:45 am the nitrators were empty and the NAC was being fed ~70 wt% HNO_3 (from the weak nitric acid tank) and ~80 wt% H_2SO_4.

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At 11:09 am, the nitric acid feed to the NAC was intentionally shut off as was the steam to the NAC reboiler; the ~80 wt% sulfuric acid feed to the NAC and the live steam to the DEN were continued.

At 11:10 am, the flow of condensate off of the NAC condenser to the nitric acid storage tank stopped, but the flow from the condenser to the top of the NAC continued. The NAC was said to be "on total reflux".

From 11:10 am to 5:41 pm, the ~80 wt% sulfuric acid feed to the NAC and the live steam to the DEN were continued. This condition produced ~65 wt% sulfuric acid as the bottoms product of the DEN. The ~65 wt% sulfuric acid was concentrated back to ~80 wt% sulfuric acid in the sulfuric acid concentrator. The ~80 wt% sulfuric acid was then returned to the NAC. The NAC was on total reflux during this entire timeframe. The temperature at the top of the NAC at 11:00 am was ~80 °C, 92 °C at 1200 pm, and ~114 °C at 1:00 pm. The top of the NAC remained at ~114 °C up to the time of the event.

At 5:42 pm, the sulfuric acid feed to the NAC tripped off (ceased) due to a high pressure interlock at the top of the column. Some steam flow was automatically reestablished to the NAC reboiler. The live steam feed to the DEN had tripped off. The temperature of the material in the reboiler was 128 °C at 5:42 pm. The reflux return flow indication to the top of the column became erratic, most likely indicating no flow. Finally, the temperature at the top of the NAC was 114 °C, and the vapor off of the condenser was 52 °C.

At 6:02 pm the NAC overheads condenser exploded. At that time, the temperature in the NAC reboiler had climbed to 153 °C because the steam to the reboiler had been automatically reestablished at 5:42 pm, and the top of the NAC was 114 °C. No personnel were in close proximity to the equipment damaged, and there were no injuries.

The body of the condenser fragmented and the condenser end plates were found intact 10 feet from their original location. The condenser tubes were crushed and fragmented. The tubes near the tube sheet were fragmented. The tube sheet is the plate where the ends of the tubes are secured (rolled to prevent leakage of coolant into the process), and this plate is bolted to the CWS (cooling water supply) and CWR (cooling water return) side of the condenser (see Figure 2). A one foot diameter hole was found in the concrete floor directly below the tube sheet of the condenser. The top of the NAC was destroyed and the DEN was cracked. The NAC reflux return line was completely fragmented but the valve bodies in the line were found intact. Failure mode experts from a consulting firm (*4*) found that the shrapnel from the metals of construction failed in a ductile manner indicating a rapid deflagration or low order detonation, as opposed to a brittle failure that would be more consistent with a high-order detonation.

The survey of the damage suggested that the event took place in the condenser and most probably in the reflux return line as well. The consulting firm determined that the extent of the damage resulted from a low-order detonation which was the equivalent of 2 to 4 pounds of trinitrotoluene (TNT) (*5*). The consulting firm also estimated that the condenser could withstand a detonation equivalent of <2 pounds of TNT, and that ~1200 psig was necessary to cause the shell of the condenser to fail. *The failure appeared to be the result of a rapid decomposition of a condensed phase forming high pressure gas.*

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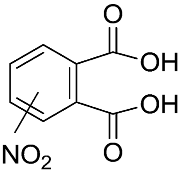
The consulting firm also determined by a series of worst case heat of reaction calculations, that the damage could not have been the result of a reaction of hydrogen with air, or carbon monoxide with air. Further, it was concluded that the failure was not the result of water leaking into the condenser, mixing with the nitric acid present, and generating heat leading to the rapid vaporization (pressure build) of nitric acid and or water.

Determination of the Probable Cause(s) of the Condenser Failure

Hundreds of samples of process streams and debris were taken immediately after the failure (*6*). Only the relevant findings are presented. The nitric acid feeding the NAC on the day of the event was 80.6 wt% HNO_3, 0.4 wt% TNM, 200 ppm of the nitro-N-alkylphthalimide (**2**), 4 ppm of nitrophthalic acid (**4**), 18 ppm of N-alkylphthalimide (**1**), 1000 ppm of nitroform (**5**, trinitromethane, bp at 12 mm 50 °C, mp 26.5 °C, freely soluble in water), 2.4 wt% oxides of nitrogen, and 5 ppm calcium.



nitrophthalic acid

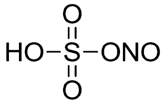
4

$(NO_2)_3CH$

Nitroform

5

The sulfuric acid feeding the NAC (analyzed just after the failure) was 80 wt% sulfuric acid, 540 ppm of nitrophthalic acid, 3100 ppm methylamine, 80 ppm TNM, 38 ppm nitroform, 25 ppm of nitro-N-alkylphthalimide, 3.7 wt% oxides of nitrogen (some of which was in the form of nitrosylsulfuric acid (**6**) and nitric acid), 100 ppm calcium, and about 300 ppm of other dissolved metals (primarily chromium, iron, sodium, nickel, magnesium and potassium).



$HO{-}\overset{O}{\underset{O}{S}}{-}ONO$

Nitrosylsulfuric Acid

6

Calcium sulfate was found partially fouling the packing of the NAC. Trace amounts of nitroform and TNM were found in the remnants of the NAC reflux return line.

Residual material was collected from the debris field. Remnants of the overheads line, the condenser, and the reflux return line were swabbed to collect residual chemical species that may have been present in the overheads system before the failure (see footnote 6). Trace amounts of nitroform, tetranitromethane, methylamine (as an acid salt), dinitrotoluene, compound 2, and nitrophthalic acid were found in all three places. The amount of these species present in these locations before the incident cannot be determined.

No evidence of corrosion was found among the remnants of the failed condenser and associated piping. Hydrogen can be formed by the corrosion of metal with dilute nitric acid and sulfuric acid (*7*). The absence of corrosion suggested that hydrogen was not involved in the event.

No foreign organic material was found in any process stream after the event. No unexpected metal contamination was found in the debris or process streams.

The damage pattern, knowledge of the process, and the ruling out of a gas-phase explosion suggested that a condensed phase, present in the condenser and/or the reflux return line, had rapidly decomposed generating high pressure gas that then over-pressured the condenser. The investigation proceeded with the hypothesis that the condensed phase was composed of an organic fuel and an oxidant. The oxidizing and oxidizable constituents could have been present in the same chemical compound. Some form of energy (e.g., thermal energy, even ambient heat, friction, electrical discharge) was necessary to initiate the rapid decomposition of a mixture of oxidant and oxidizer. We could not rule out friction (from a valve, or moving fluid or gas) as the source of the initiator. The only plausible source of an electrical discharge was the flow meter in the return reflux line to the top of the NAC, but this meter was completely destroyed and could not be examined.

The oxidants present in the NAC, the condenser, and the reflux return line from the condenser to the top of the NAC just prior to the event were nitric acid, oxides of nitrogen, oxygen, TNM, nitroform, and nitrosylsulfuric acid. The fuels present were TNM, nitroform, trace amounts of nitro-phthalic acid and N-alkylphthalimide, and methylamine. TNM and nitroform are compounds that contain both fuel (carbon) and oxidant (nitro group) but they are more effective at being an oxidant than a fuel. The cooling water fed temperature to the condenser on the day of the event was 18 °C. The boiling point of N_2O_4 is ~20 °C.

One of the guiding principles when designing a nitration facility is that low points and pockets are to be avoided, as these are places where unwanted material can collect, stagnate, and subsequently and uncontrollably react. The horizontal condenser was designed so that the condensate gravity-flowed to the drain of the condenser (see Figure 2). It could not be verified, post failure, if condensate was draining properly, since the condenser was destroyed. We also considered the possibility that the condenser was fouled with calcium sulfate (the presence of calcium resulting from a cooling water leak into the system), wherein a dam of sorts formed and then allowed the pooling of condensed material in the bottom of the condenser. There was no evidence found in the debris that suggested a

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significant amount of calcium sulfate being present in the condenser, nor were we able to determine if the condenser had been sloped properly to allow drainage. A low point in the reflux return line was present, allowing for the collection and stagnation of liquid, should the reflux return flow cease for any reason (see Figure 2).

An Aspen® Dynamics model of the NAC was developed and used to simulate the NAC column during the time period starting when the column was placed on total reflux (*8*). Physical properties for various constituents needed for the model were gleaned from the literature, estimated, or determined experimentally. Historical compositions of pertinent process streams were used in the model. The electronically captured plant trend data for process stream flow rates, and process temperatures and pressures were used in the Aspen model. The model then provided calculated values for the temperature in the top of the NAC, the DEN bottoms temperature and pressure, and the estimated composition of the NAC distillate and NAC bottoms product as a function of time.

The model predicted that the majority of the TNM, nitroform, and oxides of nitrogen (e.g., NO_2, HNO_3) present in the sulfuric acid feed to the NAC over the timeframe of 11:09 am to 6:02 pm was stripped off overhead and was condensed in the condenser. This condensate was returned to the top of the column and essentially recirculated from the top of the column to the reflux condenser and then back to the head of the column via the reflux return line. Some water was also distilled overhead. As indicated previously, during this timeframe, only the 86% sulfuric acid was being fed to the NAC, live steam was feeding the DEN, and the column was on total reflux. Further, the model predicted that the material collected overhead (the vapor and the condensate present in the condenser and reflux return line) was 60 wt% HNO_3 and contained at least two pounds of TNM with at least one pound as a second phase, and at least 0.8 pounds of nitroform. The estimated amount of phase-separated TNM was based on the known solubility limit of TNM in weak nitric acid (see note 1). It is known that the rate TNM hydrolyzes to nitroform in weak nitric acid is function of temperature (equation 2, footnote 1).

$$\underset{\mathbf{3}}{C(NO_2)_4} \xrightarrow{\text{weak nitric acid}} \underset{\mathbf{4}}{(NO_2)_3CH} \qquad \text{(Equ 2)}$$

It was estimated, based on the dimensions of the reflux return line and reflux condenser, that there were ~80 pounds of material present in the return line and as much as 70 pounds of material present in the condenser, depending on the amount of fouling in the condenser.

The amount of TNM and nitroform in the sulfuric acid feed to the NAC had been determined before the condenser failure, and in mass balance studies performed after the event. This led us to estimate that 6 to 12 pounds of TNM and nitroform had been distilled out of the sulfuric acid feed from 11:09 am to 5:42 pm and was present in both the condenser and reflux return line at the time of the event. The Aspen model also showed that the temperature of the distillate leaving the NAC was 120 °C, in fair agreement with the actual observed temperature (114 °C).

Both the Aspen model and lab studies showed only a trace of other organics (namely methylamine as a sulfate or nitrate salt, N-alkylphthalimide (**1**), nitro-N-alkylphthalimide (**2**), nitrophthalic acid (**4**), each <50 ppm) were present in the overheads at the time of the event.

We did not rule out the presence of significant amounts of NO_2 and N_2O_4 (bp 20 °C) being present in the condenser and reflux return line at the time of the failure. Recall that the cooling water on the day of the vent was running at 18 °C. It is known that mixtures of organic material and N2O4 can be extremely hazardous (*9*).

It is known that methylammonium nitrate is an explosive material (*10*) and we decided to verify that it would not come overhead of the NAC. A lab distillation of 80 wt% sulfuric acid containing 0.4 wt% methylamine at atmospheric pressure with a pot temperature of 110 °C produced a distillate that contained <2 ppm of methylamine (present as the sulfate salt). In all likelihood, the methylammonium sulfate found overhead was the result of mechanical entrainment since the vapor pressure of methylammonium sulfate is negligible.

Data collected at this juncture in the investigation led to the hypothesis that a condensed phase in both the condenser and reflux return line was most likely responsible for the condenser failure. Furthermore, it was surmised that the condensed phase was most likely composed of 60 wt% nitric acid containing oxides of nitrogen, considerable amounts of TNM and nitroform, and other trace organic materials known to be present in the process.

Thermal Stability of Probable Condensed Phase Compositions Responsible for the Condenser Failure

There was a possibility that TNM had phase separated from the condensed phase present in both the condenser and reflux return line at the time of the event. It is known that mixtures of TNM and organics can be powerful explosives (*11*). It is also know that TNM can extract organics from weak nitric acid media. It was thought that trace organic compounds and nitroform were also likely present in the condensed phase present in both the condenser and reflux return line. With all this in mind, a series of compositions were studied in the Advanced Reactive System Screening Tool (ARSST), developed by Fauske and Associates (*12*). This system is capable of heating a small amount of material (~1.0 gram) with magnetic stirring in an open 10 mL cell that is contained in a 450 mL pressure vessel equipped with a rupture disc (900 psig), Figure 3. The ARSST is an Accelerated Rate Calorimeter (ARC) of sorts, where heat of reaction is not lost to the test apparatus (*13*). The cell is insulated and heated at a controlled rate. The software can also control the heating of the cell in either a heat-wait-search mode or an isothermal operation. The open cell is equipped with a temperature thermocouple and pressure transducer (not shown in Figure 3). The sample

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container does not absorb a significant amount of reaction energy, leading to a more accurate measurement of the adiabatic rate of rise of temperature.

The compositions tested in the ARSST are shown in Table 1. The exact composition of the material present in the condenser and reflux return line will never be known, but we were confident that we would learn something from the thermal stability testing of the chosen compositions.

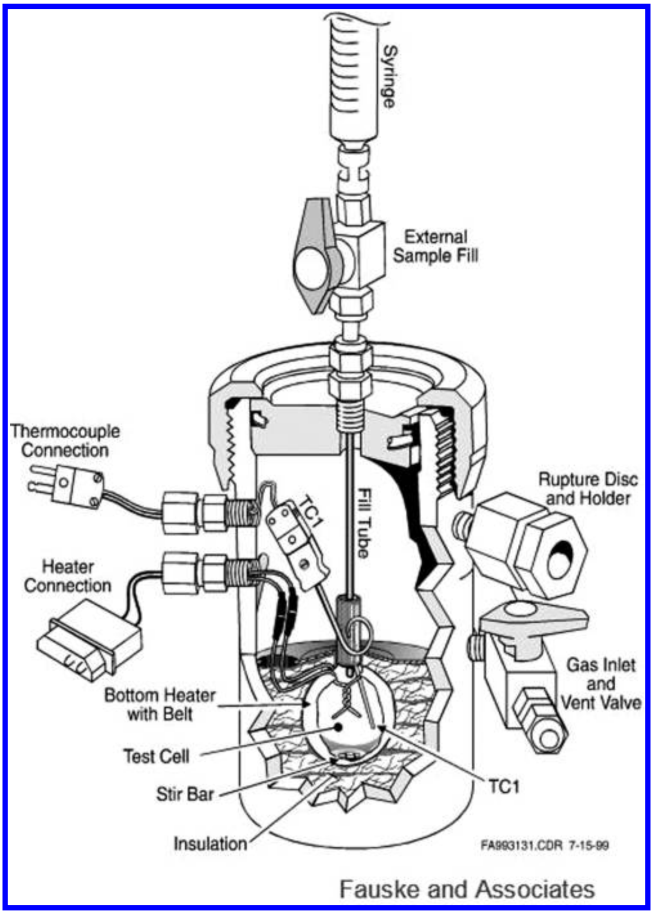

Figure 3. Fauske and Associates ARSST.

The mixtures were heated at 2.0 °C/min. The heater power would decrease when the sample began to self-heat in an attempt to maintain the desired heating rate. The sample was kept to less than 1.5 grams to accommodate the estimated peak pressure, should a detonation occur in the 450 mL high-pressure containment vessel. All tests started at ambient pressure (0 psig). Both temperature and pressure in the cell, containing the material, was measured over time. The results of the first experiment are shown in Graph 1. The mixture of TNM and

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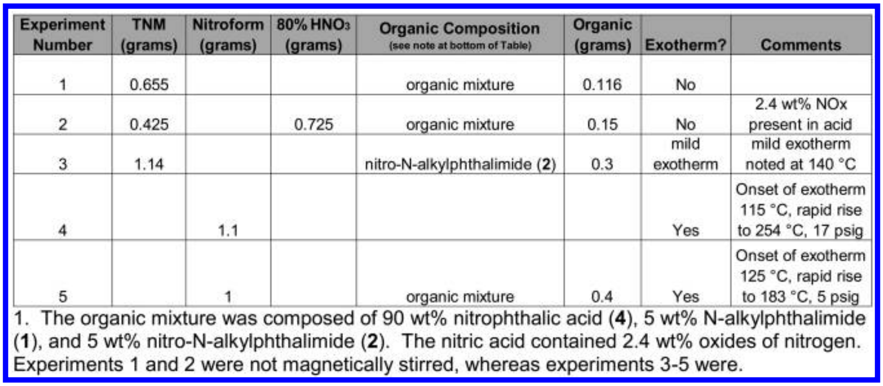
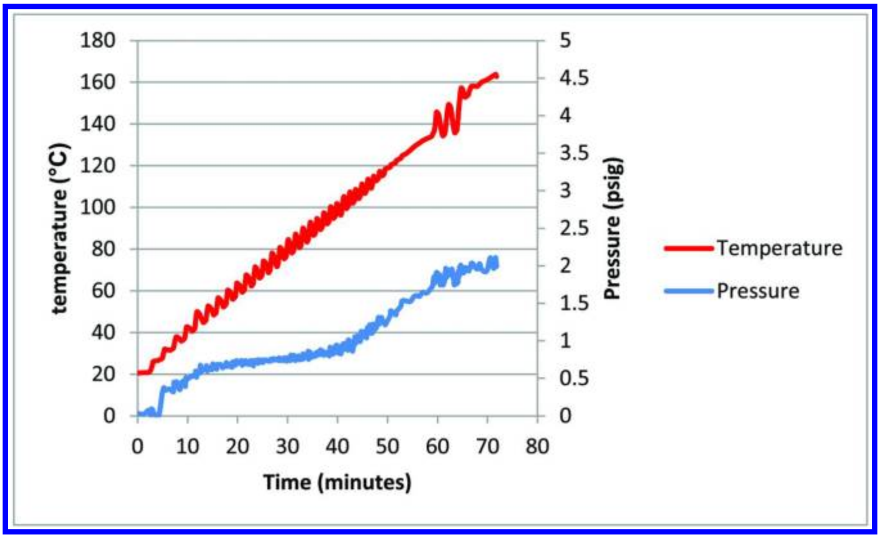
organics was not reactive up to 160 °C. Almost identical results were obtained in experiment 2 of Table 1 (graph not shown). The temperature oscillations observed in Graph 1 were due to sub-optimal default parameters used to control the heating of the sample. The parameters used were meant for a sample size of 10 grams. These parameters were adjusted in all subsequent experiments which used a sample of ~1 gram.

Table 1. Composition Tested in the ARSST (1)



Experiment Number	TNM (grams)	Nitroform (grams)	80% HNO_3 (grams)	Organic Composition (see note at bottom of Table)	Organic (grams)	Exotherm?	Comments
1	0.655			organic mixture	0.116	No	
2	0.425		0.725	organic mixture	0.15	No	2.4 wt% NOx present in acid
3	1.14			nitro-N-alkylphthalimide (**2**)	0.3	mild exotherm	mild exotherm noted at 140 °C
4		1.1				Yes	Onset of exotherm 115 °C, rapid rise to 254 °C, 17 psig
5		1		organic mixture	0.4	Yes	Onset of exotherm 125 °C, rapid rise to 183 °C, 5 psig

1. The organic mixture was composed of 90 wt% nitrophthalic acid (**4**), 5 wt% N-alkylphthalimide (**1**), and 5 wt% nitro-N-alkylphthalimide (**2**). The nitric acid contained 2.4 wt% oxides of nitrogen. Experiments 1 and 2 were not magnetically stirred, whereas experiments 3-5 were.



Scheme 1. Experiment #1 (Table 1) ARSST: TNM in the Presence of Organic Material. (see color insert)

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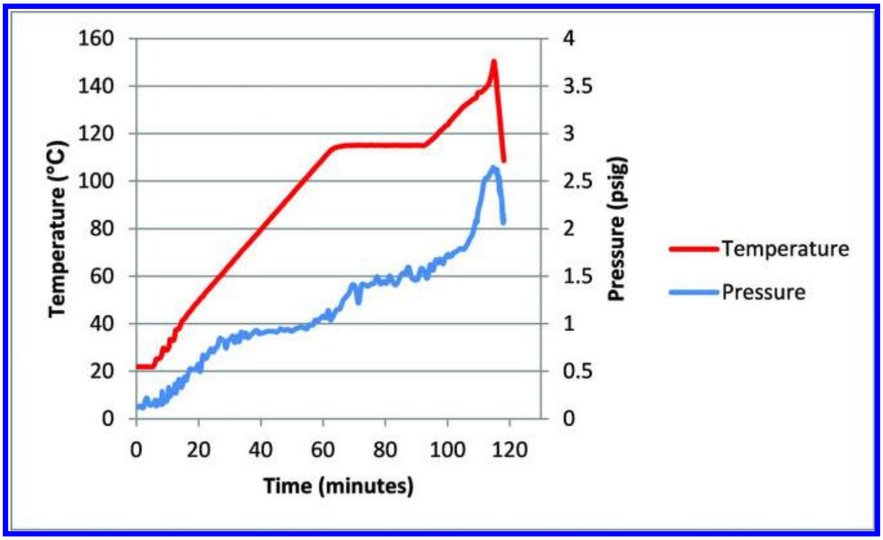
Thermal testing of a mixture of 79.2 wt% TNM (bp 126 °C) and 20.8 wt% of nitro-N-alkylphthalimide (**2**) commenced at ~20 °C, experiment 3 of Table 1. The material was heated to 115 °C and held at that temperature for 30 minutes. No exotherm was observed during that time (Graph 2). The material was then heated to 150 °C, where upon a mild exotherm at ~140 °C was observed, although no rapid reaction occurred below 150 °C. It was observed that little pressure built during the study.

The ARSST results for the thermal stability testing of pure nitroform (**5**) are shown in Graph 3 (experiment 4 of Table 1). The onset of self-heating occurred at 115 °C, resulting in a rapid temperature rise to 254 °C and a pressure rise of 17 psig. Recall that the cell in the reactor was open. It was apparent that the material rapidly decomposed at 115 °C. This thermal stability data for nitroform was not available in the open literature to our knowledge, although it was known that nitroform will rapidly decompose.

Jim Dodgen provided technical information showing that nitroform is an explosive in the pure state, and that a mixture of nitroform/water (90%/10%) was detonable with a 50 gram charge of tetryl (*N*-methyl-*N*,2,4,6-tetranitroaniline) in a one-inch pipe card gap test (*14*). It has also been reported that nitroform will rapidly decompose upon distillation (*15*).

The ARSST behavior observed for a mixture of nitroform and organics (experiment 5, Table 1) was similar to that of pure nitroform, however the peak temperature (183 °C) and peak pressure (5 psig) were lower (Graph 4).



Scheme 2. Experiment #3 (Table 1) ARSST: TNM in the Presence of Compound 2. (see color insert)

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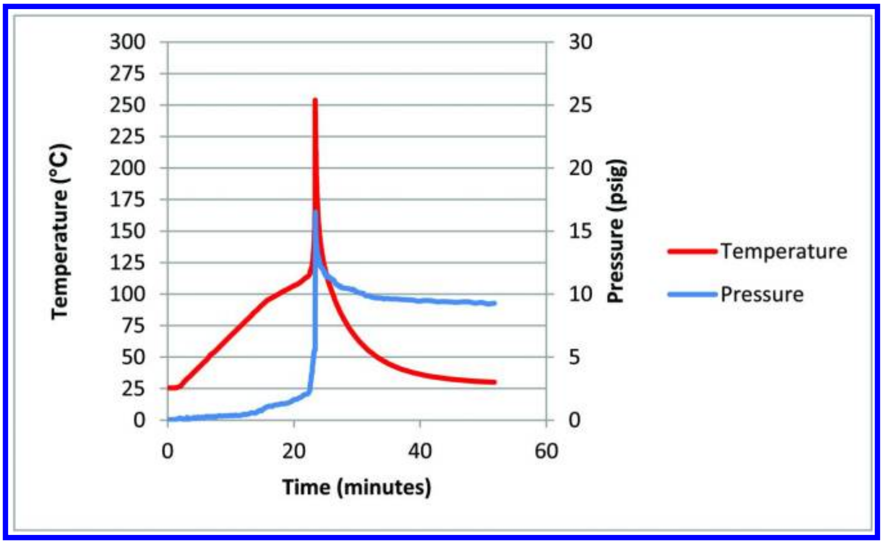
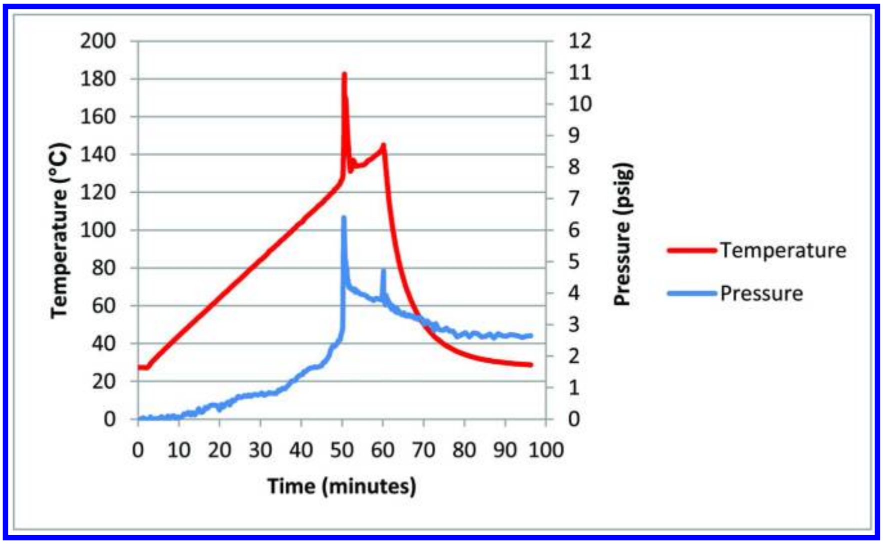


Scheme 3. Experiment #4 (Table 1) ARSST: Pure Nitroform (Compound 5). (see color insert)



Scheme 4. Experiment #3 (Table 1) ARSST: Nitrofrom (Compound 5) in the Presence of Organic. (see color insert)

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ACS Symposium Series; American Chemical Society: Washington, DC, 2013.

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Most Likely Cause of the Condenser Failure

From 11:09 am to 5:42 pm, the NAC column was fed only ~80% sulfuric acid, containing low amounts of TNM and nitroform, while the column was on total reflux. During this timeframe both the TNM (3) and nitroform (5) present in the ~80 wt% sulfuric acid feed were stripped overhead and inventoried in the condensed phase present in both the condenser and reflux return line. The TNM was hydrolyzing to nitroform during this time frame since the overhead nitric acid strength was low. The primary constituent in the overheads system was ~60 wt% nitric acid. The condenser was cooling the overheads material during this time frame.

At 5:42 pm on the day of the event, the reflux return flow stopped. As a result, the condensed material in the condenser and reflux return line was no longer being cooled by the water-cooled tubes in the condenser. The primary two organics in the condensed phase were TNM and nitroform. TNM may have phase-separated from solution. The temperature at the top of the NAC was 114 °C. The quiescent material in the overheads system self-heated through a slow exothermic degradative process reaching ~115 °C: this is the point at which the condensed phase rapidly decomposed to form a high pressure gas.

It is not clear whether the heat at the top of the NAC (the temperature indicator in the NAC overheads line showed 114 °C at the time of the event) or the rapid rise in the temperature of the reboiler at 5:42 pm (from 128 to 154 °C) contributed to the heating of the quiescent material in the overheads system. The rapid formation of the high-pressure gas caused the condenser to fail. The rapid decomposition of the condensed phase, however, was classified as a low order detonation.

The ARSST results pointed to condensed nitroform as the primary material being responsible for the condenser and reflux return line failure. Lab studies, plant analyses and Aspen modeling all suggested that other organics (compounds **1**, **2**, **4**, methylamine or an organic unknown) were not present in the overheads system in significant amounts at the time of the event. This inferred that a mixture of N_2O_4 and organics (other than TNM and nitroform) was not responsible for the event.

Redesign of the NAC Condenser System

After considering numerous potential causes of the condenser failure, an overheads system was designed that had no low spots where an unwanted condensed phase composition could collect, Figure 4. The new vertical condenser is a tube (process side) and shell (cooling side) design, equipped with a spray of 99% nitric acid to insure no material collects in the condenser.

The flow of condensate return to the top of the NAC is controlled with a flow control valve and flow indication element. Also, the return line has no low spots where material can collect should flow cease for any reason (it will self-drain to the 99% nitric acid storage tank). The valve that controls the reflux return cannot completely close by design. This design ensures that material will drain from the reflux line to a safe location in the event of a process interruption. The condensate flow from the bottom of the condenser is split between the reflux return line and the nitric acid collection tank. This configuration limits the amount of unwanted material, should it be present for any reason, that could potentially collect in both the reflux return line and the bottom of the condenser. The new process was subjected to a LOPA (Level Of Protection Analysis) and all the interlocks around the system were reviewed and documented. The documentation included a full narrative of the reasons for each interlock.

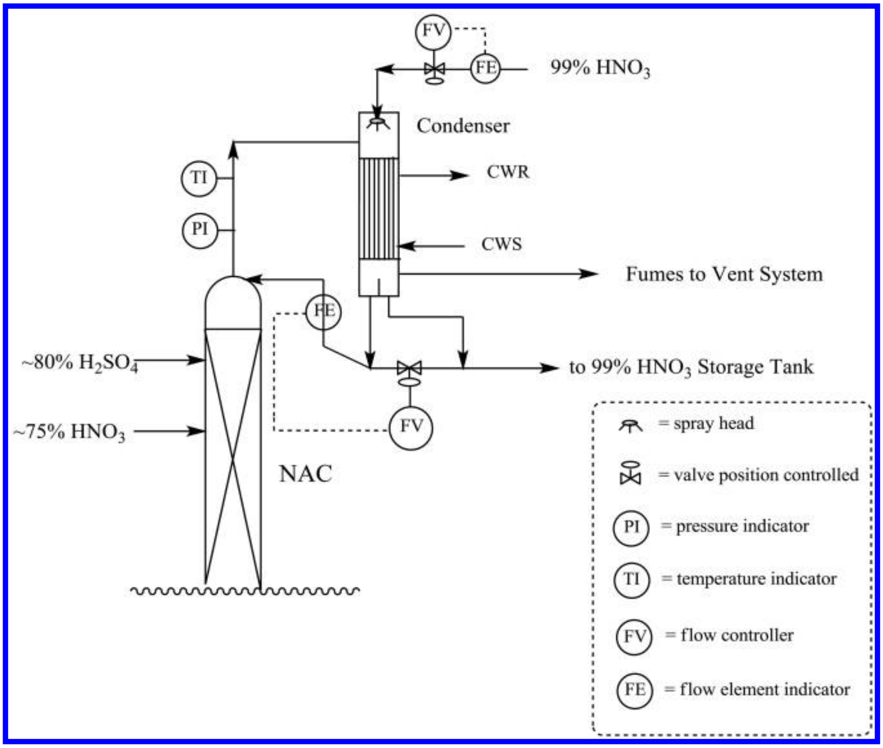

Figure 4. New Vertical Condenser.

Summary

The NAC condenser failure was most likely caused by feeding ~80% sulfuric acid to the NAC over a course of ~6 hours over which time both tetranitromethane and nitroform were efficiently stripped from the feed, thereby allowing the tetranitromethane and nitroform to collect and concentrate in the overhead condenser and reflux return line as a condensed phase, while the column was on total reflux. Some of TNM hydrolyzed to nitroform, a thermally unstable compound at 115 °C, over this time frame. The material in the overheads system lost cooling, likely self-heated, and then rapidly decomposed to form high-pressure gas that failed the condenser.

The damage pattern and metallurgical analysis was not consistent with a gas phase ignition leading to the condenser failure.

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The overheads system was redesigned with no low points where unwanted potentially hazardous material could collect and become problematic. The actual composition of the condensed phase which caused the failure will never be known. The redesign of the new system that provides an overheads configuration that prevents unsafe conditions considered the most credible causes for the explosion, as well as many other mechanisms that involve concentration of reactive species in the condenser or reflux return lines.

Experimental

Nitroform was synthesized by the method of Geckler (*16*).

TNM and 4-nitrophthalic acid were purchased from Aldrich Chemical and used as received.

The methods used to analyze the sulfuric acid and nitric acid process streams are documented in an accompanying contribution authored by R.R. Odle.

The method of using the ARSST is described in reference (*11*).

Acknowledgments

Aditya Kumar, Ganesh S, Karthik Venkataraman, and Ramesh Narayan performed the ASPEN modeling. Jim Burelbach and Hans Fauske provided guidance running the ARSST and interpreting the data. Jim Dodgen provided technical information on reactive materials. Chet Grelecki, David Ross, Robert Trebilcock, Michael Wenkoff, Colin Evans, Tracy Zhang, and Gary Davis offered insight into the cause of the event. David Mongilio and Colin Evans contributed to the redesign of the NAC condenser. Roy Odle, Mark DeLong, Karla Steele, Roger Hurst, Jessica Jarman, David Zoller, Eugene Galperin, Jim Carnahan, and Derek Lake contributed in the analysis of process samples and debris. The authors participated in the analyses of debris and process streams, mass balances of TNM and nitroform in the plant, thermal stability testing, condenser redesign, and plant data collection.

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2. Several terms are used throughout this chapter. ‘Weak nitric acid’ means nitric acid that is 30 to 75 wt% nitric acid where the balance of material is water. ‘Strong nitric acid’ means >97 wt% nitric acid (containing 3 wt% water). A process stream that is said to be 99% nitric acid is taken to mean that the nitric acid present contains 1% water and ignores other substituents

in the 99% nitric acid, such as dissolved oxides of nitrogen (NO, NO_2, and higher oxides of nitrogen), TNM, and trace organic material.

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Chapter 14

Solubility, Equilibrium, Behavior, and Analytical Characterization of Tetranitromethane, Trinitromethane, Methyl Amine, and Ammonia in a Nitration Facility

Roy R. Odle,* Thomas L. Guggenheim, and L. Mark DeLong

SABIC Innovative Plastics, 1 Lexan Lane, Mt. Vernon, Indiana 47620
***E-mail: roy.odle@Sabic-ip.com**

The safe operation of a nitration facility is very important. This chapter focuses on a framework for operating a nitration facility to inform the reader of some important safety considerations. Some detailed chemistry relating to tetranitromethane (TNM) and nitroform (NF) are discussed. More particularly, TNM can be a by-product in the nitration of aromatics. TNM and nitroform, which can be formed upon hydrolysis of TNM, can form potentially explosive mixtures with organic compounds. Furthermore, isolation of TNM and NF as separate phases is to be avoided because they are thermally unstable. The solubility of NF and TNM in nitric acid and the equilibrium between TNM and NF are dependent on nitric acid strength. In the nitration process described, methylamine and ammonia are produced as by-products. The amine impurities, present as ammonium nitrate and ammonium sulfate salts, are extremely difficult to scrub and sequester. Of particular interest is the propensity of methylammonium nitrate to form a solid in one section of the vent system. The behavior of these various by-products, both how they are formed and how they are eliminated, and an overall mass balance are discussed. Additionally, the analytical methodologies used to determine the mass balances of by-products are described.

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Introduction

The authors assume that the reader is very aware that process, product, and chemistry considerations in a nitration facility are of the utmost importance. If the reader does not know this, hopefully, this chapter will help the reader understand the importance of these considerations. However, a chapter in a book is no substitute for many years of experience, seasoned professionals, proper evaluation of hazards, knowledge of nitration chemistry, testing of hazards, and many other aspects and capabilities necessary to reduce the risk of running a nitration facility. The reader is encouraged to seek expert resources if they have questions. This is not a task for the ill-informed!

SABIC's Innovative Plastics division currently runs a nitration plant that uses an "all-nitric" process. This means that the nitration of the substrate is run in only nitric acid (+99%) with no other acids, solvents or reagents present. The all-nitric process has been used in the past in laboratories and in manufacturing facilities. However, there are reports that this type of nitration is unstable. This instability has to do with the oxidative stability of certain species in the reaction. The oxidative stability of the products and starting materials (used in the SABIC plant) makes the all nitric process feasible for commercial production. This all-nitric process has been practiced safely for well over 20 years. During this time, only one major incident occurred where plant production was disrupted by operational anomalies. The event prompted the identification of better design features of equipment to avoid such disruptions (*1*). As with all nitration reactions, the yield of the desired products of reaction is not perfect. There are some by-products that need to be managed in the plant streams.

This chapter provides some insight into how the authors used mass balance techniques to develop their understanding of the distribution of unwanted by-products in the process. The chapter also discusses how the critical analyses that were implemented are used and maintained.

The thermal stability of the desired nitrated product must also be well understood. Nitration by-products, NOx, nitric acid and other species are known to lower the on-set temperature of decomposition of nitrated products, and can lead to a runaway reaction (*2*). Runaways are not the main subject of this chapter, but one must recognize the common signs of a runaway. Those signs are an unexplained temperature rise in the reaction mass, formation of bubbles and gas, generation of NOx, mixed acid nitration reactions wherein excess nitric acid was inadvertently added to the nitration reactor, a reaction mass color change, or failure to observe the expected temperature rise that should accompany the nitration of the substrate. This list is not comprehensive so the reader is encouraged to study other causes on runaway reactions.

A runaway event can be rapid and have catastrophic consequences. The thermal stability of potential mixtures present in a nitration process must be evaluated to properly design and operate the facility.

The organization responsible for the operation of the plant applies a regular review process to prompt self-assessment of all of the chemical analysis methods, frequencies of those analysis, critical sample points, operating conditions, and process procedures.

Simple Goals for Understanding Plant Chemistry

The operation of a nitration plant is intended to produce a nitrated product. However, it is well known that no chemical reaction is perfect and no reaction yield is 100%. This is especially so in a nitration plant. Positional isomers can be formed during the nitration step. Other impurities are formed from oxygen versus nitrogen attack of the nitronium ion, or from oxidation reactions or other types of side chemistry (*3*). There are three simple rules for assessing how certain by-products (for this discussion, molecules containing C, H, N, O, and potentially X, where X is halogen) in a plant could affect the safety of that plant: (i) location, (ii) distribution, and (iii) exit.

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I. Location: Where Is the By-Product of Interest Formed?

This question raised by the "location" consideration takes one directly to the heart of the plant. The reactor is usually the place where starting material contacts the nitrating species. In most plants this place would be called the reactor. It may be in the form of a tank, stirred tank reactor, tubular reactor or many variations. This is the area of the plant where runaway reactions are probably the biggest concern. This risk has probably been assessed and provided with some means to prevent or abate such a runaway. Some of these techniques include strict control of feed rates, strict control of mixing, elimination of hot spots in the process, quickly draining the reactor into a quench basin, and means for aggressive temperature control. It is not the intent of this chapter to direct the reader to favor any one of these methods, just know that such means of control and risk abatement are considered, designed and exist in many nitration facilities.

The desired product of the nitration is usually tracked quite well in the plant as it has a direct effect on the efficiency of production. However, the isomers and side products that may also be formed during the nitration are usually separated from the main product. This separation as well as the configuration of any particular nitration train can lead to distribution of small concentrations of different types of by-products throughout the plant. These impurities may undergo reactions in areas of the plant not designed for reaction.

II. Distribution

The second question raised by the "distribution" consideration is how do the by-product compounds distribute in the plant? Other logical questions might be: Where is the compound most concentrated? Or where is the greatest risk for the compound to concentrate? The answers to these questions vary depending on the nature of the compound. The physical properties of the compound must be understood. What is its boiling point? What is its melting point? What is its vapor pressure? What is the solubility in each of the streams in the plant?

Knowledge about the risk associated with each particular by-product must be known. This is not always easy to determine. Some compounds may not be reactive and are really of no concern as long as they do not contribute to an oxygen balanced mixture somewhere in the plant. As earlier stated, some by-product compounds will lower the onset temperature of product decomposition, which can be rapid and catastrophic. Other compounds can be primary explosives! Obviously one would want to know the concentration and distribution of those kinds of risky compounds. Some compounds are not very soluble. Other compounds are highly oxidative and therefore are dangerous if mixed with other organic materials. And of course, in the real world, compounds can have varying amounts of each of these attributes. The greatest risk is usually in the place where the greatest concentrations of high risk compounds are found.

III. Exit

The third important question raised by the "exit" consideration is: How does the by-product compound leave the plant?

This can happen in a couple of ways. The preferred option is for impurities to be separated from the product and exit the plant in some sort of waste treatment stream that is designed to capture and/or destroy those compounds. Sometimes the molecule is transformed in the plant into a different form or species such that its distribution must be controlled in order to remove it. There is also the possibility that a compound can be oxidized to such an extent that it appears to be consumed in the nitration facility. Usually this means that the organic compound is nearly completely oxidized in the nitrating medium. An example of this would be an aromatic ring that has reacted in an oxonium ion fashion to produce a phenolic species. The phenolic species is quickly nitrated to form a picric acid type of impurity. This type of molecule can be further oxidized, by oxides of nitrogen or nitric acid, to finally give TNM, CO, CO_2, and oxalic acid. There is a multitude of intermediate products in this type of oxidation reaction. A molecule that is "consumed" or oxidized in the nitration plant probably generates the most difficult species on which to do a material balance.

As one can see, the goal for understanding plant chemistry becomes very complicated as one has to understand both the chemistry and the physical nature of the primary compounds as well as the isomers and the impurities. Even compounds that are produced in the parts per million ranges can build up over time if there is no way for that molecule to exit the plant. This can present a process risk if the compound is a strong oxidizer or a primary explosive, and it concentrates in one small area of the plant. Beware; this mechanism of concentration into a small area has led to disastrous results through the history of nitration. Another mechanism that increases risk is if impurities that stay with the primary product act as sensitizers for thermal degradation.

A plant mass balance of products and by-products, with understanding of reactions and physical properties, is required knowledge to aid in risk assessment.

Chemistry Considerations of Nitration: Where Are the By-Products of Interest Formed?

The principles discussed in the above section will be illustrated with examples and more discussion in this section of the chapter.

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In Figure 1, the formation of the active nitrating species is shown, the nitronium ion (*4–7*) .

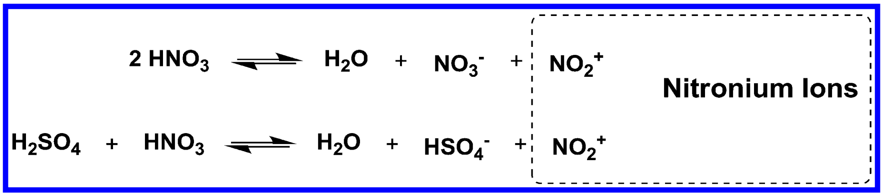

Figure 1. Formation of Nitronium Ion.

In Figure 2, note a generic chemical equation for the nitration of an aromatic species that is called the starting material (SM). Functional groups on this starting material are designated by R groups. The method of nitration is not specified except that nitric acid is being used as the nitrating agent. And of course water from nitration is formed. The equation shows three different types of product species. Two isomers are shown as a 4 isomer and a 3 isomer the yield is 91% and 5% respectively (4-P-A, and 3-P-B). The OH-C compound represents the case where the nitronium ion and has attacked from the oxo position to give a phenolic compound. Once formed, it quickly nitrates two more times to give a species that is beginning to look like picric acid. This type of reaction happens to some extent in nearly all nitration reactions of aromatic compounds (*8*). In this example, it is made at 4%.

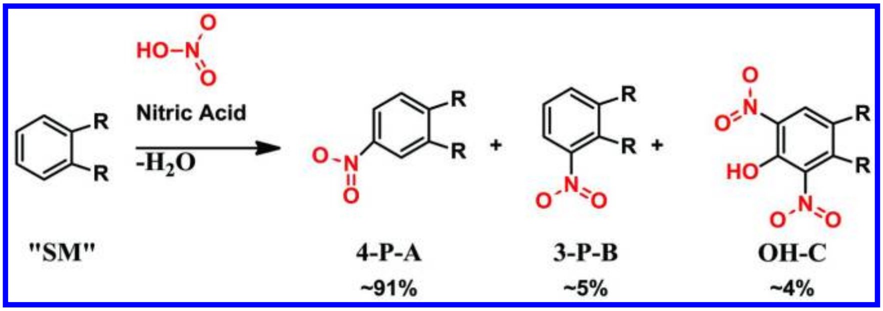

Figure 2. Desired Product/Isomers and Typical Phenolic Formation. (see color insert)

In other commercial nitration processes, this oxo-nitration species is usually washed away in some basic aqueous stream or dilute acid stream and taken to some sort of waste treatment. A lot of expense is often spent to treat and dispose of streams containing these nitro phenolic compounds. Many times, if sulfuric acid is used in conjunction with nitric acid is used (mixed acid nitration), these streams also contain sulfonated impurities and are called either red water (*9*) or black water.

It so happens that in the "all nitric" process example (Figure 3), heating the phenolic impurity to 50°C in nitric acid gives nearly complete oxidation of the compound. Nitric acid is an unusual reagent in that it can be a nitration medium as well as an oxidative medium (*10*). This reaction is very useful because most of

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the compounds formed from the oxidation, for example, carbon dioxide, carbon monoxide, and oxalic acid are removed from the plant either as a gas or with wastewater. However, one of the compounds formed by oxidation ends up being per-nitrated to give tetranitromethane. Tetranitromethane in the presence of water and nitric acid readily establishes equilibrium between itself and nitroform. Nitroform can also continue to hydrolyze, or can decompose to eventually give CO_2 and NOx.

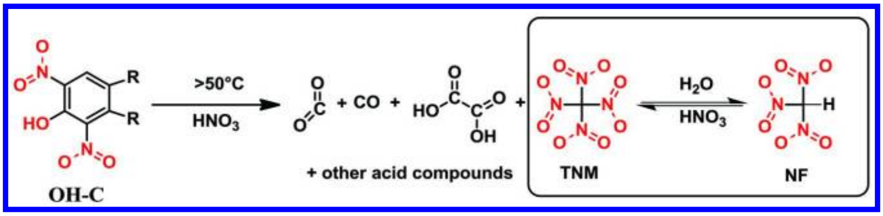

Figure 3. Nitric Acid Oxidation and Formation of TNM. (see color insert)

The equilibrium between tetranitromethane and nitroform depends on the strength of the nitric acid or one might think of it as the concentration of water (*11*).

In this particular nitration example one of the side groups or R groups can generate two different types of nitrogen compounds. In Figure 4, the top equation, an oxidation reaction gives intermediate 4-P-D with pendant R′. This is followed by hydrolysis to give a modified R″ group (4-P-E) and ammonia (AM). In the lower equation of Figure 4 simple hydrolysis of the R group gives methylamine (mono-methyl-amine; MMA) and a different pendant group R‴ (4-P-F).

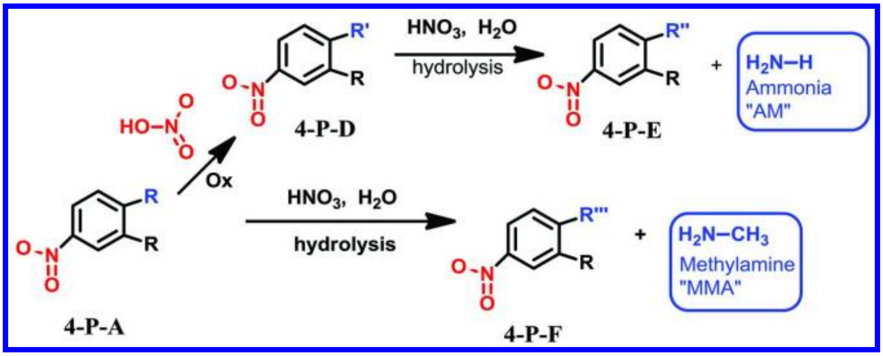

Figure 4. Formation of AM and MMA from R Group Hydrolysis. (see color insert)

The formation of these two nitrogen species was not well appreciated. Both ammonia and MMA readily form salts with nitric acid. These salts can be unstable or explosive when concentrated and subjected to certain conditions.

The equation in Figure 5 shows a mechanism where an aromatic compound in a nitration reaction readily gives a certain amount of ammonia. Without belaboring the mechanism, one observes that oxo-attack by the nitronium ion is followed by nitrosation and oxidation to give a hydroxyl imine which decomposes in nitric acid to eventually give ammonia (*12*). This reaction shows that ammonia can be generated in a nitration facility without having any side groups or nitrogen bearing moieties on the target starting material. Beware of ammonium nitrate salts, or nitrite salts for that matter, building in the overhead vents of a nitration facility. Consider the places where these salts might accumulate. This discussion in no way can cover the myriad of possible routes that high risk compounds can be formed and concentrated to give high risk situations.

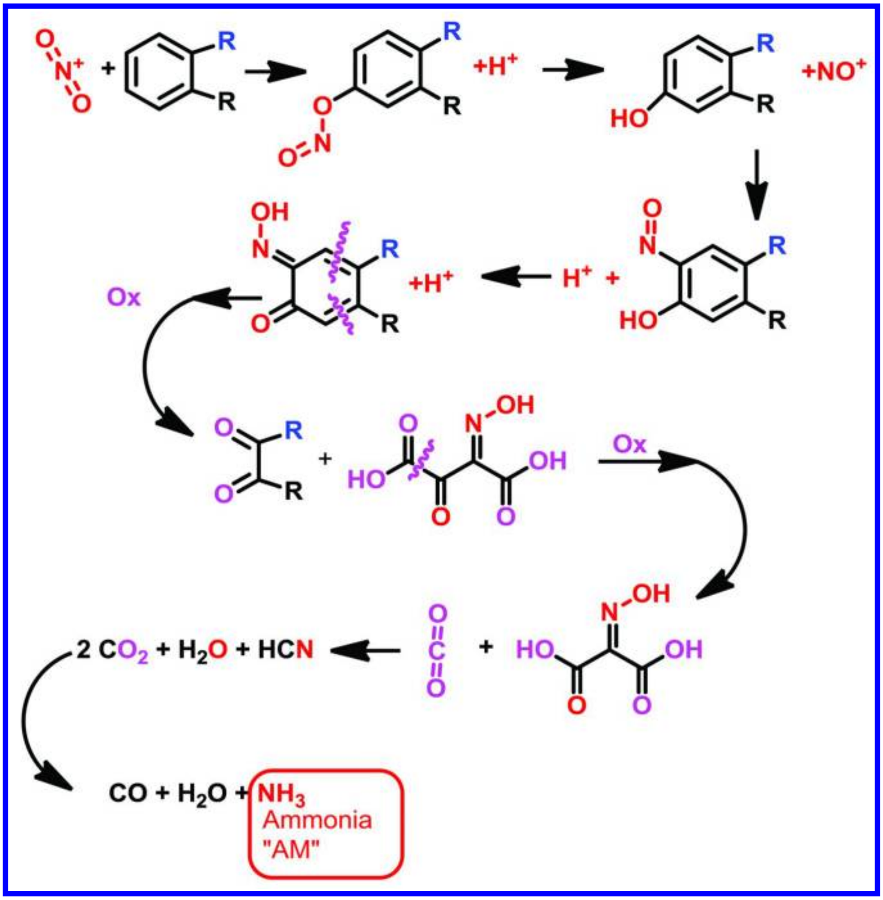

Figure 5. Side Reaction to Ammonia. (see color insert)

In the example shown in Figure 4 the primary source of methylamine is from simple hydrolysis of the SM or products, and the source of ammonia is a combination of oxidation and hydrolysis of the SM or products, as well as an impurity in the methylamine. Considerable study has been carried out in order to confirm those conclusions. Such answers do not come easy.

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By-Products of Concern in Nitration Facilities

Every nitration reaction has its own unique chemistry as far as impurities or side products that can be produced. The reader needs to be aware that the chemists and engineers running a facility or piloting a new nitration must diligently sample and analyze all process streams to understand these reactions. Again, the impact of by-products on the thermal stability of the product must be evaluated.

There are some by-products that seem to be pervasive in the nitration industry. The following is a partial list of those compounds; however, this is not an exhaustive list! Variants of these compounds are likely in different process situations. Those operating a nitration facility must be aware of these types of compounds, Table 1.

Table 1. High Risk Compounds, By-Products, and Mixtures Formed in Nitration Plants

Compound or Mixtures	***Hazard***	***Reference Number***
tetranitromethane	strong oxidant	(*13*)
nitroform	oxidant, rapidly decomposes	(*14*)
methylammonium nitrate (nitrite)	detonable in dry state	(*15*)
ammonium nitrate (nitrite)	detonable in presence of organics	(*16*)
nitric esters of organic acids	potentially detonable	(*17*)
nitro-alkanes	reactivity depends on oxygen balance	(*18*, *19*)
nitrated polyols	high energy and sensitive	(*20*)
mixtures of nitric acid and organics with little water present	oxygen balance determines energy density	(*21*)
NOx and Organics	oxygen balance determines energy density	
NOx reacting with polymeric materials in process	sensitive polynitrated polymers form	(*22*)
polynitrated aromatics	sensitive high energy density compounds present in process	
excess nitric acid with organics in mixed acid media	increased risk of runaway reactions	

Oxygen balance has been mentioned a few times in this chapter (*21*, *23*). It is simply the balance of oxidant and fuel. The more perfect the balance of oxidant and fuel, the higher the energy that can result.

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These are only a few examples of potential risk compounds and situations in the nitration plant. There are many more that could be considered. Please, know what you are doing and consult experts who can help you if you are new to the nitration world. Being proactive and taking precautions is prudent and highly advisable.

Analytical Challenges

The analytical challenges to complete a good mass balance in a nitration plant are enormous! The matrices in which the compounds exist are corrosive, reactive, and fuming. These present many challenges in sample preparation and analytical method development. However, some very straightforward methods to measure the compounds of interest have been developed. While these methods may not directly transfer to all situations, they may give some direction as to techniques that might be used to measure the by-products and compounds of interest in a nitration plant or process.

Analyzing Tetranitromethane and Nitroform

The presence and concentrations of both tetranitromethane and nitroform are very important so analyses of samples from the plant are needed. Tetranitromethane is a strong oxidant as mentioned earlier and nitroform can be a sensitizer or a detonable compound when concentrated. In one particular situation the matrix is 40 wt% to 99 wt% nitric acid. The analytical procedure involved the direct dilution of the sample with acetonitrile and water followed by analysis via HPLC-PIC using a UV-Visible detector. The details will be given later in the Experimental section. The same method can be used with either a weak or strong sulfuric acid matrix. Note that the choice of the diluent is very important so as to avoid highly reactive situations.

Analyzing MMA and Ammonia

MMA and ammonia are found in many streams in the example shown in Figure 4. These species, which distribute between several process streams, can be present in very low concentrations. The method to analyze for ammonia and MMA is performed using ion chromatography. The initial sample matrix can be sulfuric acid (30 wt% to 82 wt%) or nitric acid (20 wt% to 99 wt%). The presence of the acid complicates the analysis. Figure 6 illustrates the sample prep method. It was discovered that a sample can be diluted with water then passed through an IC-OH sample prep cartridge column (center rectangle in Figure 6), to reduce the amount or remove the acid anion. This is a way to remove or neutralize acid without the introduction of a cation (like NaOH) that may cause interference in the subsequent cation analysis. Passage of the diluted sample through the column replaces the sulfate or nitrate with hydroxide. The sample prep column is essentially an anion exchange resin in the hydroxide form. The column is first filled with water, and then the diluted sample is passed through the cartridge. The

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first material through the cartridge is discarded and additional sample is filtered through the same cartridge and the filtrate collected. This filtrate is then analyzed by Ion Chromatography.

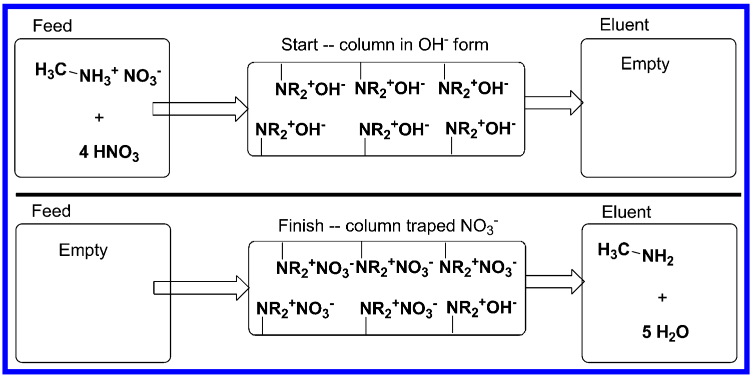

Figure 6. Ion Exchange Treatment in Nitric Acid Matrix.

Other Methods To Analyze Process Streams

Chromatography methods (like HPLC) are sufficient to quantify compounds of interest. However, what if there are unknown organics in the stream? This is a question that must be addressed while running a nitration facility. Total organic carbon (TOC) has been successfully employed to augment and verify chromatography (HPLC) methods. TOC works well in both nitric and sulfuric acid streams as well as dilute water streams. The method is sensitive as long as measures are taken to not overload the detector. This is easy to avoid by diluting the sample with distilled water. This instrument is considered essential to keeping a nitration plant safe.

The trustworthy methods are used daily to analyze plant streams and confirm that nothing has changed and concentrations are of no concern. This is especially true if something in the plant has changed. This change might have been a new piece of equipment, use of a new lubricant or seal fluid in the system, a new gasket in the system, or a new source of reactants or reagents. In many cases, an extraction of plant samples is used to concentrate species for analysis by one of the methods mentioned above. Occasionally, those same techniques of sample preparation are used with one of the following analytical methods: GC-MS (Gas Chromatography-Mass Spectroscopy), LC-MS (Liquid Chromatography-Mass Spectroscopy), NMR (Nuclear Magnetic Resonance), FTIR (Fourier Transform Infrared Spectroscopy), or ICP (Inductively Coupled Plasma). Note that ICP is used to track metal concentrations in the plant streams. This can be an early indication that corrosion is a problem in a certain area of the plant. A plant mass balance of metals was not discussed but this type of mass balance is useful for determining the aging and integrity of the plant.

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To determine the behavior of compounds and by-products in the plant, all streams need to have a method of analysis. The tough matrix is a challenge for quick and easy analysis. However, with some thought and creativity the challenge can be made manageable.

Mass Balance: Origin, Distribution, Level, and Exit of Compounds of Concern

In this section a simple box diagram of a nitration plant, encompassing the chemistry shown in Figures 2, 3, and 4, is depicted. It will be used to demonstrate how a mass balance can show the point of origin of certain impurities, how compounds distribute in the plant streams, and what the concentration levels are in each area of the plant. In order to simplify the analysis and math, whole sections of plant equipment have been included in a geometric shape to show the principle of the mass balance analysis (Figures 7, 9, and 10 below).

Mass Balance of TNM and NF Around the Reaction Area

Figure 7 depicts the reaction area of the example process encompassed by the chemistries shown in Figures 2, 3, 4, and 5. The mass balance of interest is for TNM and NF. The concentration of TNM is shown in red letters, and the concentration of trinitromethane (NF) is the second number in blue. The numbers have been normalized for flow and are expressed in relative weight/time. There is no need to do any extra math in order to understand the mass flow.

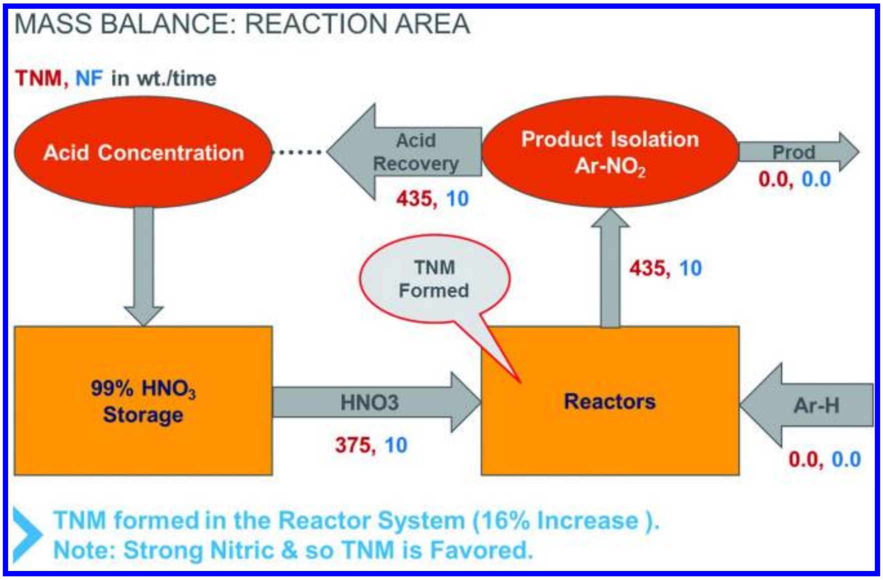

Figure 7. Mass Balance of the Reactor Area. (see color insert)

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Begin in the upper left-hand corner of Figure 7 with the oval labeled “Acid Concentration”. This is the part of the plant where the nitric acid is contacted with sulfuric acid in order to make strong nitric acid. For this discussion, strong nitric acid has a concentration of greater than 99% nitric acid, HNO_3, by weight. The strong nitric acid is collected in a storage tank. Note the wt/time of 375, 10: TNM, NF in the strong tank. Recall that the equilibrium of TNM and nitroform in nitric acid is dependent on the nitric acid strength (*11*, *24*). TNM is favored in strong nitric acid where very little nitroform exists. This will be discussed further below (Figure 8).

The strong nitric acid feeds the “Reactors” (Figure 7) where it contacts the aromatic starting material (Ar-H). There is no TNM or NF in the pure starting material. Flowing out of the reactor it the wt/time of 435, 10: TNM, NF, showing an increase in the concentration of TNM. Indeed, TNM is formed in the reactor system, as shown in Figure 3. Now this may not seem surprising to the reader, however, it is very important in the grand scheme of things to know where the TNM is being formed. There is no doubt that one point of origin for TNM is the reactor system.

Now move to the upper right-hand oval of Figure 7. This represents the “Product Isolation Area” of the plant. This area involves many different streams and process steps to wash, purify and isolate the nitration product. The product is essentially void of TNM or NF. Now to a chemist, there is never such a thing as zero, but the levels are negligible and present no safety risk downstream. The interesting observation is that the total mass flows in the acid recovery streams account for the TNM and NF from the reactors.

Thus a point of origin for TNM is in the reactor system with a 16% increase from the incoming mass flow. Analysis showed that in this strong nitric area TNM is favored over NF. The product stream is an insignificant exit point for either tetranitromethane or nitroform. Also of note is that even though the TNM and NF were distributed in the complex product isolation area, the final feed stream to the acid concentration system accounted well for both impurities of interest.

Equilibrium of TNM and NF and Solvolysis Behavior

As the concentration of nitric acid increases the ratio of TNM to NF also increases, Figure 8. One may be tempted to calculate and equilibrium constant from this data but that is not possible, as the nitroform decomposes via hydrolysis to NOx, HNO_3, nitrous acid, and presumably carbon dioxide (See Table 2). The simple take away from Figure 8 is that nitroform is favored in weak acid and tetranitromethane is favored in strong nitric acid.

Table 2 shows the solvolysis of tetranitromethane to nitroform in 40% nitric acid at 90°C, and also shows the rate to equilibrium as well as the reality of the hydrolysis in the TNM-NF system. Note that the mass balance does not close. This is because nitroform further reacts in the system to give other hydrolysis products. This experiment was performed at the solubility limit of TNM in 40 wt% nitric acid.

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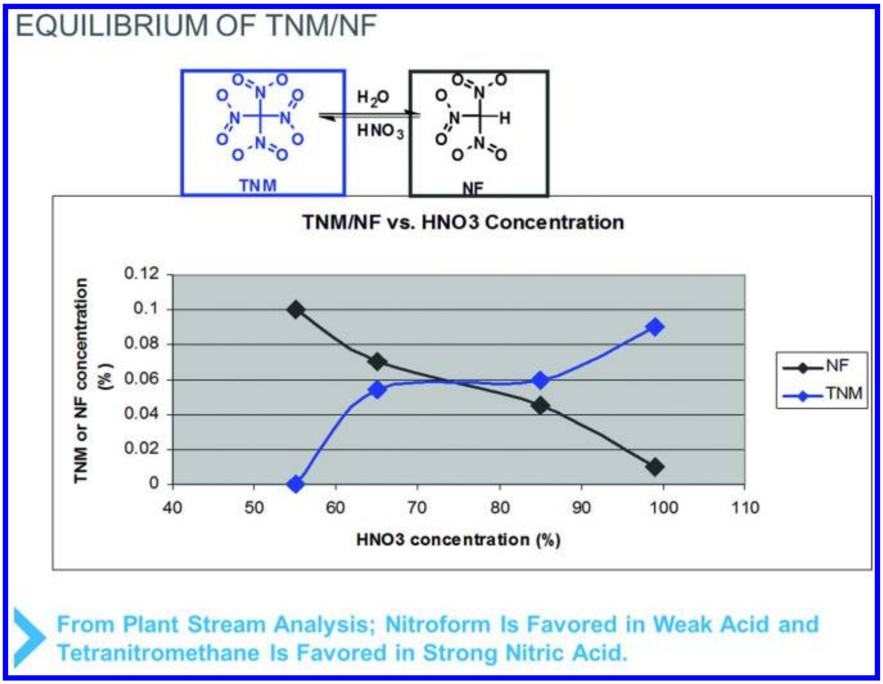

EQUILIBRIUM OF TNM/NF

From Plant Stream Analysis; Nitroform Is Favored in Weak Acid and Tetranitromethane Is Favored in Strong Nitric Acid.

Figure 8. Equilibrium of Tetranitromethane and Nitroform. (see color insert)

Table 2. Solvolysis of TNM in 40% Nitric Acid at 90°C (*24*)

Time(h)	*TNM (ppm by wt.)*	*Nitroform (ppm by wt.)*
0	4600	0
2,5	2600	270
21.5	700	800
43.5	275	1050

Mass Balance of TNM, NF, and MMA Around the Weak Nitric Acid Recovery System

Figure 9 represents the weak nitric acid recovery section of the plant encompassing the chemistry shown in Figures 2, 3, and 4. The mass balance of interest now includes TNM, NF, and MMA. Again, the units are in relative weight per time so that no complicated math needs to be done to interpret the mass balance.

Start in the upper left-hand corner of Figure 9 with the oval which represents a waste stream with organics and the wt/time of 0, 12, 0.15: TNM, NF, MMA which

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is feeding into a weak nitric acid evaporator. Going overhead of the evaporator is weak nitric acid containing: 0, 10.8, 0: TNM, NF, MMA. The evaporator overheads eventually are fed to the nitric acid recovery unit.

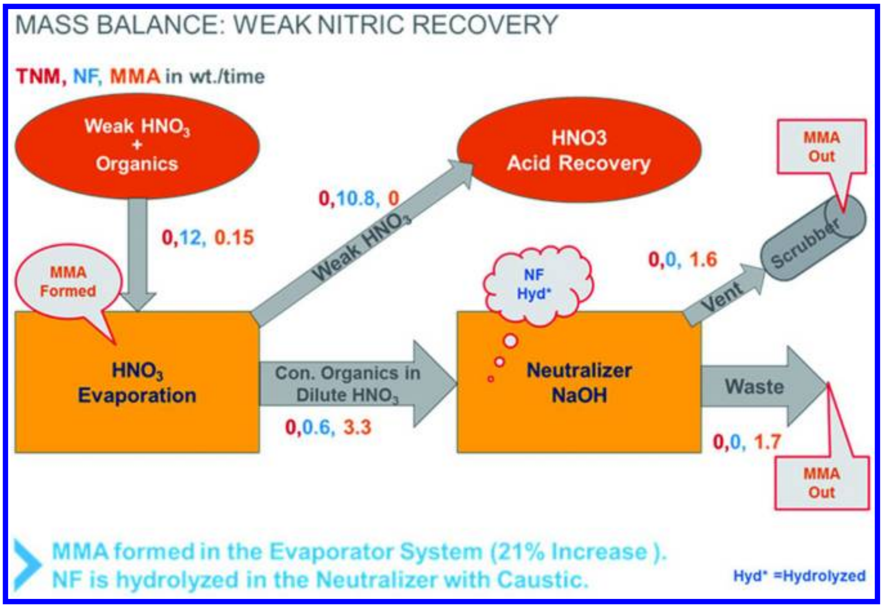

Figure 9. Mass Balance of Weak Nitric Acid Recovery. (see color insert)

Exiting the bottom of the evaporator (Figure 9) is weak nitric acid that contains concentrated organics and 0, 0.6, 3.3: TNM, NF, MMA, which is feeding the neutralizer on the bottom right-hand corner. If one does a little simple math, you will deduce that MMA was formed in the nitric acid evaporator (a 21% increase). Therefore, a point of origin for MMA is the weak nitric evaporator. This would be an area to look for methylammonium nitrate in vent systems or other stagnant places where it might form and collect. Methylammonium nitrate can collect as crystalline material that is sensitive to impact.

The bottoms of the evaporator are neutralized with sodium hydroxide in the neutralizer (Figure 9). Two process streams exit the neutralizer. The first is the vent stream where the wt/time are 0, 0, 1.6: TNM, NF, MMA and the wt/time going out the waste stream, which is an aqueous stream, containing 0, 0, 1.7: TNM, NF, MMA. The conclusion around this unit operation is that nitroform is hydrolyzed in the presence of sodium hydroxide. MMA is leaving the plant via the vent as well as the aqueous stream. Once again, this would be a good place to make sure that methylammonium nitrate is not being collected in the vent system.

Out of these very complex sample matrices the analytical results have proven useful to show that MMA is formed in the evaporator system (a 21% increase), and that nitroform is hydrolyzed and destroyed in the neutralizer, which is a sodium hydroxide rich aqueous stream. MMA is leaving the plant in both a vent system and a wastewater system.

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Mass Balance TNM, NF, and MMA Around Strong Acid Concentration

Figure 10 depicts a very complex system wherein weak nitric acid is mixed with sulfuric acid and strong nitric acid is produced. In the upper left-hand corner note the oval that represents a scrubbing system wherein sulfuric acid is used to absorb nitrogen oxides or NOx. The sulfuric acid makes for very efficient scrubbing of the NOx. First examine and consider the streams that leave the NOx scrubbing system.

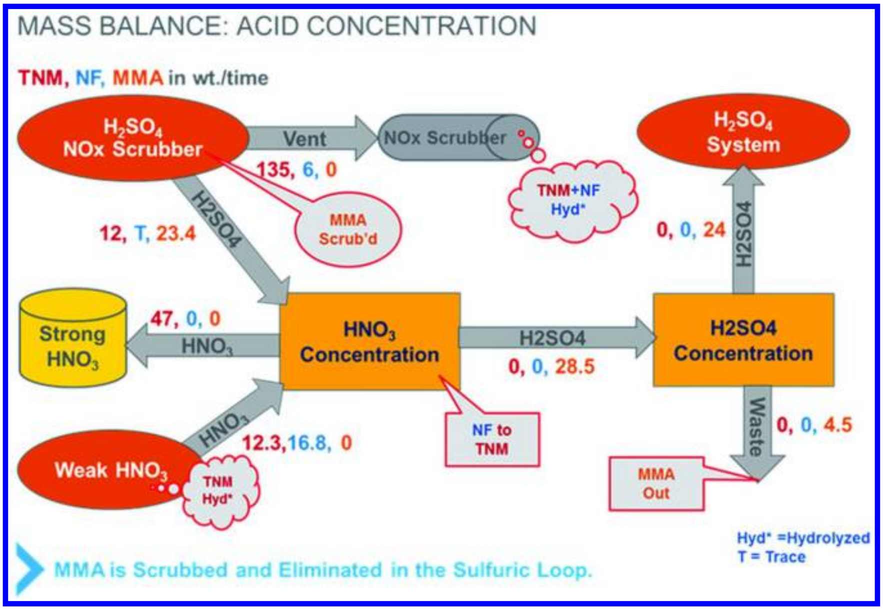

Figure 10. Mass Balance of Acid Concentration. (see color insert)

Leaving the vent system of the scrubbers is a gas stream with the wt/time of 135, 6, 0: TNM, NF, MMA. The sulfuric acid feeds the nitric acid concentrator (the center rectangle). The entering sulfuric acid stream has a wt/time of 12, T(trace), 23.4: TNM, NF, MMA. The complicated flows into the NOx scrubbing system are not explained but the mass balance showed clearly that MMA was efficiently absorbed into the sulfuric acid scrubbing system.

The bottom left-hand corner of Figure 10 has the oval labeled "Weak HNO_3". Note that TNM is hydrolyzed to nitroform, CO_2, and NOx to some extent in this area of the plant. The complete mass balance that would let the reader draw this conclusion is not shown, as the amount of equipment and streams is beyond the scope of this chapter. However, take note that the wt/time weak nitric feed to the nitric acid concentrator is 12.3, 16.8, 0: TNM, NF, MMA.

The nitric acid concentration step takes place in the orange rectangle in the middle of the page. Here two streams leave this operation. The first stream is strong nitric acid that moves to the left into the yellow strong nitric tank. Here the wt/time composition is 47, 0, 0: TNM, NF, MMA. In the concentrated nitric acid,

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99+ wt%, the equilibrium greatly favors TNM and NF is not detected. Also note that MMA is absent in this stream.

The sulfuric acid stream (Figure 10) leaves the nitric acid concentrator to the sulfuric acid concentrator process area, and contains a wt/time of 0, 0, 28.5 of TNM, NF, MMA. It is surprising that essentially neither TNM nor NF is in the sulfuric acid stream. The equilibrium favors TNM, which is volatile and so goes overhead with the strong nitric acid. The conclusion is that nitroform is transformed to TNM in this concentrator. Note that all of the MMA leaves the nitric acid concentrator with the sulfuric acid. The mass flow of MMA leaving the nitric acid concentrator is a little more than expected. There is either an error in the mass flow measurements or some mechanism of MMA formation is present in the nitric acid concentrator. Indeed, there is a small concentration of organic in this area that could give MMA upon hydrolysis, but this does not present a safety risk.

Note the sulfuric acid concentrator which is the orange rectangle in the center right of Figure 10. The concentrated sulfuric acid leaving the concentrator contains wt/time of 0, 0, 24: TNM, NF, MMA. The concentrated sulfuric acid harbors the MMA generated in the process. If the stream is monitored from the time of a clean plant startup to equilibrium, it is observed that the concentration of MMA goes from zero to a constant steady state level (~3000 ppm). Note that the MMA present in the sulfuric acid is in the form of the methylammonium sulfate form, not the nitrate form. The safety risks of MMA in sulfuric acid are much lower than when MMA is present in a nitric acid stream.

The waste water stream leaving the sulfuric acid concentrator contains a wt/time profile of 0, 0, 4.5 of TNM, NF, MMA. This stream provides an exit of MMA from the process.

The mass balance calculations from this area of the plant (Figure 10) show that MMA is scrubbed in the sulfuric acid scrubbers and eventually eliminated in a sulfuric acid loop. Nitroform is effectively transformed to tetranitromethane which stays with the strong nitric acid. The vent off the sulfuric acid NOx scrubbing unit is sent to another NOx scrubbing unit, and this provides an exit point for TNM and NF from the process. The technology of this final NOx scrubber is not discussed here. However, it is the case that the TNM and NF that exit the sulfuric acid NOx scrubbers are hydrolyzed in the final NOx scrubber. Thus Figure 10 shows the distribution and reactions of the compounds of concern which are monitored in this example.

Solubility of TNM and NF in Nitric Acid

Over the years the authors have gathered much information about the solubility of tetranitromethane in various concentrations of nitric acid. They have also observed the solubility as a function of temperature. The results are summarized in the Table 3 (*24*). One should note that the solubility changes dramatically with percent nitric acid, especially at the 60 wt% nitric acid level. It should also be observed that temperatures between zero and 80 °C have little effect on the solubility, Figure 11. The solubility of NF in water is quite high,

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16.7 gr per 100 mL of water at 0 °C. The solubility of NF in different strengths of nitric acid was not determined. This would be difficult because of the equilibrium that was discussed earlier in the chapter.

Table 3. Solubility of TNM in Acid Media

Acid Composition	*25 °C (wt%)*	*60 °C (wt%)*
water	0.1	0.08
20% nitric acid	0.25	0.23
40% nitric acid	0.54	0.53
60% nitric acid	0.72	0.7
70% nitric acid	1.0 - 1.5	1.0 - 1.5
80% nitric acid	5.4	5.4
90% nitric acid	15.3	15.3
99% nitric acid	>30	>30
98% sulfuric acid	0.8 - 1.0	2.5 - 3.1
86% sulfuric acid	0.7 - 0.8	not determined
86% sulfuric acid/90% nitric acid (2:1 by wt)	0.7 - 0.8	not determined

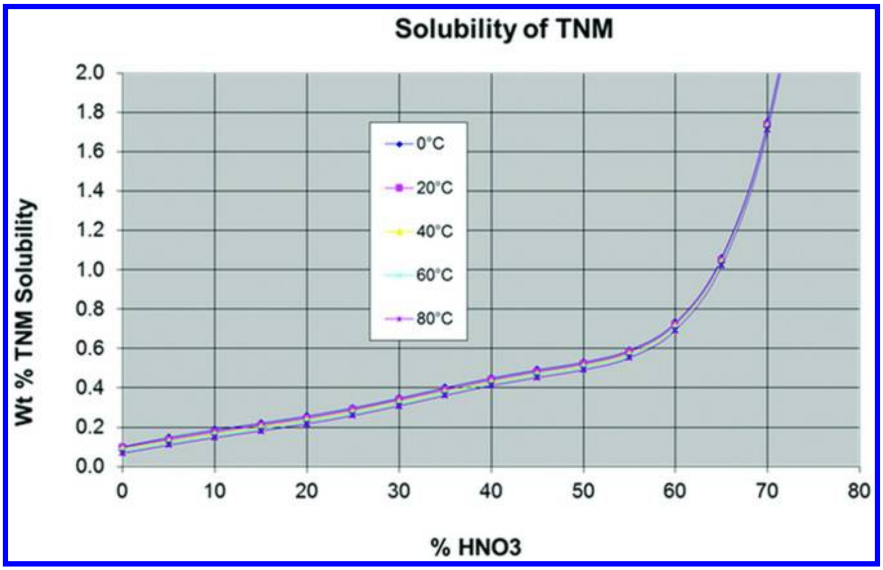

Figure 11. Solubility of TNM in Various Strengths (wt%) of Nitric Acid as a Function of Temperature. (see color insert)

TNM and NF concentrations are consistent with the process knowledge of the plant. The concentrations of TNM and NF in all process streams are well below their solubility limits. Action levels are chosen (levels at which serious action is taken in the plant which may include shutting the plant down) to be one third the TNM solubility limit in the particular strength of nitric acid. This level is easily detectable by an HPLC method (see Experimental).

Trapping Gaseous Amines in Acid Scrubbers

A strict and detailed material balance for the example plant employing the general chemistry shown in Figures 2, 3, and 4 showed that MMA gas acts differently in the presence of nitric acid than it does in the presence of sulfuric acid. This type of behavior has also been observed for ammonia in certain plants. This unusual behavior is shown in a dramatic way by the series of experiments shown in Table 4.

The laboratory equipment used for the study is shown in Figure 12. Air was passed through a flow meter at 2 SCFH (standard cubic feet per hour) into a small impinger containing 9.0 grams of 40 wt% aqueous MMA. Later in the study, we employed a bubbler instead of the jointed impinger as there was a concern that the joint leaked. The gas flow from the impinger was conveyed via a Teflon® tube to a large impinger (#1, 500 mL capacity) containing 400 mL of the desired acid. The flow from this impinger was conveyed to the second impinger (500 mL capacity) containing 400 mL of the desired acid. The exit of the second impinger was vented to the laboratory hood. The impinger (or gas bubbler) containing the aqueous MMA was heated to 45 °C using an external temperature controlled water bath (not shown in Figure 12). The air flowed to the system for 2 hours, after which it was found that the impinger containing the aqueous MMA no longer contained MMA; some water remained in the impinger after 2 hours of air flow. The large impingers were at ambient temperature. The frit at the end of dip tube in spargers #1 and #2 were a C porosity frit (20 to 50 micron). The gas bubbles emanating from the frit were small. In one experiment the frit was removed and the open end of the tube had an internal diameter of ~5 mm. The gas bubbles emanating from the open ended dip tube were large. In two experiments the frit was replaced with a short piece of plastic tubing that fit snuggly over the end of the dip tube. The end of the short piece of plastic tubing was plugged with a Teflon stopper. The sides of the short piece of plastic tubing was pierced with a utility knife to create six slits that were ~3 mm in length and ~0.5 mm wide. The gas bubbles emanating from the slits were of medium size.

The level of MMA in the fluid contained in the 500 mL impingers was measured, but that data is not presented here. However, the key observations are shown in Table 4.

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Table 4. Trapping MMA Vapor (*1*)

Exp	*MMA Delivery system*	*Sparger Type*	*Sparger #1 Contents*	*Sparger #2 Contents*	*MMAN Fog Observed in Sparger #1?*	*Break- Through of MAA to Sparger #2?*	*Conclusions*
A	from impinger	C frit (small bubbles)	water	water	no	yes	MMA is stripped from water with nitrogen sparge
B	from impinger	C frit (small bubbles)	70% nitric acid	70% nitric acid	yes	yes	white fog of MMAN formation in #1 and traveled to #2
C	from impinger	C frit (small bubbles)	32% nitric acid	32% nitric acid	yes	yes	white fog of MMAN formation in #1 and traveled to #2
D	from impinger	open tube (large bubbles)	86% sulfuric acid	86% sulfuric acid	no	no	MMAS formation in #1, no break-though to #2
E	spike MMA into Sparger #1	C frit (small bubbles)	32% HNO3 spiked with MAA	32% HNO3	no	no	MMAN once formed is not stripped out of 32% nitric acid
F	from bubbler	slit (medium bubbles)	86% sulfuric acid	32% nitric acid	no	no	MMAS once formed is not stripped out with nitrogen sparge
G	from bubbler	slit (medium bubbles)	86% sulfuric acid containing 10% nitrosyl sulfuric acid	32% nitric acid	yes	yes	MMAN fog formed in sparger #1 and traveled to sparger #21

[1] MMAN is methylammonium nitrate. MMAS is methylammonium sulfate. In all experiments that air flow was 2 SCFH for 120 minutes. The content of MAA in the spargers was determined (exact levels not shown).

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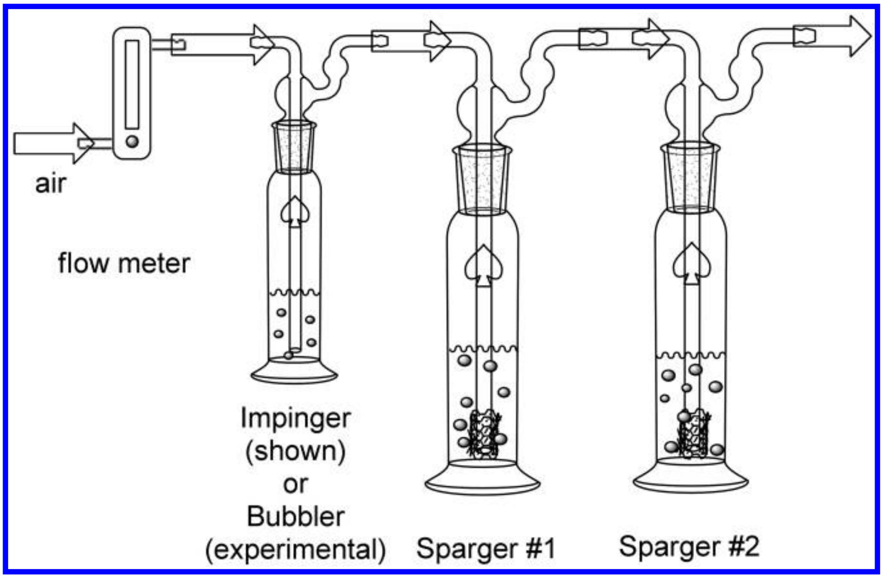

Figure 12. Laboratory Equipment Used to Study Absorption of MAA Gas by Aqueous Acids. (see color insert)

Experiment A

In this experiment 40% aqueous MMA was introduced into an impinger. Sparger #1 was filled with water and fitted with a frit on the dip tube; in like manner sparger #2 was also filled with water and fitted with a frit. Air was allowed to bubble through the impinger and through each of the spargers at 2 SCHF for 120 minutes. MMA was stripped from the water in the impinger and carried through sparger #1 and sparger #2. When sparger #2 was analyzed, MMA was present. Water was not good at sequestering MMA.

Experiment B

This experiment was exactly the same as A except that 70% nitric acid was placed in both sparger #1 and sparger #2. When the airflow was started, a white fog was noted in the headspace of sparger #1 and also in the headspace of sparger #2. The white fog in the headspace of sparger #1 actually flowed through the frit and the liquid in sparger #2. The white fog was identified as methylammonium nitrate. It was in a very finely divided liquid phase, mist, or sol. Unlike water scrubbing the nitric acid produced a white fog that moved through the scrubbing media.

Experiment C

This experiment was run as in B only 32% nitric acid was used in both spargers. The observed results were exactly the same as in experiment B.

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Experiment D

The MMA delivery system used the small impinger however the spargers both had open dip tubes rather than frits. This resulted in large bubbles emanating from the dip tubes in the large spargers. The spargers were charged with 86% sulfuric acid and the airflow was started. No fog was observed over the headspace of either sparger nor was any MMA found in sparger #2. The sulfuric acid was a more effective scrubber for vaporized MMA in this lab equipment.

Experiment E

The impinger in this case was empty and each sparger was filled with 32% nitric acid. However, sparger #1 was spiked with the aqueous MMA. In this way, the MMA was dissolved in the acid as the methylammonium nitrate salt. The airflow was started through the impinger but no fog or sol was formed in either sparger #1 or sparger #2 and no breakthrough of MMA was observed in sparger #2. The methylammonium nitrate was formed and dissolved when the nitric acid in sparger #1 was spiked with MMA, and it stayed there after being sparged with air.

Experiment F

A bubbler was charged with the aqueous MMA. The dip tubes in the large spargers were fitted a short plugged plastic tube. The plastic tube was pierced with a utility blade to form short slits. The bubbles emanating from the slits were of medium size. Sparger #1 was charged with 86% sulfuric acid while sparger #2 was charged with 32% nitric acid. The gas flow was started and the system observed. No white cloud or sol was observed above either sparger #1 or sparger #2 and no breakthrough was observed in sparger #2. This again showed the efficacy of sulfuric acid to scrub MMA.

Experiment G

A bubbler was charged with aqueous MMA. Sparger #1 was charged with 400 mL of 86 wt% sulfuric acid containing 10 wt% nitrosyl sulfuric acid. Sparger #2 was charged with 32 wt% nitric acid. Air flow was established at 2 SCFH. A white fog was observed in the head space of sparger #1 which flowed into sparger #2. MMA was observed in sparger #2. It was not verified whether the fog was methylammonium sulfate or methylammonium nitrate, but taking all the scrubbing experimental results together, it was very likely that methylammonium nitrate was formed in sparger #1 and carried forward to sparger #2 in experiment G.

These experiments were not repeated with ammonia but it is very likely that similar behavior would be observed. The conclusions are that MMA vapor was not scrubbed efficiently with nitric acid and MMA vapor was scrubbed efficiently with clean sulfuric acid. Surprisingly, if the sulfuric acid contained nitrosyl sulfuric acid (or presumably nitric acid), then methylammonium nitrate can form when MMA vapor passes through the acid solution and escape as a sol. These findings are very consistent with what was observed in the plant as shown by the mass balance. While lab experiments seem to show the large difference in the scrubbing ability of nitric versus sulfuric acid, processes are known where very minute amounts of mist can defeat scrubbers and still allow small amounts of "mist" to travel and collect in vent systems. In other words better does not mean perfect and the risk still needs to be assessed in the actual specific equipment and configurations employed.

Summary

One must consider the unique safety concerns in all process areas when operating a nitration plant. Compounds and by-products to watch for in a nitration facility have been reviewed (Table 1).

The design of a nitration plant must avoid areas where material can collect and stagnate. There should be low points that can trap material. All vessels, lines, and vents should be self-draining. Material in the process should not be allowed to be blocked in; there should always be a route to relieve pressure. A pump should not be allowed to dead head through the use of proper sensors and interlocks. Bubbles should not be allowed to form in process streams, as collapsing bubbles can create micro environments of high temperature and pressure that can cause the initiation of a fast uncontrollable reaction. Process streams should be kept moving and not allowed to stagnate, especially without proper cooling. Many accidents occur where nitration occurs in an area of the plant other than in the nitrator. One must be cognizant of factors that contribute to runaway nitration reactions.

A mixture of an oxidant and organic contains more energy as it approaches oxygen balance. These mixtures can detonate (the reaction front self-propagates faster speed of sound) or deflagrate (the reaction front self-propagates at just under supersonic velocity). Oxygen balanced mixtures of oxidant and fuel are more sensitive (easily prone to reaction via heat, shock, static spark, or mechanical energy input) than mixtures that are not. Oxygen balanced materials can be highly sensitive or not sensitive, but they should be avoided whenever possible.

This is a partial summary of items to consider when designing and operating a nitration plant. Each nitration facility presents unique challenges, and requires expertise in design, hazards testing and evaluation, and operation. The intention of this chapter is to urge you to be diligent in your quest to reduce risk in your nitration facility. A proper Level of Protection Analysis (LOPA) and hazards of operation review (Hazop) should be done when the plant is designed, and when the plant and equipment change. Other primers and experts ought to be sought out and used to plan your process design, operating rules, and risk abatement.

Good mass balances of substituents in a nitration plant are required to operate a safe facility. Solubility limits of by-products in process streams must be known to insure no phase separation occurs in the process. Phase separation can lead to a host of process issues. Clean sulfuric and nitric acid streams should be analyzed for carbon by TOC. Free amines must be tracked in process streams as nitrate/nitrite salts are sensitive materials. We have shown that ammonium nitrate salts, present in vapor streams as sols (fine solid particles), can defeat common scrubbers. Safety critical analyses need to be performed every shift every day. Some analyses are

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performed even when the plant is down to make sure nothing is changing in storage vessels. Mass balances may vary over certain time frames, and in fact seldom does the first mass balance ever close in a plant. It takes much work and diligence to catalog the organic species to track, and to develop the best analytical methods to do so. It also requires good measurement of mass flows throughout the plant.

In conclusion, the authors would like to emphasize again the importance of understanding the risks involved in performing nitration reactions and operating a nitration plant. Knowledge and experience are important tools to mitigate risk.

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Experimental

TNM Analysis by HPLC

Product streams throughout the nitration plant are analyzed for tetranitromethane (TNM). The acid streams are also analyzed for the nitration starting material, product, and side reaction products. All samples are analyzed by dissolving the sample in a large amount of acetonitrile (care must be taken to avoid a safety issue with sample preparation). The diluted sample is then injected onto a High Pressure Liquid Chromatograph (HPLC). Most results are reported as parts per million (ppm) although a few are reported as weight %.

Samples from 15 to 20 plant locations are analyzed either once per shift or once per day using this procedure. A sampling plan and a sampling matrix (with sample preparation instructions unique for the sample) are utilized. Target values of concern have been set for all streams. Appropriate standards are prepared, and analyte recovery experiments performed to verify the method.

Safety Considerations/Hazards

Acetonitrile - flammable, harmful if inhaled or absorbed through skin
Nitric acid - highly toxic, oxidizer
TNM – oxidizer
Wear proper personal protective equipment when handling all chemicals
In case of skin contact rinse thoroughly with water
In case of eye contact rinse thoroughly with water and seek medical assistance

Equipment

Waters liquid chromatographic system consisting of the following: Waters 2695 Separations Module with Model 2489 Absorbance Detector (280 nm detection), Waters Resolve C18 5 micron 8 x 100 mm Rad-Pac cartridge column, 2.5 mL/min flow rate, isocratic solvent (55/45, water/acetonitrile), 15 μL injection, column oven temperature 35 °C.

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Percent Organics, NF, and Product Analysis by HPLC

Sample prep is the same as for the analysis of TNM in acid process streams (appropriate dilution with acetonitrile). Appropriate standards are prepared, and recovery experiments from each sample matrix were performed to verify the method. Nitroform was prepared by the method of Geckler (*25*).

Samples Are Shot on an HPLC

Waters 2695 Separations Module; Model 2489 Absorbance Detector (280 nm detection); using a Phenomenex Luna 5μ, C18, 150 mm by 3 mm column; isocratic solvent system (prepared by dissolving 31.8 gr of tetramethylammonium chloride in 120 mL of methanol, then adding that to 2400 mL of deionized water, then adding to that 1080 mL of HPLC grade acetonitrile, then adding to that 0.8 mL of glacial acetic acid, finally mixing and filtering before use); at 1.0 mL/min flow rate; 5 μL injection; column oven temperature 30 °C.

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Chapter 15

Redesign for Safe Operation of a Nitric Acid Recovery Unit

John Pace[*,1] **and Colin Evans**[2]

[1]**SABIC, Parkersburg, West Virginia 26101**
[2]**Chemetics (retired), Toronto, Canada**
[*]**E-mail: john.pace@sabic-ip.com**

In an effort to improve the operability of a weak nitric acid recovery unit operated by the Innovative Plastics division of Saudi Basic Industries Corporation (SABIC), a technology team from SABIC initiated a study to understand the root cause of the occasional loss of adequate control of the operating temperature and pressure of the unit. A review of the capacity of the unit's emergency pressure relief vent was a second objective of the study. The emergency relief requirements were determined based on calorimetric data on process samples. The operating targets of the unit were modified to minimize the frequency and risk of the process excursions and the relief system was modified to protect against the estimated maximum credible relief case scenario.

Background

An extended plant outage was taken by SABIC to address issues resulting from an incident in a nitric acid concentration process (*1*). Several safety reviews were conducted during the outage for other areas of the plant that were not involved in the incident. The topic of this paper is the work done to address one of the potential issues discovered in the review of a weak nitric acid recovery unit. This unit recovers weak nitric acid from a process stream and recycles it to the nitric acid concentrator.

The weak nitric acid recovery unit consists of an evaporator (Figure 1) which receives a feed stream containing 1% to 3% (by weight) "organics" in a water/nitric acid mixture of approximately 40% acid strength. Organics, in the sense used

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ACS Symposium Series; American Chemical Society: Washington, DC, 2013.

in this discussion, are the main organic products of the nitration facility, which employs the nitric acid recovery unit. There are other organic species present in this stream, but they are not rountinely measured. These other organics are byproducts of the process, and are present at a weight ratio of no more than one to one, by-product to product organics. The term “organics”, from this point forward, refers to the product organics only. “Acid strength” refers to the weight percent nitric acid in the combined water and nitric acid portion of the stream content, ignoring the organic content.

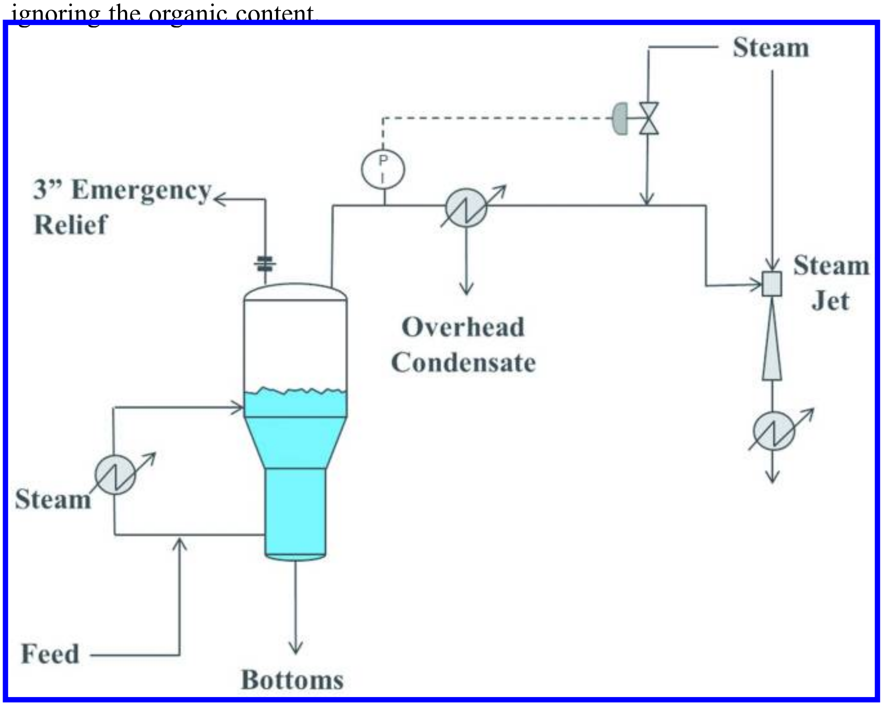

Figure 1. Weak nitric acid evaporator system. (see color insert)

The acid strength of the recovered nitric acid that is taken overhead in this evaporator is typically 35%. The bottoms stream is a waste, normally 12% to 15% organics with an acid strength of approximately 60%. The evaporator operates under vacuum, at approximately 100 mmHg absolute pressure, and at approximately 65°C. Heat is supplied to the evaporator indirectly by steam, through a thermosyphon reboiler. Pumping of the bottoms mixture is avoided to prevent overheating of the bottoms material, since it is known that nitric acid can exothermically oxidize the organics at elevated temperatures and generate NO_x, CO, and CO_2. The vapor overheads of the evaporator are condensed and steam jets are used to maintain the operating vacuum in the evaporator. The system pressure is controlled by addition of steam to the suction of the jet, as a vacuum break. A three inch emergency pressure relief vent was provided in the original design of the evaporator, with a rupture disk having a burst pressure of 13.5 psig. The emergency pressure relief header is routed to a NO_x removal system to prevent the release of NO_x to the atmosphere.

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It was noted during the review that from time to time it was difficult for operators to control the evaporator at a stable temperature and pressure. This generally occurred when the organics content in the bottoms exceeded 18% to 20%, usually due to transitions in the composition of the feed to the evaporator or to upsets in the rate of removal of the bottoms material from the evaporator. Bottoms samples were routinely taken for analysis every 16 hours and the operators typically adjusted the feed and steam rates to the evaporator to return the bottoms organics content to the normal range of 12% to 15% if the analysis indicated the organics were outside of that range. Upon examination of the past operating data, several of these disturbances in the operating temperature and pressure of the evaporator were found by the review team. The temperature and pressure trends of a typical disturbance of this type are shown in Figure 2.

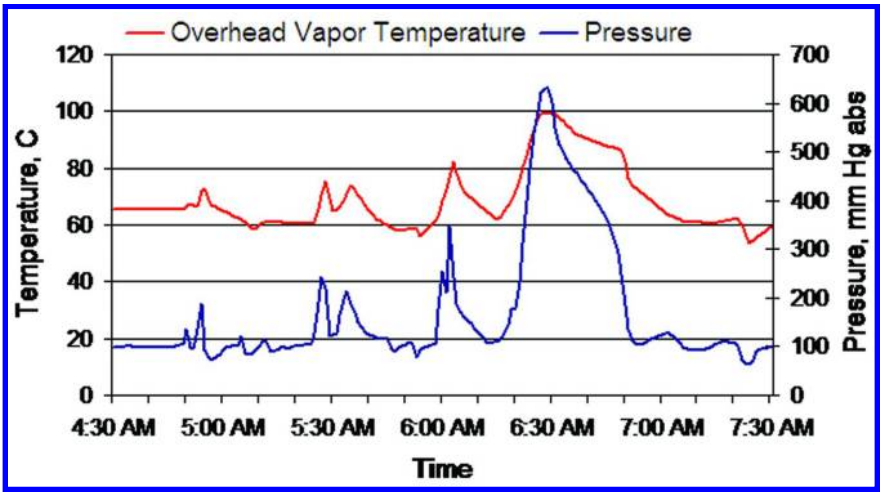

Figure 2. Pressure and temperature trends during a typical evaporator disturbance. (see color insert)

During these disturbances the operating pressure would typically increase to as much as 700 mm Hg absolute, with the temperature reaching as high as 100°C. The review team decided to study these operating upsets in more detail, particularly to see if the vessel was adequately protected from excessive pressure in the event that the bottoms organic content became excessively high, and if the usual methods of returning the evaporator to its target operating temperature and pressure were not successful.

Discussion

An investigation was initiated to gain an understanding of the source of temperature and pressure excursions in the operation of the nitric acid evaporator, and to make recommendations to help avoid these events. A second objective was to determine the adequacy of the existing emergency relief system and to make recommendations for relief system upgrades if the existing system was found to be inadequate.

To achieve these objectives, several samples were subjected to calorimetric testing techniques, further described below. Use of these test results by the reader for his or her processes should not be attempted since the test results are very dependent on the nature of the organics present in the samples.

There was only one evaporator bottoms sample available for testing after the nitric acid concentrator incident (*1*). The plant would not be re-started until the changes in procedures and equipment design recommended during that safety review were implemented. In order to have a wider range of samples available for study, an effort was made to prepare and test "synthetic samples". Synthetically prepared mixtures were found to give calorimetry results that were not consistent with the results on the available process sample. The organic content of the process sample was 17%, on the upper end of the normal operating range. There was enough of this sample to perform calorimetry for use in evaluation of the adequacy of the emergency pressure relief system under normal operation. However the quantity was insufficient to allow concentration of the material in the laboratory to a higher organic content to enable evaluation of the relief requirements under more extreme conditions. The available sample was tested in an Advanced Reactive System Screening Tool (ARSST) calorimeter (*2*). Information on the behavior of material with higher organic content would have to be to be inferred from ARC calorimetry that had been performed on plant material several years earlier, on samples ranging from 14% to 31% organics.

The 17% organics process sample that was available for calorimetric evaluation was testing using procedures developed by the Design Institute for Emergency Relief Systems (DIERS) program, sponsored by the American Institute of Chemical Engineers. Methods were developed under DIERS sponsorship for evaluating emergency pressure relief requirements for reactive systems, where the relieving flow often consists of two phases. The ARSST is one of a series of calorimeters that were developed specifically for generation of data for use in prediction of relief behavior in large production scale equipment, using the DIERS methodology. The ARSST allows generation of the required data using relatively small samples (~10 grams). Characteristics of the ARSST include:

1. A 10 cc agitated thin wall spherical glass test cell inside a 350 cc pressure containment vessel.
2. The test cell is open to the containment vessel and pressure is equalized between the two, allowing the use of the thin wall glass test cell.
3. A low phi-factor (discussed below), allowing collection of data at effectively adiabatic conditions.
4. The test cell temperature can be ramped upward at a constant rate (or alternately by a heat-wait-search routine) until an exotherm is detected.
5. A temperature controller and heater on the test cell allow maintenance of the same temperature outside of the cell as inside, to prevent heat flow to the containment vessel.

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6. The 350cc pressure containment vessel can be vented and controlled at a constant backpressure, or closed to allow the pressure to build as the experiment proceeds, depending on which mode best fits the purpose of the test. The use of the open test cell in the ARSST test method has been confirmed to give results that compare very well with test results from other DIERS developed apparatus that use closed test cells (such as the larger VSP2 Vent Sizing Package calorimeter) (*2*).

Temperature vs. time and pressure vs. time data is collected during the experiment and is later converted to rates of pressure rise and rates of temperature rise vs. sample temperature. This rate of rise data is required for the relief system design calculations.

The phi factor mentioned above is a measure of the adiabatic capability of the calorimeter. Large commercial equipment exhibits nearly adiabatic behavior during thermal runaway events. The heat losses from the contents of large-scale equipment are very slight compared to the heat being generated within the equipment. These heat losses include heat loss to the surroundings as well as heat that is absorbed in raising the temperature of the containing vessel. Failure to conduct the small-scale experiments adiabatically leads to an understatement of the heat released by the reaction, reducing the rate of temperature rise that is measured. This error in turn leads to underestimation of the emergency pressure venting requirements of the full-scale vessel. Many lab calorimeters, such as the accelerating rate calorimeter (ARC), are not truly adiabatic in that their sample cells have significant "thermal capacity" compared to that of the test cell contents. Thermal capacity is defined as the product of the mass and the specific heat of the material. The ARC sample cell, for example, is a relatively thick walled metal container, designed so that it is able to withstand the high pressures that can be generated during the experiments. The sample container of the ARSST is vented into the containment vessel; equalizing the pressure inside and outside of the sample container, allowing the use of thin wall glass with a much lower thermal capacity.

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The phi factor is calculated as:

$$\boxed{\Phi = \frac{m_S \times CP_S + m_{SC} \times CP_{SC}}{m_S \times CP_S}}$$

where:
m_S is the mass of the sample
m_{SC} is the mass of the sample container
CP_S is the specific heat of the sample
CP_{SC} is the specific heat of the sample container

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The phi factor is 1.0 for a completely adiabatic system. Phi factors of ~1.05 are typical of large scale vessels, as well as of the ARSST sample cell and sample. ARC calorimeters typically have phi factors of 2.5 to 3.0. ARC calorimeters are not typically used for the calorimetry supporting emergency pressure relief designs for this reason.

ARSST data, generated with the pressure containment vessel in the closed mode of operation, for the 17% organics sample are shown in Figures 3 and 4.

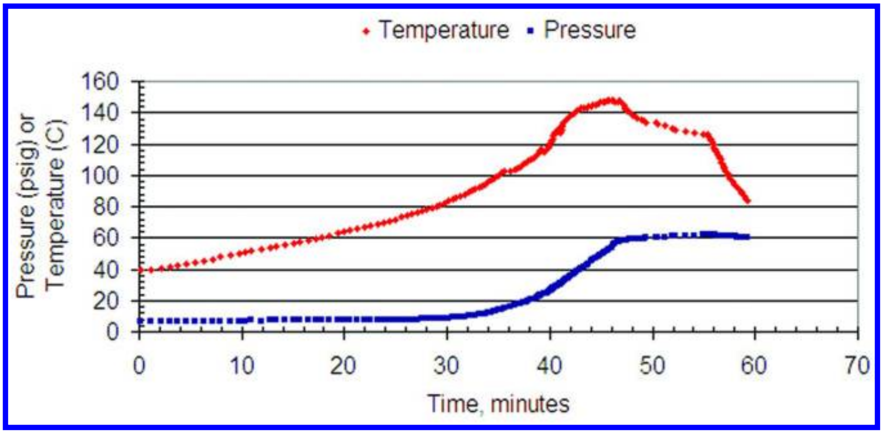

Figure 3. Temperature and pressure vs. time for the 17% organics sample. (see color insert)

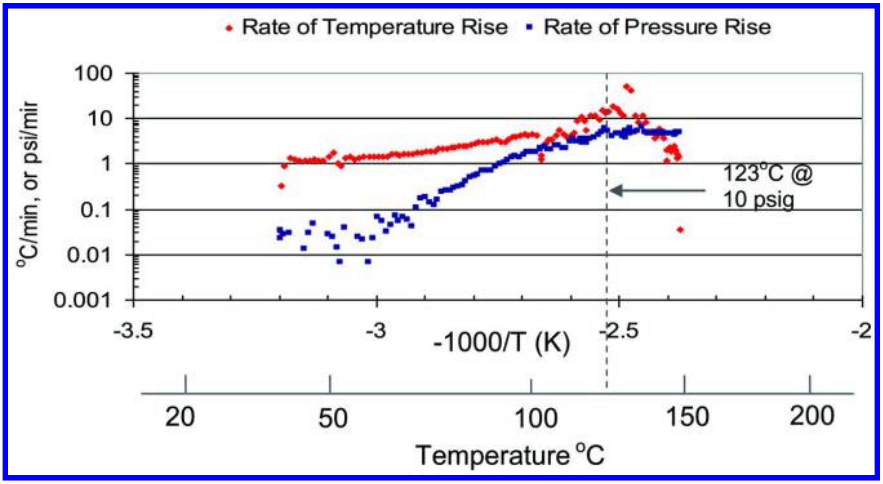

Figure 4. Rates of temperature rise and pressure rise vs. temperature for the 17% organics sample. (see color insert)

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The ARSST test on the sample containing 17% organics yielded a rate of temperature rise of ~18°C/min and a rate of pressure rise of ~6 psi/min at 123°C, the temperature required for the bottoms composition to exert 10 psig of pressure (the desired rupture disk bursting pressure) in a closed system under boiling conditions. These values could be used for design for relief for up to 17% organics evaporator bottoms material. Considering that it is possible to concentrate to above 17% in the bottoms, some additional safety margin had to be designed into the relief system so that it could accommodate relief scenarios starting from organic content in excess of 17%. The intent was for the relief system to be capable of successfully relieving the evaporator in the case of the maximum credible organics content.

Determination of the maximum credible organics content was accomplished through statistical analysis of the bottoms organic data for a period of eight years of operation prior to the nitric acid concentrator incident (*1*). The histogram of the data is shown in Figure 5.

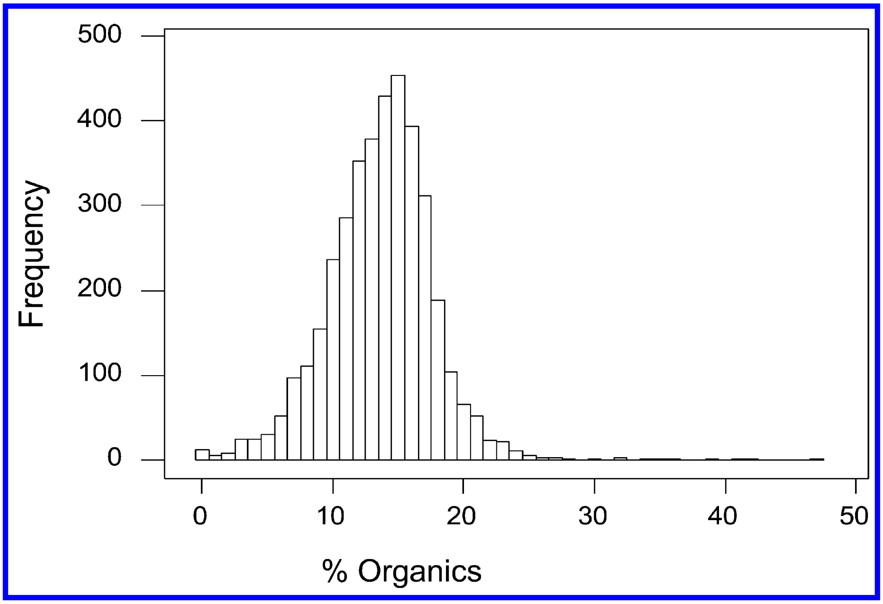

Figure 5. Histogram of the previous eight years' percent organics.

The average percent organics for this period was 13.6%, with short term and long term standard deviations of 2.7% and 4.1% respectively. From experience, organic analyses on the very high end of the histogram (>25%) are actually more likely to be due to analytical error. In order to provide a suitable design margin for the emergency relief, the existing ARC test data for 31% organics was converted to what would have been the expected behavior in a low phi factor calorimetry test. In addition it would be necessary to shift the mean of the % organics slightly lower, or to reduce the variability in the bottoms concentration, in order to reliably avoid exceeding 31% organics in the evaporator (targeting

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<1 time in a million samples). The probability of exceeding 31% organics based on the statistics from the previous eight years performance was estimated as 28 times per million samples. The accuracy of this probability estimate however is questionable, based on the long tail seen on the high end of the histogram, and on the uncertainty of the reality of the values over 25%.

In order to have information at 31% organics similar to the low phi data of Figure 4 for 17% organics, it was necessary to convert the ARC rate of temperature rise data to a low phi basis. Conversion of ARC data for this purpose is only recommended when the relative amount of "burn-up" of reactive species in the sample is relatively low between the point of initiation of the test and the point that the sample reaches the relief conditions (123°C in this case). The amount of burn-up was calculated as ~15% for the previous ARC data for a sample with 15% organics. The relative burn-up for the 31% organics ARC test would be much less than 15%, confirming that scaling of the ARC data for the 31% organics relief case is a reasonable approach in the absence of additional samples for ARSST testing.

The raw ARC temperature and pressure data for 14% and 31% organics are shown in Figure 6 below.

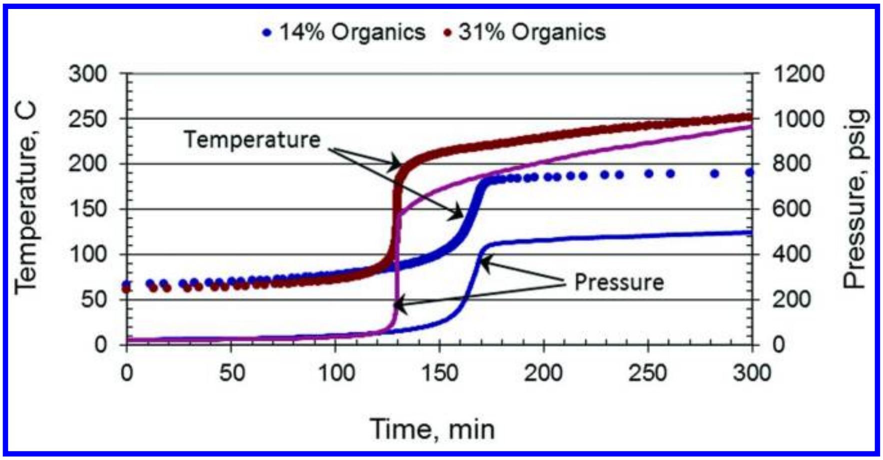

Figure 6. ARC data (prior to conversion) for 14% and 31% organics. (see color insert)

The ARC rate of temperature rise was calculated and then multiplied by the phi factor for that specific ARC test to convert it to a low phi basis. The phi factor adjusted rate of temperature rise is shown in Figure 7 for 15% and 22% organics ARC data, along with the 17% organics ARSST data.

The phi adjusted 15% organics ARC data agrees very well with the ARSST data for the 17% organics sample. When comparing the difference in organic content of those two tests, the conversion of the ARC data yielded slightly conservative results. This comparison of the temperature rise data from the two different calorimeters led to confidence that the 31% organics ARC data could be used for the relief system design. The phi adjusted rate of temperature rise and the rate of pressure rise in the ARC experiments are given in Figure 8 below for 15%, 22%, and 31% organics.

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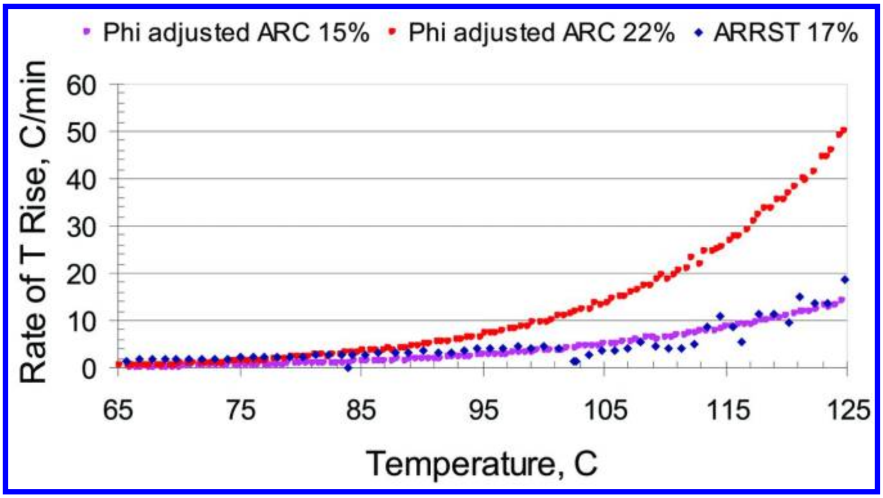

Figure 7. Phi factor adjusted ARC data compared to ARSST data. (see color insert)

This rate of rise information for temperature and pressure was used for the design of the emergency pressure relief system for the evaporator. The rates of rise used for the design were taken at 123°C, the temperature required for the bottoms composition to exert 10 psig of pressure in a closed system under boiling conditions.

The formula for calculation of the required venting area is given by:

$$A/V = \frac{3.5 \cdot 10^{-3}}{P\left[1 + \frac{1.98 \cdot 10^{3}}{P^{1.75}}\right]^{0.286}} \frac{\dot{T} + \dot{P}}{C_D}$$

where:

A is the vent area (square meters)

V is the reactant volume (cubic meters)

C_D is the discharge coefficient

P is the venting pressure (psig)

$\dot{T}$ is the self-heat rate at the relief pressure, °C/min

$\dot{P}$ is the rate of pressure rise of the ARSST test cell at the desired relief pressure, psi/min

The above equation is specific to the geometry of the ARSST, accounting for the volume of the containment vessel when the measured rate of pressure rise is used. In order to have a rate of pressure rise on an equivalent basis for the ARC generated data, the same ratio of rate of temperature rise to the rate of pressure rise of ~3 for the 17% organics ARSST test was used for the estimation of the correct rate of pressure rise to use for the 31% organics case.

The discharge coefficient is specific to the geometry of the emergency venting system. A vessel discharging to atmosphere would have a discharge coefficient close to 1.0, an ideal nozzle. In the case of the evaporator however, where the vessel is relieved to a NO_x scrubbing system remote from the evaporator, the discharge coefficient was estimated to be ~0.38 based on the number of equivalent lengths of piping between the evaporator and the ultimate discharge point.

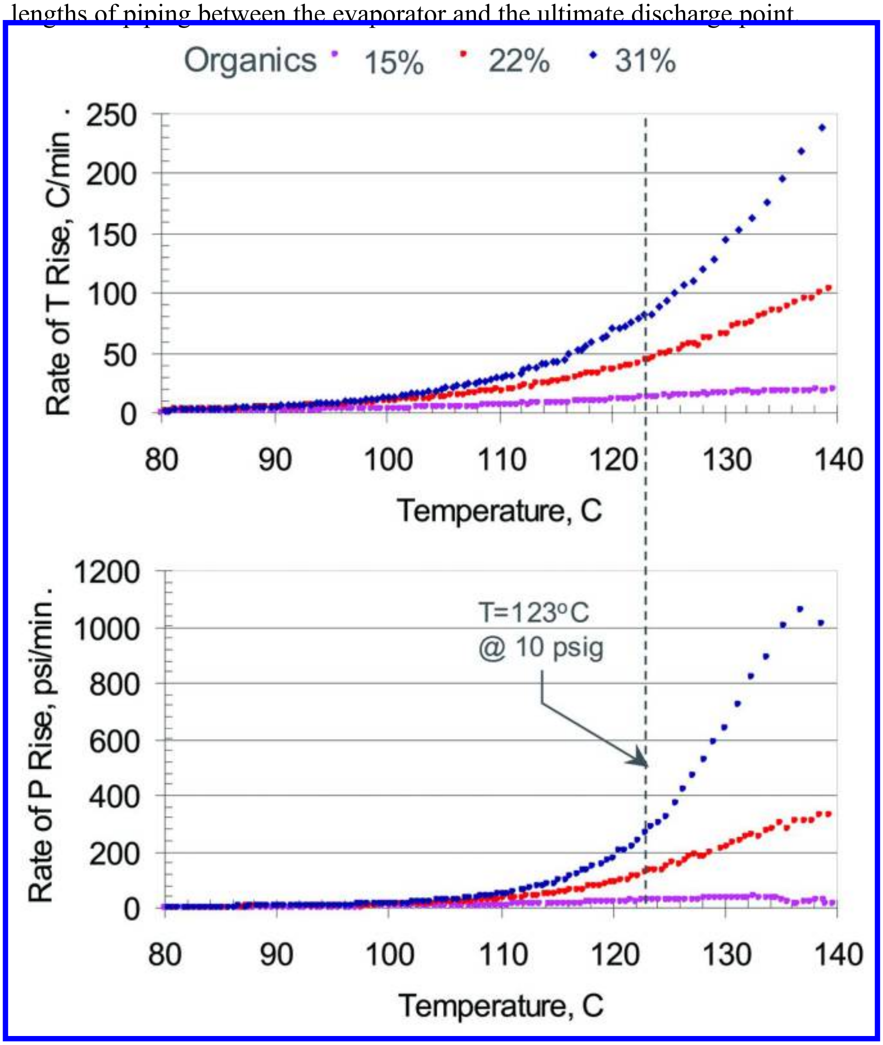

Figure 8. Phi adjusted rate of temperature rise and rate of pressure rise for 15%, 22% and 31% organics. (see color insert)

The calculated relief requirements at 17% organics are shown in Table 1. These results indicate that the relieving capacity of the existing 3 inch emergency vent is inadequate to control the pressure from a relieving event at 17% organics, even if the vessel inventory was reduced by half and the relieving pressure reduced to 5 psig.

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The calculated relief requirements at 31% organics are shown in Table 2. In the case of 31% organics a relief diameter of approximately 14 inches is necessary for relief of the normal liquid inventory at 10 psig. For the final design a new 16 inch relief line was installed, incorporating a rupture disk with a burst pressure of 10 psig. The evaporator body was replaced, utilizing a design that allowed normal operation at approximately 50% of the liquid inventory of the original design. The 16 inch relief line provides protection for the case of 31% organics content along with a higher than normal operating level, should they happen simultaneously. The existing 3 inch relief line was retained, with a 5 psig rupture disk, to allow protection of the main disk in the event of a pressure increase not related to oxidation of the bottoms material.

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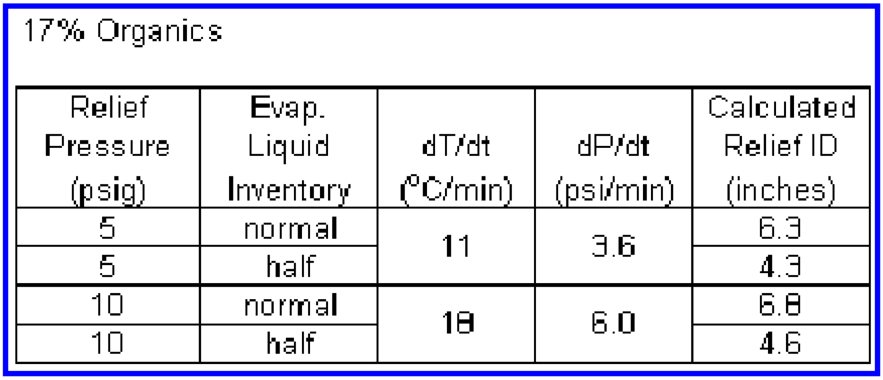
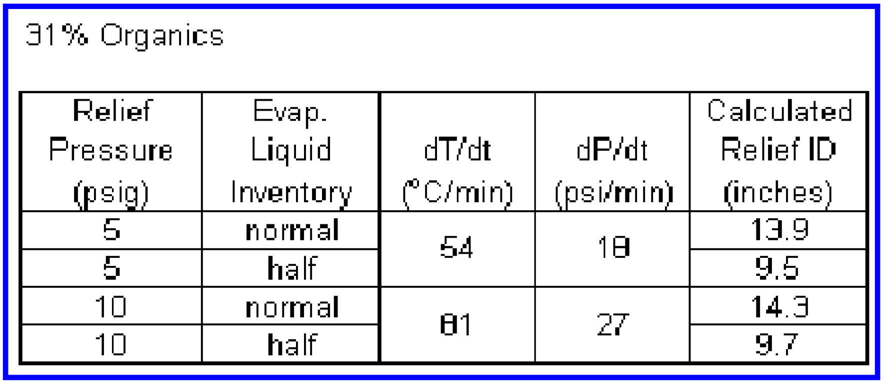
Table 1. Emergency pressure vent diameter vs. relief pressure and evaporator inventory for 17% organics



17% Organics

Relief Pressure (psig)	Evap. Liquid Inventory	dT/dt (°C/min)	dP/dt (psi/min)	Calculated Relief ID (inches)
5	normal	11	3.6	6.3
5	half			4.3
10	normal	18	6.0	6.8
10	half			4.6

Table 2. Emergency pressure vent diameter vs. relief pressure and evaporator inventory for 31% organics



31% Organics

Relief Pressure (psig)	Evap. Liquid Inventory	dT/dt (°C/min)	dP/dt (psi/min)	Calculated Relief ID (inches)
5	normal	54	18	13.9
5	half			9.5
10	normal	81	27	14.3
10	half			9.7

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A word of explanation is needed to clarify the use of the equilibrium (i.e. normal boiling) temperature and pressure of the sample mixture for determination of the parameters for vent sizing. The equilibrium temperature/pressure relationship is specifically valid only for open systems when gassy components (i.e. NO_x, CO, and CO_2 in this case) are being generated. When the containing vessel is closed, the gas components exert an additional pressure based on the quantity present, over and above the equilibrium pressure of the components in the liquid mixture. The degree to which the vessel is being vented prior to a relief event, therefore, determines the actual temperature which will be attained at the point of pressure relief. In cases where there is no venting or limited venting prior to relief, the temperature attained will be lower than the equilibrium temperature. The temperature at the point of relief determines the rate of temperature rise, which is the most significant factor determining the relief area required. Closed or partially vented vessels therefore will relieve at a lower temperature and a lower rate of temperature rise than a fully vented one. Once the emergency relief vent opens, the conditions in the vessel return quickly to conditions very close to the equilibrium conditions as the excess gassy components are released. The vent area determined, therefore, is generally conservative for the point of relief; and is specifically sized for the flow required past the initiation point of the relief.

An additional use for the rate of pressure rise data from the ARC experiments was to give insight into the loss of ability to control the pressure in the evaporator when the organics content become too high. The rate of pressure rise data was converted to kg/hr of gas generation, subtracting the rate of rise of the vapor pressures of the water and nitric acid, and converting the resulting pressure rise to an estimated gas (NO_x, CO, CO_2, average MW=44) generation rate in the evaporator, given the sample size and volume of the ARC test cell (10cc) and the normal inventory of the evaporator. The results are shown in Figure 9.

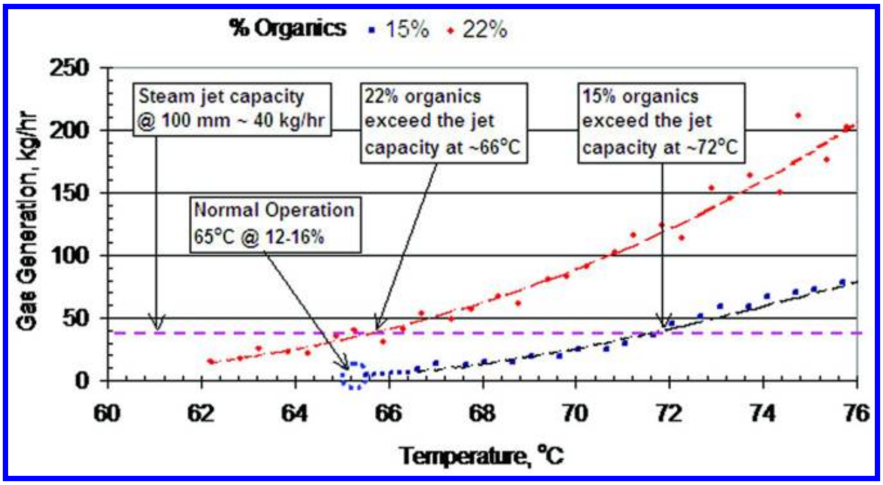

Figure 9. Rate of gas generation estimate for the evaporator as a function of the temperature and organics content of the bottoms. (see color insert)

The maximum capacity of the steam jets used for pressure control of the evaporator is 40 kg/hr. At its normal operating temperature of 65°C, the pressure in the evaporator is easily controlled when the organic content of the bottoms is ~15%. At this organic content, the capacity of the steam jets would not be exceeded unless the temperature of the evaporator is allowed to increase to ~72°C. At 22% organics, however, this estimate suggests that the steam jet capacity would be marginal at the normal operating temperature. This explains why the temperature and pressure control of the evaporator becomes difficult if the organics content of the bottoms increases beyond about 20%. A control target of a maximum of 16% organics in the bottoms stream was established to help reduce the frequency of the loss of temperature and pressure control of the evaporator.

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Conclusions

Through this investigation the SABIC team was (i) able to determine the adequacy of the existing emergency relief system and to make recommendations for relief system upgrades, and (ii) understand the causes of temperature and pressure excursions in the operation of the nitric acid evaporator, and to make recommendations to help avoid these excursions. Recommendations made from the knowledge gained from the investigation resulted in the following actions were taken to improve the safe operation of the evaporator:

1. A separate 16-inch relief vent line and rupture disk with a burst pressure of 10 psig was installed on the evaporator.
2. The burst pressure of the existing 3-inch rupture disk was reduced to 5 psig from the original 13.5 psig burst pressure.
3. The normal evaporator bottoms operating inventory was reduced by 50% through re-design of the evaporator body.
4. A maximum control limit for bottoms organics of 16% was introduced.
5. The frequency of bottoms organics testing was increased to every 8 hours from every 16 hours.
6. The capability for addition of ambient temperature water to the evaporator was added to help in control of any future significant temperature/pressure excursions.
7. Operating data are presented in the Appendix for a full year of operation after these modifications were completed. This information demonstrates the improvement that was realized in control of the bottoms organics content after the modifications were implemented.

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Appendix

Bottoms organics data is given in Figure 10 for one full year of operation, seven years after the redesign and procedural changes. The average organic content of the evaporator bottoms over that period of time was 12.2%, which is 1.4% lower than for the eight years preceding the changes. When compared with the performance shown in Figure 5 prior to the redesign, the combined effects of establishing the 16% upper target for organics and increasing the frequency of testing have combined to essentially eliminate excursions above 17% organics. In addition the variability has been significantly reduced, with short-term and long-term standard deviations of 1.7% and 2.2% respectively. With this average and standard deviation, no cases exceeding the 31% organics emergency relief design basis are statistically expected per one million samples. There has been only one instance of loss of control of the evaporator due to high bottoms organics in the eight years since the re-start. In that instance, just after the re-start, water was added to the evaporator to provide cooling in order to re-establish control. The operating pressure has not reached the 10 psig burst pressure of the 16 inch rupture disk in the eight years of operation after the modifications.

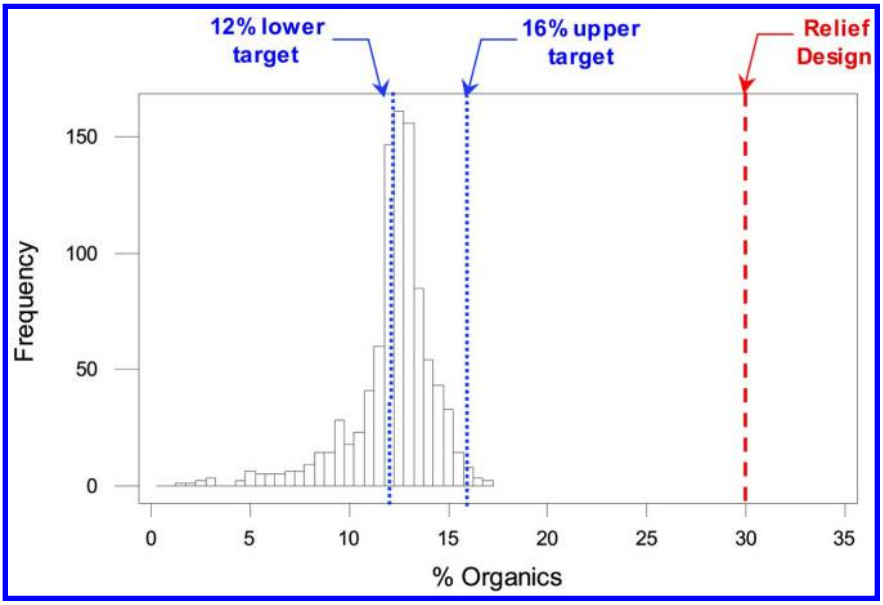

Figure 10. Histogram of organics data after the evaporator system modifications. (see color insert)

Acknowledgments

The authors would like to thank Roy Odle, Mark Delong, and Tim Allen, all of SABIC; Hans Fauske of Fauske and Associates; and James Chan (consultant) for their many contributions to this work. Appreciation is also expressed to Thomas Guggenheim of SABIC, Roy Odle, and Patrick Gallagher, formerly of General Electric, for the ARC data used in this work.

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Chapter 16

Materials Challenges in Strong Nitric and Sulfuric Acid Service

L. Mark L. Delong[*]

SABIC Innovative Plastics, 1 Lexan Lane, Mt. Vernon, Indiana 47620
[*]E-mail: mark.delong@Sabic-ip.com

Understanding of a facility's materials of construction is key to the profitable operation of any facility where both strong (>95%) nitric and sulfuric acid is used. Generally, one must be able to ferret out specific corrosion mechanisms as a function of acid concentration and temperature in order to ensure that the proper materials of construction are used in key areas. In this chapter, two corrosion events are discussed: (i) the suitability of A611 stainless steel in nitric acid service and (ii) materials of construction of steam ejectors used in the concentration of sulfuric acid. The author also discusses the lifetime of a variety of materials.

Introduction

The chemical and process conditions during the manufacture of 4-nitro-n-alkylphthalimide (*1*), can be extreme. The process employs a NAC/SAC (nitric acid concentrator/sulfuric acid concentrator) to continuously produce strong nitric acid. HNO_3 strengths are typically >95% but can range from 20% to 100%, containing as much as 2.5% NOx with respect to the nitric acid present. The concentration of H_2SO_4, used to break the 70% HNO_3 azeotrope in the distillation portion of concentrated HNO_3 production and also used to scrub NOx (thereby forming $NOHSO_4$), can vary from 70% to 90%. The concentration of NaOH, which is used to neutralize certain undesirable byproducts, can range from 20% and 50%. These corrosive chemicals exist in process conditions ranging in temperature from ambient to 165 °C, and pressure from atmospheric to 65 mm Hg.abs.

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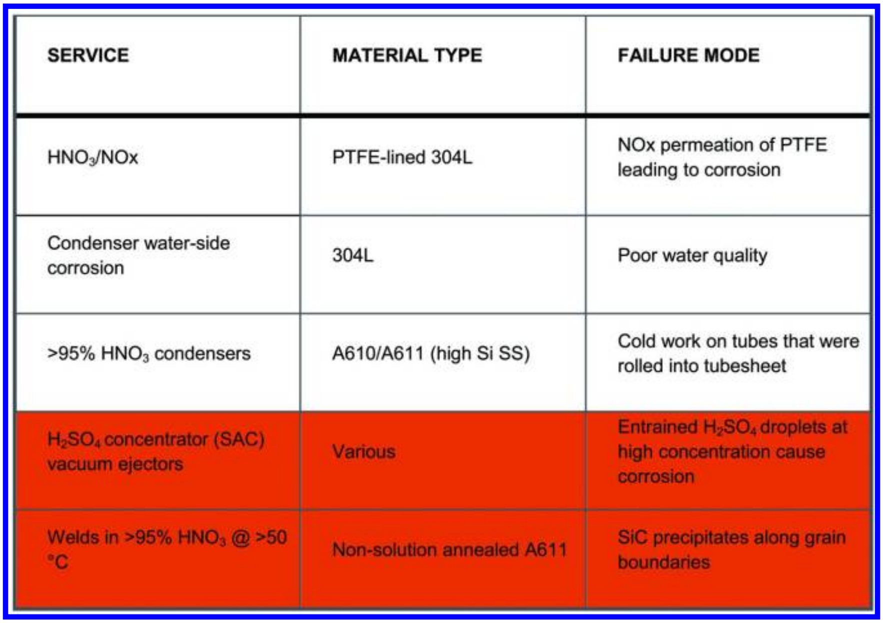
Given the dynamic nature of the manufacturing process, the materials must be both specific to its chemical and process environment as well as sufficiently flexible to maintain corrosion resistance over a wide range of chemical concentrations. Furthermore, cost and availability of the materials must be considered and in line with financial objectives. When specifying the construction materials, one must define the acceptable lifetime vs. replacement cost. Not all materials need to be expensive exotic metals. For example, polytetrafluoroethyene (PTFE)-lined 304L stainless steel eventually degrades in strong nitric acid. However, when used in conjunction with the *proper* nitric service and routine inspection, we have found that this piping can remain in use for more than five years even in strong nitric acid service.

Table 1 describes features of construction materials used in the manufacturing process. More particularly, Table 1 emphasizes proper use of construction materials that can be employed in our process. This Table describes just a few of many various material failure modes that can exist in this process. In our PTFE-lined 304L example, its service life is significantly shorter than 5 years when exposed to high concentrations of NOx. This is because NOx permeates the liner eventually corroding the surrounding stainless steel shell (*2*). In cases where the pipe is under vacuum, both liner and shell can eventually collapse leading to a potential safety hazard.

Table 1. Various Failure Modes in a NAC/SAC Environment



SERVICE	MATERIAL TYPE	FAILURE MODE
HNO_3/NOx	PTFE-lined 304L	NOx permeation of PTFE leading to corrosion
Condenser water-side corrosion	304L	Poor water quality
>95% HNO_3 condensers	A610/A611 (high Si SS)	Cold work on tubes that were rolled into tubesheet
H_2SO_4 concentrator (SAC) vacuum ejectors	Various	Entrained H_2SO_4 droplets at high concentration cause corrosion
Welds in >95% HNO_3 @ >50 °C	Non-solution annealed A611	SiC precipitates along grain boundaries

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Other factors to consider are water quality and galvanic effects. For example, when chloride levels exceed 200 ppm, 304L stainless steel is susceptible to chloride stress cracking. For the high Si alloy described in the Table 1, loss in the concentration of Si due to excessive cold work will lead to a galvanic effect. This is because the steel in the cold work section lacks passivation compared to the surrounding metal, thereby causing an anodic effect in the cold work section (*3*).

In this chapter, we concentrate on two incidents, highlighted in Table 1, that we believe will be of general interest to those who operate a NAC/SAC. These will be detailed below.

Experimental

The experimental results were obtained under contract with Hira Ahluwalia, Material Selection Resources, Pennington, NJ. In the examination of the metal failure mode of the SAC ejectors, optical microscopy, and to some extent, trial and error were the only tools required. To understand weld failures in strong nitric service, a combination of optical microscopy, scanning electron microscopy (SEM),energy dispersive x-ray (EDX) spectroscopy and Auger electron spectroscopy (AES) were employed (*4*, *5*).

SAC Ejector Failure

A 2-stage steam ejector is used to provide vacuum in the concentration of approximately 70% H_2SO_4 (recovered diluted product from the extractive distillation of HNO_3 that has had any HNO_3 removed in a prior step) to yield approximately ~85% H_2SO_4. This particular ejector is a the second stage ejector used to provide additional vacuum needed in the main concentration step for the purpose of using less overall steam.

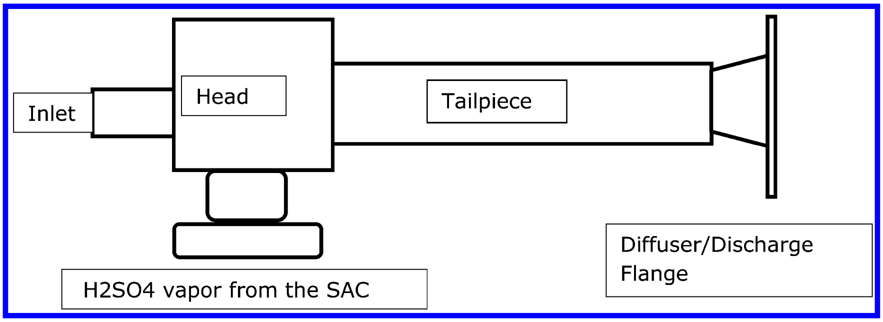

Figure 1. Ejector Schematic.

For those unfamiliar with a steam ejector, it is most easily recognized as a form of aspirator much like that used in a high school science lab. The difference is that in an aspirator the maximum vacuum is limited to the vapor pressure of water while the maximum vacuum from steam is much higher. Steam enters the ejector at the inlet and exits the diffuser/discharge nozzle. The flow of steam creates a vacuum on the overheads line from the sulfuric acid concentrator.

Routine inspection found the diffuser and the weld at the discharge flange suffered significant degradation (Figures 1-3).The nozzle is exposed to low pressure steam with entrained H_2SO_4 droplets of unknown concentration at approximately 100 °C at 400 mm Hg.

Figures 2 and 3 are pictures of the effect on Hastelloy. Various materials of construction, including 316L, Hastelloy C, and Hastelloy C lined with Ultimet (similar to Hastelloy, but contains Co for increased wear resistance) were previously trialed. The lifetime of these materials were less than12 months. In each case the head section remained pristine while the tail sections appeared as shown in Figures 2 and 3.

Initially, the degradation mechanism was thought to be erosion, in part, because the H_2SO_4 concentration entrained in the vapor was estimated at 2%. This concentration is normally suitable for Hastelloy-type material. The degradation seen in Figures 2 and 3, combined with the failure of wear-resistant Ultimet, made it apparent that corrosion was a factor to consider. For corrosion to be an issue with this material the entrained H_2SO_4 would have to be 10% or greater in concentration.

The Merck Index (*6*) indicates that Zr is “Very slightly attacked by hot concentrated sulfuric acid”. Furthermore, at the time (2008) Zr was approximately 30% cheaper than Hastelloy. Given this, a monolithic tailpiece made of nearly pure Zr was fabricated and trialed. This ejector, with a Hastelloy head and a Zr tailpiece, has now been in continuous service for five years. This trial tends to validate the hypothesis that the entrained H_2SO_4 concentration is greater or equal to 10% such that corrosion is the primary avenue of failure.

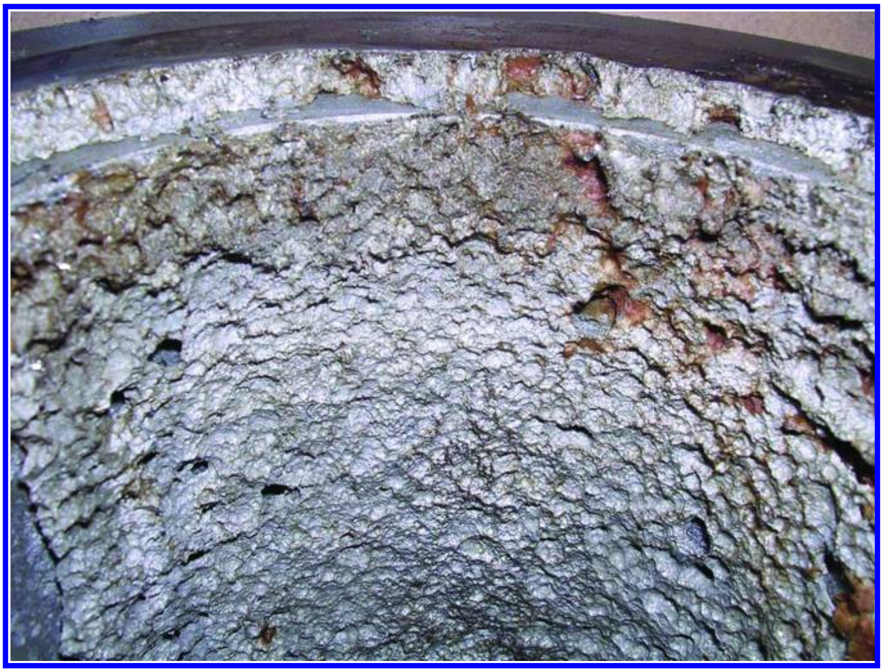

Figure 2. Diffuser Section (Hastelloy). (see color insert)

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Figure 3. Heat affected zone of weld at discharge flange (Hastelloy). (see color insert)

Heat Affected Zones in A611 for >95% HNO_3 Service

A 611 is a proprietary austenitic stainless steel containing approximately 6% Si. Si is known to aid in corrosion resistance in strong, hot (>50°C) HNO_3 acid because it is easily oxidized thereby providing a corrosion resistant layer. Corrosion was observed in A611 welded pipe at the following locations of each service temperature, with 70 °C showing the largest amount of degradation (Figures 4 and 5):

1. Weld Metal
2. Weld fusion line
3. Heat affected zone of the welding activity

The behavior observed in Figures 4 and 5 is quite different than that seen when solution annealed A610 (a slightly lower Si containing steel) is used in this facility. In fact, the non-solution annealed material in Figures 4 and 5 had a service life that was measured in months while the solution annealed material in nearly identical service had lifespans of several years.

In solution annealing, steel is heated to 50 °C above the austenitic temperature and held for sufficient time to allow the material to fully form austenite. The austenitic temperature is dependent upon the alloy (primarily upon the amount of Ni and Cr) and represents the transition of Fe from a body centered cubic crystal structure to a face centered cubic configuration (*7*). After treatment at this temperature, the material is usually quenched to form a homogenous equilibrium microstructure. This process is commonly completed after welding and/or cold

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working in order to insure that the steel is homogenous, i.e., carbon is fully solubilized and the alloy is not segregated into domains of various compositions.

Given that the material in question had not gone through the solution annealing process, we applied a combination of SEM and EDX to determine the size of the grain boundaries and its composition, respectively. These techniques were applied to areas that showed no apparent corrosion and areas that were visibly corroded, particularly the heat affected zone of the welds. AES was also employed to understand how the alloy may have changed as a function of depth through the metal along the heat affected zones.

Figure 4. Pipe in >95% HNO_3 70 °C Service. Corrosion is seen in between and along welds (white area). (see color insert)

Figure 5. Pipe in >95% HNO_3 50 °C Service. Note the corroded areas are less extensive. (see color insert)

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Figure 6 compares the SEM images of corrosion in a heat affected welding zone to that in a non-heat affected area. Round pegs were placed at the exact location of the analysis (the dark material behind the pegs held the pegs in place for the purposes of taking the top left picture). The images are taken from a pipe in the HNO_3 service in question. Intergranular corrosion is seen in the heat affected area at the field weld in 70 °C service (2nd peg from the left). The more homogeneous manufacturer's annealed fabrication weld, while not immune, shows greater resistance to attack (top right image; though hard to see, the field weld is the horizontal line in the middle of the image). The bulk pipe in the top right image appears more compositionally homogenous than either weld section.

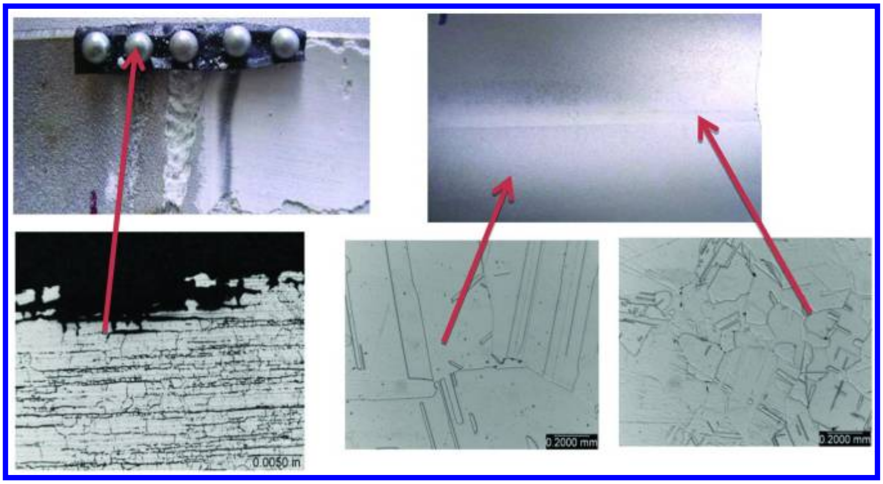

Figure 6. Micrographic Data. Arrows indicate the location of the SEM image (bottom) in relation to the optical image (top). Pictures grouped to the left are from a corroded section of piping corresponding to the heat affected zone (second dot—arrow point) or the field weld (middle dot, the weld is the vertical divot extending below the peg, that has the approximate width of the peg). The right group of pictures is from a non-corroded section of pipe where the left arrow points to the bulk of the pipe and the right arrow points to the original factory fabrication weld. (see color insert)

EDX data is presented in Figure 7. While the magnitude of the atomic spectral lines does not indicate abundance between elements, it does provide some indication of elemental abundance when comparing specific elements. In the corroded section, it is clear that Si is more abundant on the surface than in the non-corroded section. The white material seen along the sections of corroded pipe is essentially "sand" (SiO2) that has migrated to the surface. Given that Si is used in this grade of stainless to passivate the metal, it is clear that the depletion of this element in the bulk leads to more rapid corrosion than is seen in the non-heat affected zones or welds that had been solution annealed. Notice too the difference in relative abundance of Fe, Cr, Ni and O between the corroded and non-corroded areas. The non-corroded area is more homogenous and exhibits much less oxidation as evidenced by the lack of an abundance of Si “sand” deposited on its surface. It is apparent that inhomogeneity is influenced by the field weld activity.

Figure 8 is the elemental profile as a function of sputter depth from AES. There are two notable features. First, the predominance of Si, O and C at the surface of areas 1, 2 and 4 indicates that SiO2 forms at the surface. Given the data in Figure 7 and the overall obvious appearance of sand on the surface this is not surprising. At slightly greater depths, C appears. This indicates that SiC forms. Cr is seen along with C at slightly deeper sputter depths suggesting formation of CrC. This in effect lessens the amount of both Si and Cr available for passivation. It is likely that these materials form at the grain boundaries resulting in the appearance seen in Figure 6 bottom left SEM image.

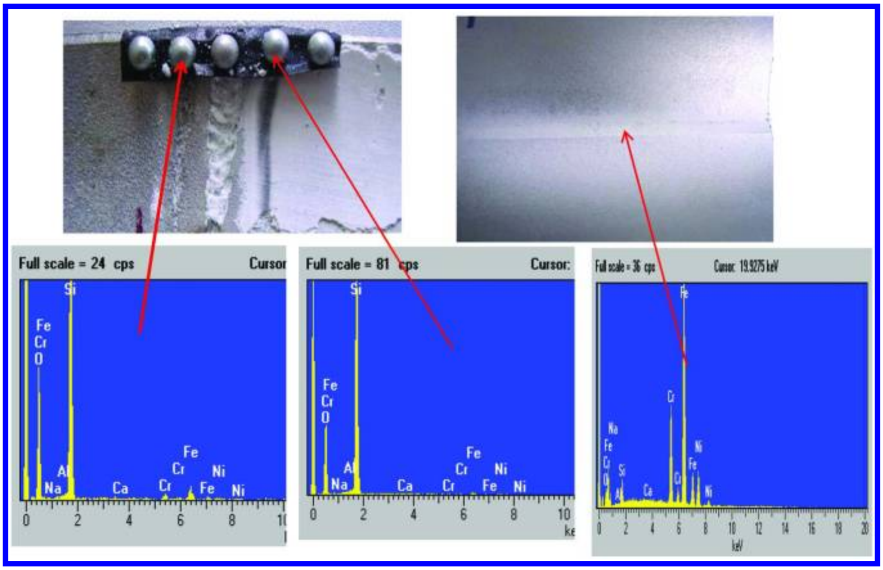

Figure 7. EDX data in relation to location. Arrows indicate the location of the EDX data (bottom) in relation to the optical image (top). The picture on the top left is from a corroded section of piping corresponding to the heat affected weld zone where the white “dust”, or “sand” seen in the optical image above (fourth dot) corresponds to the “dust” or “sand” seen in Figures 4 and 5. The second dot is in the same heat affected zone as the fourth dot; the only difference is that the white dust was removed for the sake of comparison via EDX. The top right picture is from a non-corroded section of pipe where the left arrow points to the original factory fabrication weld. (see color insert)

The second feature of note, area 3, the weld, contains Ca. This element is not inherent in the A611, but results from the weld slag. From a chemical compatibility perspective, the weld is likely the weakest point in the pipe. Since the heat affected zone is more inhomogeneous (as compared to solution annealed metal), attack at the weld leads to attack at the heat affected zone.

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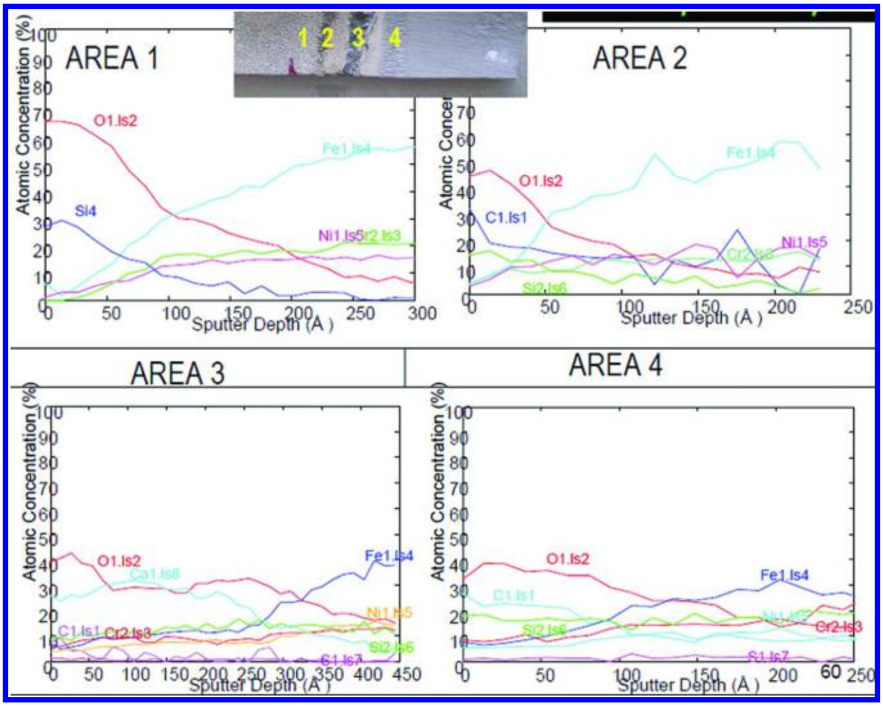

Figure 8. AES data on the corroded sections. Areas correspond to the optical image embedded in the figure, where area 3 is the weld. (see color insert)

Conclusion

Understanding the service environment of a manufacturing process is critical when choosing metallurgy for strong acid service. Accurate in-process measurements of temperature and concentration are invaluable. In the case of the SAC jet material issue process measurements can avoid the trial and error involved in specification of a construction material. However, in some cases, obtaining these measurements may be extremely difficult. In the absence of good in-process measurements, coupon testing is indispensable. Sometimes relatively inexpensive metals (e.g., Zr) yield very good lifetimes.

Cost of materials is important. Acceptable lifetimes vs. replacement cost must be defined: not all materials need to be expensive exotic metals such as Ta or Nb. Teflon-lined 304L eventually degrades, but in the proper nitric service, routine inspection demonstrates it can remain in use for >5 years.

Finally, as demonstrated in the A611 pipe example, a material is only as good as its weakest point of attack. In general, liners are chemically resistant (as opposed to impervious) and base metals/alloys are susceptible to stresses from fabrication (microstructure). These considerations must be balanced to achieve the most cost effective option to prevent unnecessary downtime.

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Editor’s Biography

Thomas L. Guggenheim

Thomas L. Guggenheim earned a B.S. degree in Chemistry from St. Olaf College in 1978 and a Ph.D. in Physical Organic Chemistry from the University of Minnesota (P.G. Gassman) in 1983. He began his career at the GE Corporate Research Center, working in the area of engineering thermoplastics, before moving to GE Plastics in Mt. Vernon, Indiana in 1989 (SABIC purchased GE Plastics in 2007). Since that time, he has worked on process chemistry optimization, new process development, process safety analysis, wastewater management, analytical method development, patent management, and is an expert in nitration chemistry and processes to manufacture polyetherimides.

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