



CHALMERS
UNIVERSITY OF TECHNOLOGY



Optimization of the Chematur Pump Nitration process for continuous production of Dinitrotoluene

Master of Science Thesis
Innovative and Sustainable Chemical Engineering Programme

Niklas Rendahl
Gabriela M. Rodríguez López

MASTER THESIS 2017

**Optimization of the Chematur Pump Nitration process
for continuous production of Dinitrotoluene**

NIKLAS RENDAHL
GABRIELA M. RODRÍGUEZ LÓPEZ



CHALMERS
UNIVERSITY OF TECHNOLOGY

Department of Chemistry and Chemical Engineering
Division of Chemical Engineering Design
CHALMERS UNIVERSITY OF TECHNOLOGY
Gothenburg, Sweden 2017

Optimization of the Chematur Pump Nitration process
for continuous production of Dinitrotoluene

Niklas Rendahl
Gabriela M. Rodríguez López

© NIKLAS RENDAHL & GABRIELA M. RODRÍGUEZ LÓPEZ, 2017.

Supervisor: Lars Stenmark, Chematur Engineering
Examiner: Gunnar Eriksson, Department of Chemistry and Chemical Engineering

Department of Chemistry and Chemical Engineering
Division of Chemical Engineering Design
Chalmers University of Technology
SE-412 96 Gothenburg
Telephone +46 31 772 1000

Cover: Toluene diisocyanate chemical plant designed by Chematur Engineering.

Typeset in L^AT_EX
Gothenburg, Sweden 2017

Optimization of the Chematur Pump Nitration process for continuous production of Dinitrotoluene

NIKLAS RENDAHL

GABRIELA M. RODRÍGUEZ LÓPEZ

Department of Chemistry and Chemical Engineering
Chalmers University of Technology

Abstract

One of the Chematur Engineering's technology specialties is the production of toluene diisocyanate (TDI). For its manufacturing, toluene is first continuously nitrated into dinitrotoluene (DNT) using their property Pump Nitration process; and further purified in a washing process. The pump nitration unit consists of two nitration stages, for MNT and DNT, using a mixed acid of nitric acid (HNO_3) and sulfuric acid (H_2SO_4) as the nitrating agent. The washing process reduces the impurities in the crude DNT product by three washing steps connected in series. First an acidic wash followed by an alkaline wash and finally a liquid-liquid extraction (LLE). The objective of this master thesis was to optimize both systems to improve the DNT yield and quality.

For the pump nitration pilot plant, the main objectives were to increase the isomer ratio of 2,4-DNT/2,6-DNT and to decrease the by-product concentration in the DNT product. A single replicate factorial design was used to find the optimum running parameters using the reaction temperature for both stages and the H_2SO_4 concentration in the DNT stage as the evaluated factors. Results from this factorial design showed that the optimum running condition were to increase the H_2SO_4 concentration in the DNT stage by 0.5% and to lower the reaction temperature in the DNT stage by 1°C calculated from the current commercial operation values. The MNT stage temperature was already at the optimum value. The optimum conditions were evaluated in a long run experiment, achieving 80.1/19.9 of DNT isomer ratio and reduction of by-products in the crude DNT. It was also found that the overall rate of reaction for the MNT stage is diffusion limited.

The main improvement for the washing station was to reduce impurities level below 50 ppm in the washed DNT. A lab scale experiment replicating the alkaline wash, showed the highest removal percentage with 99.9% of the mixed acids and 95.3% of nitrobenzoic acids at pH 7. With the extraction column, a Karr column, the optimum mass flow ratio between the DNT and fresh water was 0.8 and 128 rpm for the frequency of the reciprocating trays. The DNT produced in the long run experiment was washed using these optimum parameters. It was possible to remove 99.6% of mixed acids, 99.3% of nitrobenzoic acids and 32.3% of nitrocresols. The impurities of nitrocresols and nitrobenzoic acids were reduced below the target of 50 ppm. The mixed acids reached 83 ppm in the washed product.

Keywords: nitration, toluene, mononitrotoluene, dinitrotoluene, optimization, mass transfer, liquid-liquid extraction

Acknowledgements

I would thank Lars Stenmark of his supervision and valuable input and commenting on the thesis. I want to thank Anna Eriksson, Gert Wass and Stefan Johansson for the help that they provided during the experimental part of the master thesis. Thanks to Chematur Engineering for providing us with an apartment and possibility to use the company car. Thank my classmate Gabriela M. Rodríguez López for working with me on the thesis. I thank Gunnar Eriksson for being the examiner of the thesis. Finally, I want to thank my family for the support they have given me.

Niklas Rendahl, Gothenburg, June 2017

I would like to express my deepest gratitude to my supervisor, Lars Stenmark, for giving me the opportunity to pursue this master thesis project at Chematur Engineering. Thanks for your contribution to the project, which has been instrumental for the completion of the project goals, on such a short timeline.

I would furthermore like to thank the Chematur Technology Centre group, Anna Eriksson, Gert Wass and Stefan Johansson, for taking their time to help me during the experiments and, more importantly, making me feel at home.

My sincere thanks to all the colleges and friends for their support and encouragement to fulfill my goals in Sweden. To Carolina Braga, Anali Guzman, Ruth Garcia, Isabella Fröderberg, Jeanette Rivera, Mariangelli Colón and Divia Jimenez; thanks for all the fantastic time that we pass together, I wish you much successes in your new life chapter.

Quisiera dedicarle este trabajo a mi familia. Gracias por todo su apoyo, comprensión y buenos deseos para lograr mi sueño. Gracias por ese amor incondicional al dejarme extender mis alas en busca de un mejor futuro. Los amo con todo mi corazón!

Gabriela M. Rodríguez López, Gothenburg, June 2017

Contents

List of Figures	xiii
List of Tables	xv
1 Introduction	1
1.1 Background	1
1.2 Project Purpose	1
1.3 Limitations	2
1.4 Methodology	2
1.5 Thesis outline	3
2 Theory	5
2.1 Nitration Chemistry	5
2.1.1 Electrophilic substitution reaction	5
2.1.2 Nitration of Toluene	6
2.1.2.1 Mononitration Step	6
2.1.2.2 Dinitration Step	7
2.1.3 Effects of physico-chemicals conditions in the nitration of toluene	8
2.1.3.1 Effect of mixed acids	8
2.1.3.2 Effect of introducing reactants	10
2.1.3.3 Effect on the overall rate of reaction	11
2.1.3.4 Effect of temperature	12
2.1.4 Secondary reactions in the nitration of toluene	13
2.1.5 Purification of Dinitrotoluene	14
2.1.5.1 Liquid-liquid extraction (LLE)	15
2.1.5.1.1 Categories of LLE equipment	16
2.1.5.1.2 Mass Balance of multiple stage counter-current extraction	17
2.1.6 Treatment of waste water from purification of DNT	17
2.2 Design and Analysis of Experiment	18
2.2.1 Factorial Design	18
2.2.1.1 Statistical Analysis of single replicate 2^3 factorial de- sign	19
2.2.1.1.1 Estimated Effects	19
2.2.1.1.2 Analysis of Variance (ANOVA)	20
2.2.1.1.3 F test statistic	21

	2.2.1.1.4	Sum of Squares	22
	2.2.1.1.5	Degrees of Freedom	23
	2.2.1.1.6	P-value approach	23
3	Problem Description		25
3.1	Description of the Pump Nitration Pilot Plant		25
3.1.1	Improvement in the pilot plant		25
3.1.2	Selected parameters for optimization of the pilot plant		26
3.2	Description of the crude DNT washing step		26
3.2.1	Improvement in the washing step		27
4	Safety Aspects		29
4.1	Chemicals		29
4.1.1	Reactants		29
4.1.1.1	Toluene		29
4.1.1.2	Sulfuric acid 95-97%		29
4.1.1.3	Nitric acid fuming 99.9%		29
4.1.2	Products		30
4.1.2.1	Mononitrotoluene		30
4.1.2.2	Dinitrotoluene		30
4.1.2.3	Trinitrotoluene		30
4.1.2.4	Nitrobenzoic acid		30
4.1.2.5	Dinitrobenzoic acid		30
4.1.2.6	Mononitrocresol		30
4.1.2.7	Dinitrocresol		30
4.1.2.8	Trinitrocresol		30
4.2	Overview of risks of the pilot plant		31
4.2.1	Pump nitration pilot plant risks		31
4.2.2	Washing steps risks		31
5	Experiment		33
5.1	Factorial Design Experiment		33
5.2	Steady state experiment		34
5.3	Overall rate of reaction experiment		34
5.4	Washing step experiment		35
5.5	Analytical tools		35
5.5.1	Analytical tools for the organic phase		36
5.5.1.1	Gas chromatography		36
5.5.1.2	High-performance liquid chromatography		36
5.5.2	Analytical tools for the acidic phase		37
5.5.2.1	Acid-base Titration		37
5.5.2.2	Redox Titration		37
5.5.3	Extraction of organics in the aqueous phase		38

6	Results	39
6.1	Pump Nitration Pilot Plant Experiments	39
6.1.1	Original factorial design	39
6.1.2	Single replicate 2 ³ factorial design analysis	41
6.1.3	Steady state experiment	44
6.1.4	Mass balance results for the pump nitration system	44
6.1.5	Overall rate of reaction experiment	48
6.2	Washing step experiment	49
6.2.1	Alkaline wash pH experiment	49
6.2.2	Optimization of the Karr column	50
6.2.3	Washing of the DNT produced in the steady state experiment	51
6.2.4	Mass balance results for the washing system	53
7	Discussion	55
7.1	Factorial Design	55
7.1.1	Original factorial design	55
7.1.2	Single replicate 2 ³ factorial design analysis	56
7.2	Steady state experiment	58
7.2.1	Mass balance for the pump nitration system	60
7.2.2	Overall rate of reaction experiment	61
7.3	Washing step experiments	62
7.3.1	Alkaline wash pH experiment	62
7.3.2	Optimization of the Karr column	62
7.3.3	Washing of the DNT produced in the steady state experiment	63
7.3.4	Mass balance for the washing system	64
8	Conclusions	65
A	Appendix 1	I
A.1	Pump Nitration pilot plant flow sheet	III
A.2	DNT washing step flow sheet	V
B	Appendix 2	VII
C	Appendix 3	XI
C.1	Factorial Design data	XI
C.2	Steady state experiment	XII
C.3	Washing step experiments	XIV
D	Appendix 4	XV

List of Figures

2.1	Example of electrophile substitution reaction with nitronium ion and benzene.[9]	6
2.2	The three different isomers of mononitrotoluene: <i>ortho</i> -, <i>meta</i> - and <i>para</i> - position, respectively.[6]	7
2.3	The two intermediates formed as a result of the <i>o</i> - and <i>p</i> - attack in the production of MNT.[10]	7
2.4	The 6 isomers of DNT.[6]	8
2.5	A ternary mixture diagram of HNO ₃ , H ₂ SO ₄ and H ₂ O with the different region of MNT and DNT production.[6]	9
2.6	Oxidation secondary reaction in nitration of toluene.[17]	14
2.7	The formation of a Meisenheimer complex of TNT.[20]	15
2.8	Pulsed Columns: (a) Examples [21] and (b) Mass balance	16
2.9	Example of 2 ³ factorial design.[24]	18
2.10	Example of F distributions.[24]	21
2.11	Example of a Normal Probability Plot and Half-Normal Plot of the estimated effects.[24]	23
6.1	Half-Normal plot of 2,4-DNT% content in the final product response	41
6.2	Half-Normal plot for the MNT content in the DNT stage	42
6.3	Half-Normal plot of Toluene content in the MNT stage	43
6.4	Toluene concentration [%] in the MNT stage at different flow rates during the overall rate of reaction experiment: ▲ for base case flow rate; ● low flow rate; ■ high flow rate.	48
A.1	Flow sheet diagram of the Pump nitration pilot plant	III
A.2	Flow sheet diagram of the DNT washing step	V
D.1	GC chromatogram of the REW produced by washing the DNT product of the steady state experiment	XVII

List of Tables

2.1	Example of isomers distribution in the MNT product at different temperatures.[6]	7
2.2	The isomer distribution in the crude DNT product.[6]	8
2.3	Solubility of DNT in acids at different H ₂ SO ₄ concentrations [%] and temperatures.[6]	11
2.4	Design matrix for a 2 ³ factorial design	19
5.1	Selected parameters and levels for single replicate 2 ³ factorial design .	33
6.1	Change of mixed acid concentration [%], in both stages, during Experiment 6	39
6.2	Organic phase composition [%], in the MNT stage, for Experiment 5 and 6 of the original factorial design.	40
6.3	Organic composition [%], in the DNT stage, for Experiment 5 and 6 of the original factorial design.	40
6.4	Nitrobenzoic acids composition [ppm], at both stages, for Experiment 5 and 6 of the original factorial design.	40
6.5	ANOVA results of 2,4-DNT% content in the final product response using $F_{0.1,1,6}=3.78$	41
6.6	ANOVA results for MNT content in the DNT stage response using $F_{0.1,1,2}=8.53$	42
6.7	ANOVA results for Toluene content in MNT stage response using $F_{0.1,1,2}=8.53$	43
6.8	Comparison of the organic composition, at both stages, between the steady state experiment and Experiment 9	44
6.9	Change of mixed acids concentration [%], in both stages, during the steady state experiment	45
6.10	Overall mass balance [g] of the steady state experiment	45
6.11	Sulfuric acid mass balance [g] for the steady state experiment	45
6.12	Nitric acid mass balance [g] for the steady state experiment	46
6.13	Toluene mass balance [g] for the steady state experiment	46
6.14	Crude DNT production [g] for the steady state experiment	47
6.15	Approximation of the HNO ₃ and toluene reacted in secondary reactions during steady state experiment.	47
6.16	Summary of the results for the overall rate of reaction experiment. . .	48
6.17	Nitrobenzoic acids concentration [ppm] before and after re-heating the DNT product of Experiment 9	49

6.18	Average concentration of mixed acid concentration and nitrobenzoic acids with percentage of removal.	49
6.19	Impurities removal [%], at different flow rates of fresh water entering the Karr column	50
6.20	Impurities removal [%], at different frequency of the Karr column reciprocating trays	50
6.21	Phases composition [%] in different streams of the DNT washing step.	51
6.22	Nitrobenzoic acids mass content [g] in different streams of the DNT washing step.	51
6.23	Impurities removal [%] in the washed DNT product from the steady state experiment	52
6.24	Concentration of organics [%] in the outlet streams of the washing step	52
6.25	Overall mass balance on the washing system	53
6.26	DNT specie mass balance on the washing step	53
B.1	Chemical compounds with the code name and structure	VII
C.1	Organic phase composition [%] at both stages	XI
C.2	Products composition [ppm] of secondary reactions in the organic phase at both stages	XI
C.3	Organic phase composition [%], at both stages, for the steady state experiment at shutdown time	XII
C.4	Organic phase composition [%], at both stages, for the Experiment 9 at shutdown time	XII
C.5	Nitrobenzoic acid composition [ppm] in the organic phase, at both stages, for the steady state experiment at shutdown time	XIII
C.6	Nitrobenzoic acid composition [ppm] in the organic phase, at both stages, for the Experiment 9 at shutdown time	XIII
C.7	Organic phase composition in the MNT stage for overall rate of reaction experiment	XIII
C.8	Phases composition of crude and washed DNT at different parameters of the Karr column	XIV

1

Introduction

1.1 Background

The demand of polyurethanes are increasing globally. The main market areas are rigid and flexible foams; with 32% and 36% of the total polyurethane market, respectively.[1] One of the primarily raw material for production of polyurethanes is toluene diisocyanate (TDI).[1] In 2016, the global capacity of TDI was 3.2 million tone.[2]

In the sector of flexible foams for transportation and furniture industry, 87% of the TDI global production is used.[3] The major markets for this chemical in 2014 were Europe and Asia; mainly by the increase in the automobile market.[4] To be competitive in the TDI market, constant improvement of the technology is required to maximize production revenues of TDI.

One of Chematur Engineering's technology specialties is the production of TDI manufactured in three steps. First, toluene is nitrated into dinitrotoluene (DNT) via their proprietary Pump Nitration continuous process.[5] Then crude DNT goes through a washing step. The washed DNT is hydrogenated into toluene diamine (TDA); which is phosgenated to produce TDI.[5]

In this master thesis, the project was concentrated on studying and optimizing the first stage including the DNT washing step. With the purpose of continuing with research and development of their pump nitration technology, Chematur build a representative pilot-plant with a washing step section downstream. These equipments were facilitated for the development of this master thesis.

1.2 Project Purpose

This master thesis work has being subdivided into two main areas of study: production of DNT with pump nitration technology and purification of the crude DNT. In the first area of study, there are some indications that the DNT quality with respect to isomer distribution is somewhat different from other processes. Thus, the main objectives are to optimize the nitration of toluene and find the optimum running parameters for the pilot plant. In order to improve the DNT quality, it is also important to minimize secondary reactions that occur during nitration of toluene.

In the second area of the study a relative unproven section of the pilot plant was used. It is of interest to understand, in more detail, the washing step and to verify that it works in accordance with the separation and mass transport theory. The main goal of the washing step study is to reduce the presence of acids and impurities to as low level as possible.

1.3 Limitations

All the master thesis work was conducted at Chematur Engineering Technology Centre in Karlskoga, Sweden. A re-design of the pump nitration plant with the washing step was outside the scope for this project. The main limitation was the experimental time required for the pump nitration pilot plant. It was necessary to make an extensive literature study related to the subject to identify the most significant parameters for the pilot plant optimization. In order to complete all the experiments inside the time frame available, the equipment provided by the company was used. Moreover, the crude DNT produced in the pilot plant optimization experiments was used for studying the DNT washing step. Therefore, a careful planing of the DNT washing step experiments was needed in order to accomplish the goals with the quantity of DNT available.

1.4 Methodology

To accomplish the optimization of the pump nitration goals, a single replicate full factorial design experiment was performed. It composes a total of 9 experiment where 3 selected parameters were studied. Furthermore, the result from this factorial design was tested in an additional experiment for a longer period of time. The main idea was to analyze the pilot plant behavior and product, at steady state condition. Lastly, changes in flow rates entering the mononitrotoluene (MNT) reactor were tested to evaluate if the overall rate of reaction is kinetic or diffusion limited.

For the DNT washing step, laboratory experiments were initially done replicating the first two washing stages of the pilot plant. In this way, it was possible to minimize the amount of crude DNT used for studying and optimizing these washing stages. The laboratory experiment results, where implemented in the actual DNT washing pilot plant to further optimize the last washing stage.

Results from these two experiments, laboratory scale and optimization of the third washing stage, were used to study washing of the crude DNT obtained from the long run experiment of the pump nitration pilot plant. In such matter, the washing capacity of the pilot plant was analyzed to verify that the DNT washing step goals were accomplished.

1.5 Thesis outline

This project is divided into 8 chapters, as follows.

Chapter 1, introduction of the master thesis project; including background, project purpose, limitations, methodology and outline.

Chapter 2, present the scientific literature study and chemical engineering theory used to accomplish the master thesis work. This includes the nitration chemistry and the Design of Experiment background in depth, as well as, basic knowledge of liquid-liquid extraction. In the nitration chemistry section the reaction of toluene into MNT and DNT is discussed; and how different parameters affect the nitration. In the Design of Experiment section, the factorial design is discussed, including the evaluation of the effects of the selected parameters.

Chapter 3, a detailed version of the problem description, including the pilot plants description, is given.

Chapter 4, all the used chemicals are presented with their general physical and chemical properties, including hazards. Also, an overview of risks in the pilot plants and the safety protocols used.

Chapter 5, present the experiments procedure used. Also, a description of the sample handling and analytical tools used.

Chapter 6, present all the results.

Chapter 7, a discussion of all experimental results.

Chapter 8, conclusions with recommendation for future work.

2

Theory

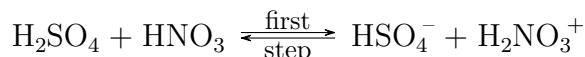
2.1 Nitration Chemistry

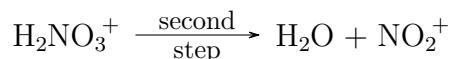
Nitration of aromatic compounds is one of the earliest organic reactions to be investigated, around the 18th century and developed at industrial level in the earliest years of the 19th century.[6, 7] In 1742, Rudolf Glauber was the first chemist to obtain picric acid by acting on wool and horn with nitric acid (HNO_3).[6] After this discovery, reactions with HNO_3 and different organic compounds started to be investigated. In 1834, the German chemist Eilhardt Mitscherlich, nitrated benzene into nitrobenzene. But it was not until 1842 Nikolay Zinin when reduced nitrobenzene into aniline, that a rapid development of nitrating organic compounds on industrial scale was made.[6, 8] Throughout time, a variety of practical uses for nitrated compounds has been discovered. They can be used as intermediate organic compounds or as end products. For examples, in the production of dyes, perfumes and medical substances, the nitrated compounds are used as intermediates.[6] In explosives, like trinitrotoluene (TNT), the nitrated compound is the final product.

2.1.1 Electrophilic substitution reaction

An electrophilic substitution reaction is a reaction that has, as the first step, an attack of an electrophile. This is an ion or molecule deficient of an electron and can therefore accept one.[9] This reaction is characteristic of aromatic compounds, like toluene, due to the delocalized electrons in the ring. One example of this substitution reaction is the nitration of aromatic compounds; the nitro groups ($-\text{NO}_2$) are introduced on to the aromatic ring.[6]

This reaction can be carried out as a direct or indirect introduction of the nitro group. With indirect introduction of the nitro group; a different compound group is introduced first and later then substituted with the nitro group. One example of this indirect substitution reaction is the nitration of phenols, where a sulphonic acid group ($-\text{SO}_3^-$) is introduced first and then the nitro group. Direct substitution requires a nitrating agent to introduce the nitro group by substitution of a hydrogen from the ring. Example of these nitrating agents are concentrated HNO_3 or a mixture of it with sulfuric acid (H_2SO_4), among others.[6] In the mixed acid process, the electrophile nitronium ion (NO_2^+) is produced in two step:





Then the NO_2^+ will react with the aromatic compound, producing an intermediate known as the sigma complex. Its name refer to the creation of a *sigma*-bond in the ring.[9] The complete reaction, using benzene as the aromatic compound, can be seen in Figure 2.1.

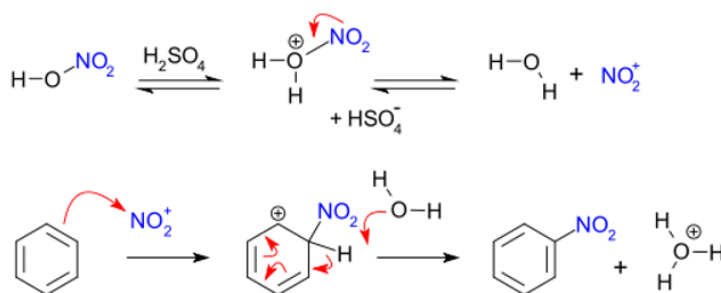


Figure 2.1: Example of electrophile substitution reaction with nitronium ion and benzene.[9]

As the number of nitro group substitutions increases, it becomes more difficult. This phenomena is due to that the intermediate has a higher activation energy (E_a) to go through another electrophile substitution reaction.[10] The sigma complex tend to be a resonance stabilizer as a result of only containing 4 π electrons.[9]

2.1.2 Nitration of Toluene

Compared to nitration of benzene, the nitration of toluene occurs faster. The methyl group attached to the benzene ring is an electron donating group promoting the rate of reaction.[10] This methyl group will also affect the position of the first nitro group attached to toluene.

2.1.2.1 Mononitration Step

In the mononitration step, toluene is reacting with the NO_2^+ to form three possible isomers: *ortho*(*o*)-, *meta*(*m*)- and *para*(*p*)- MNT. The *o*- group refer to a group located at the adjacent carbon of the methyl group. The *m*-group will be located at the carbon number 3, starting counting with the carbon linked to the methyl group. The *p*-isomer has the nitro group opposite to the methyl group. The three MNT isomers are shown in Figure 2.2.

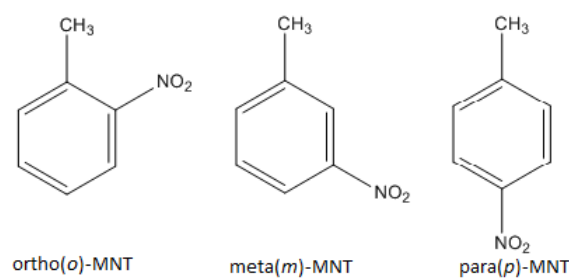


Figure 2.2: The three different isomers of mononitrotoluene: *ortho*-, *meta*- and *para*- position, respectively.[6]

Table 2.1: Example of isomers distribution in the MNT product at different temperatures.[6]

Temperature [°C]	Composition of the product [%]		
	<i>o</i> -isomer	<i>p</i> -isomer	<i>m</i> -isomer
30	56.9	39.9	3.2
60	57.5	38.5	4.0

The predominant isomers of the mononitration product, are the *ortho* and *para*; see Table 2.1. This is due to that the methyl group creates an inductive electron release promoting the *o*- and *p*- substitution; see Figure 2.3.[10] For that reason, the methyl group is known as an *o*-/*p*- director.[9]

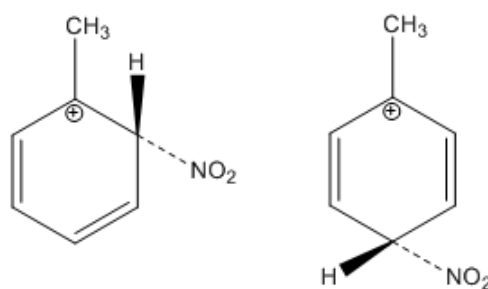


Figure 2.3: The two intermediates formed as a result of the *o*- and *p*- attack in the production of MNT.[10]

2.1.2.2 Dinitration Step

A second nitro group substitution in toluene is done by the dinitration step; where the MNT is further nitrated into DNT. It has 6 possible isomers, which are shown in Figure 2.4.

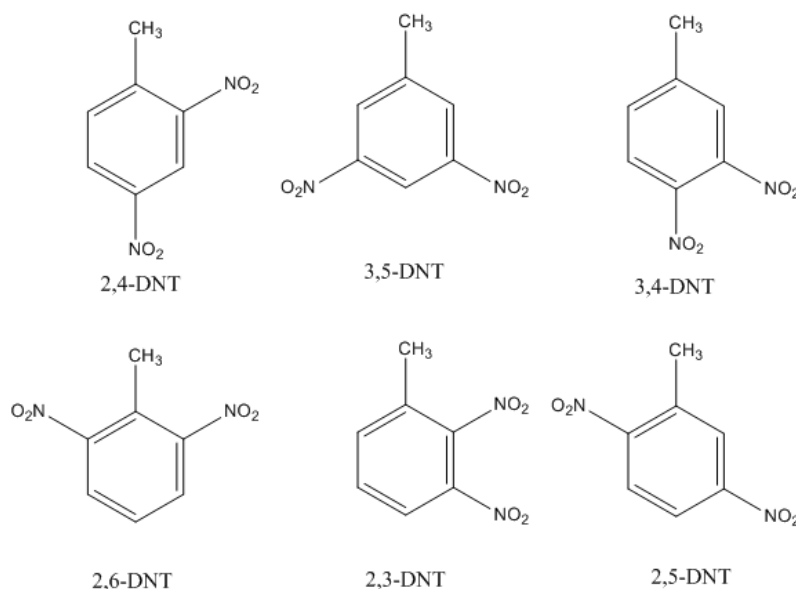


Figure 2.4: The 6 isomers of DNT.[6]

The isomers produced in the MNT reaction, are responsible for the DNT isomers that are formed. The *o*- and *p*-nitrotoluene has a tendency to form 2,4-DNT while only the *o*-nitrotoluene gives the 2,6-DNT isomer. The *m*-isomer is responsible for creating the rest of the DNT isomers. The 2,4-DNT and 2,6-DNT isomers are the most abundant.[6] Usually, the percentage, by only considering these two isomers, are 80% of 2,4-DNT and 20% of 2,6-DNT.[11] A normal composition example of the DNT final product is shown in Table 2.2.[6]

Table 2.2: The isomer distribution in the crude DNT product.[6]

DNT isomers	Percentage [%]
2,4-dinitrotoluene	76.1
2,6-dinitrotoluene	19.8
3,4-dinitrotoluene	2.25
2,3-dinitrotoluene	1.23
2,5-dinitrotoluene	0.54
3,5-dinitrotoluene	0.08

2.1.3 Effects of physico-chemicals conditions in the nitration of toluene

2.1.3.1 Effect of mixed acids

The presence of H_2SO_4 in the nitration mixture has two purposes. To increase the solubility of the aromatic compound in the mixture; and the production of nitronium ions (NO_2^+) by ionizing the HNO_3 . [10] The production of NO_2^+ will increase

the speed of reaction. The water content will increase during the nitration process and will tend to dilute the acids.[6] H_2SO_4 has the ability to bind the water, thus higher H_2SO_4 concentration is preferable to create a buffer conditions to prevent the dilution of the nitrating acids too much, otherwise the nitration of toluene could be affected. If the final product is required to have a lower concentration of *m*-nitrotoluene, a higher H_2SO_4 concentration is preferred.[6]

HNO_3 is acting, as both, a nitration agent and an oxidation agent.[6] The type of reaction is dependent of the concentration of HNO_3 . At higher concentration of HNO_3 , it acts more as a nitration agent. If the HNO_3 is diluted, it behave as an oxidizing agent.[6] This behavior is further discussed in Section 2.1.4.

It is also important to consider the composition of each acids in the the nitrating mixture: HNO_3 , H_2SO_4 and water.[6] Kostevish and Sapozhnikov developed a ternary diagram showing the areas that favor a specific nitration product with respect to the acid composition.[6] This can be seen in Figure 2.5.

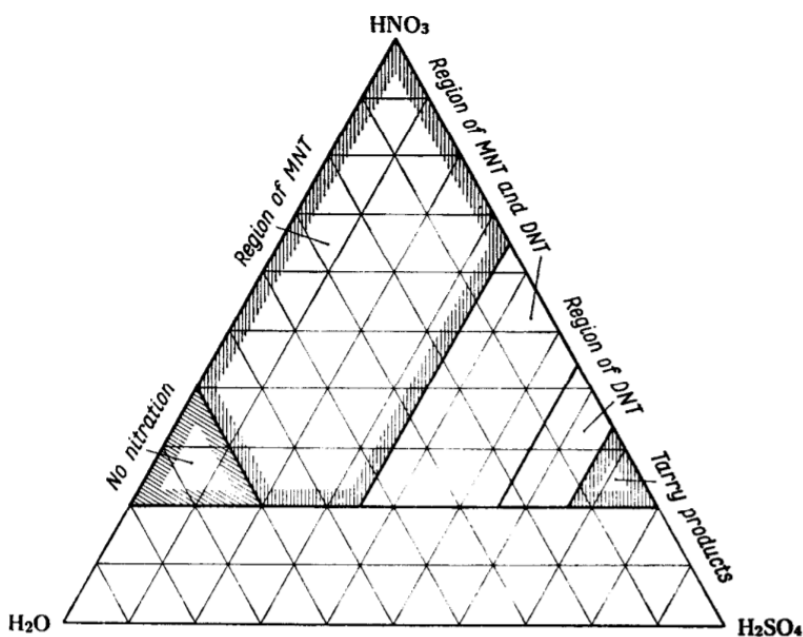


Figure 2.5: A ternary mixture diagram of HNO_3 , H_2SO_4 and H_2O with the different region of MNT and DNT production.[6]

The composition of the nitrating mixed acid affect the desired product and needs to be chosen carefully. As can be seen in Figure 2.5, if the HNO_3 is relative low in the mixed acid, tarry products can be obtained. This region is not favorable because it ruin the nitrating mixed acid and not desirable products are going to be obtained. For that reason, an excess of HNO_3 is preferable in each nitration stage to avoid this zone.

In MNT production, only a slightly excess of HNO_3 is needed; around 0.5-2.0%.[6] If the desired product is DNT, around 2.0% of HNO_3 is preferable in order to avoid

the tarry region. If further nitration is required, a higher excess of HNO_3 and strong fuming H_2SO_4 is needed due to the difficulty to introduce a third nitro group.[6]

2.1.3.2 Effect of introducing reactants

The mixed acid used in each nitration stage is called spent acid (SPA). The spent acid is recycled in each stage mainly to reduce acid consumption. All of the excess of acid from the DNT stage is recycled to the MNT stage. The way of introducing the SPA can affect the reaction and product formation. Two different methods has been proposed:

- In the first alternative, the SPA is mixed with concentrated HNO_3 to obtain the correct nitration mixture before adding it to the organic reactant.[6] The first drawback is an increment in temperature due to the heat of dilution between concentrated HNO_3 and a SPA that has a significant water content. The second drawback is that the organics is put in contact with a high concentration mixed acid. This results, that in the beginning, the reaction is vigorous and produce another increase in temperature. Hence, these increment in temperature can produce an uncontrolled reaction; which should be avoided for safety purposes.
- The second method is introducing the organic to the SPA and then introduce the concentrated HNO_3 slowly.[6] With this approach the nitration proceeds slowly and in a more controlled way. This second method is safer than option one.

The addition of the organic reactant can affect the overall reaction; existing three different ways:

- Adding the toluene to mixed acid
- Adding the mixed acid to toluene
- Introduce them simultaneously into the reactor

As T. Urbański explained in [6], the first alternative is the most applied. However, as a drawback, the first amount of organic substance added to the acid will have a higher HNO_3 excess with a risk to over nitrate. If the substance is sensitive to a higher concentration of acid it can decompose. In the second alternative, there is an insufficient amount of HNO_3 because it will react instantaneously with the high concentration of toluene at the beginning. As advantage, this will avoid to go beyond mononitration. However, with aromatic compounds like toluene, nitrating with an insufficient amount of HNO_3 would form the tarry matter that will ruin the nitrating acids. The best alternative is the third option. It can be use for a continuous nitration process. The nitration reaction takes place in the acidic phase; thus it is required to first saturate this phase with the organic before the reaction takes place. This will provide a control of the reaction, avoiding violent reactions or over-nitratation.

Even though the DNT reaction is performed at harsher conditions of mixed acid concentration and temperature, this reaction occur more slowly due to the difficulty of introducing a second nitro group. Because of this, the order of mixing of the organic and nitrating acids is not that important.

2.1.3.3 Effect on the overall rate of reaction

The MNT and DNT reaction are heterogeneous reactions which will cause the overall rate of reaction dependent of kinetic and mass transport effects. In a heterogeneous reaction, an interface between the organic and aqueous phases is produced. Thus, it is necessary to overcome diffusion effects in order to increase the reaction rate.

An alternative is to increase the solubility of the organic phase into the acidic phase. In Table 2.3 it is shown that the solubility of DNT in the mixed acid increases with temperature and H_2SO_4 concentration.[6] The same behavior is valid for MNT, see reference [6, p. 269].

Table 2.3: Solubility of DNT in acids at different H_2SO_4 concentrations [%] and temperatures.[6]

H_2SO_4 %	Solubility of DNT [g/100 g acid]					
	20°C	40°C	50°C	70°C	100°C	120°C
80.0	1.2	-	2.5	3.8		
83.6	-	3.6	4.7	6.3	6.4	6.5
88.7	6.1	10.0	12.8			17.4
90.0	8.5	-	16.8	20.0	-	-
93.0	-	26.4	33.8	58.3	82.4	66.6
99.8	-	72.6	14.4	1121	1360	-

By saturating the acid phase with the organic phase, diffusion limitations are minimized leading to an increase of the overall rate of reaction.

Creating a good mixing inside the reactor will also increase the mass transport. In a batch or continuous stirred-tank reactor (CSTR), good mixing is achieved by increasing the rotational speed of the stirrer (rpm). In a continuous system, the adequate plug-flow reactor (PFR) that enhance good mixing is known as a static mixer. This PFR reactor promotes in-line turbulent conditions to increase the mixing of two fluids with different properties like viscosity and density.[12]

By having a good mixing, the overall rate of reaction will be similar to the kinetic reaction rate; which is only dependent on temperature and reactants concentration. If the mixing is poor, the nitration rate is dependent on diffusion transport effects, decreasing the overall rate of reaction. This can also lead to a uneven distribution of acid molecules, known as dead space, where the acid is trapped without organics due to it higher density.[6] The problem that can occur is if the mixing suddenly

increases and the dead volume start disappearing, the organic will be in contact with the acid causing a vigorous reaction and rapid increase in temperature. This can lead to an increase of by-products and secondary oxidation reactions.[6]

One way to quantify this mixing effect in the reactor, is calculating the Reynolds (Re) number inside the static mixer at different feeding flow rates. The Re is a ratio between the inertia forces and the viscosity forces acting on the fluid.[13] This dimensionless number give an idea of the flow condition inside the static mixer. Higher flow rate will produce higher Re; as can be seen in Equation 2.1.

$$Re = \frac{\rho \vartheta D_H}{\eta} \quad (2.1)$$

where ρ is the density of the fluid [kg/m^3], ϑ is the mean velocity entering to the static mixer [m/s], D_H is the hydraulic diameter [m] and η is the dynamic viscosity of the fluid [$\text{Pa}\cdot\text{s}$]. It is important to use the D_H in the calculations because a percentage of the volume inside the static mixer is occupied by the mixer blades. Higher Re is an indication of better mixing. Therefore, if the rate increases when Re increases it indicates that the overall rate of reaction is diffusion limited. On the contrary, if the rate stay unaffected, the overall rate of reaction is only limited by the kinetics.

Additionally, a kinetic limited reaction can be evaluated by changing the residence time (τ) for reaction; the time where reactants stays inside the reactor (see Equation 2.2).

$$\tau = \frac{V}{Q} \quad (2.2)$$

where V is the total volume of the reactor [m^3] and Q is the volumetric flow entering the reactor [m^3/s]. Without any physical changes in the static mixer length or volume, this property can be evaluated by changing the flow rate to the reactor. Higher flow rate will give lower τ ; while decreasing the flow rate increases τ . Higher τ means higher time for the reaction to occur inside the reactor. Thus, it is expected an increment in product yield if the reaction is limited by the kinetic. The opposite behavior will show up if the reaction is diffusion limited due to decreased mass transport efficiency.

2.1.3.4 Effect of temperature

The nitration of toluene is an exothermic reaction where the temperature will have a significant effect on yield and selectivity. As it is known, the rate of reaction is dependent on temperature by a rate constant (k) that follow the Arrhenius equation.[13]

$$k = A * e^{\left(\frac{-E_a}{RT}\right)} \quad (2.3)$$

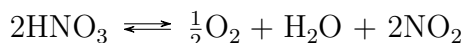
where A is the pre-exponential factor of, E_a the activation energy, R the gas constant and T is the absolute temperature.

For the MNT reaction, the E_a for the *ortho* and *para* isomer are lower than the *meta* isomer because, as it was discussed in Section 2.1.2.1, the first two isomers are more favoured. However, as the nitro groups substitution increases, the E_a also increases due to the difficulties in adding a new group (See Section 2.1.1).[10] For that reason, the temperature condition for the MNT reaction is lower than what is required for the DNT reaction.

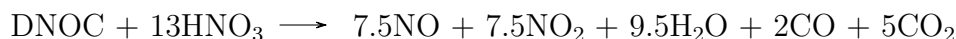
On the other hand, if the temperature is increased, more substitution of nitro group and oxidation side reactions will occur. Thus, the temperature is preferable kept as low as possible. Especially at the start-up of the MNT process it is important to avoid violent reaction and decreases in product yield. Lastly, the DNT reaction has a restriction limit where the temperature can not be more than 120°C because it is consider dangerous with risk of explosion and not lower than 70°C because of risk of crystal formation.[6, 14]

2.1.4 Secondary reactions in the nitration of toluene

Every time a nitro group is added to toluene, it withdraws an electron, deactivating the ring. With a highly deactivated aromatic compound, elevated temperature and high acid concentration will promote oxidation side reactions. For 3,5-DNT, oxidation is the only reported way of continued reaction.[15] D. Ross et. al. concluded in [15] that the thermal decomposition of HNO_3 is responsible for the oxidation side reactions in MNT and DNT production. The nitrogen dioxide NO_2 produced by thermal decomposition, is considered as the oxidizer.[15] The net reaction of HNO_3 decomposition is the following:



The two pathways of oxidation reactions in nitration of toluene are, the oxidation of the methyl group and ring oxidation.[16] Toluene, without any substitution, can ready be oxidized. This is the reason of finding cresols in the MNT product.[6] After this, the introduction of nitro groups produce nitrocresols.[6] Oxidation of the methyl group produce, for example, phenols, benzaldehyde and benzoic acids in the reaction product. These compounds can be nitrated into nitrophenols, nitrobenzaldehyde and nitrobenzoic acid; respectively.[16] See Figure 2.6 for the chemical reaction path for these by-products. Further oxidation of these products, including their isomers, will lead to creation of more by-products. One example is the total oxidation of dinitrocresols, according to following chemical reaction¹:



Finally, a dark colored complex can be produced when the system contains too low excess of HNO_3 and high content of nitrogen oxide (NO) in the nitrating acid.[6] The composition of this complex is $\text{C}_6\text{H}_5\text{CH}_3 \cdot 2\text{ONOSO}_3\text{H} \cdot 3\text{H}_2\text{SO}_4$. This complex can be broken down by adding more HNO_3 if the concentration of the mixed acid is high enough, obtaining nitrotoluene. On the other hand, if the HNO_3 concentration is

¹Based on Aspen Plus database

practically nonexistent, the complex will start decomposing, forming tarry matter.[6]

It is important to minimize or stop these secondary reaction in nitration of toluene as they create a reduction in yield, problems in the purification process and creation of volatile materials (eg.NOx).[15]

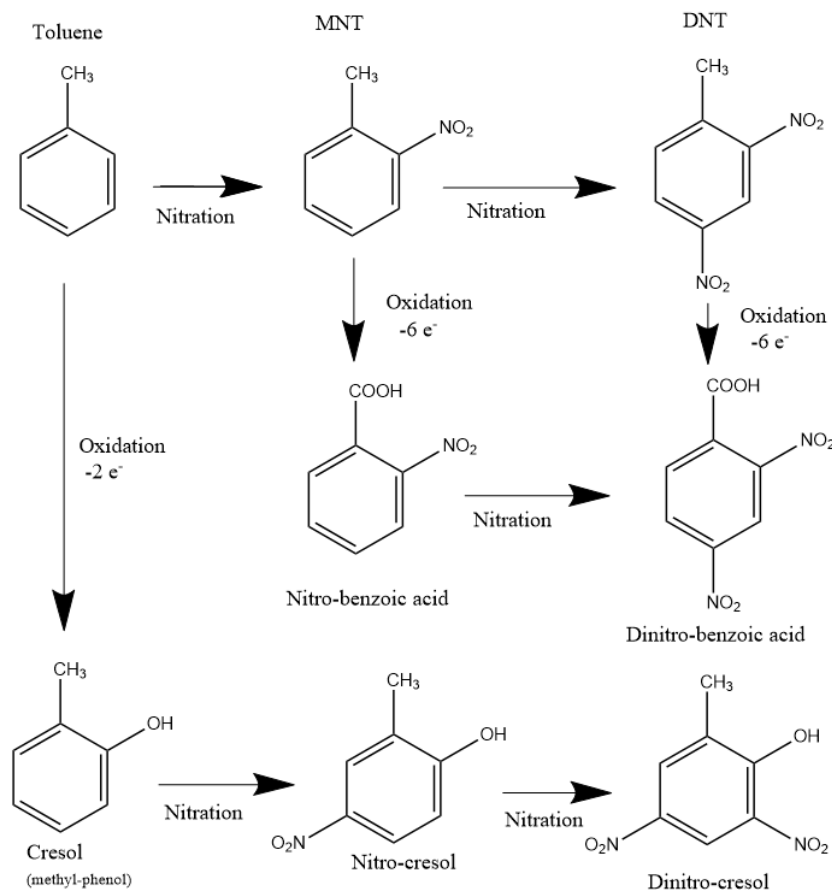


Figure 2.6: Oxidation secondary reaction in nitration of toluene.[17]

2.1.5 Purification of Dinitrotoluene

The crude DNT from the nitration process contains impurities like nitrating acids and by-products from secondary reactions. Before using DNT in the production of TDI, these impurities need to be removed. Washing with water is done to remove the acids in the crude DNT. The waste washing water turns into a yellow color due to the high concentration of acid residues. Thus, this waste water is known as yellow water (YEW).[18]

For the removal of nitrocresols and aromatic carboxylic acids (eg. nitrobenzoic acids), an alkaline wash is used. They are converted into water-soluble salts corresponding to the base used and recovered in the aqueous phase.[19, 18] Examples of bases are sodium carbonate (Na₂CO₃), sodium bicarbonate (NaHCO₃), ammo-

nia (NH_3) and sodium hydroxide (NaOH).[18] The pH value for this washing stage should be above 7 and the base used should have a concentration of 2-10%. [19] The waste water of the alkaline solution will turn to dark red due to the presence of salts of nitrocresols. This is why it is called red water (REW).[18, 6]

As the pH increase above 9 the hydroxide ion in the aqueous phase can form a Meisenheimer complex with the aromatic compound.[20] This complex adds a hydroxide ion to the aromatic ring of DNT and/or TNT (see figure 2.7).[20]

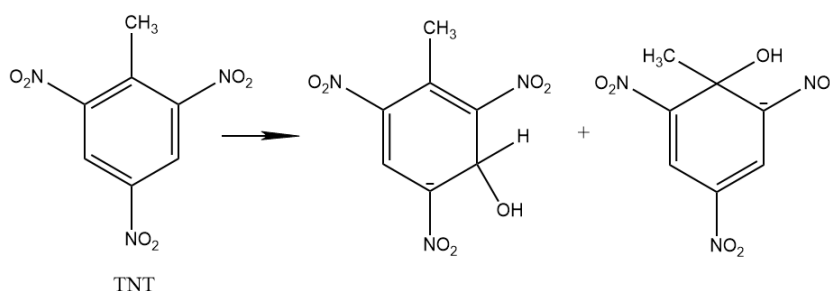


Figure 2.7: The formation of a Meisenheimer complex of TNT.[20]

The DNT is more resistance to the alkaline hydrolysis than TNT; as consequence TNT Meisenheimer formation is more common.[20] When this complex is formed, the final color of DNT and TNT is reddish being difficult to remove.[20] The Meisenheimer complex will cause downstream problems during the TDI production lowering the total product yield.

The third washing step is using a liquid-liquid extraction (LLE) to remove traces of acids, organics and any excess of the base used.[18, 6]

2.1.5.1 Liquid-liquid extraction (LLE)

In a LLE, a specific solute is removed from a solution by using a liquid solvent.[21] The main requirement for this separation technology is that the solvent is immiscible with the solution to be extracted. Only the solute will be soluble in both liquids. The efficiency will be enhanced by a two-phase system with a large interfacial area. Increasing the interfacial area between the phases, will enhance the mass transport of the solute from the solution to the solvent.[21]

However, a real extraction is not ideal. Small traces of solvent can be soluble in the treated solution. This can make the density and interfacial tension of each phase will be similar; making the separation between them difficult. Thus, LLE can not be used if the difference in density ($\Delta\rho$) and interfacial tension ($\Delta\gamma$) between the solution and the solvent is not large enough.

2.1.5.1.1 Categories of LLE equipment The most efficient and used method industrially for LLE is counter-current feeding of the solution to be extracted and the solvent.[12] There exist different equipment designs for this separation technique because sometimes $\Delta\rho$ between the two liquids phases is not large enough to enable good phase separation. If low $\Delta\rho$, one is forced to use low velocities of the inlet streams and, as consequence, reduce the interfacial mass transfer rate.[21] External motion can be included in the equipment design to improve the interfacial mass transfer rate.[21] Solvent extraction equipment can be classified in three categories:

1. **Static:** Spray, sieve trays and packed columns are example of this category. This category has relatively low efficiency. For the spray column, the interfacial area relays only in the size of dispersed phase droplets created by the spray nozzle. The sieve tray and packed columns has an increased mass transfer efficiency by adding the trays and packing material respectively. Both trays and packing material improve the interfacial area for mass transfer in comparison with the spray column.[22]
2. **Pulsed:** Pulsed columns has the feature to periodically and vertically move the two phases at a specific frequency.[21] This pulsation effect causes a decrease in droplet size which increase the interfacial area of mass transfer. This category of LLE column can be found with sieve trays and packed material. A modification of the pulsed sieve tray column is the Karr column. The distinction of this column from the others is the reciprocating perforated trays in vertical direction with a specific amplitude and frequency.[23] It has a gear on top to create the movement of the trays (See Figure 2.8). Some advantages for this type of columns are higher extraction efficiency and lower power requirement, lower axial mixing area and higher extraction yield.[23, 22]
3. **Agitated:** This category of extraction devices are equipped with agitator elements inside. They have high efficiency of separation but the lowest capacity.[22]

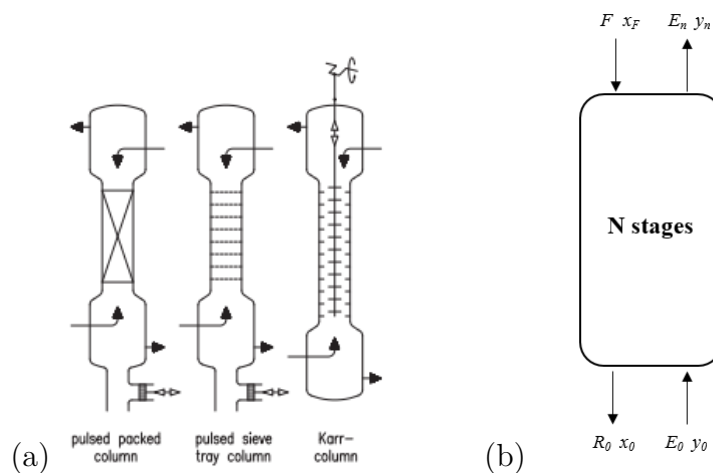


Figure 2.8: Pulsed Columns: (a) Examples [21] and (b) Mass balance

2.1.5.1.2 Mass Balance of multiple stage counter-current extraction The feed solution (F) and the solvent (E_0) enter counter-currently into the column. The feed solution will decrease the concentration of the solute, impurities, from x_F to x_0 . The solvent will increase its solute concentration from y_0 to y_n . Index 0 and n referred to the first and last stage of the system, respectively. At the end, the solute outlet stream is known as extract (E_n) and the treated feed stream is known as raffinate (R).

The total mass balance is:

$$F + E_0 = R_0 + E_n = M \quad (2.4)$$

where M represent the overall concentration of both phases. The solute mass balance is the following:

$$Fx_F + E_0y_0 = R_0x_0 + E_ny_n = Mz \quad (2.5)$$

where z is the solute fraction in M . The larger the E_0 flow rate, the lower solute content will be in R_0 . However, lower concentration of solute will be present in E_n . This makes it difficult to regenerate the extract before recycling it back into the LLE. For that reason it is important to determine the minimum amount of solvent needed to be fed into the column in order to achieve the required purity level in the raffinate and to be easier to regenerate the extract afterward.

2.1.6 Treatment of waste water from purification of DNT

All the waste water produced during the purification of DNT needs to be recovered for further treatment. This waste water has high levels of soluble DNT and MNT, which can be extracted in order to increase the product yield before it is sent to further treatment. From the YEW, up to 98% of H_2SO_4 and HNO_3 can be recovered.[19] This allows to recycle back these acids into the nitration plant. However high concentration of nitrocresols and nitrobenzoic acid in the REW needs to be treated before the waste water is disposed. The main reason is that these nitro compounds are toxic to the bacteria used in biological waste water treatment plants.[19]

2.2 Design and Analysis of Experiment

During optimization of products or processes, different scientific experiments can be designed in order to gather more information, understand the system and obtain a robust process.[24] Through these experiments it is possible to change deliberately one or more variables, also known as factors, in order to observe an effect in the studied response(s).[24] One alternative of experimental design is known as the classical. It consist in varying one variable at the time. The main disadvantage of this method is that it does not consider possible interactions between the selected factors in the study. In order to consider the interaction effects between factors, a factorial experimental design is an alternative. This experimental design increases the precision of results while it reduces the amount of experiments needed to make conclusions valid for the studied range of experimental conditions.[24]

2.2.1 Factorial Design

In factorial experiment design, all possible combination of the levels of the selected factors (k) are tested in a statistical approach.[24] These levels are normally addressed as low ($-$) and high ($+$) values for each factor as can be seen in Figure 2.9. The total number of experiments needed to complete a specific factorial design will depend on the number of selected factors and levels. For example, if only two levels are going to be tested for each factor; the total number of experiments is 2^k .

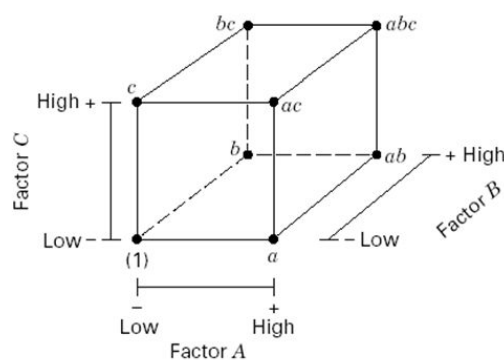


Figure 2.9: Example of 2^3 factorial design.[24]

In Figure 2.9, three factors were selected giving a total of 8 experiments; plus experiment 9 known as the center point. The design matrix containing all the experiments needed for this factorial design is shown below in Table 2.4.

Table 2.4: Design matrix for a 2^3 factorial design

Experiments	A	B	C	AB	AC	BC	ABC	Label
1	-	-	-	+	+	+	-	(1)
2	+	-	-	-	-	+	+	a
3	-	+	-	-	+	-	+	b
4	+	+	-	+	-	-	-	ab
5	-	-	+	+	-	-	+	c
6	+	-	+	-	+	-	-	ac
7	-	+	+	-	-	+	-	bc
8	+	+	+	+	+	+	+	abc
9	0	0	0	0	0	0	0	0

In Table 2.4, two different notations are used to describe the treatment combination in each experiment. First, the effect coding is shown, where $-$ and $+$ signs are used to indicate the low and high value selected for each factor.[24] The second form is called the label form where lower capital letters are used to indicate the high level of each factor; and the (1) indicates that all the factors are at the low level.[24] Both notations are presented in Figure 2.9.

The experiments or runs should ideally be performed in a complete randomized order. The main reason is due to the statistical method used for the evaluation of the results. As it is established in [24], the observations must be independently distributed random variables. However, there exists situations, like in chemical processes, where performing a complete randomization of the experiments is extremely difficult because of the added time and cost. In those situations, nested-designs are useful. Here, all the experiments in one of the levels were performed randomly; and then the experiments with the other level were performed randomly.

2.2.1.1 Statistical Analysis of single replicate 2^3 factorial design

In this section it will be explained how to perform the statistical analysis of a single replicate 2^3 factorial design.

2.2.1.1.1 Estimated Effects First it is required to calculate the estimated effects for each factor, including their interactions. As it is explained by D.C. Montgomery in [24], the effect can be defined as the change in a response (Y) produced by a change in the level of the evaluated factor. To explain how this is calculated it is necessary to refer back to Figure 2.9. Using factor A as an example, the right side of the cube correspond to results obtained when the factor A is at high level (Y_+); and the left side of the cube contain the results corresponded when factor A is at the low level (Y_-). Thus, the estimated effect of a factor is calculated by a change of averaged results between the high and low level. This is demonstrated in the following formula:

$$\text{Effect} = \frac{\sum Y_+}{n_+} - \frac{\sum Y_-}{n_-} \quad (2.6)$$

where n refer to the number of observations at each level.[25] Using Equation 2.6 the estimated effects for each main factor is the following:

$$A = \frac{(a + ac + abc + ab)}{4} - \frac{((1) + b + c + bc)}{4} \quad (2.7)$$

$$B = \frac{(b + ab + abc + bc)}{4} - \frac{((1) + a + c + ac)}{4} \quad (2.8)$$

$$C = \frac{(c + bc + abc + ac)}{4} - \frac{((1) + a + b + ab)}{4} \quad (2.9)$$

Looking at Equation 2.7, it is noticed that the signs that complement each label are equals to the multiplication of the effect coding column of factor A with the label column presented in Table 2.4. The same occur for B and C factor. Thus, to calculate the estimated effects of the interactions, the effect coding column needs to be obtained for them (See Table 2.4). The effect coding column for an interaction is the product of the corresponded columns of the factors that compose it. For example, the AB interaction, is the product of the effect coding column of A and B. At the end, each factor should have the same amount of + and -; this property is known as orthogonality. This property indicate that no correlation exist among the factors; thus their effect estimation are completely independent.[25]

After calculating the estimated effects for each factors connected to an specific response, the magnitude and direction of each result can be preliminary evaluated. Both, magnitude and direction will gave an indication in which level these factors should be to influence the evaluated response. The sign of the estimated effect results will correspond to the direction. Thus, a + sign indicates that the factor should be increased from the low to the high level in order to favor the studied response; while a - sing correspond to the opposite behavior. Additionally, the magnitude of the estimated effect will preliminary establish which of the included factors in the factorial design has an influence in the studied response. However, from these results it can not be concluded which factor is more significant to have an effect in a specific response. For that reason, an analysis of variance, also known as ANOVA, is needed.

2.2.1.1.2 Analysis of Variance (ANOVA) It is a statistical method used to test the difference between two or more means (μ_i); also it can be expressed in term of the variance (σ^2).[24] For the statistical test of a factorial design, two hypothesis can be drawn. First, the null hypothesis (H_0) said that all the means corresponded to each factors are equal; or no difference in variance occur. This suggest that non of the factors included in the factorial design has a significant effect in the evaluated response.[24] If the H_0 is rejected, the alternative hypothesis (H_1) indicates that at least one means is different; or there is at least a difference in variance. This suggest that at least one factor included in the factorial design has a significant effect in the evaluated response. The statistical significant test can be summarized in terms of

the μ as follow:

$$\begin{aligned} H_0 : & \mu_A = \mu_B = \mu_C = \mu_{AB} = \mu_{AC} = \mu_{BC} = \mu_{ABC} \\ H_1 : & \mu_i \neq \mu_j \text{ for at least one pair (i, j)} \end{aligned}$$

And in terms of the σ^2 is the following:

$$\begin{aligned} H_0 : & \sigma_A^2 = \sigma_B^2 = \sigma_C^2 = \sigma_{AB}^2 = \sigma_{AC}^2 = \sigma_{BC}^2 = \sigma_{ABC}^2 = 0 \\ H_1 : & \sigma_i^2 \neq 0 \text{ for at least one factor (i)} \end{aligned}$$

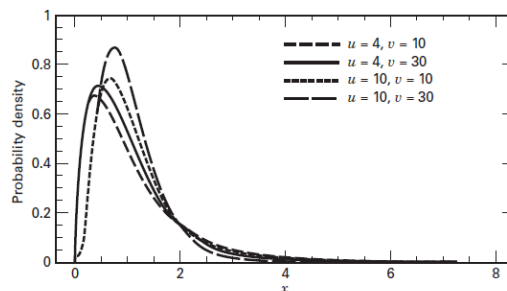


Figure 2.10: Example of F distributions.[24]

2.2.1.1.3 F test statistic To evaluate the statistical hypothesis, the F distribution is used. An example of a F distribution is showed in Figure 2.10 where is characterized by having non negative values and skewed to the right. The random variable F is defined as the ratio of two independent chi-square (χ^2) random samples; each one divided by their degrees of freedom (ν).[26] The formula for the F distribution is the following:

$$F_{\nu_1, \nu_2} = \frac{\chi_1^2 / \nu_1}{\chi_2^2 / \nu_2} \quad (2.10)$$

where the index 1 and 2 referred to the two evaluated random samples.

The χ^2 distribution is used when a sampling distribution can be defined in terms of normal random variable.[24] In the evaluation of the statistical hypothesis for factorial design and using the Cochran's Theorem (see in [24, p. 74]); the χ^2 distribution can be expressed as follow:

$$\chi^2 = \frac{SS}{\sigma^2} \quad (2.11)$$

where SS is the sum of squares of the evaluated samples. This makes possible to re-write Equation 2.10 as follow:

$$F_0 = \frac{SS_1 / \nu_1}{SS_2 / \nu_2} \quad (2.12)$$

where SS/ν equals to the mean square, MS which is used as an estimation of σ^2 for each evaluated sample.[24]

In the factorial design the index 1 correspond to the evaluated factors and the index 2 correspond to the error. The MS_{Error} is actually the estimation of σ^2 within the selected factors of the factorial design. If H_0 is true, MS_{Factor} is an estimation of σ^2 as well. However, if H_0 is rejected, the MS_{Factor} is greater than the true variance; indicating that the numerator of Equation 2.12 is larger than the denominator. Thus, is possible to re-write the H_1 as $\sigma_{Factor}^2 > \sigma_{Error}^2$. This indicates that the region to reject the H_0 is located at the upper region of the one-tail F distribution showed in Figure 2.10; known as the critical region.[24] In conclusion, test statistic to reject the H_0 is the following:

$$F_0 > F_{\alpha, \nu_1, \nu_2}$$

where: F_0 is the F value calculated with Equation 2.12 and F_{α, ν_1, ν_2} is the F value obtained in the F-table corresponded to the chosen significance level (α), degree of freedom of the numerator (ν_1) and denominator (ν_2). The F_{α, ν_1, ν_2} will define the critical region or rejection region for the hypothesis test; also known as F-test.[24]

Due to the fact that this statistical hypothesis test is based on experimental data, it can lead to miscalculation of the critical region in the F distribution. For that reason it is necessary to selected a significance level which will indicate the probability of rejecting the H_0 when this is true.[24] In the majority of the experiments, it is known that a certain deviation in μ_i occurs; for that reason a certain level of error needs to be assumed. The most common α assumed is 0.05; equivalent to a 95% of confidence level.[25] This indicates that exist a 95% of probability that the H_0 could or couldn't be rejected. Being F tests statistic as a fixed significance level testing.[24]

2.2.1.1.4 Sum of Squares In order to evaluate the F-test, it is important to calculate the SS with it respective ν . For the ANOVA of a single replicate full factorial design, 3 different SS are necessary: a sum of square for each factor (SS_{Factor}), the sum of square of the error (SS_{Error}) and the total sum of square (SS_{Total}). The SS for each factor (including the interaction) in a single replicate 2^3 full factorial design can be expressed in terms of the already calculated estimated effect with Equation 2.6:

$$SS_{Factor} = 2 \times \text{Effect}^2 \tag{2.13}$$

And for the SS_{Total} , a summation of each SS_{Factor} is done.

The determination of SS_{Error} is done by evaluating which factors does not have a significant effect into the evaluated response. Usually, as their is an increment in the interaction order, less significant those factors are; for example ABC interaction. However, statistical tools can be implemented in order to select insignificant factors for the estimation of SS_{Error} . Examples of that are the normal and half-normal probability plots.[24] Negligible effects are normally distributed, which means that has a zero μ and a variance σ^2 . These factors will tend to follow the line of the normal or half-normal probability plot (See Figure 2.11).

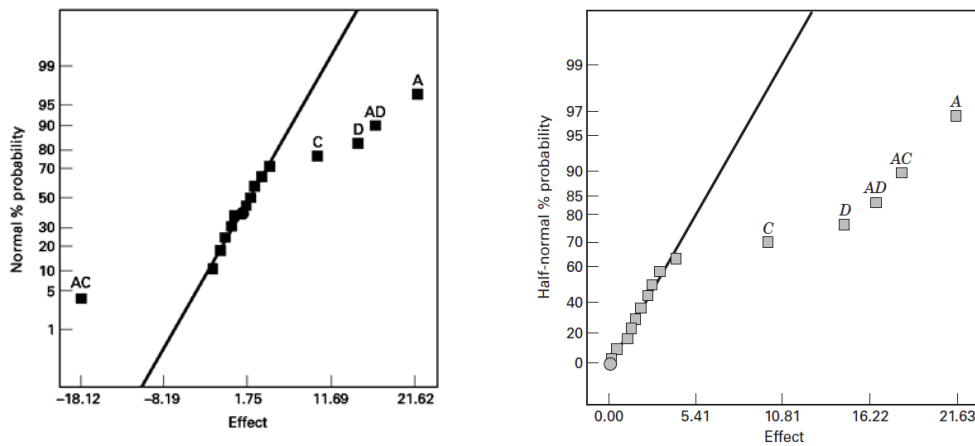


Figure 2.11: Example of a Normal Probability Plot and Half-Normal Plot of the estimated effects.[24]

The difference between the normal and half-normal probability plot is that this last one contain the absolute value of the estimated effects; making it easier to interpret the graph when working with fewer factors, like 2^3 factorial design. In both graphs, those factors that follow the straight line, their respective SS can be summed up to estimate the SS_{Error} .

2.2.1.1.5 Degrees of Freedom As is established by D. C. Montgomery in [24], the numbers of ν for sum of squares correspond to the numbers of independent elements in that sum of squares. For each factor, including the interactions, the ν equals to one; while ν for SS_{Total} is the total number of factors minus 1. For the error, the degrees of freedom will correspond to the number of factors used for the estimation.

2.2.1.1.6 P-value approach Statistical soft-wares, like Minitab® and JMP®, use the p -value approach together with the F test statistic to determine significance factors in hypothesis testing. The main reason is that the critical region defined with the F-test statistic does not established how far away the computed F_0 is from this region. The p -value approach will determine the risk of falsely reject the H_0 with the calculated F_0 ; by calculating the smallest α value that will lead to a false rejection of H_0 . [25] Thus, to consider a factor significant the F test statistic inequality should be true and the p -value as small as possible.

3

Problem Description

3.1 Description of the Pump Nitration Pilot Plant

The process flow diagram is shown in A.1. The pilot plant consists of two reaction loops, one for the MNT stage and one for the DNT stage. In each loop an acidic phase is circulated at a relatively high flow rate by a loop pump which also serves as the primary mixing of reactants. Before the pump the organic species to be nitrated is introduced as well as the required amount of HNO_3 to maintain a stable HNO_3 concentration in the loop. To the DNT loop, concentrated H_2SO_4 is also added to absorb the water generated in the nitration and hence maintain a stable H_2SO_4 concentration at the desired level in the loop.

Following the pump, is a static mixer section with a few seconds' residence time where the intensive mixing of the organic and the acidic phase is maintained to complete the reaction. The reaction is exothermic and there is no cooling in the reaction zone, meaning that the reaction is in adiabatic mode. Temperature transducers are mounted in this section to follow the progress of the reaction by the temperature increase, approximately 10°C in each loops. After the static mixers, the heat of reaction is removed in a cooler before the mixture is fed to a static separator where the organic and acidic phase is separated. Most of the acidic phase is returned to the suction side of the loop pump to complete the loop. The organics and excess acid, equal to what has been fed to the loop, overflows into a second separator where the organic and acidic phase are separated.

In the DNT loop, crude DNT is collected as the light phase and the acidic phase, mostly H_2SO_4 , is transferred by gravity to the MNT loop to serve as the reaction media for the MNT loop. In the MNT loop, crude MNT is separated as the light phase, collected in a vessel, and then pumped to the DNT loop to be further nitrated. The heavy acidic phase is collected as spent acid (SPA). As there is no addition of concentrated H_2SO_4 in the MNT loop, the H_2SO_4 concentration in the SPA will be lower than in the acid flowing from the DNT loop.

3.1.1 Improvement in the pilot plant

Although being used commercially for a long time, there are aspects of the process that still needs investigation. It is of interest to see if the isomer ratio 2,4-DNT /2,6-DNT can be increased above 80/20 by optimizing the conditions. A decrease in the formation of by-products, like nitrocresols and nitrobenzoic acids is also of

interest. Additionally, it is of interest to decrease the MNT and TNT present in the final DNT to levels below 1000 ppm.

3.1.2 Selected parameters for optimization of the pilot plant

In order to accomplish the above requirements, a single replicate 2^3 factorial design was chosen. The factors included in this factorial design are: Reaction temperature for the MNT and DNT stages and H_2SO_4 concentration in the DNT stage. As was discussed in Section 2.1.3; the reaction temperature in both stages affects the rate of reaction and slightly the isomer ratio. The H_2SO_4 concentration in both stages is also significant for improvement of the isomer ratio of the DNT product as discussed in Section 2.1.3. However, in the pump nitration technology there is no direct control of the H_2SO_4 concentration in the MNT stage. As explained in Section 3.1, a recycle stream of the mixed acid from the DNT stage is transferred to the MNT stage which is diluted by the water generated in the nitration. To fulfill the overall mass balance the acid must flow unrestricted from the DNT stage to the MNT stage. The H_2SO_4 concentration in the MNT stage will therefore be directly linked to the corresponding concentration in the DNT stage.

Additionally, it is of interest to evaluate if the reaction in the MNT stage has mass transport limitation affecting the overall reaction rate. The aim is to maximize toluene conversion in this stage by making the overall reaction rate dependant only on the intrinsic kinetics. Therefore, the loop flow rate was another parameter in the evaluation.

3.2 Description of the crude DNT washing step

Crude DNT obtained from the pump nitration plant contains residues of acids, NO_x and products from side reactions (see Section 2.1.5). In Section 2.1.4 is discussed that these impurities consists of nitroresols and aromatic carboxylic acid caused by secondary reactions of toluene. These impurities can cause further problems in the downstream steps in the production of TDI. The washing process is divided in 3 stages connected in series, to remove all impurities as shown in Figure A.2.

The first stage consists of washing the crude DNT with fresh water to remove the dissolved and suspended acids: H_2SO_4 , HNO_3 and HNO_2 . This stage is known as the acidic washing with YEW as waste water. Then, the washed DNT and the YEW is separated using a static separator. The YEW is stored in a small container in order to recirculate a portion of it to reduce the fresh water consumption in this stage and to minimize the DNT losses due to its solubility in the YEW.

Next, the DNT passes to the second section, the alkaline wash, where NaOH is fed into the second washing tank to remove the residual mineral acids and the weak acids produced by side reactions. A pH meter is used to maintain pH between 7-8.

The organic and aqueous phase, the REW, is separated in another static separator.

Finally, the third stage is composed of a counter-current column of the Karr type where LLE is done in order to remove the sodium salts of impurities and mineral acids. The solvent is fresh water, which enters counter-current to DNT. Wash water from the Karr column is used in the alkaline wash in order to minimize fresh water consumption and increase the recovery of washed DNT.

Both REW and YEW are collected in separated containers to be treated to recover acids and DNT.

3.2.1 Improvement in the washing step

The goal of the washing step is to reduce the impurities in the washed DNT below 50 ppm. For that reason, it is important to optimize each washing step. For the second stage, it is important to determine the optimum pH value to decrease the impurities but avoid new side reactions. In the third stage, an optimization of the Karr column is required. Therefore, the feed flow of the solvent and DNT, and variation in the frequency of the reciprocating trays are the parameters selected for evaluation.

3. Problem Description

4

Safety Aspects

To perform the experiment in a safer way all the hazards of the chemicals are needed to consider in order to make a risk assessment.

4.1 Chemicals

All the chemicals used during this master thesis work were handled as highly pure components or as mixtures. The information provided in this section is based on the PubChem Substance and Compound databases and the book "*Thermophysical properties of chemicals and hydrocarbons*".[14, 27]

4.1.1 Reactants

4.1.1.1 Toluene

A colorless liquid with a molecular weight (M.W.) of $92.13g/mol$; has a density of $0.867g/cm^3$ at $20.0^\circ C$. Toluene is highly flammable with a flash point at $4.0^\circ C$. It can causes skin irritation.

4.1.1.2 Sulfuric acid 95-97%

It is an oily colorless liquid with a M.W. of $98.08g/mol$. It has a boiling point of $290.0^\circ C$, a density of $1.84g/cm^3$ at $25.0^\circ C$ and it is strongly corrosive. May be harmful if it is swallowed and fatal if it is inhaled. It can cause skin burns and eye damage.

4.1.1.3 Nitric acid fuming 99.9%

It is pale yellow liquid with red-brown fuming gases, with a density of $1.512g/cm^3$ at $20.0^\circ C$ and M.W. of $63.012g/mol$. Its boiling point is $83.0^\circ C$, it is miscible with water and an oxidizer. This chemical is very toxic when it is inhaled. It is corrosive to metals, tissue and skin, causing severe skin burns and eye damage. It does not produce fire but can intensify it. Thus precaution with fire hazards needs to be taken into consideration. Fuming HNO_3 is decomposed into NO_2 which react with the methyl group of toluene creating nitrous acid (HNO_2).[15]

4.1.2 Products

4.1.2.1 Mononitrotoluene

The color of MNT is pale yellow with an odor close to bitter almond. It is soluble in most organic solvents. It has a M.W. of $137.138g/mol$. The boiling point is $83^{\circ}C$ and density of $1.16g/cm^3$ at $25.0^{\circ}C$. MNT is toxic if inhaled and contact with skin.

4.1.2.2 Dinitrotoluene

DNT is a pale yellow crystalline material that has a density of $1.3210g/cm^3$ at $25.0^{\circ}C$ and a boiling point at $300.0^{\circ}C$. It also has a slight odor of bitter almonds. The M.W. is $182.135g/mol$. Soluble in organic solvents. Toxic when inhaled and on skin contact. It has a carcinogenic substance. Very toxic to aquatic life.

4.1.2.3 Trinitrotoluene

TNT has physical properties of yellow crystals with a density of $1.625g/cm^3$ at $70.0^{\circ}C$ and a M.W. of $227.132g/mol$. It has a boiling point of $240.0^{\circ}C$ and it can explode at elevated temperatures, being a major hazard. TNT is soluble in organic solvents. It can cause serious irritations on the skin and eyes and it is very toxic for aquatic life.

4.1.2.4 Nitrobenzoic acid

Yellowish-white crystals with a density of $1.55g/cm^3$ at $32^{\circ}C$ and a M.W. of $167.12g/mol$. It is slightly soluble in water. It can cause skin irritations and serious eye irritation.

4.1.2.5 Dinitrobenzoic acid

It is a solid with a M.W. of $212.117g/mol$ and a density of $1.6517g/cm^3$ at $25.0^{\circ}C$. Causes skin irritation and serious eye irritations.

4.1.2.6 Mononitrocresol

A powder with a yellow to orange color with a M.W. of $153.14g/mol$ and at density of $1.034g/cm^3$ at $20.0^{\circ}C$. It can cause skin irritation and serious eye irritation.

4.1.2.7 Dinitrocresol

A yellow solid with no smell. M.W. of $198.134g/mol$ and a density of $1.3723g/cm^3$ at $89.3^{\circ}C$. It has a boiling point at $312.0^{\circ}C$. Soluble in organic solvents. It can cause serious eye damage and is very toxic to aquatic life.

4.1.2.8 Trinitrocresol

A yellow solid with M.W. of $243.131g/mol$ and a density of 1.556 at $47.5^{\circ}C$. Explosive and harmful in contact with skin.

4.2 Overview of risks of the pilot plant

By analyzing the material safety data sheet of the chemicals, a general review of the safety precautions was done. The safety gear provided was lab coat, lab goggles, rubber gloves, extra strong rubber gloves to handle fuming HNO_3 and safety shoes resistance to chemicals. A gas mask with extra filtration (Sundstrom SR 500) was near the pilot plant as a precaution if any chemical spill and if needed when loading of chemicals.

4.2.1 Pump nitration pilot plant risks

The most likely event for an accident was during the refilling of chemicals and loading of the mixed acids or liquid DNT. To perform it in a safe way, the refilling of chemicals bottles were done in a ventilated hood. To remove acid stains, paper with water was used and, before discarding the used paper, more water was added to avoid possible ignition. The pure reactants for the reaction were stored in glass containers, while the products were stored in plastic containers. Usually, the DNT produced was stored in a plastic container that allows re-heat up to 80.0°C in order to melt the crude DNT for later use in the washing step. The SPA, REW and YEW contain high concentration of acids, which required them to be handled in a safe way for disposal. They were collected in specific containers, labeled, to later be sent to the disposal facility.

One of the most important safety aspect was the constant supervision of the pump nitration pilot plant during operation. Because of the exothermic reaction, one person had to always be present to check that no runaway of the reaction occurred. Also, it was important to check that the temperature inside each stage was controlled. For the cooling system, the supervisor needs to make sure that the temperature is re-established to the feeding temperature. Finally, it is important to keep track of the H_2SO_4 concentration in the DNT stage to make sure that the concentration were at the desired value. If the H_2SO_4 concentration increases above 82.0%, uncontrolled reaction will occur, forcing the need to shut-down the plant and restore the acid concentration into a safe zone.

4.2.2 Washing steps risks

In the washing step it is important to maintain the DNT levels in the separators. The equipment is design to use gravity to promote the flow of DNT between each washing stage. The flow of washed DNT leaving the acidic and alkaline washers are regulated by increasing the height, using adjustable legs mounted to be washing tanks. If the leg is too high, the DNT flow increases, filling the static separators after each wash. This can produce a flooding of the Karr column used for the last washing step.

5

Experiment

5.1 Factorial Design Experiment

A single replicate 2^3 factorial design was done to find the optimum running conditions of the pump nitration pilot plant to study the points discussed in Section 3.1.1. The experiments needed to complete the factorial design are shown in Table 2.4 and the selected parameters and levels are presented in Table 5.1.

Table 5.1: Selected parameters and levels for single replicate 2^3 factorial design

Parameters	Factors	Levels		
		-	0	+
Temperature MNT stage [°C]	A	-2.0	0	+2.0
Temperature DNT stage [°C]	B	-2.0	0	+2.0
H ₂ SO ₄ concentration [%]	C	-1.0	0	+1.0

The middle point values of the factorial design are the actual parameters that Chematur's pump nitration technology is running at industrial stage. To choose the values of the factorial design, $\pm 2.0^\circ\text{C}$, for factor A and B; and $\pm 1.0\%$, for factor C, from the middle point was decided. Explanation of this decision is discussed in Section 7.1.

It is not possible to perform a complete randomized experiments for this factorial design. The main reason was the time required for changing the H₂SO₄ concentration randomly. For that reason the randomization was performed for the experiments that compose each level of factor C. The plan was to first run all experiment for the low level of factor C in a random order. For the first runs to be performed, both loops were filled with the correct concentration of acids. For the DNT stage, a pre-mixture of SPA with a concentration that meets the experimental requirement was prepared. Then, part of this pre-mixture was diluted to lower the H₂SO₄ concentration, by 9.0%, in other to meet the concentration requirements for the MNT stage. The acid mixtures were left running for 12 hours in their respective loops in order to achieve an homogeneous concentration in all zones of each loop.

Before starting with the experimentation, a start-up run of 2 consecutive days was required to lower the toluene concentration in the MNT loop below 10.0% and to reduce the TNT concentration in the DNT loop below 1.0%. Additionally, this

start-up run, permits to find the correct feed flows for each acid in order to maintain the correct concentration of the acids in each loop. Once the required values were achieved, the experimental runs were started. The first 4 experiments at low level of H_2SO_4 concentration were done. During these experiments, the MNT stage increased its H_2SO_4 concentration by 3.0%.

After completing the first four experiments, the sulfuric acid concentration in the DNT loop needed to be concentrated in order to run the middle point of the factorial design. Different alternatives of how to concentrate this SPA were tested. However, the best reliable way was to drain half of the acid and concentrate it to the required H_2SO_4 concentration. Then, pouring the concentrated acid back until an over-flow through the recycle stream that connects the DNT and MNT loops was seen. Finally the concentrated acid was left 12 hours running inside the loop to ensure that every zone had the same concentration. After that, the middle point experiment could be accomplished. Thereafter, the DNT acid was once again concentrated to perform the last 4 experiments, using the same method as described above.

Each experimental run required a minimum of 3 hours to reach steady state. During this time, adjustment in the cooling system was done to reach the desired temperature values for each experiment. Also, during this time period, analysis of the acidic phase was done in order to ensure that acid concentration in each loop was at the stipulated values. If not, adjustments of the feeds were made. When the HNO_3 concentration in the DNT and MNT loops remained constant, it was assumed that the system was at steady state. At this point, sampling of the organic phase began. The frequency of sampling was approximately every 30 minutes for a total time of 5-8 hours. The analysis of the organic and acidic samples are described in Section 5.5.

5.2 Steady state experiment

For the optimum point found in the factorial design, a long run was done to ensure that steady state was reached. For this experiment, the run time was approximately 15 hours. The acid concentration of both loops needed to be adjusted to the optimum values from the factorial design analysis. The same procedure as described in Section 5.1 was followed. Thereafter, the run was started. The same sampling procedure as described earlier was used but with lower sampling frequency (every hour) to minimize the disturbances of the system. All weights of reactants and product entering and leaving the pump nitration system were also measured. With this data, an overall mass and compound mass balance was done.

5.3 Overall rate of reaction experiment

Using the optimum point from the factorial design, changes in the loop flow rate of the MNT circuit was made in order to test how the overall rate of reaction is affected. For this experiment, a change of ± 5.0 kg/h ($\pm 25.0\%$) from the company's

base case value was tested. Before starting the experiment, the acid concentrations were analyzed to confirm that they were at the required value. In the first hour, the pump nitration plant was run using the flow rate at the base case value as a reference value. Then, the lower flow rate was run approximately 4 hours. Next, the same procedure was done with the higher flow rate after returning to the base case value for 1 hours. Sampling was done as described before.

5.4 Washing step experiment

A lab-scale experiment was first done to optimize the first two stages of the washing process. In these experiments, 4 different pH values (5,7,8 and 9) were selected to analyze its effect on the alkaline wash. The DNT samples were tested for acidity before and after the lab-scale washing. This allowed the determination of which pH value favors the removal of impurities without promoting any new side reaction.

With the optimum pH value for the alkaline wash, optimization of the Karr column was done. As explained in Section 3.2.1, two parameters were tested. The flow rate of fresh water entering the column and the frequency (rpm) for the reciprocating trays of the column. From previous knowledge, the maximum rpm value for the column is 130 rpm. Above this value, the DNT droplets starts to accumulate in the upper section of the column causing flooding of the column. Thus, two different frequencies below the limit value were tested, 128 and 118 rpm. The DNT used in the experiment was the one produced during the factorial design experiment.

Two experiments were run varying the mass ratio DNT to fresh water. The two mass ratios tested were 0.8 and 1.2. Samples of the washed DNT, REW and YEW were taken at the beginning, at the equilibrium and at end of the experiments. The equilibrium point was defined as the moment where all the old DNT accumulated in the DNT washing pilot plant was removed, equivalent to approximately 4.0 L of new crude DNT. The analysis of the samples is described in Section 5.5.

5.5 Analytical tools

Through out the experiments, samples of the organic and acidic/aqueous phases were collected in order to track how both systems were responding. For the organics the weight percent of the different compounds involved in the reaction was measured. That includes the main organic compounds and the impurities from side reactions. For the acidic phase, it was important to constantly measure the concentration of the nitrating acids: H_2SO_4 , HNO_3 and HNO_2 . The available analytical tools were: Gas chromatograph with flame ionization detector (GC-FID), high-performance liquid chromatography (HPLC) and titrations. As it is known that some organics is dissolved in the aqueous phase, an extraction method was also used.

5.5.1 Analytical tools for the organic phase

The organic compounds were analyzed by using a GC-FID and the impurities of side reactions were analyzed with HPLC.

5.5.1.1 Gas chromatography

The principle of GC is to separate an organic sample into its components, using their relative volatility.[28] The sample, is injected into a heated inlet, and carried with a carrier gas; mostly helium (He) or hydrogen (H) through a column specific to the type of organic sample to be analyzed.[28] The column of the GC is a capillary tube with a stationary phase coated on the inner wall. This type of column has a high resolution, shorter analysis time, greater sensitivity and lower sample capacity than traditional packed columns.[29] The sample of interest is dissolved in a suitable solvent such as methanol, dichloromethane or acetonitrile.[28] The separation of compounds is achieved by the distribution of the individual components between the mobile phase (carrier gas) and the stationary phase (the column).[28]

In the equipment used, the detector is a flame ionization detector (FID). One of the advantages with this detector is the high sensitivity.[28] The main disadvantage is that the compounds detected are destroyed during the analysis.[28] After separation in the column, the compounds are directed to the FID, where they are burnt in a flame to produce ions which are detected, giving an electrical signal. The FID is a good detector for hydrocarbons.[28]

The signal from the FID is recorded to create a GC chromatogram with peaks at different retention times. To calibrate the GC, standards containing pure substances was injected to find their retention time and, if necessary, their response in the FID. The compounds with shortest retention time have the highest volatility. The lowest volatility have the longest retention time. For example TNT is always the last compound to be detected because of lowest volatility. The area of each peak is a good approximation of the compounds concentration in weight %. Therefore, all peaks were integrated using the computer software connected to the GC-FID.[29].

The aromatic compounds detected with the GC-FID were the following. Toluene, the 3 isomers of MNT, the 6 isomers of DNT, nitrocresoles, nitrobenzaldehydes and TNT.

5.5.1.2 High-performance liquid chromatography

A HPLC is a good tool when the compounds are not volatile enough, decomposes at higher temperatures or are too hydrophilic. An HPLC uses high pressure to push the solvent (eluent) through a column containing fine particles (silica particles).[29] It is composed of a solvent delivery system, a sample injector valve and a high-pressure column followed by a detector.[29]

The sample is carrier with a mobile phase (a liquid), for instance a mixture of acetonitrile and an aqueous buffer, through the column (stationary phase).[29] The separation of the sample is based on the polarity of the components. The detector is a UV detector, where a ultraviolet light beam is sent through the detector flow cell and a sensor measure the light passing through. By integrating this signal the concentration of the compound can be measured as described in Section 5.5.1.1.

HPLC was used to detect and measure the concentration of nitrobenzoic acids (NBA). Specifically the isomers 2-NBA, 4-NBA, 2,4-DNBA, 2,6-DNBA. The calibration curve was in two different ppm levels. One with a range of 1-9 ppm and one with 0.1-0.9 ppm.

5.5.2 Analytical tools for the acidic phase

The mixed acid used for nitration of toluene is composed of strong acids which are completely ionized in the presence of water.[30] Therefore, titration was used to calculate the concentration of each acid in weight percent.

In a titration, a standard solution, or titrant, with known concentration is gradually added into a solution sample (known as analyte) until the chemical reaction between them is completed.[30] This point is known as the equivalence point.[30] Different types of electrodes can be used to determine when this point is reached depending on the type of titration.

5.5.2.1 Acid-base Titration

If the reaction involved is an acid-base neutralization, a pH meter or indicator can be used. During this reaction, regardless the strong base or acid, it measured the moles of hydrogen ions (H^+) that have reacted at the equivalence point which will be equal to the hydroxide ions (OH^-) that has also reacted.[30] By adding an indicator to the sample, a change in color can be seen when the equivalence point is reached. In a more accurate way, the pH of the sample can be measured while titrating. The pH indirectly measure the concentration of the H^+ by 10^{-pH} . With this type of titration the total acidity for the samples was determined. From this the H_2SO_4 concentration can be calculated when the concentration of the other acids are known.

This titration method was also used in the DNT washing step. The total acidity of the crude and washed DNT, and REW, YEW and Karr column waste water were measured.

5.5.2.2 Redox Titration

Another reaction used for titration is a reduction/oxidation (REDOX) reaction. In a REDOX reaction, transfer of electrons occur where one component is oxidized and the other component is reduced.[31] Commonly, oxidizing agents are used as titrant during the REDOX titrations. This titrant contain the atom that will show a reduction in the oxidation number; reduction of electrons.[31] To find the equivalence

point, a potentiometer is used to measure the difference in voltage with respect to the added volume of titrant. With the Nernst equation (see [31, p 43]) it is possible to obtain the concentration value of the compound being titrated (reducing agent). Using this method, the concentration of HNO_3 and HNO_2 was measured. Also, the water content in the organic phase can be measured using this type of titration, the Karl Fisher method.[31]

5.5.3 Extraction of organics in the aqueous phase

To measure the organics dissolved in the aqueous phase, an extraction with dichloromethane as solvent was used. This method follow the same principles as discussed in Section 2.1.5.1. By adding this solvent, two immiscible phases are created. The solute, in this case DNT, is soluble in the solvent producing the organic phase. The extractions were made at ambient conditions. The solvent is evaporated by using a Rotovapor and the organic phase is weighed to determine its concentration in the aqueous phase.

6

Results

In this section all the results are presented. The code names used for the chemical compounds are presented in Appendix 2, Table B.1. If a chemical compound wasn't detected during analysis, it is denoted as n.d.(not detected). If the chemical compound was not measured, then a dash (-) is used. Finally, the terminology of nitrocresols and NBA, for nitrobenzoic acids, refers to the sum of all the isomers found.

6.1 Pump Nitration Pilot Plant Experiments

6.1.1 Original factorial design

In addition to the selected levels shown in Table 5.1, a different factorial design was initially done. It is denoted as the *original factorial design* and the results from Experiment 5 and 6 of Table 2.4 are included below for the purpose of the later discussion.

The results of mixed acids concentration in both stages are shown in Table 6.1. This data is presented as the difference between the start and shutdown results ($\Delta I = X_{Shutdown} - X_{Start}$) for each strong acid and water.

Table 6.1: Change of mixed acid concentration [%], in both stages, during Experiment 6

Mixed acids	ΔMNT [%]	ΔDNT [%]
H ₂ SO ₄	2.8	-9.1
HNO ₃	-0.45	2.5
HNO ₂	-0.3	-0.1
Total Acidity	2.1	-7.8
H ₂ O	-2.1	7.8

In Table 6.2 the organic composition result in the MNT stage for both experiments is shown.

Table 6.2: Organic phase composition [%], in the MNT stage, for Experiment 5 and 6 of the original factorial design.

Compounds	MNT composition [%]	
	Experiment 6	Experiment 5
ONT	31.8	38.8
MNT	2.36	3.04
PNT	21.9	26.4
2,6-DNT	5.64	5.38
2,5-DNT	0.17	0.132
2,4-DNT	28.2	23.4
2,3-DNT	0.392	0.323
3,4-DNT	0.509	0.422
2,6-DNPC	n.d	0.0210
TNT	8.98	2.12

The same data is presented in Table 6.3 for the organic composition in the DNT stage.

Table 6.3: Organic composition [%], in the DNT stage, for Experiment 5 and 6 of the original factorial design.

Compounds	DNT composition [%]	
	Experiment 6	Experiment 5
PNT	0.00633	0.00563
2,6-DNT	16.9	11.5
2,5-DNT	0.559	0.388
2,4-DNT	72.2	43.9
2,3-DNT	1.46	1.44
3,5-DNT	n.d	0.00399
3,4-DNT	2.18	2.01
2,4-DNBAld	n.d	0.0231
TNT	6.75	40.7

The results for the different isomers of nitrobenzoic acids in the organic phase of both stages, are shown in Table 6.4

Table 6.4: Nitrobenzoic acids composition [ppm], at both stages, for Experiment 5 and 6 of the original factorial design.

Compounds	MNT stage [ppm]		DNT stage [ppm]	
	Experiment 6	Experiment 5	Experiment 6	Experiment 5
2-NBA	43.84	164.8	124.9	143.6
4-NBA	13.59	109.6	164.3	83.99
2,4-DNBA	21.39	329.5	246.5	251.9
2,6-DNBA	5.348	74.14	96.94	68.03
Total	84.17	678.0	632.6	547.5

6.1.2 Single replicate 2^3 factorial design analysis

A second single replicate factorial design was performed. The results of the organic phase composition are shown at Appendix C.1 in Table C.1 and Table C.2. This data was used to perform the ANOVA analysis using 90% confidence level. Minitab® and JMP® software were selected for the data analysis. Half-Normal plots and ANOVA results are shown below.

In Figure 6.1, it is presented the Half-Normal plot for the 2,4-DNT% content in the final product.

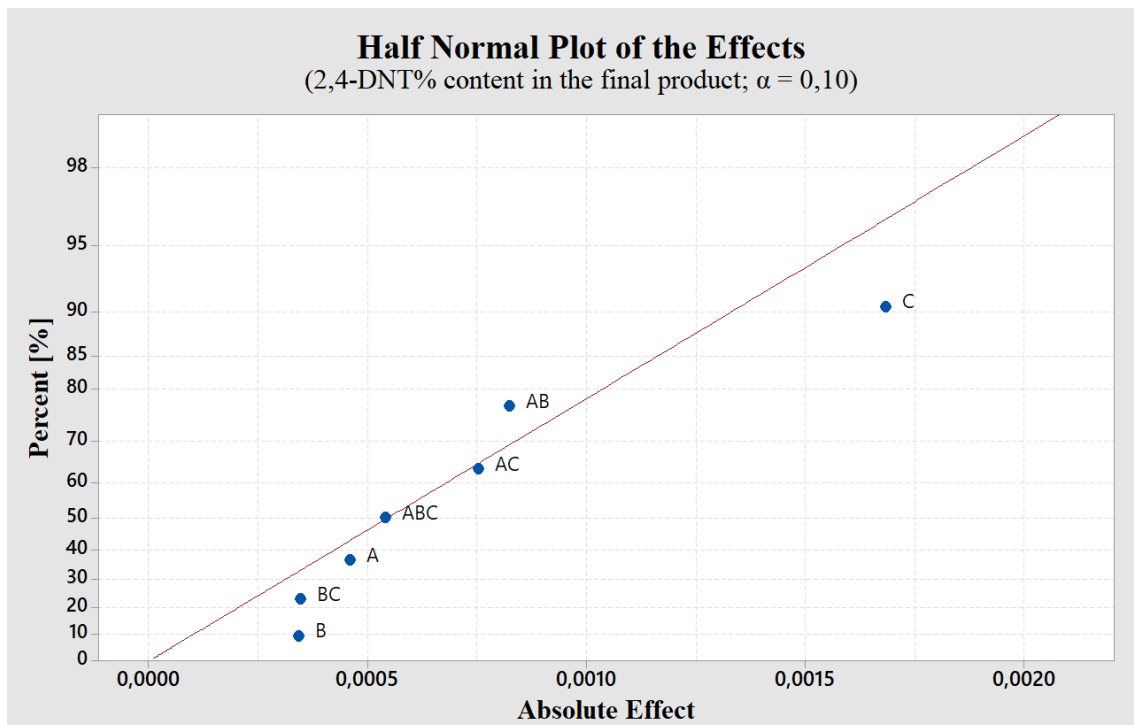


Figure 6.1: Half-Normal plot of 2,4-DNT% content in the final product response

The ANOVA results for this response is presented below:

Table 6.5: ANOVA results of 2,4-DNT% content in the final product response using $F_{0.1,1,6}=3.78$

Factors	Estimated Effect	<i>SS</i>	DF	<i>MS</i>	F_0	<i>Prob > t </i>
A	0.0004586	4.205E-07	1			
B	-0.0003413	2.329E-07	1			
C	0.001682	5.659E-06	1	5.659E-06	8.586	0.0263
AB	0.0008221	1.352E-06	1			
AC	0.0007522	1.132E-06	1			
BC	-0.0003448	2.378E-07	1			
ABC	0.0005384	5.798E-07	1			
Error		3.954E-06	6	6.59062E-07		
Total		9.613E-06	7			

6. Results

where significant parameters proved by the F-test and the p-value statistical tools are presented in **bold**.

Another response that showed significance in the Half-Normal plot was the MNT content in the DNT stage, shown in Figure 6.2.

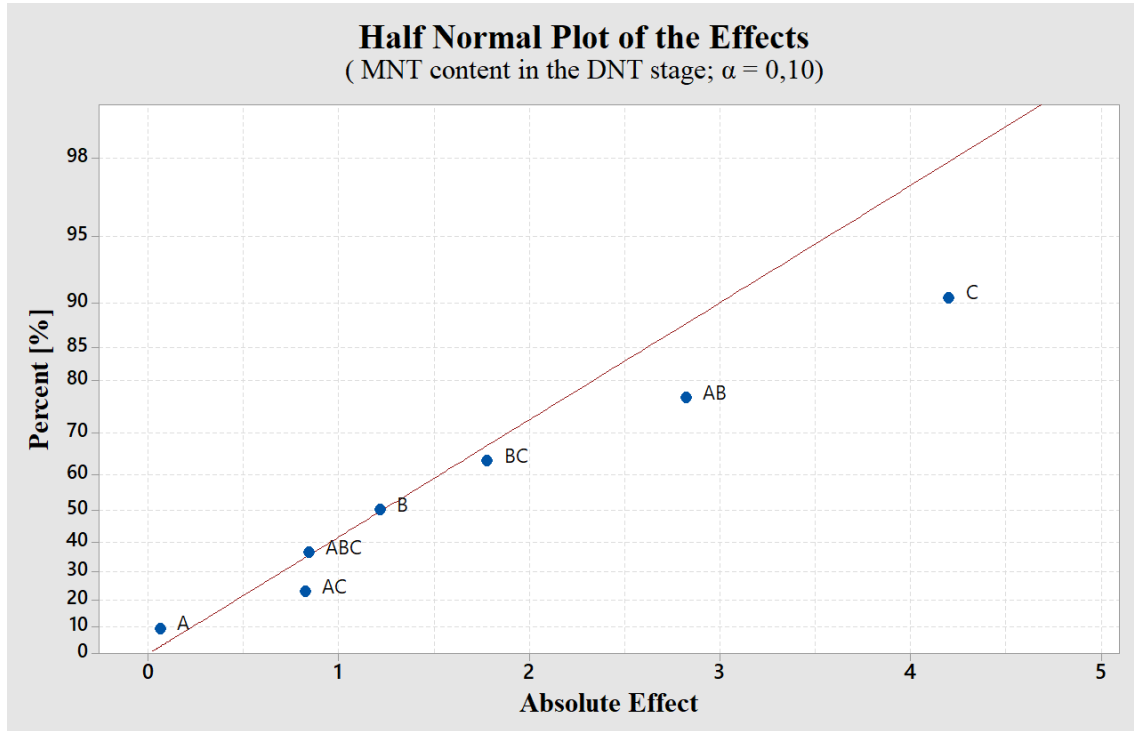


Figure 6.2: Half-Normal plot for the MNT content in the DNT stage

The ANOVA results for this response is shown below:

Table 6.6: ANOVA results for MNT content in the DNT stage response using $F_{0.1,1,2}=8.53$

Factors	Estimated Effect	<i>SS</i>	DF	<i>MS</i>	F_0	$Prob > t $
A	0.05922	0.007014	1	0.007014	0.005097	0.9496
B	-1.213	2.941	1	2.941	2.137	0.2813
C	-4.198	35.24	1	35.24	25.61	0.0369
AB	-2.819	15.89	1	15.89	11.55	0.0768
AC	-0.8199	1.345	1			
BC	1.775	6.302	1	6.302	4.579	0.1657
ABC	0.8389	1.408	1			
Error		2.752	2	1.376		
Total		63.13	7			

where significant parameters proved by the F-test and p-value statistical tools are presented in **bold**.

For the Toluene content in the MNT stage response, the Half-Normal plot is shown in Figure 6.3.

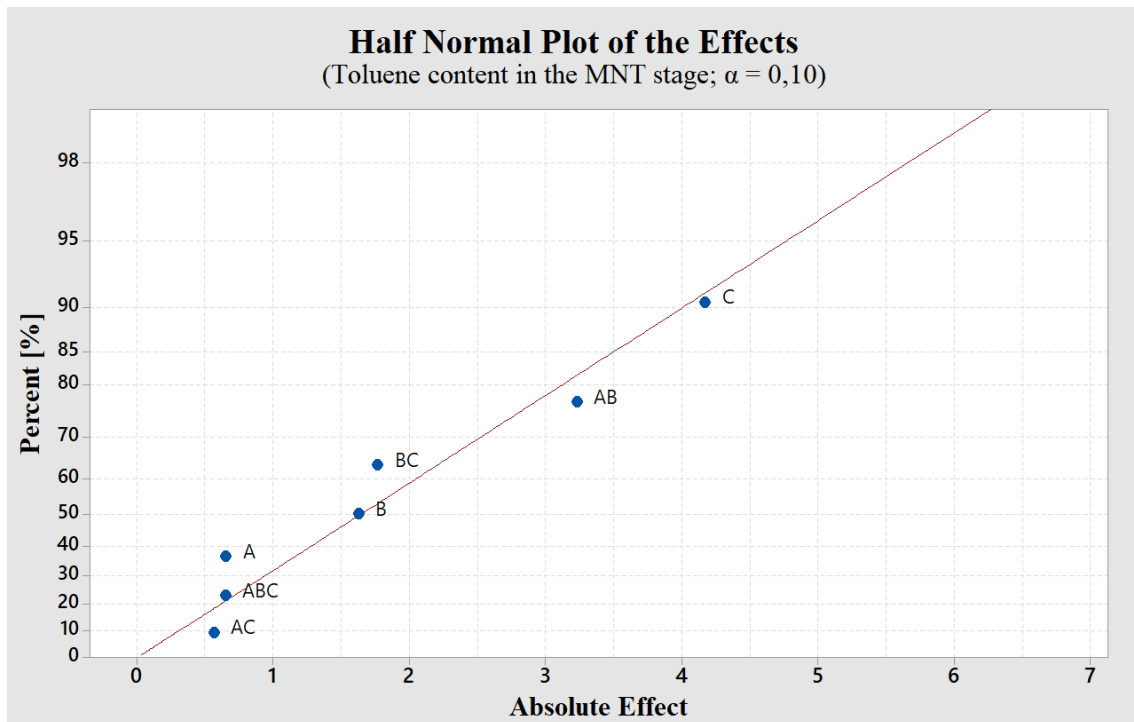


Figure 6.3: Half-Normal plot of Toluene content in the MNT stage

Its ANOVA results are presented below:

Table 6.7: ANOVA results for Toluene content in MNT stage response using $F_{0.1,1,2}=8.53$

Factors	Estimated Effect	<i>SS</i>	DF	<i>MS</i>	F_0	$Prob > t $
A	-0.6496	0.8439	1	0.8439	1.158	0.3944
B	-1.621	5.258	1	5.258	7.216	0.1151
C	-4.168	34.74	1	34.74	47.67	0.0203
AB	-3.225	20.79	1	20.79	28.54	0.0333
AC	-0.5606	0.6286	1			
BC	1.763	6.218	1	6.218	8.533	0.0999
ABC	-0.6438	0.8289	1			
Error		1.457	2	0.7287		
Total		69.31	7			

where the significant parameters proved by using F-test and p-value statistical tools are presented in **bold**.

The remaining responses that were tested did not show any correlation with the studied factors in the Half-Normal Plot and ANOVA analysis. For that reason, these results are not presented.

6.1.3 Steady state experiment

A comparison between the steady state experiment with Experiment 9 is presented in Table 6.8. The compounds in the table shows the sum of all isomers of the respective compound group. The data used to develop this table is provided in Appendix C.2, from Table C.3 through Table C.6.

Table 6.8: Comparison of the organic composition, at both stages, between the steady state experiment and Experiment 9

Compounds	Steady State	Experiment 9	Difference
	MNT stage		
Toluene [%]	2.30	2.73	-0.44
MNT [%]	89.6	90.2	-0.60
DNT [%]	7.80	6.84	0.96
TNT [%]	0.08	0.04	0.04
Nitrocresols [%]	0.19	0.21	-0.02
NBA [ppm]	95.41	95.41	0.0
	DNT stage		
MNT [%]	0.22	0.27	-0.05
DNT [%]	99.64	99.63	0.01
TNT [%]	0.140	0.087	0.05
Nitrocresols [%]	0.000	0.0012	-0.001
NBA [ppm]	152.1	154.1	-2.05
	Isomers distribution in the DNT stage ¹		
2,4-DNT [%]	80.1	79.9	0.20
2,6-DNT [%]	19.9	20.1	-0.20

6.1.4 Mass balance results for the pump nitration system

To perform a mass balance it is important to identify the inlets, outlets, accumulation in the system and any reaction that may have occurred. Looking at Figure A.1, there is 4 inlets of reactants and 2 outlet streams. Additionally, the sampling process is considered as an outlet of material from the system. For that reason, every sample was weighed to keep track of the material removed from the system. The difference in mass between the inlet and outlet stream is named as **Balance** in the result tables. If no accumulations and losses occurred this will equal to zero. It was identified 2 forms of accumulation in the system. Changes in the MNT tank level and changes of mixed acids concentration in both stages (see Table 6.9).

¹Considering only 2,4-DNT and 2,6-DNT as the total organic composition in the crude DNT.

Table 6.9: Change of mixed acids concentration [%], in both stages, during the steady state experiment

Mixed acids	Δ MNT [%]	Δ DNT [%]
H ₂ SO ₄	+2.6	+0.3
HNO ₃	+0.5	-0.4
HNO ₂	+0.1	+0.3
Total Acidity	+3.1	+0.3
H ₂ O	-3.1	-0.3

For the overall mass balance, the change in the MNT tank level was identified as the only possible source of accumulation in the system. The result of this mass balance is presented in Table 6.10.

Table 6.10: Overall mass balance [g] of the steady state experiment

	Description	Value	Unit
Inlet:	H ₂ SO ₄	5271	g H ₂ SO ₄
	HNO ₃ DNT stage	2790	g HNO ₃
	HNO ₃ MNT stage	2587	g HNO ₃
	Toluene	3665	g Toluene
Outlet:	Crude DNT produced	7050	g DNT
	SPA	6642	g SPA
	Sampling	295.2	g SPA
Inlet-Outlet = Balance		325.8	g total
Accumulation:	MNT tank	204.2	g MNT
Balance - Accumulation = Losses		121.6	g total
	Percentage	0.85	%

For each species, a mass balance was calculated as well; see Tables 6.11-6.13. The identified source of accumulation is presented at the row named **Accumulation** in the mass balance for each species.

Table 6.11: Sulfuric acid mass balance [g] for the steady state experiment

	Description	Value	Unit
Inlet:	To DNT stage	5271	g
Outlet:	In the SPA	4849	g
	Sampling	177.2	g
	In the crude DNT product	0.0	g
Inlet-Outlet = Balance		244.8	g
Accumulation:	Change of H ₂ SO ₄ % in DNT stage	8.6	g
	Change of H ₂ SO ₄ % in MNT stage	84.8	g
	In MNT tank	1.4	g
Balance - Accumulation = Losses		150.0	g
	Percentage	2.8	%

Differently to H_2SO_4 , HNO_3 is a reactant. Thus, the difference between **Balance** and **Accumulation** represents the amount of HNO_3 that has reacted; named as **Reacted** in Table 6.12.

Table 6.12: Nitric acid mass balance [g] for the steady state experiment

	Description	Value	Unit
Inlet:	To both stages	5377	g
Outlet:	In the SPA	79.7	g
	Sampling	5.04	g
	In crude DNT product	70.50	g
Inlet-Outlet = Balance		5222	g
Accumulation:	Change of $\text{HNO}_3\%$ in the DNT stage	-12.1	g
	Change of $\text{HNO}_3\%$ in the MNT stage	16.4	g
	In the MNT tank	0.0	g
Balance - Accumulation = Reacted		5218	g
Actual reacted	Total HNO_3 mass used for crude DNT production	4876	g
	Reacted - Actual Reacted = Losses		342.0
	Percentage	6.4	%

To calculate the HNO_3 amount required to produce the crude DNT obtained in the experiment, the final composition of the crude DNT was used (shown in Table C.3). The total weight of crude DNT produced was multiplied by the composition and converted into moles of each compound. Then, the moles of HNO_3 needed to produce each compound was calculated; using stoichiometric coefficients of each reaction. The **Actual Reacted** was calculated by summing the required moles of HNO_3 to produce each compound and converting it into mass.

Table 6.13: Toluene mass balance [g] for the steady state experiment

	Description	Value	Unit
Inlet:	To the MNT stage	3665	g
Outlet:	In the SPA	1.07	g
	Sampling	0.31	g
Inlet-Outlet = Balance		3664	g
Accumulation:	In the MNT tank	4.69	g
Balance - Accumulation = Reacted		3659	g
	Actual Reacted	3567	g
Reacted - Actual Reacted = Losses		92.0	g
	Percentage	2.5	%

The toluene mass balance was performed similar to the HNO_3 mass balance. To

determine the **Actual Reacted**, shown in Table 6.13, the total weight of crude DNT produced is multiplied by the ratio of toluene and DNT molecular weights.

For the DNT mass balance, the actual amount of crude DNT produced was compared to the theoretical maximum from the reacted toluene. See the mass balance calculation in Table 6.14 below:

Table 6.14: Crude DNT production [g] for the steady state experiment

Description		Value	Unit
Actual Reacted	Actual crude DNT produced	7050	g
Reacted	Possible crude DNT production	7232	g
Reacted - Actual Reacted= Losses		182.0	g
Percentage		2.6	%

An estimation of the HNO₃ and toluene reacted in secondary reactions at the steady state experiment is presented in Table 6.15.

Table 6.15: Approximation of the HNO₃ and toluene reacted in secondary reactions during steady state experiment.

	Composition [%]	Total mass [g]	Total moles	HNO ₃ reacted [mole]	Toluene reacted [mole]
Nitrocresols formation ²	0.19	13.51	0.0682	0.205	0.0682
Complete oxidation of nitrocresols	0.19	13.5	0.0682	0.887	-
NBA	0.015	1.07	0.00641	0.0192	0.00641
			Total moles	1.11	0.0746
			Total mass [g]	69.9	6.88
			New losses [g]	271.8	85.4
			New percentage	5.06	2.33
			Difference [%]	1.30	0.19

²Formation of 4,6-DNOC and 2,6-DNPC

6.1.5 Overall rate of reaction experiment

A summary of the results from the overall rate of reaction experiment is presented in Table 6.16. The original data used to construct this table is available in Appendix C.2, Table C.7.

Table 6.16: Summary of the results for the overall rate of reaction experiment.

Flow rate [kg/s]	Low -5.0	Base case 0	High +5.0
Re	93.5	124.7	155.0
τ [s]	6.21	4.66	3.73
MNT conversion [%]	89.4	89.7	90.1
NBA [ppm]	90.4	62.8	61.5

The toluene concentration behavior during the overall rate of reaction experiment is shown in Figure 6.4. The \blacktriangle represent base case flow rate, \bullet represent low flow rate, \blacksquare represent high flow rate and the black line is the transition period after changing MNT loop flow rate. The first \blacktriangle is the result of the base case flow rate after 1 hour of steady state run. Then, the MNT loop flow rate was changed to the low flow rate and after one hour the first sample at low flow rate was taken. Two more samples were taken for a total period of 3 hours. The MNT loop flow rate was again changed to the base case flow rate for one hour before taking new samples. The same procedure described for low flow rate was done for the high flow rate.

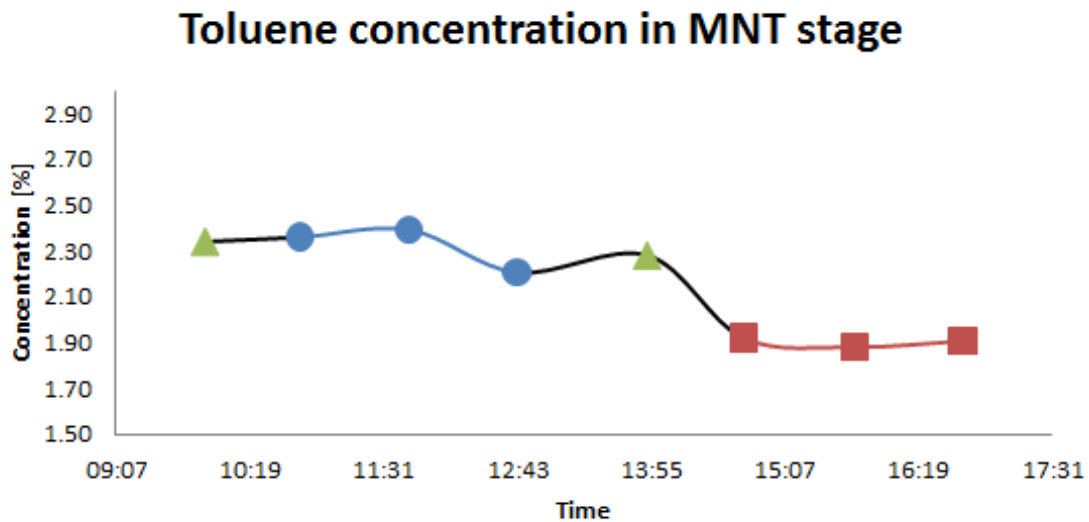


Figure 6.4: Toluene concentration [%] in the MNT stage at different flow rates during the overall rate of reaction experiment: \blacktriangle for base case flow rate; \bullet low flow rate; \blacksquare high flow rate.

6.2 Washing step experiment

6.2.1 Alkaline wash pH experiment

A comparison was made between the nitrobenzoic acids concentration in the re-heated DNT and analysis of DNT in Experiment 9 of the *original factorial design* was made before starting the pH experiment. The results are shown in Table 6.17.

Table 6.17: Nitrobenzoic acids concentration [ppm] before and after re-heating the DNT product of Experiment 9

	Re-heating DNT [ppm]	Experiment 9 [ppm]	Change [%]
2,6-DNBA	154.0	112.3	37.1%
2,4-DNBA	1269	167.6	657.0%
2-NBA	154.0	167.6	-8.10%
4-NBA	231.0	167.6	37.8%
Total	1808	615.1	194.0%

The results of the percentage of removal for the mixed acid concentration and the nitrobenzoic acids are shown in Table 6.18.

Table 6.18: Average concentration of mixed acid concentration and nitrobenzoic acids with percentage of removal.

	Average Value					
	Mixed acid			NBA		
	Initial [%]	Final [%]	Removal [%]	Initial [ppm]	Final [ppm]	Removal [%]
pH 5	2.30	0.00425	99.8%	1817	104.1	94.3%
pH 7	1.94	0.00183	99.9%	1800	84.48	95.3%
pH 8	2.15	0.0184	99.1%	2294	161.7	93.0%
pH 9	1.94	0.00680	99.7%	1800	84.54	95.3%

Each pH experiment was done in triplicate and an average was taken.

6.2.2 Optimization of the Karr column

The data used to create the following tables is found in Appendix C.3, Table C.8. Results of impurities removal, by varying the feeding of fresh water flow rate to the Karr column at a frequency of 128 rpm, are presented in Table 6.19 below:

Table 6.19: Impurities removal [%], at different flow rates of fresh water entering the Karr column

Removal [%]	Mass Ratio (crude DNT/water)	
	0.8	1.2
Mixed acids	99.1	99.1
NBA	97.6	95.9
Nitrocresols	66.0	30.9
2,4-DNBAld	14.1	14.0

At a ratio of 0.8, 2 frequencies for the reciprocating trays of the Karr column were tested. See the results in Table 6.20 below:

Table 6.20: Impurities removal [%], at different frequency of the Karr column reciprocating trays

Removal [%]	Frequency	
	118	128
Mixed acids	98.7	99.1
NBA	98.7	97.6
Nitrocresols	13.9	66.0
2,4-DNBAld	3.71	14.1

6.2.3 Washing of the DNT produced in the steady state experiment

The results for the washing of crude DNT produced in the steady state experiment are presented in this section. The composition of the organic and aqueous phase, are shown in Table 6.21. The results for the nitrobenzoic acids content are shown in Table 6.22.

Table 6.21: Phases composition [%] in different streams of the DNT washing step.

Compounds	Crude DNT [%]	Washed DNT [%]	REW [%]	YEW [%]	Wash water [%]
ONT	0.00858	0.0111	0.0322	0.112	0.0322
MNT	0.00369	0.00413	0.00617	0.0179	0.00617
PNT	0.0179	0.0201	0.216	0.214	0.216
2,6-DNT	19.1	19.0	30.5	27.2	30.5
2,5-DNT	0.539	0.535	0.870	0.776	0.870
2,4-DNT	76.4	76.4	63.3	67.4	63.3
2,3-DNT	1.49	1.48	1.55	1.24	1.55
3,4-DNT	2.23	2.22	2.88	2.23	2.88
2,4-DNBAld	0.0302	0.0397	0.245	0.251	0.245
2,6-DNPC	0.000620	0.000420	0.00458	0.00459	n.d.
TNT	0.247	0.256	0.447	0.564	0.447
Unknown	-	-	0.817	-	-
Unknown	-	-	0.282	-	-
Unknown	-	-	0.596	-	-
Mixed acids	1.93	0.00830	-	8.08	0.00590

Table 6.22: Nitrobenzoic acids mass content [g] in different streams of the DNT washing step.

Compounds	Crude DNT [g]	Washed DNT [g]	REW [g]	YEW [g]	Wash water [g]
2,6-DNBA	1.26	n.d.	0.787	0.0203	n.d.
2,4-DNBA	5.37	0.0358	9.71	0.338	6.37
2-NBA	0.497	0.179	0.797	0.0363	0.708
4-NBA	0.716	n.d.	1.00	0.0289	n.d.
Total	7.85	0.0537	12.3	0.423	7.08

The total removal percentage for each impurity achieved in this experiment is presented in Table 6.23. In Table 6.24 the percentage of organic phase dissolved in different outlet streams it is presented.

Table 6.23: Impurities removal [%] in the washed DNT product from the steady state experiment

	Removal [%]
Mixed acids	99.6
Nitrocresols	32.3
2,4-DNBAld	none
NBA	99.3

Table 6.24: Concentration of organics [%] in the outlet streams of the washing step

	Organic phase [%]
REW	0.18
YEW	0.15
Waste water	0.05

6.2.4 Mass balance results for the washing system

Looking at Figure A.2, 4 inlets are identified: crude DNT, water to acidic washing, water to Karr column and NaOH inlet. For the outlets, 3 streams were identified: REW, YEW and washed DNT. Additionally, the sampling process is considered as an outlet of material from the system. In this experiment only one sample of washed DNT was taken at the end. The same table construction described in Section 6.1.4 for the mass balance of the steady state experiment was used.

The only source of accumulation determined for this system is the wash water tank; explanation of this is provided in Section 7.3.4. The results of the overall mass balance are presented below:

Table 6.25: Overall mass balance on the washing system

	Description	Value	Unit
Inlet:	Crude DNT	7.6	kg crude DNT
	Water to Karr column	8.6	kg fresh water
	Water to acidic washing	1.7	kg fresh water
	NaOH	0.23	kg NaOH
Outlet:	REW	6.7	kg REW
	YEW	1.5	kg YEW
	Washed DNT	7.6	kg washed DNT
	Sampling	0.1	kg washed DNT
Inlet-Outlet = Balance		2.3	kg total
Accumulations:	Wash water tank	0.1	kg wash water
Balance- Accumulations = Losses		2.3	kg total
	Percentage	12.5	%

Only DNT was considered for species mass balance. The result of it is shown in Table 6.26; where Table 6.24 was used to approximate the DNT content in the outlet streams.

Table 6.26: DNT specie mass balance on the washing step

	Description	Value	Unit
Inlet:	crude DNT	7.6	kg
Outlet:	washed DNT	7.6	kg
	REW	0.012	kg
	YEW	0.0022	kg
	Sampling	0.12	kg
Inlet - Outlet = Balance		-0.10	kg
Accumulations:	wash water tank	3.4E-05	kg
Accumulations - Balance = Losses		-0.10	kg
	Percentage	-1.4	%

7

Discussion

7.1 Factorial Design

7.1.1 Original factorial design

In the *original factorial design* a larger variation between the – and + levels of the single replicate 2^3 factorial design was chosen. The aim was to get clear responses for the factors studied, and a higher probability of drawing good conclusions from the factorial design analysis. The *original factorial design* was based on $\pm 5^\circ\text{C}$ for factor A and B; and $\pm 2\%$ for factor C. However, when experiments with the high level of factor C were made, an uncontrolled reaction occurred. Results for these experimental runs are presented in Table 6.2 and Table 6.3; for the MNT and DNT stage respectively.

The first column of both tables corresponds to Experiment 6 of Table 2.4. By looking at the results for the SPA analysis for this particular run it can be seen that the mixed acid concentration of the MNT loop increased. All HNO_3 reacted, with only H_2SO_4 and HNO_2 as components in the MNT loop. The H_2SO_4 concentration increased by 2.8%. The DNT loop was at the same time diluted. The water increased by 7.8%.

This increase of water content has different origins, such as secondary oxidation reactions and water produced by the trinitration reaction. The severe conditions in these experiments increased the rate of secondary oxidation reactions. It was difficult to detect total oxidation with the available analytic tools as no measurement of gaseous reaction products (eg. NO_x , CO and CO_2) could be made. However, by measuring 2,6-DNPC in the MNT loop (see first column in Table 6.2) and nitrobenzoic acids in both stages (see Table 6.4), the presence of secondary reactions was detected. It was confirmed that nitrocresols present in the MNT loop were fully oxidized in the DNT stage, as they were not detected at this stage. The nitrobenzoic acids increased when passing from the MNT to the DNT loop as expected. For TNT, 6.8% was detected in the DNT loop with an additional production of water as a consequence.

The first run at a high level of factor C was Experiment 6 which also had the higher temperature condition in the MNT loop. To rule out the temperature variable as a possible reason for the vigorous reaction observed, also Experiment 5 with the low temperature condition in both loops was done. In the MNT loop, similar results to Experiment 6 were observed. However, as can be seen in Table 6.3, the DNT loop

was even worse with 40.7% TNT formation.

No information of mixed acids concentration are available because this experimental run reached the dark coloured complex rapidly 30 minutes after starting the pilot plant. It is important to address, that this experimental run was made after 2 attempts of running at the high level of C, Experiment 6 and a repetition of it. These attempt, resulted in that the mixed acid of both stages had a higher organic content dissolved, promoting an even more vigorous reaction when the pilot plant was started up again.

The organic results presented for Experiment 5 in the MNT stage were when the pilot plant was initiated with accumulated product from previous runs mixed with a small quantity of new product. No other sample was taken, since all the MNT stage reached the tarry zone. By looking at the results of Experiment 5 in Table 6.4, the total of nitrobenzoic acids in the MNT stage is greater than in the DNT stage. It is known that any kind of re-heating of a stored product, like starting up a pilot plant with organics accumulated inside, will lead to an increase of these acids. This phenomena will be explained further in Section 7.3.1. By comparing the nitrobenzoic products at the DNT stage, lower temperature favours less production of these compounds. This is in agreement with the theory discussed in Section 2.1.4; where lower temperature minimize side reactions.

With all the problems described above, a new factorial design was made with less change in the levels of the factors, as presented in Table 5.1.

7.1.2 Single replicate 2^3 factorial design analysis

To accomplish the improvements discussed in Section 3.1.1; the following responses were evaluated in the factorial design analysis:

1. 2,4-DNT% content in the final product
2. MNT content in the DNT stage
3. Toluene content in the MNT stage
4. DNT content in the MNT stage
5. TNT content in the MNT stage
6. TNT content in the DNT stage
7. Nitrocresols in the MNT stage
8. Nitrocresols in the DNT stage
9. Nitrobenzoic acids in the MNT stage
10. Nitrobenzoic acids in the DNT stage

In the ANOVA analysis for each of the responses, it was important to determine which factors are not significant in order to use them for the estimation of SS_{Error} . As discussed in Section 2.2.1.1.4, the Half-Normal plot method was used to determine the significant factors. Of the above tested responses, only Response 1 and 2 showed significant response. These plots are showed in Figure 6.1 and Figure 6.2. To validate the results from the Half-Normal plots the ANOVA analysis for all the

selected responses were done.

For those responses where the Half-Normal plot did not demonstrate significant factors, the SS_{Factor} of each factor, including their interactions, were compared. Those that has small SS_{Factor} can be used to estimate the SS_{Error} . By doing this, it was also found that Response 3 has significant factors. In this case, the AC and ABC interaction were discarded. It is important to address that even though main factors were found insignificant, if some of the interactions containing them is significant, the main factors were left for the ANOVA.

In Table 6.5 is shown the ANOVA result for Response 1. All the factors, except C, were used to estimate the error; leaving factor C as the only significant parameter. Here the F-test, $F_0 = 8.586 > F_{0.10,1,6} = 3.78$, determine that the H_0 can be rejected and adopt the H_1 ; concluding that at least for factor C the μ_C is different. This result is in agreement with the Half-Normal plot, as well. From the theory it is known that H_2SO_4 concentration has a higher effect on the isomers than the reaction temperature. The statistical analysis is therefore in agreement with the theory. The p-value statistical test was done, obtaining $Prob>|t| = 0.0263$, indicating that this factor is significant. The estimated effect for this factor equal to 0.001682. The interpretation of this result is that to increase the factor C should be between the middle point value towards the high level for factor C.

In Table 6.6 the ANOVA analysis for Response 2 is shown. The Half-Normal plot and the ANOVA analysis showed that factor C is the significant factor also for this response. The interaction ABC and AC were used to estimate the error. The F-test, $F_0 = 25.61 > F_{0.10,1,2} = 8.53$, indicates that the H_0 can be rejected and the H_1 is adopted. The same conclusion is obtained with the p-value analysis for factor C. The F-test indicated that the interaction AB, is significant but the p-value result is not small enough to consider it significant. These results can be improved by adding another factor to the SS_{Error} . However, the next factor needed to be discarded is A. This is not possible because it is one of the main factors of the in AB interaction. The next possible factor to be discarded is B, but this is not possible for the same reason. It is concluded that the AB interaction has a slight effect on the evaluated response.

The effect of factor C is -4.198. It is interpreted as the presence of MNT content in the DNT stage occur when factor C is at the the low level selected for the factorial design. This is in agreement with the theory discussed in Section 2.1.3.1, where decreasing the H_2SO_4 concentration, less NO_2^+ is available, decreasing the rate of nitration. Hence, in the pump nitration optimization it is of interest reduce the MNT content in the DNT stage; then the opposite action is needed. For the slightly significant AB factor, the estimated effect is -2.819. Similar interpretation is done; a low level of the AB gives more MNT content in the DNT stage. Thus, the opposite is needed to fulfill the optimization requirements in Section 3.1.1.

The Half-Normal plot for Response 3 is presented in Figure 6.3, where no significant

factors were found. But, using ABC and AC factors to estimate the SS_{Error} for the ANOVA, factor C and AB were found significant with the F-test and p-value. The ANOVA result for Response 3 is presented in Table 6.7. The estimated effect of C is -4.168 and for AB is -3.225. The same interpretation as for the estimated effects for Response 2 can be made. This is logical as both responses are considering the unconverted reactant in respective loops.

The other studied responses showed no correlation with the evaluated factors. For the best quality product and highest yield they were to be minimized as much as possible. Based on the theory, to minimize Response 5 through Response 10, a lower H_2SO_4 concentration is preferred to control additional substitution of nitro group at both stages and avoid secondary reaction products. Thus, factor C should be chosen close to the middle point of the factorial design. The same reasoning can be made for the temperature in the two loops.

When the experiments with high level for the A and B factors were performed, it was noticed a fluctuation in the inlet temperature of both static mixers. This was also true for the middle point value for factor B. This is interpreted as an indication of being close to an unsteady state for this exothermic reaction. As a consequence of this temperature fluctuation, back-flow and production of gases were detected. The gas detection was done qualitatively. From the control system used to manage the pump nitration pilot plant, it was possible to watch the fluctuation of the inlet flow to the static mixer. Getting a lower value than the set point is an indication that gases interfere with the centrifugal pump. To achieve stable operation, the temperature in each loop should not be increased to the high level of factor A and above the middle point value for factor B.

Another observation is related to the high level of factor C. In the MNT loop a vigorous reaction was noted. The temperature difference between the inlet and outlet of the static mixer was constantly monitored in both loops (ΔT). This ΔT is the adiabatic temperature rise as explained in Section 3.1. At more than $10.0^\circ C$ in the MNT loop, dinitration and trinitration can be occurring. During these runs, the ΔT reached $12.0^\circ C$.

The presented results and discussion in this section, suggests that the optimum point for the pump nitration pilot plant is: +0.5% from middle point for H_2SO_4 concentration in the DNT stage; the middle point for the temperature in the MNT stage and a decrease of $1.0^\circ C$ for the temperature in the DNT stage.

7.2 Steady state experiment

The steady state experimental run was performed with the optimum point decided from the factorial design analysis. Results from this experimental run were compared with the Experiment 9 results of the factorial design. Experiment 9 is based on the conditions that Chematur currently uses at industrial level for their pump nitration technology. Comparison results are shown in Table 6.8.

In the MNT stage, it was possible to decrease the unreacted toluene by 0.44% and nitrocresols by 0.02% in comparison with Experiment 9. But, it was noticed a reduction in MNT produced by 0.56% and an increase of DNT by 0.96%. This phenomena is as a consequence of 0.40% higher HNO_3 concentration in the steady state run compared to Experiment 9. At both experimental runs, the same HNO_3 flow rate to this stage was used. However, during the steady state run a problem with the automatic system controlling the feed flow caused a change in the mixed acid concentration in the MNT loop. After 8 hours of running the steady state experiment, it was needed to refill the reactant bottles. Therefore, a shutdown for 10 minutes was done. The automatic feeding system requires some lead time to stabilize before start feeding the correct set point value. This phenomena caused an overfeeding of HNO_3 to the MNT loop. This problem also affected the TNT content in this loop by increasing the content by 420 ppm in comparison with Experiment 9. This is in agreement with the theory, where increasing the HNO_3 excess promotes second or higher order nitro group substitution of toluene.

In the DNT stage, the MNT content was reduced by 0.05% and the DNT content remained equal to Experiment 9. However, the MNT content is still over the required limit of 1000 ppm in the crude DNT (see Section 3.1.1). The conversion of MNT for the steady state run was 99.8%; and for Experiment 9 99.7%. By increasing the H_2SO_4 concentration with 0.5% the MNT conversion will improve in comparison with Experiment 9. But, as the temperature at the same time was reduced by 1.0°C, this effect was minimized. Hence, the conversion was up by 0.1% only.

An increase of the TNT content in the crude DNT was observed. This is a consequence of the MNT stage problem discussed above. In the steady state experiment only 42.8% of the total TNT was produced in this loop while the corresponding value for Experiment 9 was 56.3%. The nitrobenzoic acids showed a reduction of 2.05% in comparison to Experiment 9. It is interesting to notice that in the MNT stage the same amount of it was produced but less in the DNT stage. Reducing the temperature at the DNT stage produce less TNT and nitrobenzoic acids. However, TNT and nitrobenzoic acids are still 395 ppm and 50 ppm above their quality limits. It is expected that in a perfect experimental run, both compounds will achieve their required levels.

The nitrocresols produced in the MNT loop goes to complete oxidation since they were not detected in the DNT stage. They were actually produced in less quantity than for Experiment 9. In the MNT loop, a reduction of 0.02% was achieved for the steady state experiment in comparison to Experiment 9. This improves the toluene conversion for the steady state experimental run somewhat.

It was possible to increase the 2,4-DNT isomer production from 79.9% to 80.1% of the total of the 2,4- and the 2,6-isomers. This value is achieving the product requirement discussed in Section 3.1.1. In summary, with the optimum point chosen it was possible to decrease secondary reactions and TNT production while maximizing the

toluene conversion to the desired product.

7.2.1 Mass balance for the pump nitration system

During the experiment it was tried to minimize any source of accumulation. However, the MNT tank level and mixed acids concentrations in both loops did not remain constant. For the MNT tank level, a manually controlled pump was used to control it. Even though precautions were taken in the experiment, the level did not remain perfectly constant. At the beginning of the experiment, the line that feeds MNT into the DNT static mixer got clogged. Before it was noticed, the system continued to run for a few minutes causing a level increase of approximately 200 mL.

The second source of accumulation identified was the H_2SO_4 in the system. As can be seen in Table 6.9, both stages got concentrated in H_2SO_4 . The MNT loop always concentrate during the first hours of running until steady state with respect to the H_2SO_4 concentration in the DNT loop was reached. This is due to the recycle stream of mixed acids from the DNT loop to the MNT loop. The change of H_2SO_4 concentration in the DNT loop was negligible.

A main source of error is the MNT tank level. This tank has a scale with intervals of 50 mL, giving a low precision when estimating the level. Another source of error was the problems in the measurement of the acids dissolved in the organic phase. The titration methods described in Section 5.5.2 were used for these measurements; but the presence of organic crystals caused interference during the titration. Acetone was added to dissolve most of the crystals, but uncertainties in the measurements were still present.

Another error was not to save the SPA outlet material of the experiment to measure its average acids concentration. Instead the amount of each acid present in the SPA outlet stream were approximated with the mixed acids composition at shut down of the MNT stage. All these errors constitute part of the losses obtained for each mass balance.

The mass balance for HNO_3 had he highest amount of losses, 6.4% of the total acid fed into the system (see Table 6.12). However, the losses due to thermal decomposition and secondary reactions was not considered. This will also affect the toluene mass balance. From the organic phase composition data in Table C.3 and Table C.5, it was possible to estimate the amount of HNO_3 and toluene that reacted to produce nitrocresols and nitrobenzoic acids. The results for these calculations are showed in Table 6.15.

As discussed nitrocresols are formed in the MNT stage but fully oxidized in the DNT stage. As an approximation, it is assumed that no other production of nitrocresols occur at the DNT stage. Thus, the same concentration of them in MNT stage enter to the DNT stage and is completely oxidized. Therefore, the shut down composition of nitrocresols in the MNT loop is used to estimate the amount of HNO_3 and toluene

needed for their creation and complete oxidation. The same calculation is made for the total amount of nitrobenzoic acids detected in the shutdown sample of the DNT stage.

Approximately 69.98g of HNO_3 and 6.88g of toluene reacted in secondary reactions. This reduces the percentage of losses by 1.30% for HNO_3 and 0.19% for toluene. But there is 5.06% HNO_3 unaccounted for. The second source of losses for this reactant is the thermal decomposition of it caused by the temperature of the system. This thermal decomposition produces NO_x . These gases escape through open spots in the pilot plant and are therefore not easy to quantify. The presence of NO_x was noted by fluctuation of the centrifugal pump located before the static mixer at the DNT stage. For all but HNO_3 , less than 3.0% was lost.

7.2.2 Overall rate of reaction experiment

Changing the flow rate in the MNT loop give the following effects. A change in the conversion of toluene and a variation of the adiabatic temperature rise, ΔT . In Table 6.16, it is shown that rising the flow rate increases the Re and decrease the τ , while the opposite is true when reducing the flow rate. With higher flow rate more acid was there to absorb the heat generated from the exothermic reaction, reducing the ΔT . The opposite behavior occur if the flow rate is decreased.

Looking the Figure 6.4, it is noticed that at higher flow rate, the toluene conversion increased, even though the τ was lower. This prove that the overall rate of reaction for the mononitration is diffusion limited. At higher Re , the mixing of the organic and aqueous phase is improved, reducing the interface thickness and increasing the contact area between the phases. This enhances the diffusion of reactants into the organic phase, obtaining a higher reaction rate. For +5.0 kg/h flow rate from the base case, 90.1% of total MNT is produced; while for the base case and -5.0 kg/h, 89.4% and 89.7% was obtained. The *ortho*- and *para*- isomers where the only MNT isomers that increased; with 0.07% *o*-MNT and 0.03% *p*-MNT by increasing to high flow rate. This will eventually improve the yield of 2,4-DNT and 2,6-DNT. See Table C.7 for more detailed results.

Variation of the ΔT affects the formation of secondary reaction products. High temperature promotes secondary reactions. The nitrobenzoic acids results in Table 6.16, shows a higher formation at lower flow rate and vice versa. This is as consequence of the change of ΔT inside the MNT static mixer. At high flow rate, the ΔT is lower and less nitrobenzoic acids is produced.

7.3 Washing step experiments

7.3.1 Alkaline wash pH experiment

For the alkaline pH experiment the DNT produced in Experiment 9 from the *original factorial design* was used. An interesting finding was made. The nitrobenzoic acids concentration increased from the original results obtained during the experimental run. To make the pH experiment, the crude DNT needed to be re-heated until it melts. A sample was taken prior to starting the experiments to analyze the initial concentration of mixed acids and nitrobenzoic acids. The results are compared in Table 6.17, and a significant increase of 194.0% of total nitrobenzoic acids was analyzed due to the re-heating of the crude DNT.

Looking at the different isomers of nitrobenzoic acids, 2,4-DNBA was the one with a significant increase of 657.0%. For 2,6-DNBA and 4-NBA the increase was 37.0%. Only 2-NBA decreased with 8.1%. It obvious that when re-melting the crude DNT, secondary reactions producing nitrobenzoic acids took place.

In Table 6.18 it can be seen that pH 7 showed the highest percentage of removal for mixed acids and nitrobenzoic acids in comparison to the other pH values analyzed. For the mixed acids, 99.9% were removed; and 95.3% of nitrobenzoic acids were removed. The experiment with pH 8 had the lowest percentage of removal for both mixed and nitrobenzoic acids. This abnormal behavior can be explained by the fact that the experiment was performed another day where the DNT had to be re-melted a second time.

As discussed in Section 3.2, the alkaline wash needs to be above 7 pH to remove the excess of the mixed acids and oxidation products. However, increasing the pH above 9, the DNT product becomes more reddish. This is as consequence of the addition of the hydroxide ion to the ring to form Meisenheimer complex with DNT and TNT. This behavior is discussed in Section 2.1.5. No analysis was done after the different pH experiments to evaluate the reduction of nitrocresols and presence of the complex at this stage of the washing step.

It can be seen in Table 6.18 that the percentage of removal for the mixed acids stayed unchanged independently of the pH value selected for the alkaline wash. This demonstrate the importance of the acidic wash stage for the removal of mixed acids dissolved in the DNT product. In order to improve their removal, the feeding of fresh water flow rate should be increased. Further explanation is provided in the section below.

7.3.2 Optimization of the Karr column

A mass flow ratio of 0.8 and 1.2, between crude DNT and fresh water, were set in the Karr column to evaluate the removal of impurities in the DNT product. A frequency equal to 128 rpm was used for the reciprocating trays in these experiments. As can

be seen in Table 6.19, the mixed acid and 2,4-DNBAlD achieved the same removal percentage, independently of the ratio. This indicates that the previous wash steps, specifically the acidic wash, has a higher efficiency in removing these impurities. As explained in Section 2.1.5, the focus of the acidic is in removing mixed acids. However, the percentage of removal for 2,4-DNBAlD is only 14.0% because this molecule has low solubility in the aqueous phase.

For the nitrocresols and NBA, a lower percentages of removal were obtained at the mass ratio 1.2. This follow the theory discussed in Section 2.1.5.1 where low solvent flow entering the LLE column reduces the purification efficiency. Therefore, a high fresh water flow feeding the column is required to maximize their removal, as discussed in Section 3.2.1.

By comparing the effect of the frequency changes at ratio 0.8, the nitrobenzoic acids removal increased by 1.3% at lower frequency. However, for nitrocresols and 2,4-DNBAlD there was a significant reduction in the removal efficiency at the lower frequency, with 52.1% and 10.4% respectively. This behavior follow the theory discussed in Section 2.1.5.1. At low frequency, the droplet size will increase, causing a reduction in the interfacial area of mass transfer. Looking at the results for the mixed acids removal, both frequencies showed similar results. The acidic wash step is more important for the removal of these acids. Nitrobenzoic acids didn't follow the expected behavior. This can be due to systematic or other errors.

Based on the above, Ratio=0.8 and frequency=128 rpm were used as the conditions for the washing of crude DNT from the steady state experiment.

7.3.3 Washing of the DNT produced in the steady state experiment

Looking at Table 6.21 and Table 6.22, the initial amount of impurities dissolved in the crude DNT were relatively small. In the washing step, it was possible to remove 99.6%, 99.3% and 32.3% of mixed acids, nitrobenzoic acids and nitrocresols respectively (see Table 6.23). During this experiment no removal of 2,4-DNBAlD was detected.

For the nitrocresols, 6.2 ppm was initially detected. After the washing, 4.2 ppm remained, a negligible amount. In Section 7.2 it was discussed that no nitrocresols were detected during the experimental run. Thus, the appearance of them could be due to the re-heating of the crude DNT. The limit content of 50 ppm for the nitrocresols and the nitrobenzoic acids was achieved. The mixed acids in the washed DNT was 33 ppm over the limit. A way to come within the specification also for the mixed acids is to increase the ratio between the fresh water and crude DNT entering to the acidic wash stage. In summary, a good quality washed DNT product was obtained.

Two observations concerning the REW stream must be highlighted. In Figure D.1

the GC chromatogram of the REW analysis is shown. Three unknown peaks were detected after the TNT peak, in total 1.70% of the organics dissolved in the REW (see Table 6.21). The sample was also analyzed with gas chromatography - mass spectroscopy (GC-MS) in an attempt to identify these compounds. The GC-MS results indicates that the last two peaks might be the Meisenheimer complex discussed earlier. The total amount of nitrobenzoic acids found in the REW was almost double the amount initially found in the crude DNT (see Table 6.22). One possible explanation for this, is the heating of the crude DNT tank to maintain it as a liquid during the experimental run. As discussed earlier, re-heating crude DNT increases these acids.

7.3.4 Mass balance for the washing system

Before the start up of the washing system, an old crude DNT product was fed in order to establish the levels inside each tank and static separators shown in Figure A.2. This procedure stabilized the system to minimize the accumulation and avoiding losses of good quality washed DNT. This procedure left the wash water tank as the only possible source of accumulation during the experimental run. Even though precautions were taken to maintain the level of this tank constant; the recycle stream that connects the waste washed water tank with the alkaline wash tank got clogged. This resulted in a slight increase of 100 mL in the level of the wash water tank.

In the overall mass balance of the washing system, the losses equals to 2.3 kg. This represent 12.5% of total mass fed into the system. The equipment used to construct the pilot-scale washing step can not accumulate 2.3 kg of mass inside the system. The only possible source of error are the inlet streams of fresh water. These inlet streams are controlled by manual flow meters with a scale division of 5 mL/min reducing the precision of the measurement. It was also noticed a constant fluctuation of the pressure of the district water service which also can contribute to the overestimation of the fresh water fed into the system.

For the DNT mass balance, the losses equals -0.10 kg. This negative indicates that more DNT was removed from the system in comparison of what was fed. This difference represent 1.4% of the crude DNT fed, it can be considered as a reasonable error. In Table 6.24 the amount of organics dissolved in the REW, YEW and wash water streams. The high level of organics demonstrates the importance of recovering the DNT before sending these waste streams to a waste water treatment plant.

8

Conclusions

Optimization of the Chematur's pump nitration technology including the washing step was achieved. For the optimization of the pump nitration a single replicate 2^3 factorial design was used. The three evaluated factors were reaction temperature in the MNT stage and the H_2SO_4 concentration and reaction temperature in the DNT stage. An *original factorial design* was initially performed, reaching an unstable region for the reaction. Therefore, a more narrow range were selected for these factors in order to obtain stable reaction in all experiments. Responses were evaluated with Half-Normal plots and ANOVA hypothesis test. It was concluded that the optimum values to run the pump nitration plant are: +0.5% from the middle point for H_2SO_4 concentration, the middle point for the MNT stage temperature and -1°C for the DNT stage temperature.

With the optimum values presented above it was possible to improve the isomer ratio between 2,4-DNT and 2,6-DNT from 3.99:1 to 4.02:1. At the same time the secondary reactions and the TNT formation was minimized, maximizing the crude DNT yield. A good overall mass balance, as well as for H_2SO_4 , DNT and toluene were achieved. All of them showed less than 3.0% of loss from what was fed into the system. The HNO_3 mass balance showed a higher percentage of loss, 5.06%, due to difficulties to quantify the amount involved in secondary reactions. It was found that the overall rate of reaction for the MNT stage is diffusion limited. By increasing the flow rate inside the static mixer, the conversion of toluene increased and less production of nitrobenzoic acids were detected.

The optimization of the washing step was focused in the alkaline wash and the LLE wash with the Karr column. For the alkaline wash the optimum pH value was 7 showing the highest removal percentage in comparison to other pH values evaluated. For the LLE wash, the optimum parameters are a mass flow ratio between the crude DNT and wash water equal to 0.8 and a frequency of 128 rpm for the reciprocating trays. Using these optimum parameters it was possible to achieve the target limit of less than 50 ppm for nitrocresols and nitrobenzoic acids in the washed DNT. The mixed acids in the washed DNT was 33 ppm over the target limit. The overall mass balance loss were 12.5% but the loss of DNT was negligible.

In future work, a simulation of the pump nitration process can be done. To obtain a reliable simulation model, experiments determining the kinetic rate of reaction for the mono and dinitration of toluene is required. The overall rate of reaction for the DNT stage should also be evaluated. This will allow the determination if

8. Conclusions

the results found for MNT stage can be transferred to the DNT stage, resulting in an increased yield of DNT and specifically the 2,4-DNT isomer. Furthermore, to overcome diffusion limitations in the overall rate of reaction, changes in the static mixer design can be tested to improve product yield.

For improvement regarding the mixed acids impurities in the washed DNT, the feed ratio of fresh water and crude DNT in the acidic wash can be analyzed. An improvement in the mass balance of this system is needed. Changes from manual flow meter to automatic flow control allow to control and calculate the fresh water flow rate entering the system. Analytical methods to detect nitrates and Meisenheimer complex in the washing step will also be helpful. These compounds can cause problems in the conversion of DNT to TDI.

References

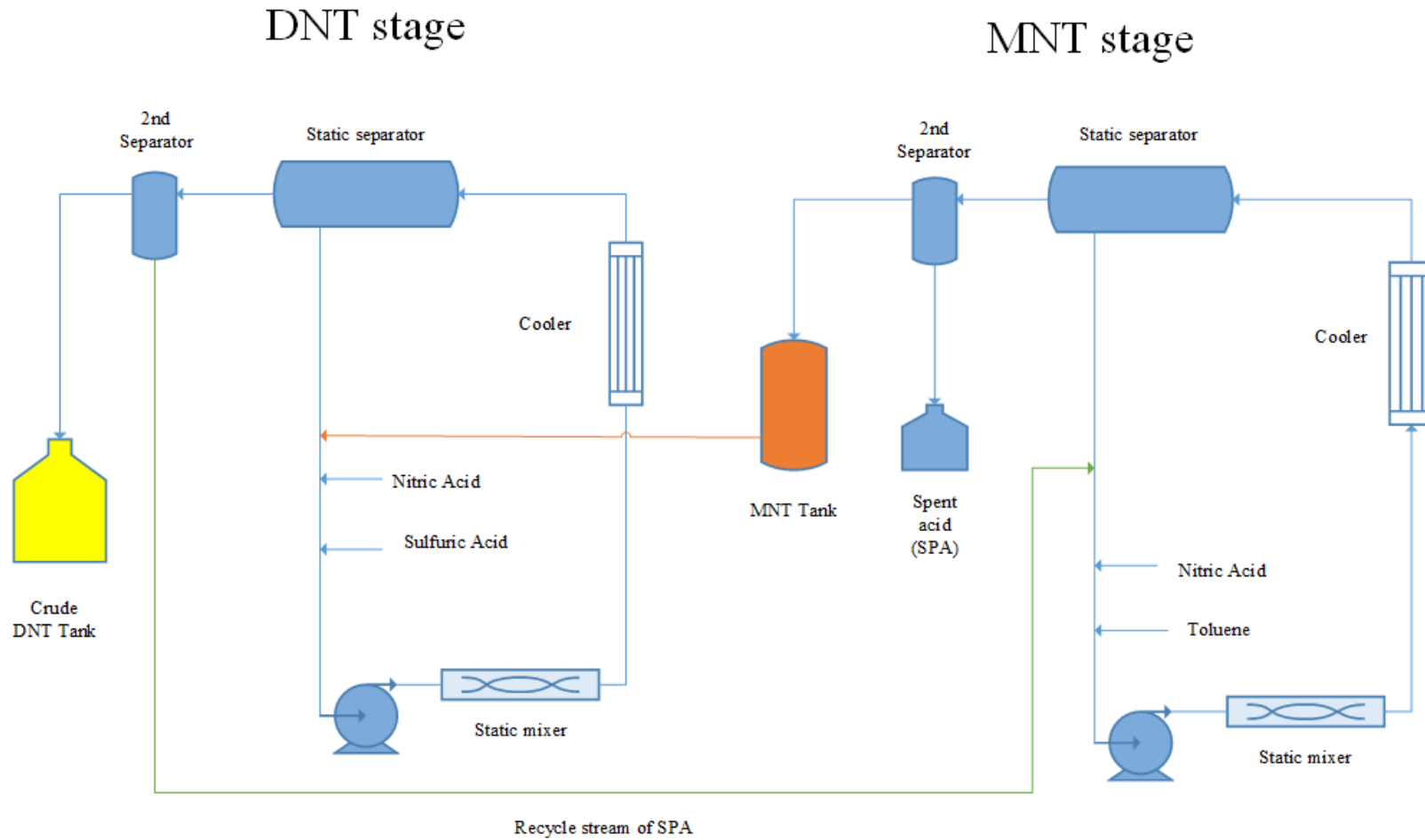
- [1] “Polyurethane chemicals and products in europe, middle east and africa (2014).” http://www.ialconsultants.com/uploads/CUBE_press_release/2014-09-30/polyurethane_EMEA_press_release_2014.pdf, 2014. Accessed: 2017-04-20.
- [2] D. Kyriacos, “Mdi, pmdi, tdi aliphatic di-isocyanates: All producers and plant capacities.” <http://www.gem-chem.net/capacity.html>, 2016. Accessed: 2017-05-24.
- [3] Merchant Research & Consulting ltd, “Tdi manufacturers in europe restructure and expand their production capacities.” <https://mcgroup.co.uk/news/20150505/tdi-manufacturers-europe-restructure-expand-production-capacities.html>, 2017. Accessed: 2017-04-19.
- [4] “Toluene diisocyanate market-global industry analysis and forecast 2023-2017.” <http://www.transparencymarketresearch.com/toluene-diisocyanate-market.html>, 2017. Accessed: 2017-04-19.
- [5] “TDI - Toluene Diisocyanate - Chematur Engineering AB-2017.” <http://chematur.se/polyurethane-chemicals/tditoluene-diisocyanate/>.
- [6] T. Urbanski, M. by Jurecki, and S. by Laverton, *Chemistry and technology of explosives*, vol. 2. Pergamon Press New York, NY, 1965.
- [7] P. A. Quadros, N. M. Oliveira, and C. M. Baptista, “Continuous adiabatic industrial benzene nitration with mixed acid at a pilot plant scale,” *Chemical Engineering Journal*, vol. 108, no. 1, pp. 1–11, 2005.
- [8] M. S. Conroy, “The Imperial Laboratory: Experimental Physiology and Clinical Medicine in Post-Crimean Russia,” 2012.
- [9] R. J. Ouellette and J. D. Rawn, *Organic chemistry*. Boston;Amsterdam;: Elsevier, 1 ed., 2014.
- [10] P. W. G. Smith and A. R. Tatchell, *Fundamental Aliphatic Chemistry : Organic Chemistry for General Degree Students*, vol. 1. Pergamon, 2014.
- [11] K. J. Saunders, *Organic polymer chemistry: an introduction to the organic chemistry of adhesives, fibres, paints, plastics and rubbers*. Springer Science & Business Media, 2012.
- [12] G. Towler and R. K. Sinnott, *Chemical engineering design: principles, practice and economics of plant and process design*. Elsevier, 2012.
- [13] G. W. Roberts, *Chemical reactions and chemical reactors*. John Wiley & Sons Hoboken, NJ, 2009.

- [14] S. Kim, P. A. Thiessen, E. E. Bolton, J. Chen, G. Fu, A. Gindulyte, L. Han, J. He, S. He, B. A. Shoemaker, *et al.*, "Pubchem substance and compound databases," *Nucleic acids research*, p. 951, 2015.
- [15] D. S. Ross and N. A. Kirshen, "Nitration and oxidative side reactions of dinitrotoluenes," ACS Publications, 1976.
- [16] L. F. Albright, "Nitration," *Kirk-Othmer Encyclopedia of Chemical Technology*, 1981.
- [17] M. Gattrell and B. Louie, "Adiabatic nitration for mononitrotoluene (mnt) production," in *Chemistry, Process Design, and Safety for the Nitration Industry*, pp. 27–48, ACS Publications, 2013.
- [18] S. Neto, R. Fritz, R. Hempel, H. Allardt, B. Becker, J. Leschinski, S. Ahrens, H. Hermann, M. Haendel, and J. Poehlmann, "Method for washing dinitrotoluene." <http://www.freepatentsonline.com/EP2841412B1.html> note=EP2841412, April 2016.
- [19] J. Münnig, D. Wastian, W. Lorenz, and B. Keggenhoff, "Process for working up the waste water obtained in the preparation of dinitrotoluene," Aug. 30 2005. US Patent 6,936,741.
- [20] L. Sviatenko, C. Kinney, L. Gorb, F. C. Hill, A. J. Bednar, S. Okovytyy, and J. Leszczynski, "Comprehensive investigations of kinetics of alkaline hydrolysis of tnt (2,4,6-trinitrotoluene), dnt (2,4-dinitrotoluene), and dnan (2,4-dinitroanisole)," *Environmental Science & Technology*, vol. 48, no. 17, pp. 10465–10474, 2014. PMID: 25083594.
- [21] A. Mersmann, M. Kind, and J. Stichlmair, *Thermal Separation Technology*, vol. 646. Springer, 2011.
- [22] A. Prabhakar, G. Sriniketan, and Y. Varma, "Dispersed phase holdup and drop size distribution in pulsed plate columns," *The Canadian Journal of Chemical Engineering*, vol. 66, no. 2, pp. 232–240, 1988.
- [23] A. Stella, K. H. Mensforth, T. Bowser, G. W. Stevens, and H. C. Pratt, "Mass transfer performance in karr reciprocating plate extraction columns," *Industrial & Engineering Chemistry Research*, vol. 47, no. 11, pp. 3996–4007, 2008.
- [24] D. C. Montgomery, *Design and analysis of experiments*. John Wiley & Sons, 2008.
- [25] M. J. Anderson and P. J. Whitcomb, *DOE simplified: practical tools for effective experimentation*. CRC Press, 2016.
- [26] D. C. Montgomery and G. C. Runger, *Applied statistics and probability for engineers*. John Wiley & Sons, 2010.
- [27] C. L. Yaws, *Thermophysical properties of chemicals and hydrocarbons*. William Andrew, 2008.
- [28] F. G. Kitson, B. S. Larsen, and C. N. McEwen, *Gas chromatography and mass spectrometry: a practical guide*. Academic Press, 1996.
- [29] D. C. Harris, *Quantitative chemical analysis*. Macmillan, 2010.
- [30] R. Chang and K. A. Goldsby, *General chemistry: the essential concepts*. New York: McGraw-Hill, 7th, international ed., 2014.
- [31] S. M. Khopkar, *Basic concepts of analytical chemistry*. New Age International, 1998.

A

Appendix 1

A.1 Pump Nitration pilot plant flow sheet



III

Figure A.1: Flow sheet diagram of the Pump nitration pilot plant

IV

A.2 DNT washing step flow sheet

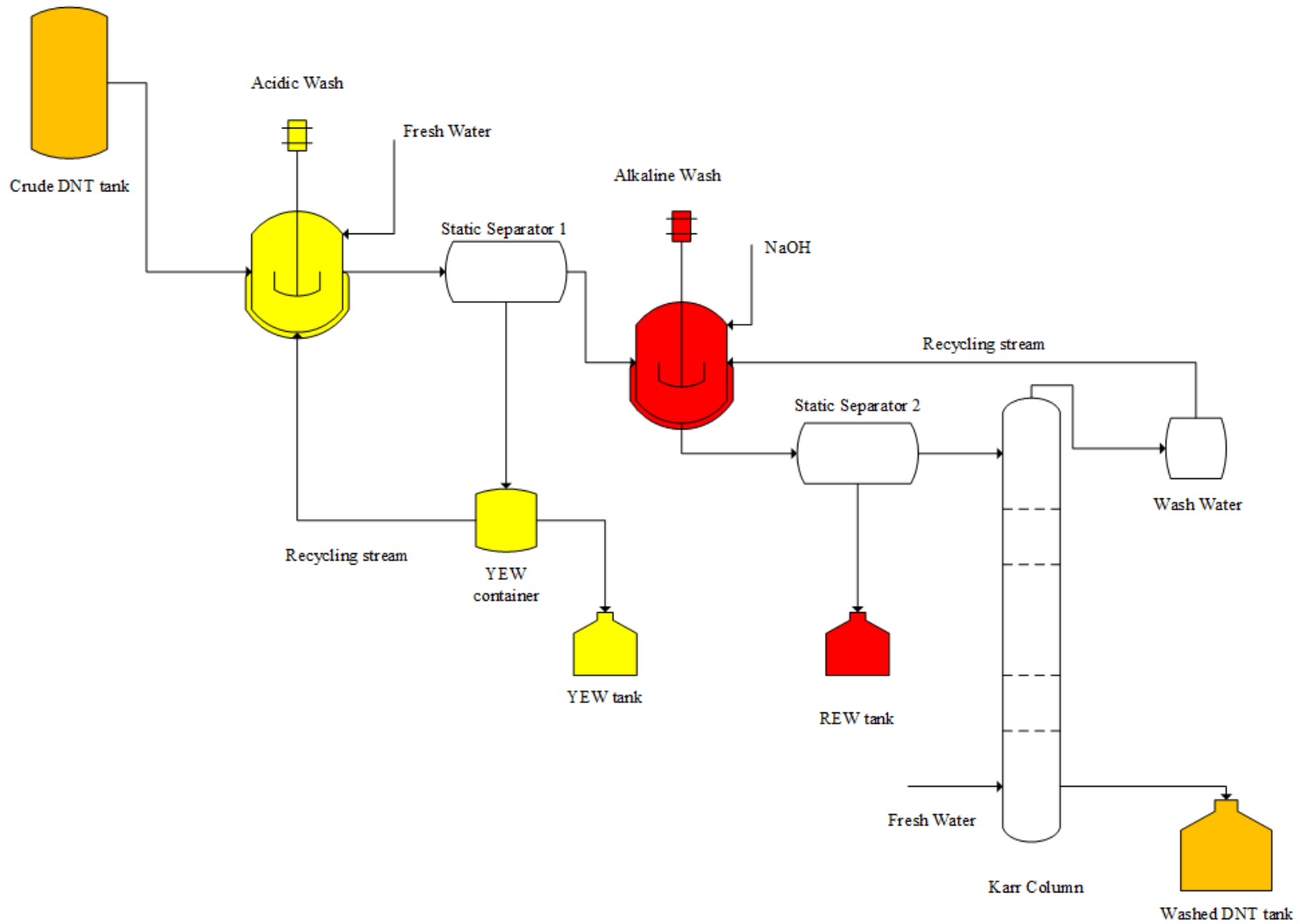
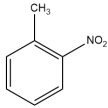
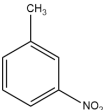
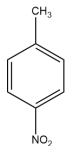
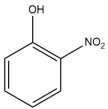
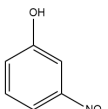
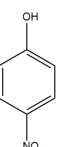
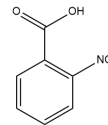


Figure A.2: Flow sheet diagram of the DNT washing step

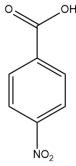
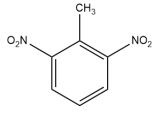
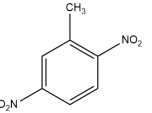
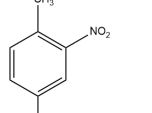
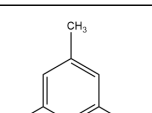
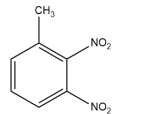
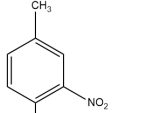
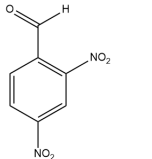
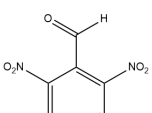
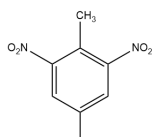
B

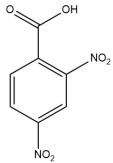
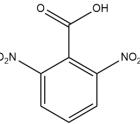
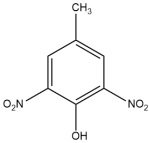
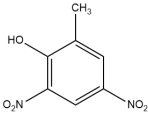
Appendix 2

Table B.1: Chemical compounds with the code name and structure

Components	Code	Structure
2-Nitrotoluene	ONT	
3-Nitrotoluene	MNT	
4-Nitrotoluene	PNT	
2-Nitrobenzaldehyde	2-NBAld	
3-Nitrobenzaldehyde	3-NBAld	
4-Nitrobenzaldehyde	4-NBAld	
2-Nitrobenzoic acid	2-NBA	

B. Appendix 2

4-Nitrobenzoic acid	4-NBA	
2,6-Dinitrotoluene	2,6-DNT	
2,5-Dinitrotoluene	2,5-DNT	
2,4-Dinitrotoluene	2,4-DNT	
3,5-Dinitrotoluene	3,5-DNT	
2,3-Dinitrotoluene	2,3-DNT	
3,4-Dinitrotoluene	3,4-DNT	
2,4-Dinitrobenzaldehyde	2,4-DNBald	
2,6-Dinitrobenzaldehyde	2,6-DNBald	
2,4,6-Trinitrotoluene	TNT	

2,4-Dinitrobenzoic acid	2,4-DNBA	
2,6-Dinitrobenzoic acid	2,6-DNBA	
2,6-Dinitro-p-cresol	2,6-DNPC	
4,6-Dinitro-o-cresol	4,6-DNOC	

C

Appendix 3

C.1 Factorial Design data

Table C.1: Organic phase composition [%] at both stages

Experiments	MNT Stage			DNT stage		
	Toluene [%]	DNT [%]	TNT [%]	2,4-DNT[%] ¹	MNT[%]	TNT[%]
1	9.30	4.35	0.00985	79.6	4.55	0.0239
2	11.8	5.82	0.0207	79.6	9.09	0.0292
3	8.50	4.07	0.00859	79.6	5.22	0.0256
4	5.83	3.95	0.0119	79.6	3.44	0.0268
5	3.29	6.01	0.00681	79.8	0.235	0.0498
6	5.95	4.99	0.00528	79.8	1.45	0.0332
7	7.30	4.32	0.00191	79.6	2.78	0.0221
8	2.22	7.99	0.0284	79.9	0.036	0.104
9	2.75	6.85	0.0404	79.9	0.270	0.0856

Table C.2: Products composition [ppm] of secondary reactions in the organic phase at both stages

Experiments	MNT Stage		DNT stage	
	Nitrocresols [ppm]	NBA [ppm]	Nitrocresols [ppm]	NBA [ppm]
1	3050	185.6	n.d.	438.3
2	2430	128.1	64.15	286.5
3	2860	181.8	n.d.	285.9
4	2680	100.4	12.50	180.6
5	2400	287.1	18.05	259.3
6	2630	95.24	25.05	174.3
7	2730	84.63	n.d.	74.83
8	1770	145.6	n.d.	231.9
9	2142	147.2	11.90	154.1

¹Considering only 2,4-DNT and 2,6-DNT as the total organic composition in the crude DNT.

C.2 Steady state experiment

Table C.3: Organic phase composition [%], at both stages, for the steady state experiment at shutdown time

Compounds	MNT stage [%]	DNT stage [%]
Toluene	2.29	-
ONT	52.9	0.0974
MNT	3.63	0.0226
PNT	33.1	0.0977
2,6-DNT	1.21	19.02
2,5-DNT	0.0315	0.528
2,4-DNT	6.45	76.4
2,3-DNT	0.0482	1.49
4,6-DNOC	0.0194	n.d.
3,5-DNT	0.0667	n.d.
3,4-DNT	n.d	2.21
2,6-DNPC	0.172	n.d.
TNT	0.0797	0.139

Table C.4: Organic phase composition [%], at both stages, for the Experiment 9 at shutdown time

Compounds	MNT stage [%]	DNT stage [%]
Toluene	2.73	-
ONT	53.3	0.125
MNT	3.67	0.0266
PNT	33.2	0.119
2,6-DNT	1.00	19.09
2,5-DNT	0.0300	0.538
2,4-DNT	5.71	76.1
2,3-DNT	0.0286	1.67
4,6-DNOC	0.0254	0.00183
3,4-DNT	0.0604	2.21
2,6-DNPC	0.189	0.00119
TNT	0.0378	0.087

Table C.5: Nitrobenzoic acid composition [ppm] in the organic phase, at both stages, for the steady state experiment at shutdown time

Compounds	MNT stage	DNT stage
	[ppm]	[ppm]
2,6-DNBAlD	n.d	12.54
2,4-DNBAlD	41.63	84.65
2-NBA	16.48	19.59
4-NBA	37.29	35.27
Total	95.41	152.1

Table C.6: Nitrobenzoic acid composition [ppm] in the organic phase, at both stages, for the Experiment 9 at shutdown time

Compounds	MNT stage	DNT stage
	[ppm]	[ppm]
2,6-DNBAlD	23.33	61.95
2,4-DNBAlD	47.56	16.62
2-NBA	15.26	18.13
4-NBA	61.03	57.41
Total	147.9	154.1

Table C.7: Organic phase composition in the MNT stage for overall rate of reaction experiment

Compounds	Low flow rate		Base case flow rate	High flow rate	
	Start	Shutdown	Reference	Start	Shutdown
Toluene [%]	2.36	2.21	2.28	1.92	1.91
ONT [%]	52.7	52.6	52.2	53.1	53.2
MNT [%]	3.68	3.72	3.62	3.59	3.59
PNT [%]	33.0	33.0	33.1	33.3	33.3
2,6-DNT [%]	1.19	1.22	1.17	1.19	1.19
2,5-DNT [%]	0.0334	0.0339	0.0320	0.0329	0.0305
2,4-DNT [%]	6.72	6.78	6.45	6.54	6.46
2,3-DNT [%]	0.0495	0.0481	0.0476	0.0494	0.0492
4,6-DNOC [%]	0.0160	0.0152	0.0154	0.0149	0.0159
3,4-DNT [%]	0.0659	0.0688	0.0657	0.0651	0.0637
2,6-DNPC [%]	0.160	0.151	0.146	0.147	0.142
TNT [%]	0.0729	0.0667	0.0572	0.0592	0.0567
NBA[ppm]	280.4	90.39	62.80	68.84	61.54

C.3 Washing step experiments

Table C.8: Phases composition of crude and washed DNT at different parameters of the Karr column

Compounds	High Frequency (128 rpm)				Low Frequency (118 rpm)	
	R=1.2		R=0.8		R=0.8	
	crude	washed	crude	washed	crude	washed
ONT [%]	3.60	3.50	0.665	0.637	1.62	1.60
MNT [%]	0.429	0.385	0.195	0.0918	0.216	0.195
PNT [%]	2.87	2.79	0.555	0.533	1.30	1.28
2,6-DNT [%]	18.4	18.4	19.2	19.2	18.9	18.9
2,5-DNT [%]	0.482	0.480	0.551	0.542	0.520	0.520
2,4-DNT [%]	70.7	71.0	74.8	75.1	73.9	74.0
2,3-DNT [%]	1.37	1.35	1.51	1.48	1.41	1.41
3,4-DNT [%]	1.94	1.92	2.20	2.18	2.03	2.03
2,4-DNBAlD [%]	0.0838	0.0721	0.0227	0.0195	0.0208	0.0200
2,6-DNCP [%]	0.0242	0.0167	0.0128	0.00435	0.00497	0.00428
TNT [%]	0.0916	0.0948	0.272	0.275	0.0536	0.0568
Mixed Acids [%]	1.38	0.0123	1.61	0.0147	1.39	0.0183
NBA [ppm]	4461	183.0	2076	49.40	2713	29.32

D

Appendix 4

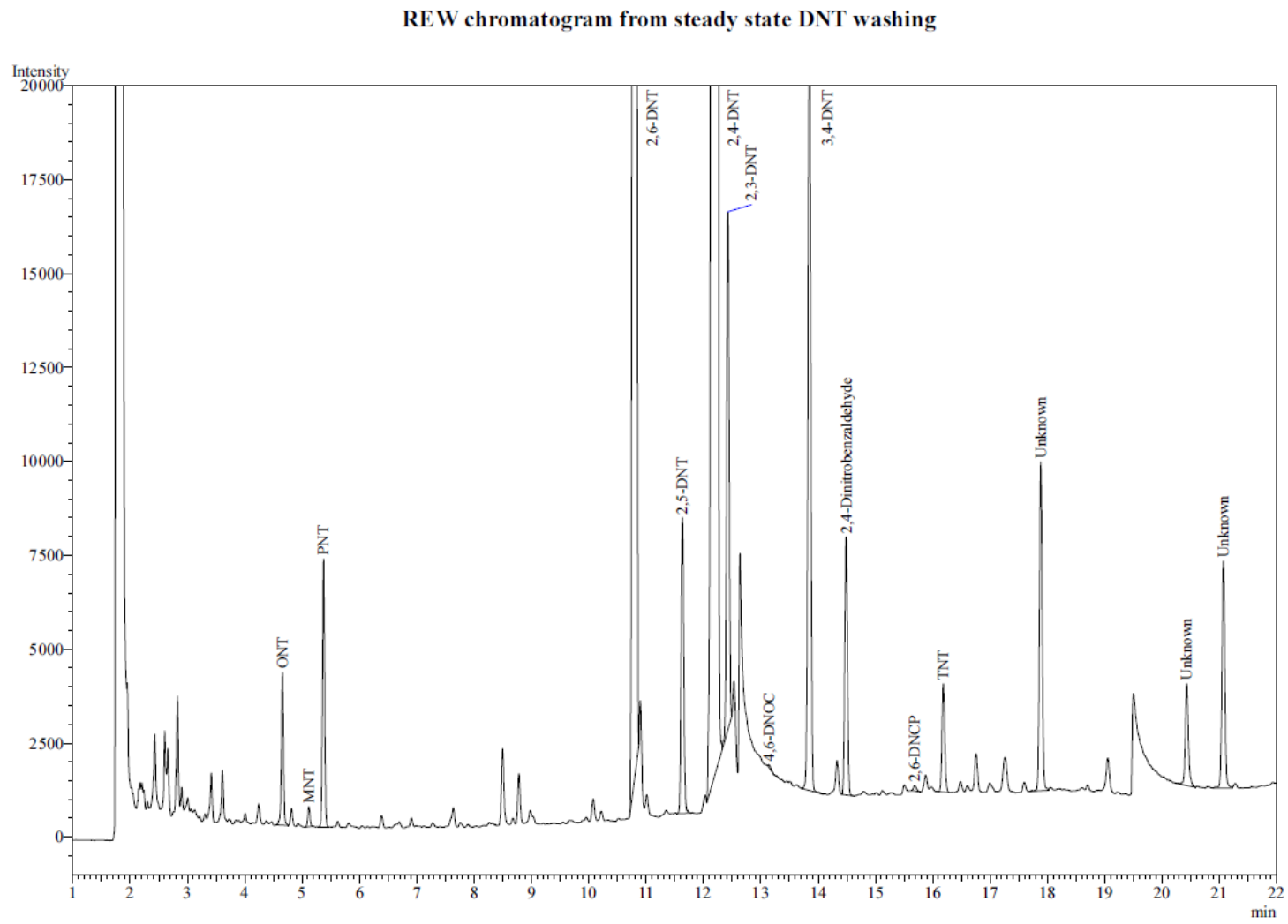


Figure D.1: GC chromatogram of the REW produced by washing the DNT product of the steady state experiment