SYNTHESIS AND CHARACTERIZATION OF TOLUENE DIISOCYANATE

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SYNTHESIS AND CHARACTERIZATION OF TOLUENE DIISOCYANATE

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I hereby declare that all information in this document has been obtained and presented in accordance with academic rules and ethical conduct. I also declare that, as required by these rules and conduct, I have fully cited and referenced all material and results that are not original to this work.

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ABSTRACT

SYNTHESIS AND CHARACTERIZATION OF TOLUENE DIISOCYANATE

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November 2014, 52 pages

Toluene diisocyanate (TDI) is one of the important components of solid rocket propellants. It is used for the construction of polyurethane network by reacting with hydroxy terminated polybutadiene (HTPB) and functions as a curing agent. The aim of project, supported by Ministry of Science Industry and Technology under SANTEZ program in collaboration with ROKETSAN, is to synthesize TDI at laboratory scale by determining the best method/methods that give the product in high yield with desired isomer ratio and quality. Although TDI is in industrially important compound, most of the studies concerning the synthesis of this compound are patented. To the best of our knowledge, TDI is not produced in Turkey and there is no study related to the production of this chemical. In this project TDI synthesis was planned in three steps which are nitration of toluene, reduction of dinitrotoluene, and phosgenation of toluenediamine. Standard nitration method was applied in the first step but optimizations were necessary in order to get the product in required isomer ratio. In the second step, Raney Nickel was found to be the ideal catalyst for the reduction of nitro groups. Finally conversion of amine groups to isocyanate groups was achieved by triphosgene reagent. Structural characterizations were carried out via NMR and FT-IR.

Keywords; Toluene diisocyanate, polyurethane, curing agent, triphosgene

ÖZ

TOLUEN DİİZOSİYANAT MADDESİNİN SENTEZİ VE KARAKTERİZASYONU

Hisar Telli, Ayşegül
Yüksek Lisans, Kimya Bölümü
Tez Yöneticisi: Prof. Dr. Özdemir Doğan

Kasım 2014, 52 sayfa

Katı roket yakıtlarının önemli bileşenlerinden biri olan toluen diizosiyanat (TDI) malzemesi hidroksi sonlu polibütadien (HTPB) polimeri ile tepkimeye girerek poliüretan ağ yapısını oluşturur ve yakıt formülasyonu içerisinde olgunlaşma ajanı olarak görev yapar. Bilim Sanayi ve Teknoloji Bakanlığı destekli SANTEZ projesi kapsamında ROKETSAN ile ortaklaşa yürütülen bu araştırma projesinde TDI malzemesinin laboratuvar koşullarında istenilen izomer oranında, yüksek verim ve saflıkta sentezlenmesi için uygun yöntem/yöntemlerin bulunması amaçlanmıştır. TDI maddesi endüstri için çok önemli olmasına rağmen yapılan birçok çalışma patentlidir. Türkiye'de henüz TDI maddesinin üretimi ve bu alanda yapılmış olan bir çalışma yoktur. TDI maddesinin sentezi üç basamaktan oluşmaktadır. Bunlar; toluenin nitrolanması, dinitrotoluenin indirgenmesi ve toluendiaminin fosgenlemesidir. Birinci basamak için standart nitrolama tepkimesi uygulanmıştır ancak istenilen izomer oranını tutturabilmek için tepkime koşullarının optimize edilmesi gerekmiştir. İkinci basamakta nitro gruplarının indirgenmesini içeren Raney Nikel'in ideal katalizör olduğu bulunmuştur. Son olarak amin gruplarının izosiyanat gruplarına dönüştürülmesi trifosgen reaktifi ile gerçekleştirilmiştir. Ürünlerin karekterizasyonu NMR ve FT-IR ile yapılmıştır.

Anahtar kelimeler: Toluen diizosiyanat, poliüretan, olgunlaşma ajanı, trifosgen

To my beloved family and my husband…

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LIST OF ABBREVIATIONS

BTC	Bis(trichloromethyl) carbonate
d	Doublet (spectral)
o-DCB	*ortho*-dichlorobenzene
DMC	Dimethyl carbonate
DNT	Dinitrotoluene
equiv.	Equivalence
EtOAc	Ethyl acetate
HDI	Hexamethylene diisocyanate
HTPB	Hydroxyl terminated polybutadiene
Hz	Hertz
IPDI	Isophorone diisocyanate
FT-IR	Infrared
J	Coupling constant
m	Multiplet (spectral)
MDI	Methylene diphenyl diisocyanate
NT	Nitrotoluene
NMR	Nuclear magnetic resonance
OxCl	Oxalyl chloride
ppm	Parts per million (in NMR)
q	Quartet (spectral)
rt	Room temperature
s	Singlet (spectral)
t	Triplet (spectral)
TDA	Toluenediamine
TDI	Toluene diisocyanate
TLC	Thin layer chromatography
TLV	Threshold Limit Value

CHAPTER 1

INTRODUCTION

Organic isocyanates have been known for a long time, but they became interesting targets commercially in the last decades due to developments based on the work by O. Bayer in 1937. It was shown that reaction of di- and/or polyisocyanates with di- and/or polyols resulted in formation of polyurethanes, which have numerous applications in many different fields.[1] The various applications of polyurethane can be classified as flexible or rigid foams (i.e. thermal insulation, furniture, packaging, household furniture, automotive seating, textile laminates), sealants, coatings, elastomers (i.e. shoe soles, vehicle body panels, rollers wheels) and others.[2] The global consumption for common diisocyanates was 4.4 million tons in the year 2000. These common diisocyanates are methylene diphenyl diisocyanate (MDI), toluene diisocyanate (TDI), hexamethylene diisocyanate (HDI), isophorone diisocyanate (IPDI), Figure 1 depicts pie chart for global consumption[3] and Figure 2 shows the structures.

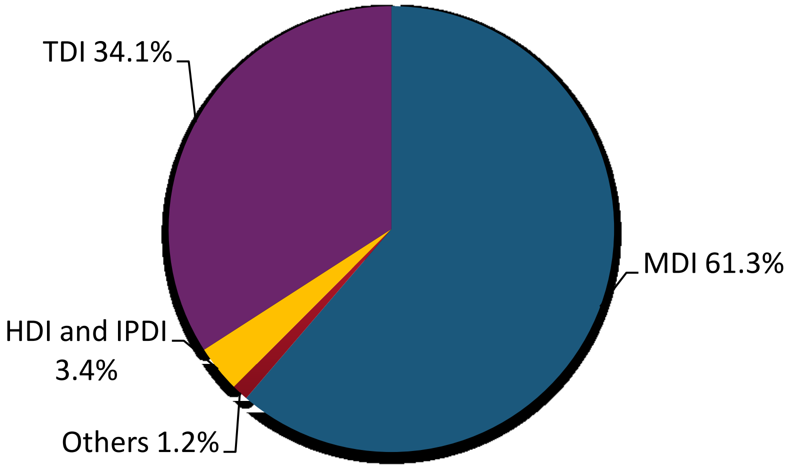
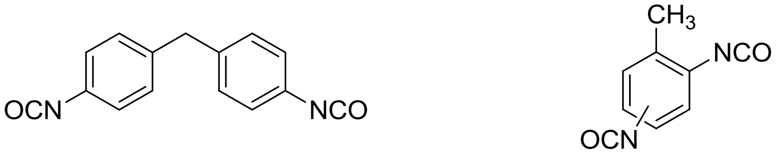


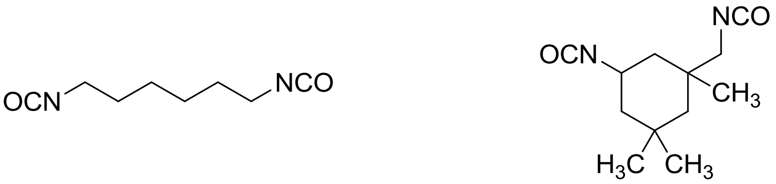
Figure 1. Global consumption of common diisocyanates.

The diisocyanates are highly reactive organic compounds due to free isocyanate groups (N=C=O). However, the reactivity of the common diisocyanates can vary by their structure. Therefore, reactivity can be increased by the substituents enhancing the electropositive nature of the –NCO carbon atom. Hence, aliphatic diisocyanates such as HDI and IPDI have lower reactivity than aromatic diisocyanates such as MDI and TDI. On the other hand, steric hindrance also affects the reactivity of diisocyanates. Thus, MDI has higher reactivity than TDI due to lower steric hindrance. Moreover, the –NCO groups of the aromatic diisocyanates have different reactivity. For instance, 2,4-TDI has -NCO groups at *para* and *ortho* positions. Reactivity of -NCO group at *para* position is higher than the one at *ortho* position with a ratio of 100:12 at room temperature. According to the rate studies, the reactivity of 2,6-TDI for the first -NCO group is about 0.56 and for the second group it is about 0.17. On the other hand, when the temperature is increased to 100 ºC, the steric effects are surpassed, and the reactivity of both –NCO groups is similar. In addition, MDI has –NCO group in different aromatic rings. Hence, the reactivities of NCO groups are the same.[4]



Methylene diphenyl diisocyanate (MDI)

Toluene diisocyanate (TDI)



Hexamethylene diisocyanate (HDI)

Isophorone diisocyanate (IPDI)

Figure 2. Structures of common diisocyanates

TDI is one of the highly reactive diisocyanates with the formula of $CH_3C_6H_3(NCO)_2$. There are six possible isomers as shown in Figure 3. TDI has unique properties and functional versatility due to free isocyanate functional groups (N=C=O).

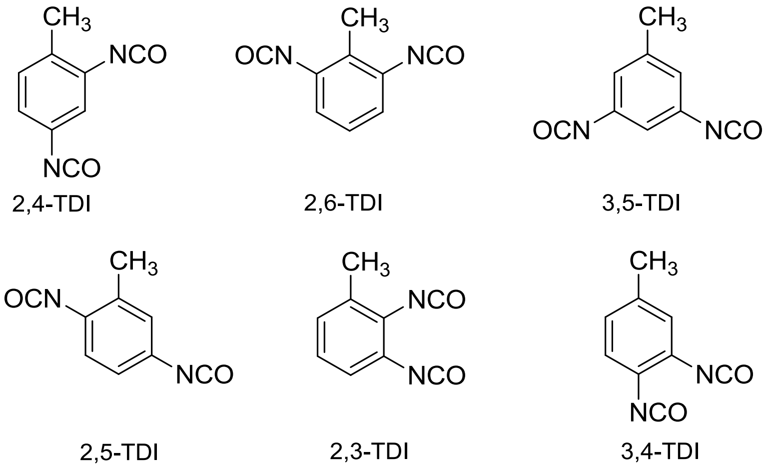


Figure 3. TDI isomers

Toluene diisocyanate (TDI), in the form of its 2,4-TDI and 2,6-TDI isomers, has been one of the most studied diisocyanate. The main product of commerce is an 80/20 mixture of 2,4-TDI and 2,6-TDI. 80/20 TDI is a colorless liquid which crystallizes at 14 ºC and boils at 251 ºC. It exerts a vapor pressure of 2.3×10^{-2} mm Hg at 25 ºC.[5] There is also a smaller market for a 35/65 mixture of 2,4-TDI and 2,6-TDI isomers.

Toluene diisocyanate is an essential intermediate compound in the production of polyurethanes due to highly reactive isocyanate groups. As described before, the main application is in the area of flexible polyurethane foams which are used in furniture, automotive seating, carpet underlay, and bedding. In addition it is used for coatings, adhesives, sealants, and urethane elastomers.[6] The world demand of TDI has been increasing day by day. Hence, approximately over 1.5 billion kilograms of TDI are produced annually.[4] According to the market research which was done by Merchant Research and Consulting Ltd., 87% of TDI demand was for flexible polyurethane foams in 2013 (Figure 4.).[7]

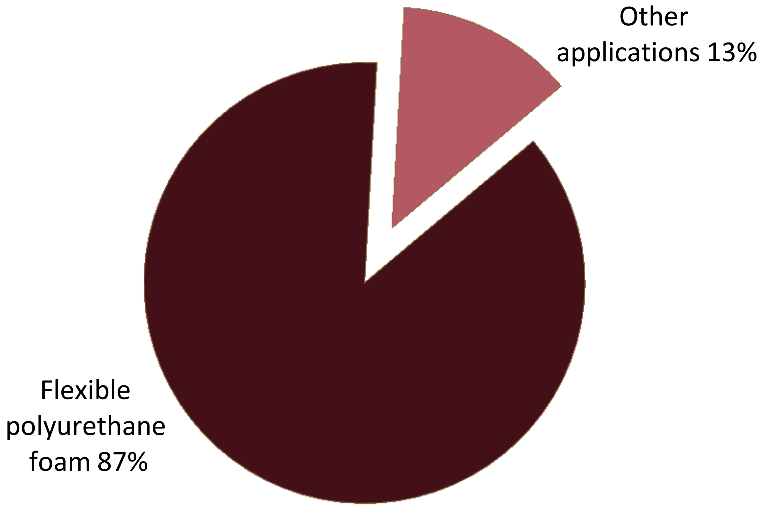
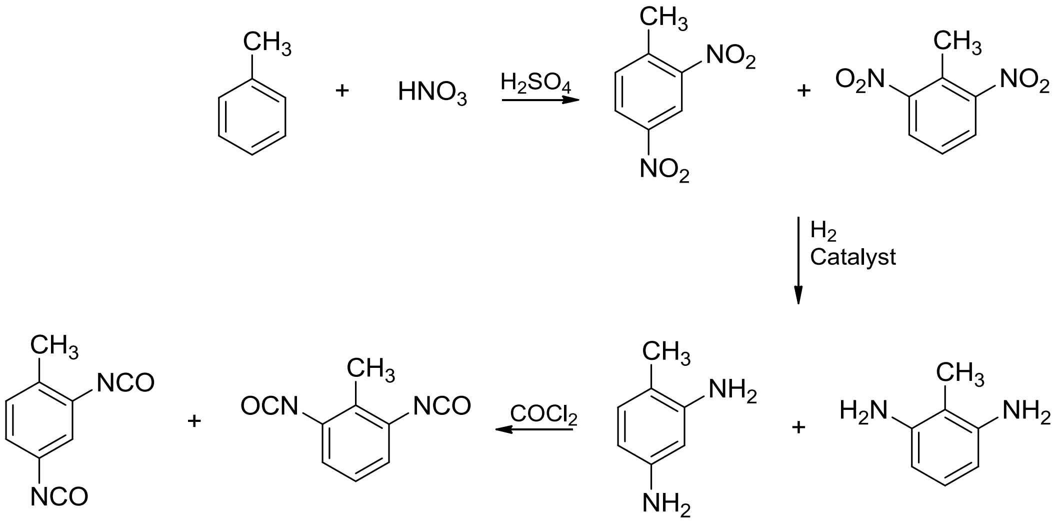


Figure 4. Global TDI consumption by end use sector in 2013

1.1. Synthesis of Toluene Diisocyanate

1.1.1. Current Processes

Several different strategies for the synthesis of toluene diisocyanates are known.[8] However, the most common and industrially applicable TDI production consists of three steps; nitration of toluene to dinitrotoluene (DNT), reduction of dinitrotoluene to toluenediamine (TDA) and conversion of amino groups to isocyanates (Scheme 1).



Scheme 1. Synthesis of TDI via conventional way

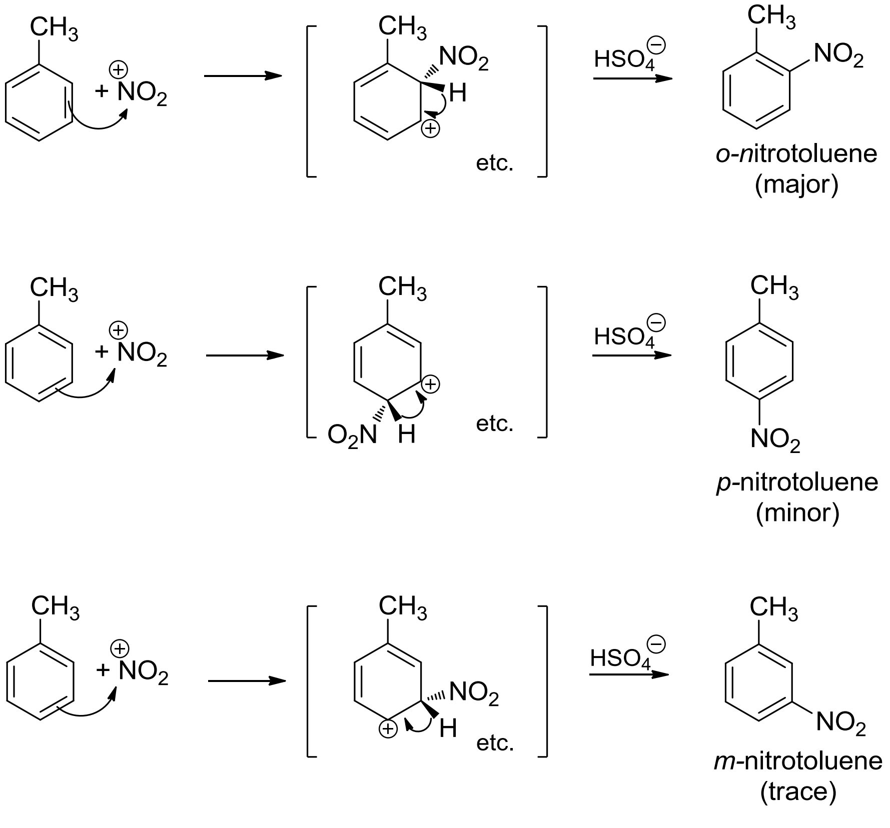
1.1.1.1. Nitration of Toluene to Dinitrotoluene (DNT)

Dinitrotoluene (DNT) as a bifunctional compound offered a relatively cheap starting material for the development of polymer systems. Moreover, a 80/20 mixture of 2,4-DNT and 2,6-DNT is now manufactured on an extensive scale and used as the raw material for toluene diisocyanate. Aromatic hydrocarbons can be nitrated (i.e. the hydrogen atoms replaced by nitro (NO_2) groups by using mixed 60-70 wt% of sulfuric acid and 30-40 wt% of nitric acid depending on the strength of nitric acid available. The strength of the nitric acid is important for the yield of DNT and also formation of TNT).[3] Sulfuric acid behaves as a catalyst to convert the nitric acid into the highly reactive, nitronium ion, which is essential for nitration. Moreover, sulfuric acid prevents dissociation of nitric acid into an oxidizing NO_3 by binding water as a hydrate. It also increases the solubility between the organic and aqueous phases.

$$HNO_3 + 2H_2SO_4 \rightleftharpoons NO_2^+ + H_3O^+ + 2HSO_4^-$$

$$HNO_3 + H_2O \rightleftharpoons NO_3^- + H_3O^+$$

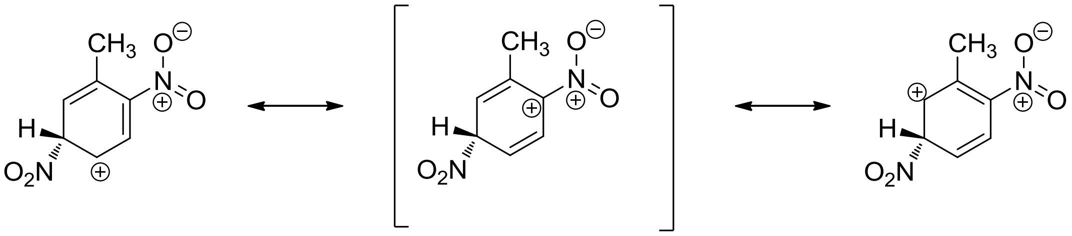
The mechanism of nitration of toluene consists of two-step process. The first step is nucleophilic attack of the π-electrons of toluene to the nitronium ion to form the intermediate mesomeric ion and the second step is removal of a proton by hydrogen sulfate ion. The methyl group of toluene molecule is an *ortho-para* activating group by forming a more stable 3˚ carbocation in their mesomeric structures of arenium ion (Scheme 2). Hence, *ortho*-nitrotoluene (major) and *para*-nitrotoluene (minor) are formed. Formation of *meta*-nitrotoluene may also take place in a very small quantity.



Scheme 2. Mechanism of nitrotoluene synthesis

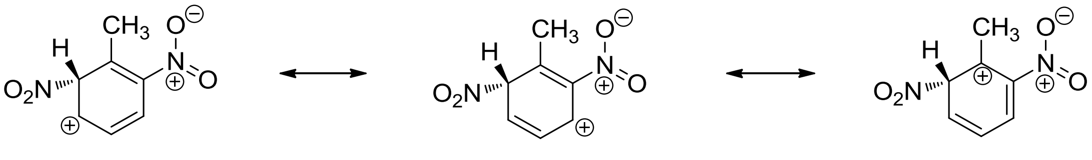
In order to prevent the formation of di- and tri-substituted nitrotoluene and form only nitrotoluene (NT), nitration reaction needs to be performed at low temperature. Introduction of the second nitro group generally takes place at higher acid concentration and temperature. For this reason, the temperature control is very important to avoid formation of trinitrotoluene (TNT) as final product which is an explosive.

Dinitrotoluene synthesis is carried out by nitration of nitrotoluene. In general, nitro groups are *meta*-directing substituents. The deactivation by nitro group is the result of its mesomeric effect (-M) with π-electron system of toluene ring which is supplemented by the inductive (-I) effect. Moreover, in the molecular structure of nitrotoluene, *ortho* and *para* positions are subject to the greatest reduction in electron density. The *ortho* and *para* attacks with respect to nitro group lead to energetically unfavorable mesomeric structures as shown in Scheme 3.



Scheme 3. *Para* attack to the nitro group

On the other hand, the *meta* attack leads to a more favorable intermediate (mesomeric structure) corresponding to dinitrotoluene (Scheme 4). Hence, the final products of dinitrotoluene consists of two isomers 2,4-DNT and 2,6-DNT with the ratio of about 80/20 respectively.

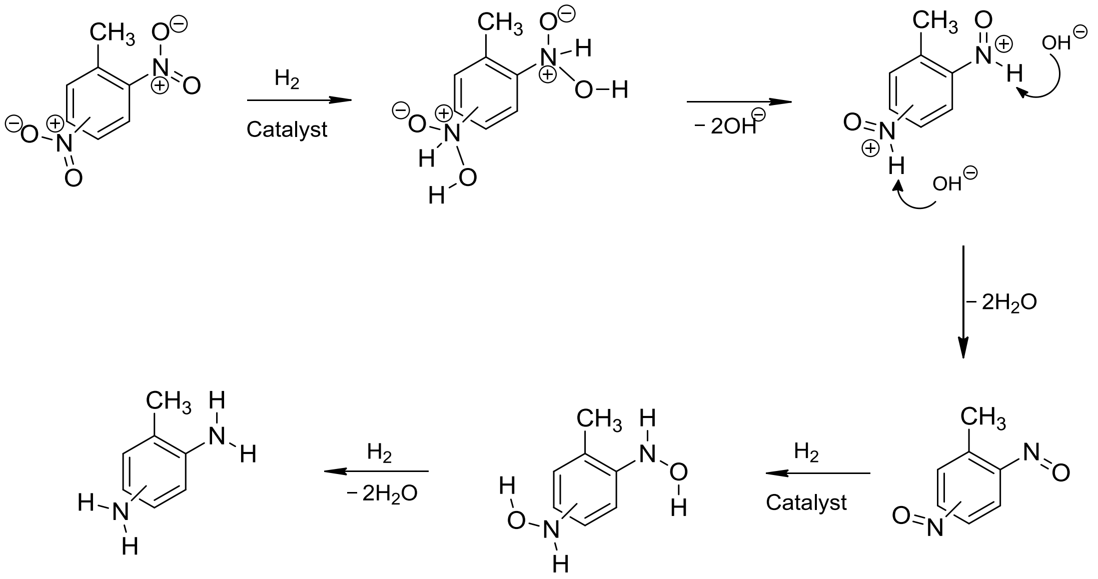


Scheme 4. *Meta* attack to the nitro group

1.1.1.2. Reduction of Dinitrotoluene (DNT) to Toluenediamine (TDA)

Toluenediamine is a valuable chemical especially for the production of toluene diisocyanates. Although numerous methods have been applied for, synthesis of toluenediamine, the reduction (hydrogenation) of dinitrotoluene is most applicable one.[9] Reduction of nitro groups to amino groups can be carried out with powerful reducing agents such as tin or tin (II) chloride and iron with hydrochloric acid.[10] However, these reagents are not convenient for mass production. Dinitrotoluene can be hydrogenated by using a wide variety of catalysts and various reaction parameter combinations of temperature, pressure and solvents were found to be effective. The common catalyst systems include supported noble metals especially Palladium (Pd) supported by Carbon, Platinum (Pt) and Nickel (Raney type). Although Pd and Pt are highly active catalysts even at low temperatures and low pressure of hydrogen, these catalysts are not economically viable. For this reason, Raney Nickel catalyst which is prepared by leaching out aluminum under controlled conditions is an economically feasible catalyst for the production of toluenediamine in high yields.[11] Furthermore, it has been reported that Bayer uses a modified Raney catalyst for conversion of DNT to TDA in high yields.[4]

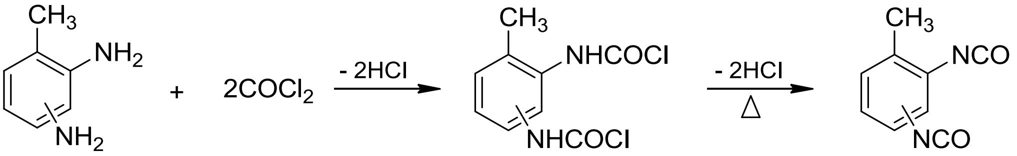
Numerous publications concern the mechanistic understanding of the catalytic reduction of dinitrotoluene to toluenediamine by heterogeneous catalysis.[12] Generally rapid hydrogenation proceeds by a complex reaction pathway from the dinitro compound via nitroso- and hydroxylamine intermediates to the aromatic diamine as shown in Scheme 5.



Scheme 5. Mechanism of hydrogenation of dinitrotoluene

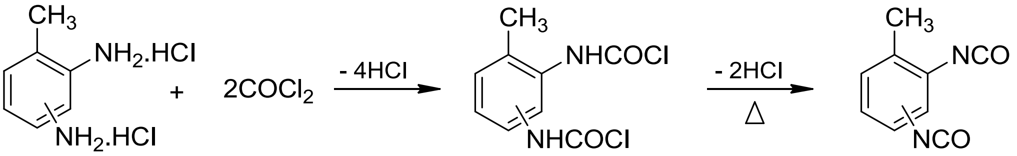
1.1.1.3. Conversion of Toluenediamine (TDA) to Toluene Diisocyanate (TDI)

Conversion of toluenediamine to toluene diisocyanate can be carried out via phosgenation of toluenediamine which is most widely employed by using phosgene as a reagent. The first step is called as cold phosgenation. In this step, toluenediamine and phosgene react with each other to form intermediate carbamoyl chloride. This stage as described before, is taking place at 0-50 ºC in an inert solvent such as *o*-dichlorobenzene, monochlorobenzene, toluene or xylene.[1] The reaction temperature is increased to 170-180 ºC to form toluene diisocyanate from intermediate product (Scheme 6). This step is called as hot phosgenation. At the end of heating period, dark colored polymeric side products may form, which the material can be separated from easily by fractional distillation.



Scheme 6. Dicarbamoyl chloride formation

Furthermore, phosgenation of the toluenediamine can be achieved by using the HCl salt of toluenediamine that can be obtained easily by injecting dry HCl to TDA solution (Mitsubishi Chemical process). In this method, phosgene reacts with the amine hydrochlorides at elevated temperature and with strong agitation to form diisocyanate (Scheme 7). The excess HCl can be stripped by inert gas such as nitrogen.



Scheme 7. Mitsubishi Chemical process

Phosgene is highly reactive reagent used for the production of fine chemicals and also very toxic substance which was used as a chemical weapon in World War I.[13]

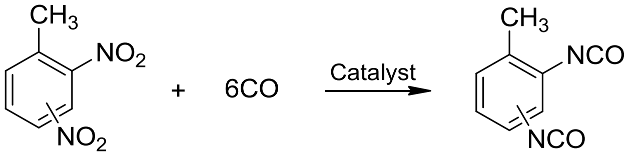
To avoid the application of extremely toxic phosgene gas, phosgene equivalents such as oxalyl chloride, trichloromethyl chloroformate (diphosgene) or bis(trichloromethyl) carbonate (triphosgene) can be used as a phosgenation reagents.[14] These compounds have advantages for handling in laboratory scale synthesis. In summary, phosgene can be considered more dangerous than the other phosgene derivatives.

However, there are many alternative routes (i.e. reductive carbonylation, carbonylation of DNT via toluene diethyl carbamate and EniChem urethane pyrolysis) for the synthesis of toluene diisocyanate; none are as simple or as attractive as the carbonylation of primary amines with phosgene. This is reflected by the widespread employment of phosgene in the industrial manufacture of isocyanates; the use of phosgene continues despite numerous attempts to find suitable alternatives.

1.1.2. Alternative Synthetic Pathways for Toluene Diisocyanate (TDI)

The synthesis of toluene diisocyanate can be carried out with phosgene and phosgene derivatives which are very toxic materials. Hence, there has been an increasing interest in developing alternative methods. However, they are all in pilot-plant operations, none of them have been scaled-up to commercial production scale due to the economical feasibility problems.

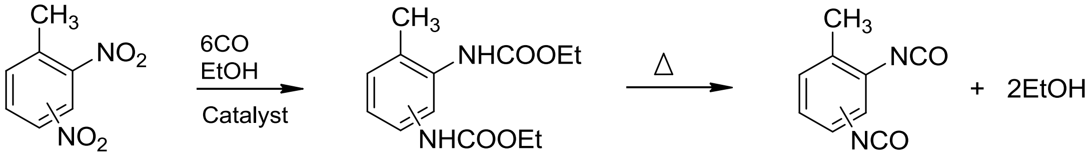
The most convenient alternative pathway compared to the phosgenation of the corresponding amines is the reductive carbonylation of nitro arenes. This method can be described as reductive carbonylation where toluene diisocyanate was synthesized by the direct conversion of dinitrotoluene with carbon monoxide and using different catalytic systems (Scheme 8).



Scheme 8. Reductive carbonylation of nitro arenes to toluene diisocyanate

The direct high pressure carbonylation of DNT to TDI was explored by Olin between 1965 and 1969. This study had a remarkable result compared to the research for direct carbonylation for the synthesis of TDI. According to Olin's research various catalyst/co-catalyst systems were examined at mostly 190 ºC under carbon monoxide pressures of 150-300 bar.[15] Best yields were obtained by using Palladium chloride combined with one or more metal oxides. Moreover, several organic compounds were tried as co-catalyst, in particular pyridine. Unfortunately, this carbonylation route is still not industrially applicable for TDI synthesis. The lifetime of catalysts is short and regeneration of expensive catalysts is difficult. Furthermore, highly-toxic catalyst residues were detected in the final products.[16]

The other significant alternative method for the synthesis of TDI is carbonylation of DNT via toluene diethyl carbamate. The chemical route includes two stages as shown in Scheme 9.



Scheme 9. Carbonylation of DNT via toluene diethyl carbamate

For the first stage, the yield is up to 90% and as the catalysts usually precious metal halides and selenium catalysts are used. The second stage is endothermic and achieved by pyrolysing the biscarbamate at high temperatures (up to 200 ºC), vaporizing the TDI-ethanol mixture and partially condensing the TDI.[17]

Moreover, TDI synthesis can be done with EniChem urethane pyrolysis method. In this method, oxidative carbonylation of methanol is used to give dimethyl carbonate (DMC). Then, TDA is reacted with DMC and urethane intermediate is formed. This intermediate product is cracked at very high temperature (up to 350 ºC) and at low pressure to produce TDI. Unfortunately, for the pyrolysis step temperature is very high. Hence, this method is also not economically convenient for mass production.[18]

1.2. Properties of TDI

Commercially available in three isomer ratios; 100% 2,4-TDI, 80% 2,4-TDI; 20% 2,6-TDI, 65% 2,4-TDI; 35% 2,6-TDI

Table 1. Properties and Characteristics of 80/20 2,4-TDI/2,6-TDI[19]

Physical State	Liquid
Approximate Flash Point	127 ºC
Boiling Point	251 ºC
Color	Colorless or pale yellow (undistilled grades are dark color)
Corrosivity	Relatively non-corrosive at normal temperature
Freezing Point	14 ºC
Decomposition Point	287 ºC
Hygroscopicity	Reacts with water with evolution of carbon dioxide
Light Sensitivity	Under light color becomes yellow
Reactivity	Reacts with compounds containing active hydrogen, rate depends on the nature of active hydrogen. Can be violent.
Specific Gravity (25 ºC)	1.22
Vapor Density (Air = 1)	6.0
Viscosity at 25 ºC	Approx. 3 cps
Vapor Pressure	2.3×10^{-2} mbar at 20 ºC
Oral LD_{50}	5800 mg / kg
Inhalation LC_{50} Rat	1 Hr Aerosol 500-600 mg / m^3 4 Hr Aerosol 110 mg / m^3

1.3. Toxicity of TDI

The most important toxic effect of TDI on humans is on the respiratory system. Some cases of skin reactions to TDI have been reported and it is also an irritant to the eye. TDI has low oral toxicity.

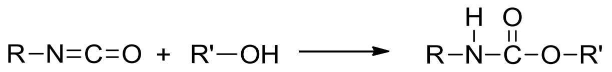
The effects of TDI on the respiratory tract can be divided into two separate responses. Firstly, TDI is irritable to the respiratory tract and exposure to high concentration above the Threshold Limit Value (TLV) of 0.02 ppm can cause coughing and difficulty in breathing. In other words, inhalation of TDI at above TLV can irritate mucous membranes in the respiratory tract (nose, throat, lungs) causing runny nose, sore throat, coughing, chest discomfort, shortness of breath and reduced lung function (breathing obstruction).[20] These symptoms are usually reversible provided the person concerned is removed from the TDI atmosphere. Secondly, TDI may also act as a respiratory sensitizer. The sensitivity reaction takes the form of asthmatic type symptoms which progress to a condition of severe respiratory distress. Its onset can be immediate or delayed. There is also evidence that a small percentage of people who have become sensitized by over-exposure to isocyanates have suffered loss of respiratory capacity more easily.[21]

The characteristic odor and strong irritating effect on the eyes may be resulted conjunctivitis.

The described toxic effects of TDI are warnings of the presence of excessive concentrations of TDI vapors in the air. However, at the TLV (0.02 ppm) for prolonged exposure it is difficult to detect. Therefore, odor and irritation should not be relied upon as indication of hazard levels.

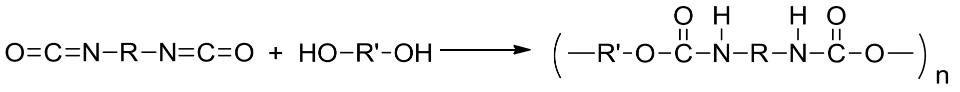
1.4. Chemistry of TDI

Toluene diisocyanate is one of isocyanates with two isocyanates groups. Firstly, toluene diisocyanate reacts with hydroxyl functional groups (-OH) to form urethane linkages. If TDI is reacted with a molecule that possesses two or more –OH groups, polymers with urethane linkages are formed which are named as polyurethanes. This material is essential for industrial applications especially in polymer industry.



$$R{-}N{=}C{=}O + R'{-}OH \longrightarrow R{-}\overset{H}{N}{-}\overset{O}{\overset{\|}{C}}{-}O{-}R'$$

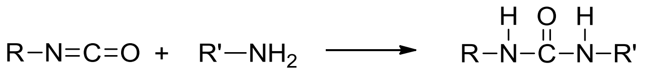
urethane



$$O{=}C{=}N{-}R{-}N{=}C{=}O + HO{-}R'{-}OH \longrightarrow \left(-R'{-}O{-}\overset{O}{\overset{\|}{C}}{-}\overset{H}{N}{-}R{-}\overset{H}{N}{-}\overset{O}{\overset{\|}{C}}{-}O-\right)_n$$

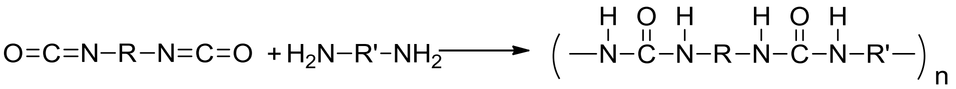
polyurethane

Toluene diisocyanate can also react with amine functional groups (-NH_2). The result of the reaction between TDI and a compound containing two or more amine groups is long polymer chains known as polyureas.



$$R{-}N{=}C{=}O + R'{-}NH_2 \longrightarrow R{-}\overset{H}{N}{-}\overset{O}{\overset{\|}{C}}{-}\overset{H}{N}{-}R'$$

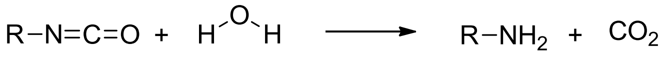
urea



$$O{=}C{=}N{-}R{-}N{=}C{=}O + H_2N{-}R'{-}NH_2 \longrightarrow \left(-\overset{H}{N}{-}\overset{O}{\overset{\|}{C}}{-}\overset{H}{N}{-}R{-}\overset{H}{N}{-}\overset{O}{\overset{\|}{C}}{-}\overset{H}{N}{-}R'-\right)_n$$

polyurea

Moreover, isocyanate groups of TDI react with water to form carbon dioxide (CO_2). Carbon dioxide is a blowing agent (leads to bubbling) which is used for production of polyurethane foam.[22]



$$R{-}N{=}C{=}O + H_2O \longrightarrow R{-}NH_2 + CO_2$$

1.5. Rocket Propellant

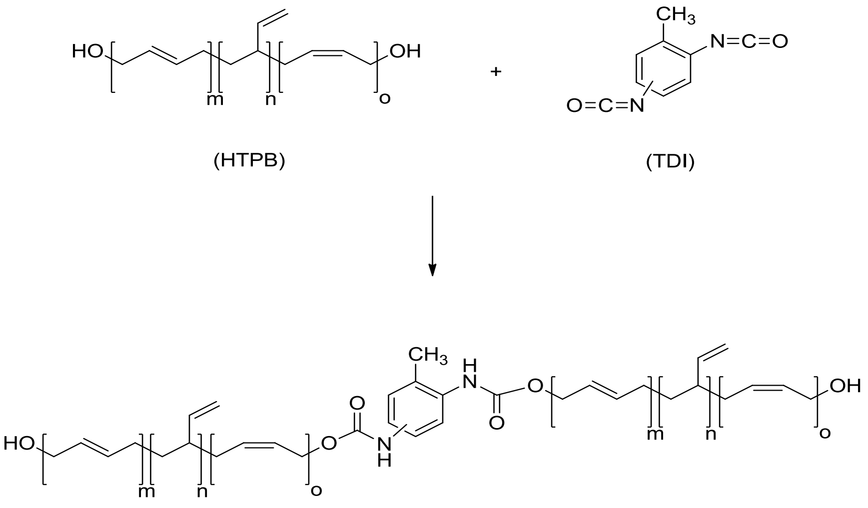
A rocket propellant is an energetic material which produces energy or pressurized gas that leads to motion of vehicle, projectile or other object. Moreover, rocket propellant is the chemical mixture which is composed of basically a fuel and an oxidizer. [23] The fuel is a material, which produces gas when combined with oxygen. The oxidizer is an agent which supplies oxygen for burning. The chemical propellants can be categorized according to their state. There are basically solid, liquid and gas propellants. The hybrid is also another type of propellants including different phase of fuel and oxidizer.[24]

Solid rocket propellants divide into two basic groups, which are composite and homogeneous propellants. Solid propellants can be used in rockets which are very simple compared to other types of rockets. These kinds of propellants have advantages; much easier to store, handle, stable at ordinary temperature, and cost effective than the other type of propellants. Therefore, these features make it more convenient for military applications. Homogeneous propellants can be simple or double base. A simple base propellant is usually nitrocellulose and a double base propellant is composed of nitrocellulose and nitroglycerine.

Composite propellants are heterogeneous mixtures basically composed of fuel, oxidizer, and polymeric binder. Additionally, plasticizers, stabilizers, burn rate modifiers and etc. can also be used in composite rocket propellants. A typical composite rocket propellant contains finely ground mineral salt generally ammonium perchlorate (NH_4ClO_4) as an oxidizer in 69-70% and powder aluminum (Al) as fuel in 16-20%. The reaction between fuel and oxidizer is shown below.

$$10\,Al + 6\,NH_4ClO_4 \longrightarrow 4\,Al_2O_3 + 2\,AlCl_3 + 12\,H_2O + 3\,N_2$$

The polymeric binders (11-14%) are used in order to hold together the composite ingredients.[25] Hydroxyl terminated polybutadiene (HTPB) is a bi-functional polymeric binder generally used in composite rocket propellants. In order to increase the mechanical properties, homogeneity, shelf-life, and control the burning rate, bi-functional isocyanates such as TDI are used. Isocyanates are converted to polyurethanes by reacting with HTPB as shown in Scheme 10. In this reaction, the hydroxyl groups (-OH) of HTPB and isocyanate groups (-NCO) of TDI react with each other to form urethane linkages. In other words, the hydroxyl group attacks to the isocyanate carbon and form carbamate. Furthermore, HTPB and TDI are bi-functional compounds. Hence, matrix polymer is formed (curing reaction).



Scheme 10. General representation of the reaction between HTPB and TDI

The fuel (Al powder) and oxidizer (NH_4ClO_4) gets diffused into the network polymer. The composite propellant can be produced by mixing these compounds as shown in Figure 5.

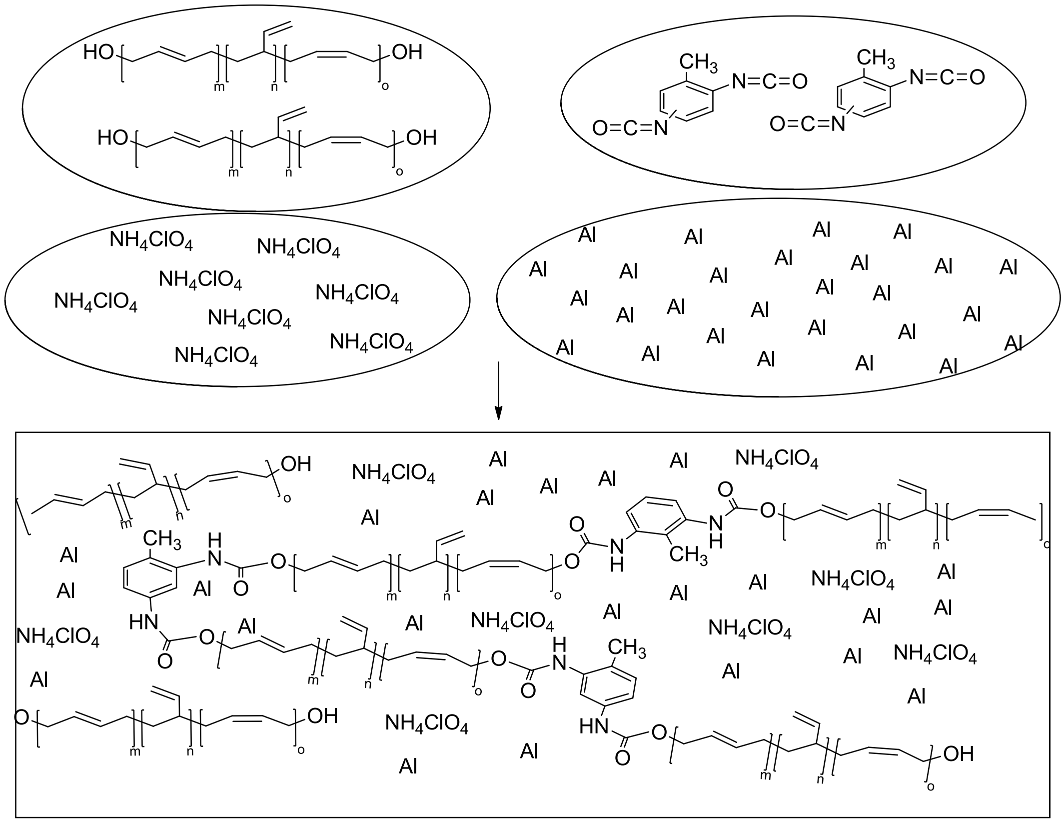


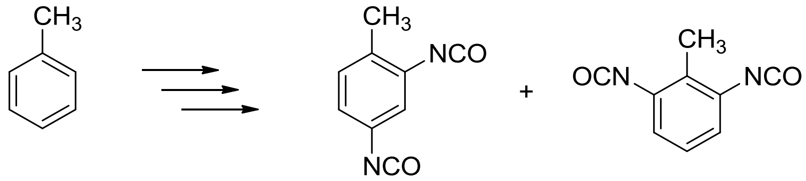
Figure 5. Representation of solid rocket propellant

Liquid propellants are another type of rocket propellants. There are three types for liquid propellants; petroleum, cryogens, and hypergols. Petroleum is refined crude oil and is a mixture of complex hydrocarbons. Highly refined kerosene is a common example of petroleum type of liquid propellant. Cryogens are composed of liquidized gases generally hydrogen and oxygen. Hypergenic propellants (hypergols) are composed highly toxic and corrosive liquids such as combination of dinitrogen tetroxide and hydrazine.[26] Liquid propellants are usually used in more complex engine systems than solid propellants. Their ingredients which are fuel and oxidizer are stored in different tanks and fed simultaneously when the motor is working. Therefore, they have the advantage of controlling the flow of propellant. Another advantage is that liquid propellants can have a high combustion temperature and exhaust gases with small molecular weight. However, due to low density of liquid propellants, storage area is a big problem. This leads to increase in weight of the vehicle. Moreover, the storage temperature of the liquid is very important because most of them exist as liquid at very low temperatures. Therefore it requires insulation system. Hence, the weight and cost of vehicle can be raised. As a result of cost and usage complexity, liquid propellants are used in very special and complex engine systems.

Gas propellants are composed of some compressed gases. This sort of propellant usage area is very limited due to the very low density and high weight of the pressure vessels.[27]

Hybrid propellants are new type of propellants. These propellants composed of different physical state of fuel and oxidizer. Usually, fuel is in solid state and oxidizer is in liquid state.[28] An example of hybrid propellant can be given as HTPB rubber (solid fuel) and nitrous oxide (liquid oxidizer). They have an advantage for having high performance such as solid propellant. However, there are some problems in the combustion process (i.e. stopped or restarted). Hence, hybrid propellants have very limited use.[29]

1.6. The aim of this work



Scheme 11. TDI synthesis starting from toluene

Toluene diisocyanate (TDI) is highly reactive bifunctional organic compound. This compound is used in industry for different purposes. Most importantly, TDI is also used as one of the raw materials of the solid rocket propellants hence it is an essential compound for the defense industry. Unfortunately, TDI is currently imported from abroad. Companies producing missiles and explosives can have difficulties in buying TDI in large quantities and sometimes specific permission may also be required. For such companies, it is important that Turkey has the knowledge and expertise to synthesize these types of compounds. In this thesis we aimed to synthesize TDI starting from toluene in three steps. For each step it is important to find industrially applicable methods.

CHAPTER 2

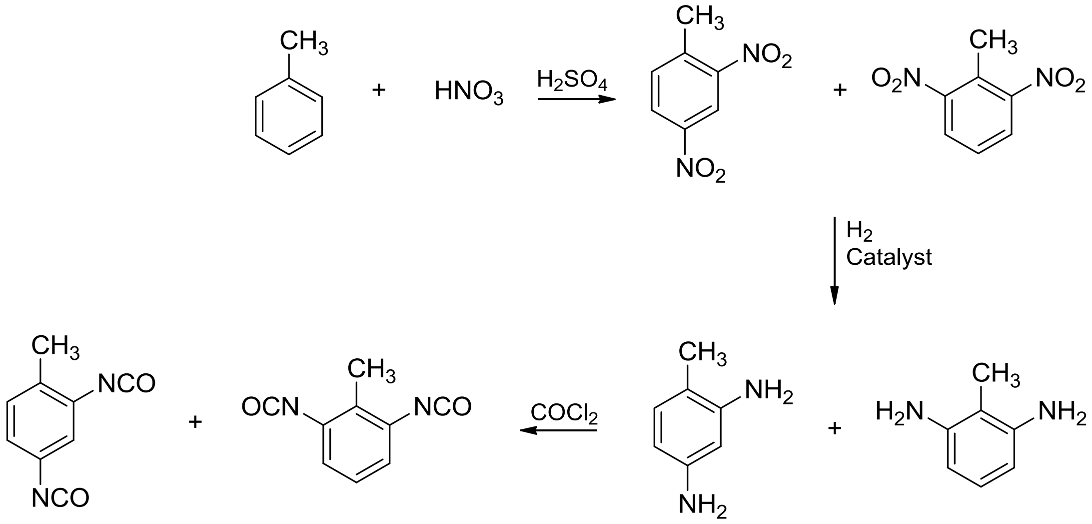
RESULTS AND DISCUSSION

In this thesis work our aim is to achieve the lab-scale synthesis of toluene diisocyanate (TDI) with required specifications in collaboration with ROKETSAN as a SANTEZ project. Synthesized TDI must have the same specifications as shown in Table 2.

Table 2. Specifications of TDI

Property	Required results range
Appearance	Colorless or light yellow, liquid
Purity, %, minimum	99.0
2,4-Isomer Ratio, %	78-82
2,6-Isomer Ratio, %	18-22
Isocyanate content, %	47.90 – 48.32
Hydrolyzed Chlorine content, %	0.01
Density (20°C), g/cm^3	1.21 – 1.23
Refractive Index	1.564 – 1.568
Total chlorine content, %, maximum	0.04

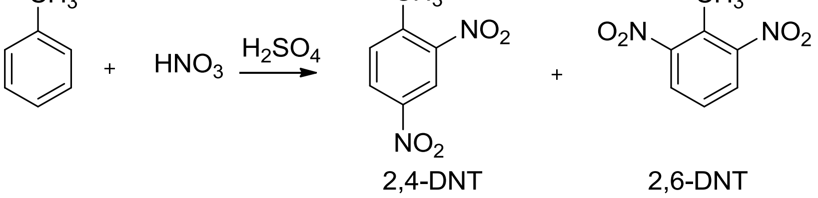
TDI synthesis was carried out in three steps which are in turn nitration of toluene to dinitrotoluene (DNT), reduction of dinitrotoluene to toluenediamine (TDA) and conversion of amino groups to isocyanates (Scheme 12). This synthetic pathway is more economic and industrially applicable when compared to the other alternative pathways as reported by Nexant.[8]



Scheme 12. Synthetic pathway of toluene diisocyanate

2.1. Nitration of Toluene to Dinitrotoluene

In order to synthesize dinitrotoluene (DNT), H_2SO_4 mediated nitration method was developed based on information of literature.[36] This method uses nitric acid (HNO_3) and sulfuric acid which is the catalyst of the reaction (Scheme 13).



Scheme 13. Nitration of toluene to dinitrotoluene

In order to synthesize DNT with the required isomer ratio, it was necessary to perform some optimizations. The required isomer ratio is 2,4-DNT in 78-82% and

2,6-DNT in 22-18%. In order to get this ratio, it was necessary to optimize the reaction time, amount of HNO_3 and temperature. In this method, other isomers like 2,5-DNT were not observed. The reason is that after mononitration, the second nitro group can only go to the *ortho* and *para* positions of the methyl group due to its directing effect. The methyl group is an electron donating group. Therefore, it is an *ortho-para* director which can easily be deduced from the resonance structures shown in Scheme 2 (page 6). The nitro group is an electron withdrawing group and *meta* director. Therefore, mainly 2,4-DNT and 2,6-DNT were formed as the result of second nitration. The optimization studies were summarized in Table 3. The results are based on experiments that are repeated 3-4 times.

Table 3. Optimization studies of DNT synthesis

Entry	**Amount of Toluene** (g)	**Time** (h)	**Ratio of Toluene:HNO₃**	**NT** (%)	**2,4-DNT** (%)	**2,6-DNT** (%)	**Yield** (%)
1	1	3	1:2.0	67	26	7	ND
2	1	3	1:2.5	9	73	18	ND
3	1	3	1:2.8	2	78	20	ND
4	1	3	1:3.0	---	81	19	90
5	1	3	1:3.2	---	80	20	93
6	5	3	1:3.2	---	80	20	94
7	10	3	1:3.2	---	81	19	97
8	10	24	1:3.4	---	82	18	98
9	10	6	1:3.4	---	79	21	97
10	10	3	1:3.4	---	78	22	95
11	10	1.5	1:3.4	---	78	22	96
12	50	3	1:3.2	---	78	22	95
13	130	3.5	1:3.2	---	82	18	90
14	230	1.5	1:3.2	---	80	20	94

ND: Not determined.

Optimization studies for nitration of toluene to dinitrotoluene started with determination of HNO_3 equivalence. Therefore, the isomer ratio of DNT, amount of NT and yield were examined by altering HNO_3 equivalence. As can be seen from Table 3, the amount of HNO_3 was found to be as at least 3.0 equivalents (entries 1-5). otherwise, minor amount of NT was detected. However, the HNO_3 equiv. was not enhanced drastically because trinitrotoluene (TNT) formation could take place. Moreover, in order to prevent formation of TNT the temperature was not higher than 80 ºC. Then, with determined HNO_3 amount scale up studies were done. The results did not change drastically on the 5-10g scale experiments (entries 6 and 7). Secondly, the effect of reaction time on isomer ratio of DNT and yield was examined. According to the results, increase in reaction time didn't affect the yield and isomer ratio significantly (entries 8-10); it was still in the desired range. Under optimized conditions, the reaction was repeated with 50g, 130g, and 230g of toluene without a significant change on the results (entries 12-14). The characterization of the products was done by using ^1H NMR and FT-IR. The isomer ratio was determined by integrating the methyl protons on the ^1H NMR spectrum (Figure 8) where, 2,4-DNT methyl signal appeared at 2.66 ppm and that of 2,6-DNT appeared at 2.49 ppm. TLC was also quite helpful in following the reaction and controlling the product formation. Besides NMR, characterization was also done by FT-IR which showed the signals corresponding to nitro groups at 1515 cm^{-1} and 1342 cm^{-1} (Figure 9).

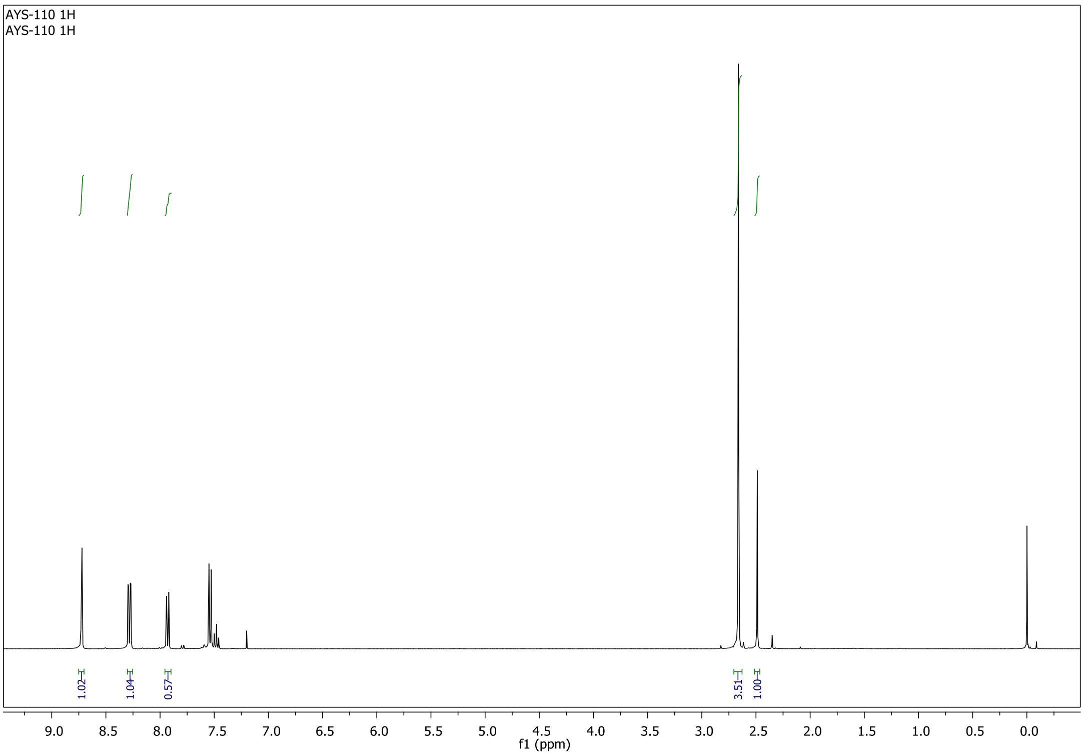


Figure 6. ^{1}H NMR spectrum of mixture of 2,4-DNT and 2,6-DNT

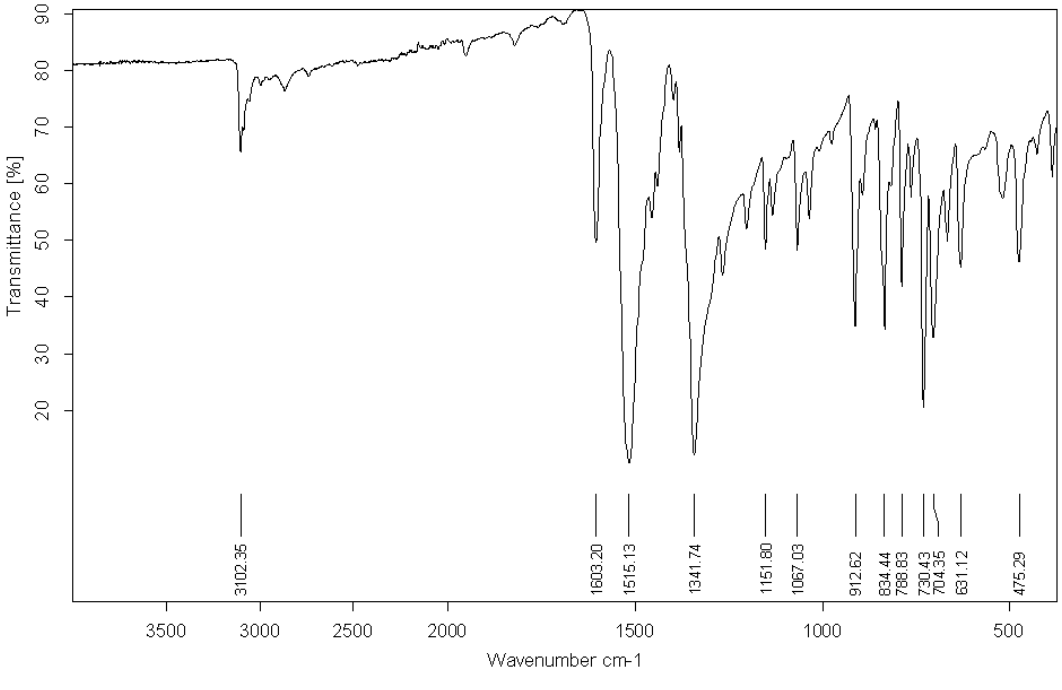
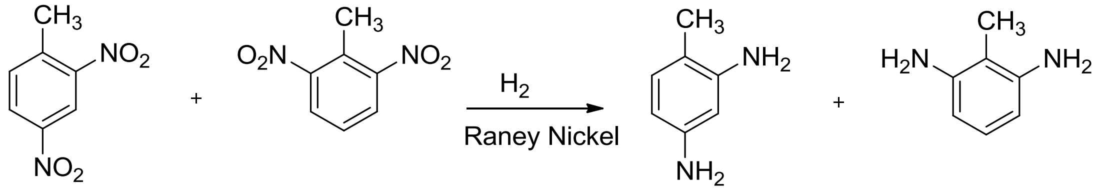


Figure 7. FT-IR Spectrum of a mixture of 2,4-DNT and 2,6-DNT

2.2. Reduction of Dinitrotoluene to Toluenediamine



Scheme 14. Reduction of dinitrotoluene to toluenediamine

After obtaining satisfactory results from the nitration step of the TDI synthesis, we were ready to try the second step which was reduction of nitro groups. In the literature, different catalysts were used for this purpose but in terms of industrial application, it was necessary to find a catalyst with a suitable price, ease of application, ease of availability, and form the product in high yield. Based on the literature studies, it was realized that Raney Nickel could provide all the requirements mentioned before. Therefore we started our studies with this catalyst. In order to form the product in high yield, it was necessary to do some optimization studies. These studies were done by using the H-Cube reactor (Figure 8). It is a continuous type of a reactor with advantages of being user friendly, safer and faster in comparison to a Batch type reactor (Figure 12). In addition, it produces its hydrogen by electrolysis of water. The main disadvantage of this device is that the experiments can be run only on a small scale. For this reaction the important parameters were temperature and pressure.

Figure 8. Image of H-Cube Reactor[30]

First, the pressure was set to 10 bar and temperature was scanned. As can be seen from Table 4 at room temperature or 50 ºC, product formation was not observed (entries 1 and 2). Increasing the temperature to 75 ºC product was observed with starting material (entry 3). Increasing temperature further by keeping the pressure at 10 bar didn’t change the result significantly (entries 4 and 5), starting material and the product were monitored by TLC. Then the pressure was increased to 20 bar and temperature screening studies were carried out starting with 50 ºC (entry 6). The results were very similar, even at 75 ºC (entry 7), to the previous results where DNT and TDA were together. At this pressure, when the temperature was increased to 100 ºC, it was observed on the TLC that there was no starting material. However, there were some uncharacterized compounds (entry 8). Same result was also observed at 125 ºC (entry 9). We continued pressure and temperature screening studies at 25 bar. At this pressure product formation was achieved with satisfactory results only at 100 ºC (entries 10-13).

Table 4. Optimization studies of TDA synthesis by H-Cube

Entry	Pressure (bar)	Temperature (°C)	Result
1	10	25	DNT was recovered.
2	10	50	DNT was recovered.
3	10	75	DNT and TDA were together.
4	10	100	DNT and TDA were together.
5	10	125	DNT and TDA were together.
6	20	50	DNT was recovered.
7	20	75	DNT and TDA were together.
8	20	100	TDA and uncharacterized side products were together.
9	20	125	TDA and uncharacterized side products were together.
10	25	50	DNT and TDA were together.
11	25	60	DNT and TDA were together.
12	25	75	TDA and uncharacterized side products were together.
13	25	100	100% conversion.
14	30	50	TDA and uncharacterized side products were together.
15	30	75	100% conversion.
16	30	100	100% conversion.
17	30	125	100% conversion.
18	40	50	TDA and uncharacterized side products were together.
19	40	75	100% conversion.
20	40	100	100% conversion.
21	50	50	TDA and uncharacterized side products were together.
22	50	75	100% conversion.
23	50	100	100% conversion.
24[a]	40	120	100% conversion.

[a] This experiment was done with 80g of DNT by using the Parr reactor.

In order to find out optimum pressure and temperature, experiments were also carried out at 30 bar (entries 14-17). At this pressure it was possible to achieve complete conversion of DNT to TDA at lower temperature as compared to results at 25 bar. Further studies at 40 and 50 bars also provided similar results (entries 18-23), complete conversion was achieved at 75 ºC. Higher temperatures than 75 ºC seemed to be unnecessary. From these optimization studies it was concluded that the pressure should be around 30 bar and temperature should be around 75 ºC. In order to adapt these experimental parameters to a large scale synthesis, it was necessary to do some experiments by the batch reactor (Figure 12).

Figure 9. Image of Parr Reactor (Batch-type reactor)

In order to make sure that the complete conversion of DNT was achieved, pressure was set at 40 bar and temperature at 120 ºC. Under these conditions, in order to obtain enough material for tests, about 15 experiments were done at different times. For these experiments 80 g of DNT in ethyl alcohol was used and product was isolated in quantitative yield (entry 24). Product was confirmed by ^{1}H NMR spectrum (Figure 13). Aromatic protons of 2,4-TDA and 2,6-TDA appeared at around 6.00-7.00 ppm, amine protons appeared as a broad singlet at 3.49 ppm, and methyl protons appeared as a singlet at 2.15 and 1.95 ppm.

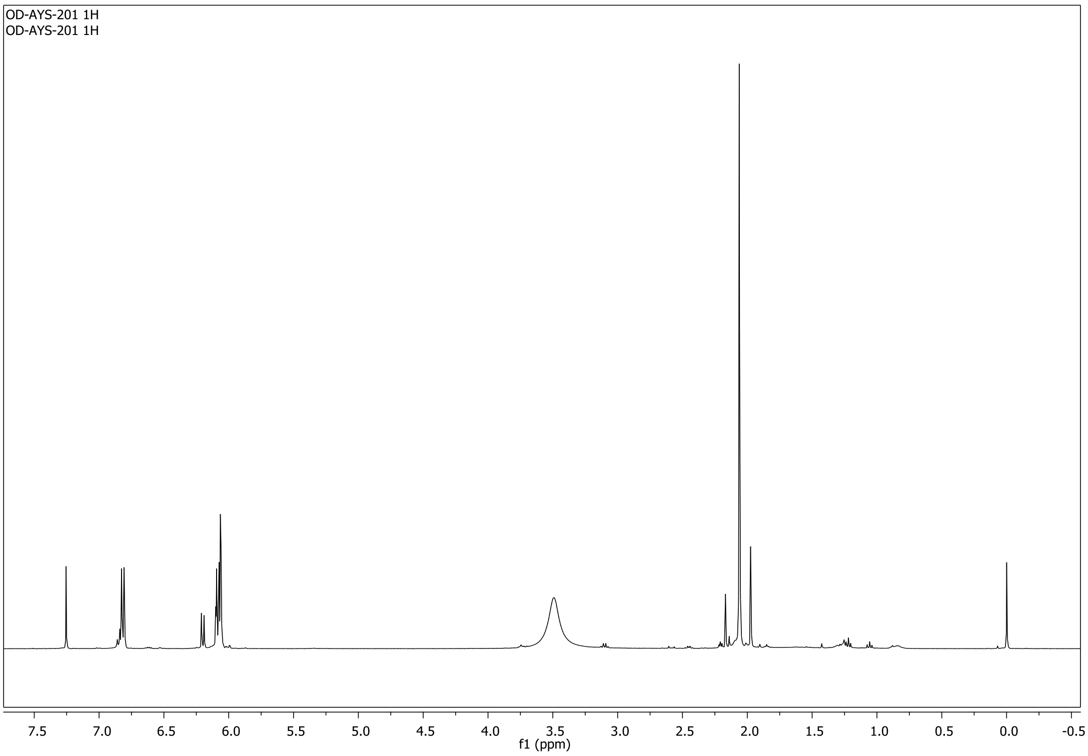
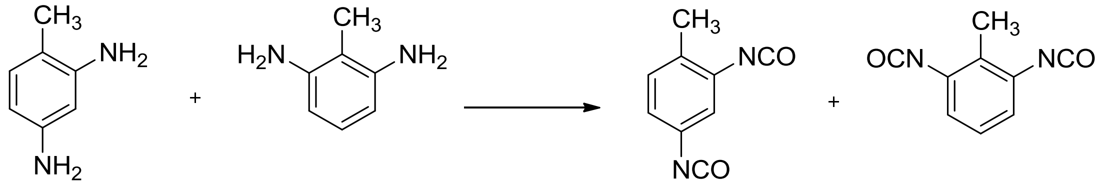


Figure 10. ^{1}H NMR spectrum of 2,4-TDA and 2,6-TDA mixture

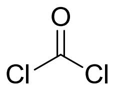
2.3. Conversion of Amino Groups to Isocyanates

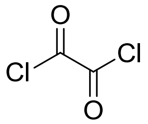


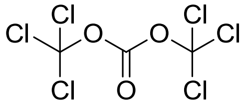
Scheme 15. Conversion of amino groups to isocyanates

This step was the most critical one for the TDI synthesis. There are many methods; however, most of them are not industrially applicable. Industry uses phosgene or its equivalents (diphosgene and triphosgene) for the production of isocyanates including

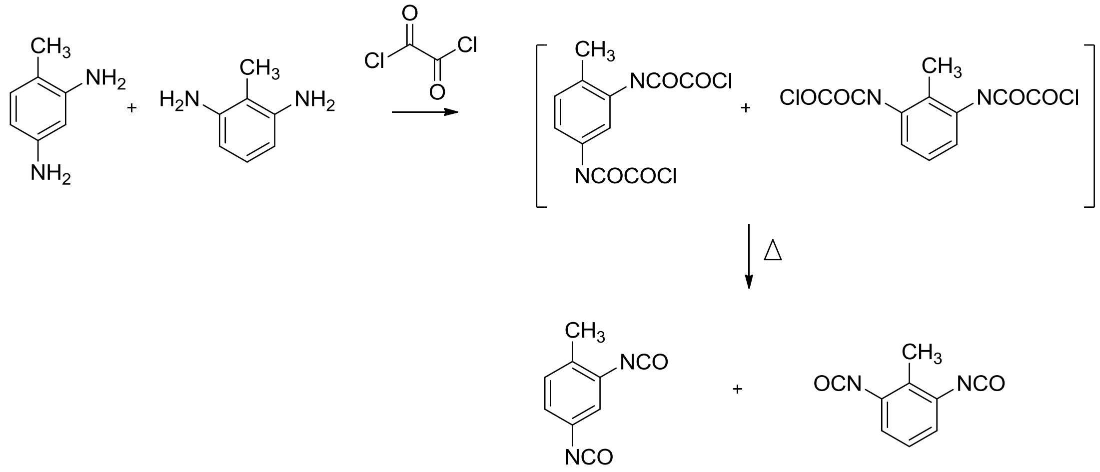
TDI.[31] For the lab scale synthesis oxalyl chloride is another alternative to phosgene or its equivalents.


Phosgene


Oxalyl chloride


Bis (trichloromethyl) carbonate
Triphosgene

Phosgene is the most reactive compound among all the reagents for isocyanate synthesis. Hence, we planned our studies with phosgene. However, phosgene is highly toxic gas and it can be used as chemical weapon. Therefore, it is difficult to import phosgene. Therefore we started our lab scale synthesis by using oxalyl chloride (OxCl).[32]



Scheme 16. TDI synthesis with OxCl

According to this reaction pathway, OxCl reacts with amine groups of TDA to form 2-oxo(arylamino)acetyl chloride which is converted to isocyanate at elevated temperature up to 170 ºC. At low temperature isocyanate peaks are not observed on the FT-IR spectrum. We have used both high (*o*-dichlorobenzene) and low (ethyl acetate) boiling solvents. The results of some of these studies were summarized in

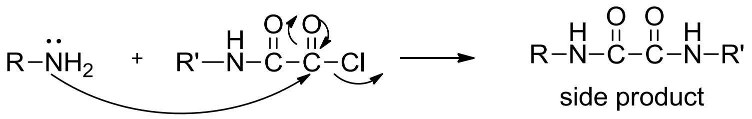
Table 5. Unfortunately, the product was obtained just in trace amount. Mainly dark colored polymeric material was obtained.

Table 5. Isocyanate formation by OxCl

Entry	Concentration (M)	Solvent	Temperature (°C)	Time (h)	Addition Type	Result
1[a]	0.50	*o*-DCB	90-160	2	Dropwise	No product
2[a,b]	0.50	*o*-DCB	50-160	3	Dropwise	No product
3[b]	0.50	*o*-DCB	50-160	3	Dropwise	Trace amount
4	0.10	EtOAc and *o*-DCB	10-130	3	Dropwise	Trace amount
5[a]	1.50	$EtCl_2$	0-80	5	At once	Trace amount
6	1.50	$EtCl_2$	0-80	5	At once	Trace amount

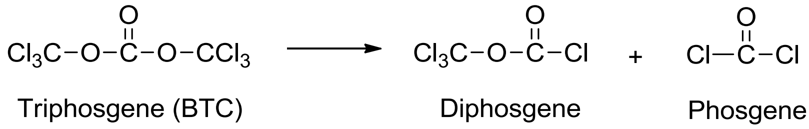
[a]TDA salt
[b]Repeated via 1 g and 4 g of TDA

Formation of polymeric material can be explained by the reaction of one of amine group of TDA and intermediate product as shown below.[33]



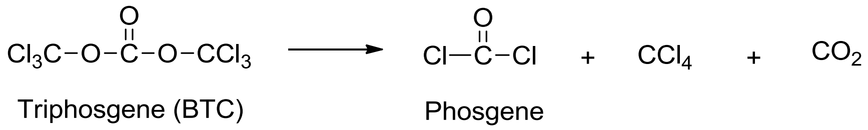
Scheme 17. Mechanism of side product formation

After unsuccessful results with oxalyl chloride, we looked at the alternative reagent and decided to use triphosgene. Triphosgene (bis(trichloromethyl) carbonate, BTC) has advantages as compared to phosgene. It is solid and stable at room temperature. Therefore, it is safer, more practical, easy to handle, store, and transport. Conversion of triphosgene to phosgene has been identified in three different ways depending on the reaction conditions as reported in the literature. Triphosgene produces phosgene and diphosgene at low temperature, even during its distillation under reduced pressure (Scheme 18).[34]



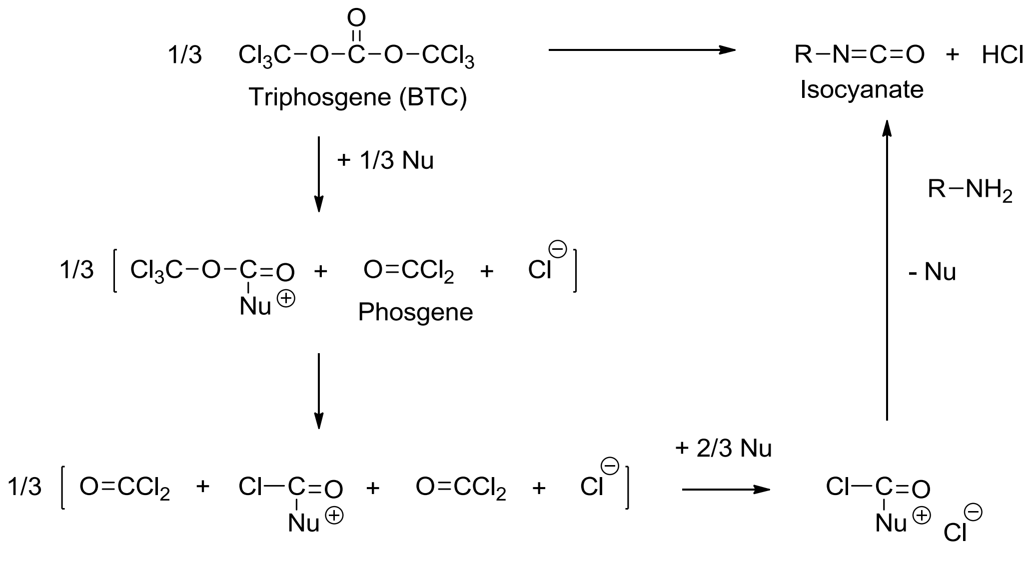
Scheme 18. Diphosgene and phosgene formation from BTC

It also produces phosgene, tetrachloromethane, and carbon dioxide in the presence of activated carbon or a Lewis acid when heated at melting temperature of BTC (80 °C).



Scheme 19. Phosgene, tetrachloromethane, and carbon dioxide formation from BTC

Moreover, triphosgene can also produce 3 moles of phosgene in the reaction medium when reacted with amines to form isocyanates as shown in Scheme 20.[35]



Scheme 20. Isocyanate formation from triphosgene

Studies carried out with BTC were summarized in Table 6. As can be seen from this table, we examined the concentration of TDA, addition type, solvent and equivalence of BTC by monitoring the reaction with FT-IR. In the FT-IR one can easily observe the disappearance of amine signals at around 3300 cm^{-1} and appearance of very characteristic strong isocyanate signal at around 2200 cm^{-1}. In order to find out the difference between free amine form of TDA and its HCl salt, reactions were performed both with free amine form and salt form (entries 1 and 2). The experiments showed that the free amine form of TDA formed the product in higher yield. Therefore the optimization studies were continued with the free amine form of TDA. Next, we examine the effect of time of addition (entries 3 and 4). Clearly, slow addition produced TDI in high yield. This may be attributed to the lower TDA concentration in the reaction medium.[34] At high concentration of TDA, it can react with the intermediates shown in Scheme 16 to form urea type side products. Further optimizations were carried out to find the optimum ratio of TDA to BTC. From these studies the ratio of 3:2.4 (1.2 mol of phosgene was used for 1.0 mol of amino group) was found to be the optimal values. Using higher amount of BTC lowered the yield of TDI (entries 1 and 7). Among the solvents chlorobenzene, butylacetate and toluene, toluene formed the product in higher yield (entries 8-10). Finally, under the optimized conditions (toluene as the solvent, 5.5 mL/min addition rate, 3:2.4 ratio of TDA: BTC) the reaction was repeated with 48 g of TDA which formed TDI in 58% isolated yield. FT-IR spectrum of synthesized TDI is shown in Figure 17.

Table 6. Optimization studies of TDI synthesis by triphosgene

Entry	TDA:BTC	Addition (mL/min)	Solvent	Yield[a] (%)
1	3:4	5.5	Toluene	33
2[b]	3:4	5.5	Toluene	12
3	3:4	At once	Toluene	10
4	3:4	3	Toluene	40
5	3:5	3.5	Toluene	26
6	3:4	3.5	Toluene	33
7[c]	3:2.4	5.5	Toluene	40
8[d]	3:2.4	5.5	Toluene	58
9	3:2.4	5.5	Butylacetate	28
10	3:2.4	5.5	Chlorobenzene	30

[a] Isolated yield
[b] Toluenediamine hydrochloride was used.
[c] 20 g of TDA was used.
[d] This experiment was performed with 48 g of TDA.

From the FT-IR spectrum, sharp and strong isocyanate signal at 2239 cm^{-1} can be easily observed (Figure 17). Moreover, the isomer ratio of the TDI can also be determined by using FT-IR spectrum using the signals at around 810 cm^{-1} and 782 cm^{-1}. By the quantitative analysis of the spectrum, the percentage of 2,4-TDI and 2,6-TDI could be calculated. For the specification of TDI, required isomer ratio is 78-82% for 2,4-TDI and 18-22% for 2,6-TDI.

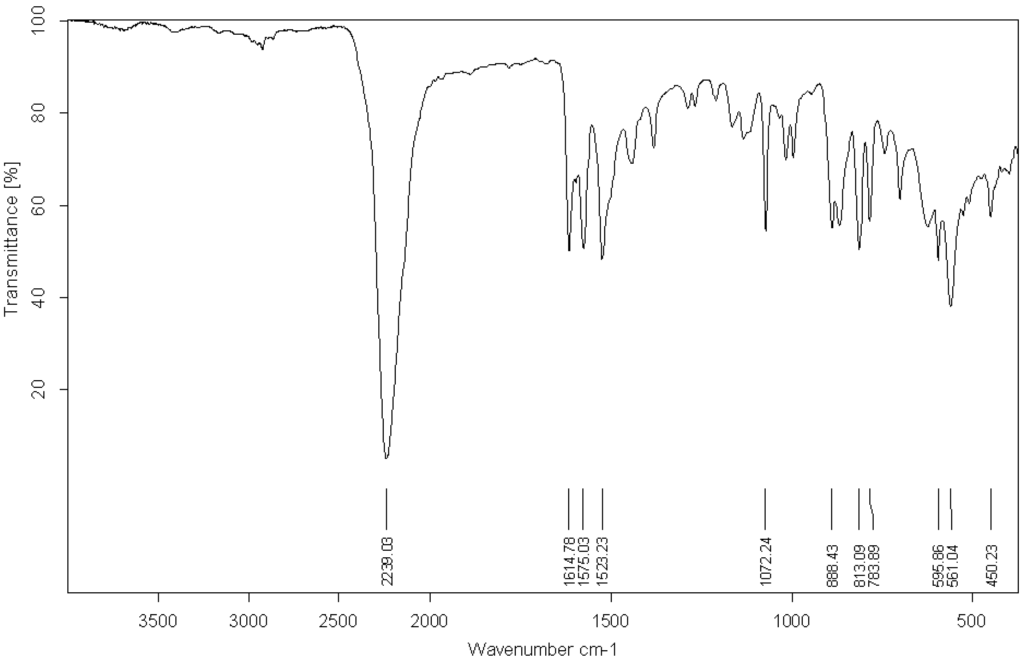


Figure 11. FT-IR spectrum of a mixture of 2,4-TDI and 2,6-TDI

^{1}H NMR spectrum of the synthesized TDI was also consistent with the literature (Figure 18).

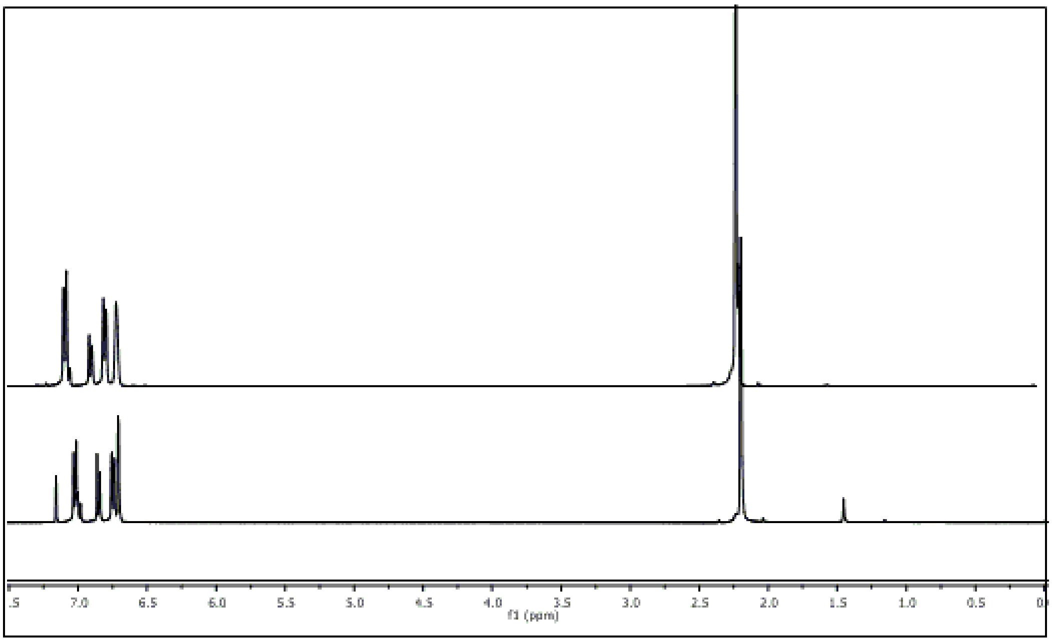
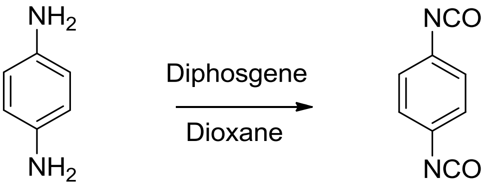


Figure 12. ^{1}H NMR spectrum of synthesized TDI (below) and reference TDI (upper)

Although, the isolated yield of TDI is 58% which can be considered as low, it is better than the literature. In the literature *p*-phenylenediamine was reacted with diphosgene to produce corresponding isocyanate in 47% yield (Scheme 21). Same reaction was also done with HCl salt of *p*-phenylenediamine but the yield was 23%. In general literature studies showed that aryldiamines form isocyanates in low yields.[35] This may be attributed to the high reactivity of aryldiamines. They can react with intermediates or isocyanates formed in the reaction medium to give urea type side products.



Scheme 21. Reaction of *p*-phenylenediamine with diphosgene

In industry, the high mass production for TDI was achieved by Bayer gas phase reaction. This method is said to be more economical. It is patented by Bayer Material Science.[36] In this method, TDA is vaporized at 250-450 ºC and diluted with inert gas or solvent. Phosgene is also heated at 200-600 ºC and diluted with inert gas or solvent. The gaseous reactants are injected to the plug flow reactor (continuous type) with the residence time of 0.5-1.5 s. Gases coming out of the reactor are condensed to isolate TDI in liquid form.

2.4.Determination of Hydrolyzable Chlorine in TDI

One of the specifications of TDI is the hydrolyzable chlorine content which is 0.01%. The source of hydrolyzable chlorine is believed to be intermediate carbamoyl chloride and dissolved phosgene. In order to decrease hydrolyzable chlorine content, stripping process was done by purging N_2 gas at 60 ºC. Our studies for reducing hydrolyzable chlorine content were summarized in Table 7.

Table 7. Studies for reducing hydrolyzable chlorine content of TDI

Entry	**Temperature** (ºC)	**Time of Stripping Process** (h)	**Initial Hydrolyzable Chlorine Content** (%)	**After Stripping Hydrolyzable Chlorine Content** (%)
1	40	20	0.823	0.531
2	40	30	0.531	0.254
3	60	38	0.254	0.03

2.5.Studies Related for Other Specifications

Besides hydrolyzable chlorine content other specifications for TDI were summarized in Table 8 and compared to the required value of specifications.

Table 8. Results of synthesized TDI

Property	**Required results range**	**Synthesized TDI**
Appearance	Colorless or light yellow, liquid	Colorless liquid
Purity, %, minimum	99.0	99.3
2,4-Isomer Ratio, %	78-82	79
2,6-Isomer Ratio, %	18-22	21
Isocyanate content, %	47.90 – 48.32	47.97
Hydrolyzed Chlorine content, %,	0.01	0.03
Density (20°C), g/cm^3	1.21 – 1.23	1.21
Refractive Index	1.564 – 1.568	1.567
Total chlorine content, %, maximum	0.04	---

It can be seen from Table 8 that synthesized TDI was satisfied most of the specifications, purity, isomer ratio, isocyanate content etc.

CHAPTER 3

CONCLUSION

Toluene diisocyanate (TDI) is one of the industrially important material especially for companies producing beds, car seats etc. It is also one of the important components of solid rocket propellants. It is a highly reactive compound and used for the synthesis of network polymers composed of urethane linkages. TDI is not produced in Turkey and has to be imported from abroad. Depending on the purpose of use, it can be limited in terms of amounts or it may require special permission. Therefore the production of this compound in Turkey is important. In this project the synthesis of this compound was achieved in three steps on a 100 g scale starting from toluene. First step was the nitration of toluene which was accomplished in 95% yield with desired quality and isomer ratio. Second step was the reduction of nitro groups. This step was also succeeded after some optimization studies by using Raney Nickel catalyst in about quantitative yield. The last step of the TDI synthesis was the conversion of amino groups to isocyanate groups. This critical step was also achieved successfully by an easily applicable procedure using triphosgene in 58% yield. All the steps were repeated more than once. Therefore they are reliable and can easily be applied by the industry. Although the experiments were done on a 100 g scale, it can easily be performed on a kg scale. In addition, the method developed for the isocyanate formation was also applied successfully for the synthesis of isophorone diisocyanate (IPDI) which is also an industrially important compound.

CHAPTER 4

EXPERIMENTAL

4.1. Instrumentation

Following instruments and materials were used for the characterization of products during the study.

^{1}H NMR spectra were obtained in $CDCl_3$-CCl_4 (1:1) solvent system, recorded in a Brucker Spectrospin Avance DPX-400 Ultra shield instrument at 400 MHz and 100 MHz respectively. The ^{1}H NMR data was reported as chemical shifts (δ, ppm) relative to tetramethylsilane (δ 0.00), peak multiplicity (abbreviations are as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad) and coupling constants in Hertz integrated number of protons.

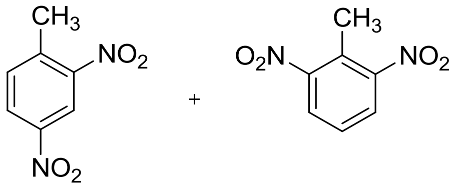
FT-IR instrument were used with ATR apparatus. The FT-IR spectra are reported in reciprocal centimeters (cm-1).

Reactions were monitored by TLC using 250 µm Silica Gel 60 F254 plates and visualized by UV-light at 254 nm. Phosphomolybdic acid in ethanol was used for TLC dye. The relative portions of solvents are in volume:volume ratio used in TLC monitoring as eluent.

Continuous hydrogenation was done by using H-Cube Hydrogenation. Batch type hydrogenation was done by 5L autoclave Parr reactor.

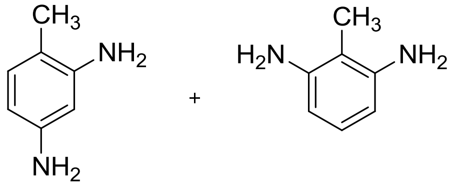
4.2. Synthesis and Characterization of Compounds

4.2.1. Synthesis of Dinitrotoluene



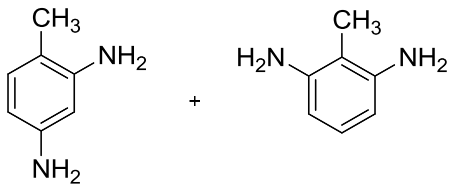
Concentrated nitric acid (15.30 mL, 347.3 mmol) was placed in a 100 mL round bottom flask with a reflux condenser, and concentrated sulfuric acid (28 mL, 52 mmol) was added in small portions with vigorous stirring. During the addition, temperature of the mixture was kept low by placing in an ice-bath. To this mixture was added toluene (11.6 mL, 109 mmol) dropwise by stirring the mixture vigorously. The temperature was controlled and kept below 55 °C. When the addition of toluene was finished, the reaction temperature was increased to 80 °C (but not appreciably higher in order to prevent TNT formation) and stirred at this temperature for 3 hours. At the end of this time, crushed ice was added to the reaction medium and stirred well in order to wash out as much acid as possible from dinitrotoluene and then allow standing. Next, the acid liquor was poured off completely and the solids were taken into a separatory funnel. After dissolving the solids in dichloromethane (100 mL), it was washed with cold water (2x100 mL). Then the organic layer was dried over $MgSO_4$, filtered, and concentrated by using rotary evaporator to get the product as pale yellow solid (19.2 g, 97% yield). The product was controlled by TLC plate (Hexane:EtOAc, 3:1, R_f = 0.74). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.72 (d, *J* = 2.4 Hz, major-1H), 8.28 (dd, *J* = 8.5, 2.4 Hz, major-1H), 7.93 (d, *J* = 8.1 Hz, minor-2H), 7.53 (d, *J* = 8.5 Hz, major-1H), 7.47 (t, *J* = 4.2 Hz, minor-1H), 2.66 (s, major-3H), 2.49 (s, minor-3H). FT-IR (cm^{-1}) 3102, 1603, 1515, 1343, 1152, 1067, 913, 834, 789, 730, 704, 631, 475.

4.2.2. Synthesis of Toluendiamine by Continuous Reactor (H-Cube)



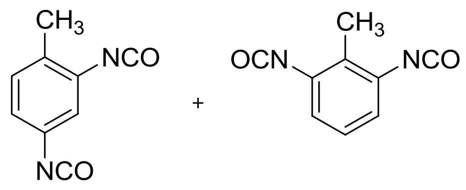
The mixture of 2,4-DNT and 2,6-DNT (92 mg, 0.50 mmol) was dissolved in ethanol (100 mL) in order to prepare 0.05 M, dinitrotoluene solution. The flow rate of H-Cube reactor was adjusted as 1 mL/min and Raney-Nickel Cad-Cart was used as the catalyst. In order to get optimum conditions different pressures (10-50 bar) and temperatures (25-125 ˚C) were screened as listed in Table 4 (page 25) with the range as, respectively. Reaction progress was monitored by TLC (Hexane:EtOAc, 3:1, R_f= 0.05).

4.2.3. Synthesis of Toluenediamine by Batch Reactor



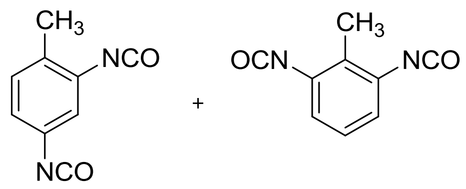
The mixture of 2,4-DNT and 2,6-DNT (80.0 g, 0.655 mol) was dissolved in ethanol (2 L) at 50 ˚C. Then the solution was introduced into the Parr reactor. Then Raney Nickel catalyst (8 g) was also added to the reactor. In order to remove oxygen the reactor was vacuumed and filled with nitrogen twice. Then the same process was also repeated with hydrogen once. The reactor was filled with hydrogen until 40 bar and the temperature was set at 120 ˚C. The reaction was continued until the pressure was reached to a constant value. At constant pressure stirring was continued for another hour. Then the reactor was cooled to 50 ˚C and purged with nitrogen to remove excess hydrogen. The reaction mixture was filtered from charcoal which was washed initially with 1 N of HCl in order to inactivate the catalyst. Finally the filtrate was evaporated to yield TDA in 92 % as a mixture of isomers (48.5 g, 0.397 mmol) The product was controlled by TLC plate (Hexane:EtOAc, 3:1, R_f = 0.05). The color of the product was light brown, as it interacted with atmospheric oxygen it became dark brown. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.83 (dd, *J* = 13.1, 7.8 Hz, major&minor-2H), 6.20 (d, *J* = 7.9 Hz, minor-2H), 6.11–6.04 (m, major-2H), 3.49 (broad, major&minor-4H), 2.06 (s, major-3H), 1.97 (s, minor-3H).

4.2.4. Synthesis Toluene Diisocyanate by Oxalyl Chloride



Under a nitrogen atmosphere, a mixture of 2,4-TDA and 2,6-TDA (2.800 g, 22.92 mmol) was dissolved in ethylacetate (150 mL) at 5-10 ˚C. OxCl (8.727 g, 68.76 mmol) was introduced to the reaction medium dropwise. Then 50 mL of *o*-dichlorobenzene was added. Under the Dean-Stark set-up, the reaction temperature was increased to 130 ºC which removed EtOAc and excess OxCl. The crude reaction mixture was distilled under vacuum. Product was formed in trace amount.

4.2.5. Synthesis of Toluene Diisocyanate by Triphosgene



For this reaction, all operations were done in a hood. Isocyanate, triphosgene and phosgene must be handled carefully. It is better to use a phosgene detector. Reaction was carried at 500 mL two necked round bottom flask having double jacked condenser which is connected to a trap (20% of NaOH solution). To this flask was added BTC (95.9 g, 323 mmol in 490 mL of toluene). Then TDA (49.3 g, 404 mmol in 2.50 L of toluene) was added to the reaction flask drop by drop. When the addition was completed, the reaction flask was heated at reflux temperature of toluene for 2 hour. The reaction was monitored by FT-IR which showed disappearance of amine signals and appearance of isocyanate signal (2200 cm^{-1}). The reaction mixture was filtered by suction filtration. Then the filtrate was concentrated by using rotary evaporator. Then the crude product was purified by vacuum distillation to TDI as a colorless liquid with 58% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.07–6.96 (m, major&minor-2 H) 6.85 (d, J = 8.0 Hz, minor-2H), 6.75 (dd, J = 8.1, 2.2 Hz, major-1H), 6.71 (d, J = 2.1 Hz, major-1H), 2.20 (s, major&minor-6H).). FT-IR (cm^{-1}) 2239, 1614, 1523, 1072, 888, 813, 784, 561.

4.2.6. Determination of Hydrolyzable Chlorine of Toluene Diisocyanate

TDI sample (10 g) was taken into a 400 mL beaker. Then, methanol (50 mL) was added and stirred. Then beaker was filled with 150 mL of water quickly to keep the reactants from solidifying and to minimize the loss of HCl. Then, the mixture was boiled gently for 30 min. The reaction temperature was decreased about 10°C with the help of icebath. Then 10 drops of HNO_3 was added. Titration was done potentiometrically with 0.01 *N* $AgNO_3$ solutions using a silver-silver chloride electrode pair. Calculation of the hydrolyzable chlorine as weight percent was done with the formula as folllows:

$$\text{Hydrolyzable chlorine, } \% = 3.55AN/W$$

where:
A = $AgNO_3$ solution required for titration of the sample, mL
N = normality of the $AgNO_3$ solution, meq/mL
W = sample used, g
3.55 = constant combining the atomic weight of chlorine (35.5), mg, the conversion from milligrams to grams (1000), and conversion to percent (100).
Hydrolyzable chlorine, % = $35.5AN(100)/1000W = 3.55AN/W$

4.2.7. Determination of Total Chlorine of Toluene Diisocyanate

The 25 mL of Na_2CO_3 was placed absorbing solution in an empty combustion flask. Then the flask was purge with oxygen for about 30 s to displace air. The 200 mg of sample was added to the absorbent cotton from a weighing buret containing a known amount of sample weighed to the nearest 0.5 mg by avoid contamination from fingerprints. While holding the flask nearly horizontal in one hand and the stopper in the other, light the filter-paper was fused with a Bunsen flame and quickly and smoothly inserted the stopper. In the same motion and after the stopper was firmly seated, tilt the flask beyond the horizontal so that the liquid would run down and form a seal around the stopper. The stopper was hold firmly in place. (**Warning—** Ignition may cause a sudden buildup of pressure within the flask. While the sample is being combusted, handle the flask with leather or heavy vinyl gloves behind a safety shield. Alternatively, the risk of explosion can be minimized using a Thomas-Lisk combustion flask with a rubber balloon attached to a side arm for the safe expansion of gas. The combustion should be carried out in a safety cabinet such as the Schöniger Combustion Ignitor. This apparatus uses an infrared lamp to ignite black filter paper in the combustion flask.) After the combustion was completed, the flask to was rotated in order to wet the flask wall being careful not to wet the platinum basket. The flask was stand 5 to 10 min. Then, the stopper was removed and again purged with oxygen. Moreover, two more 200 mg portions of the same sample were burned in the same flask in accordance with same procedure. To the nearest 0.5 mg, the weighing buret was reweighed to determine accurately the total amount of sample burned. The solution was transferred into a 100-mL beaker. The flask was rinsed with small portions of Na_2CO_3 solution, adding the rinsed to the 100-mL beaker. Acidify the solution to methyl red by adding HNO_3 drop wise, then added 0.1 mL excess. The solution was titrated potentiometrically with standard 0.01 N $AgNO_3$ solution, by using a silver-silver chloride electrode system. Calculation the total chlorine as weight percent was done with the formula as follows:

$$\% \text{ Total chlorine} = 3.55(A-B)N/W$$

A = $AgNO_3$ solution required for titration of the sample, mL
B = $AgNO_3$ solution required for titration of the blank, mL
N = normality of the $AgNO_3$ solution
W = sample used, g
3.55 = constant combining the milligram atomic weight of chlorine (35.5), conversion from milligrams to grams (1000), and conversion to percent (100).

$$\% \text{ Total chlorine} = (A-B)\ 35.5(100)/\ (1000) = 3.55(A-B)N/W$$

4.2.8. Determination of Isocyanate content of Toluene Diisocyanate

N-butylamin-dioxane solution was prepared as 25 g of N-butylamine was dissolved in 1.0 L dioxane. Moreover, methyl red methylene blue indicator was prepared with dissolving 0.100 g of methyl red and 0.0821 g of methylene blue in 100 mL of ethyl alcohol (%90). Then, 0.15 g of TDI sample was placed into the flask and 10 mL of dioxane was added. 10 mL of N-butylamin-dioxane solution was introduced the mixture and left to stand for 5-6 minutes. Moreover, 25 mL of distilled water and 3-4 drops of indicator was added to the mixture. Then, titration was done with 0.1 M of H_2SO_4 until light purple color was observed. Furthermore, the blank was also analyzed. Calculation of the isocyanate as weight percent was done with the formula as follows:

$$\text{Isocyanate, \%} = [0.08707(V2-V1)\ C * 100] / m$$

where:

V1 = Volume of H_2SO_4 consumed for blank, mL

V2 = Volume of H_2SO_4 consumed for TDI sample, mL

C = Molar concentration of H_2SO_4

m = mass of TDI sample, g

0.08708 = 0.5 equiv g of TDI/mmol

4.2.9. Determination of Purity of Toluene Diisocyanate by Isocyanate Content

The data from determination of isocyanate content of TDI was used. Calculation the purity of TDI as percent was done with the formula as follows:

$$\text{Purity, \%} = (\text{Isocyanate,\%})\ 2.074$$

where:

2.074 = 1.0 equiv g of TDI/2.0 equiv g of NCO

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