

## **FORMATION OF TARS IN THE TDA-TDI SYNTHESIS AND EXPERIMENTAL STUDY OF ITS REMOVAL IN THE TDI RECOVERY PROCESSES**

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Based on experimental investigations of toluene-diamine (TDA) and toluene-diisocyanate (TDI) synthesis as well as TDI distillation in the TDI recovery processes theoretical study of chemical reactions of tar formation was considered. Summarizing our theoretical study, we conclude that tars formation chemical reactions in TDA and TDI synthesis are unavoidable by-product formation reactions, which have large influence on realization of industrial technology of TDA and TDI manufacturing. Vacuum distillation was used for the TDI recovery from the TDI-TAR mixture and the chemical reactions, the complex process of decomposition and phase transformation of TAR-TDI mixture were tested. The effect of different factors as presence of residues of catalyst in the feed material, ingress of oxygen and water into the process chamber of TDI recovery equipment also were considered.

**Keywords:** formation of tars, chemical reactions, removal of tars, phase transformation, oligomer formation, polymerization, decomposition

### **Introduction**

In our former investigations we have investigated recovery technology of toluene-diamine (TDA) content of TDA-tar mixture and method of disposal of TDA-tar [1], as well as mixability of TDA-tar and ortho-toluene-diamine (OTDA) liquid streams [2]. In the present study based on experimental investigations of TDA-tars formation as byproduct of TDA synthesis and phosgenation reactions of TDA with formation of toluene diisocyanate (TDI) in the synthesis and TDI recovery processes, theoretical study of chemical reactions of tar formation, and tars removal as well as study of physical-chemical processes were performed. We describe the TDA-tars formation reactions during TDA synthesis, as well as TDI-tars formation during TDA phosgenation step of TDI synthesis in the present study.

### **1. TDA tars formation as byproduct of TDA synthesis**

#### ***1.1. Formation of pre-tars***

During toluene-diamine (TDA) synthesis by hydrogenation of dinitro toluene (DNT) TDA is produced, but simultaneously side reactions take place with formation of so-called pre-tars [1]:

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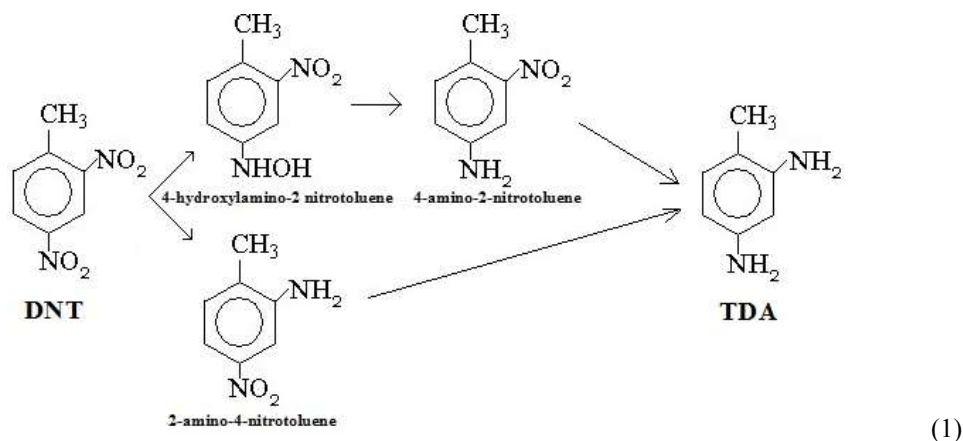
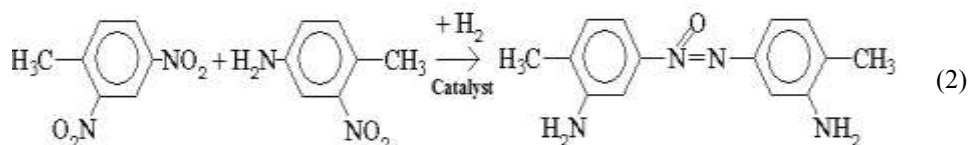
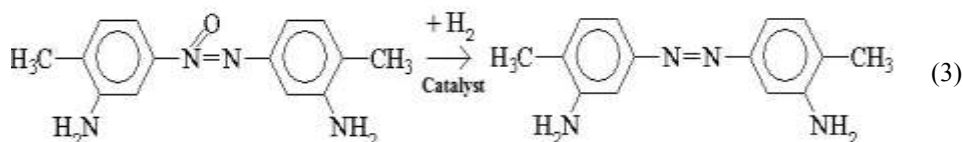


Figure 1. TDA pre TAR-s formation during the TDA productions

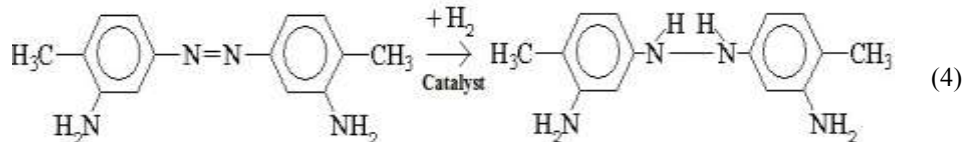
Components yet unconverted to TDA can be considered as the so-called pre-tars. If these components remain adsorbed on the surface of hydrogenation catalyst for too long time they can react to each other to form dimers. During dimerization reactions azoxy-, azo-, and hydrazo-benzene derivatives are formed. Approx. 20% of tar components are produced by these reactions. Different combination of pre-tars will produce TDA-tars as it is illustrated below:



Pre-tars                      TDA-tar (2,2'-diamino-4,4'-azoxytoluene)



TDA-tar (2,2'-diamino-4,4'-azoxytoluene) TDA-tar (2,2'-diamino-4,4'-azotoluene)

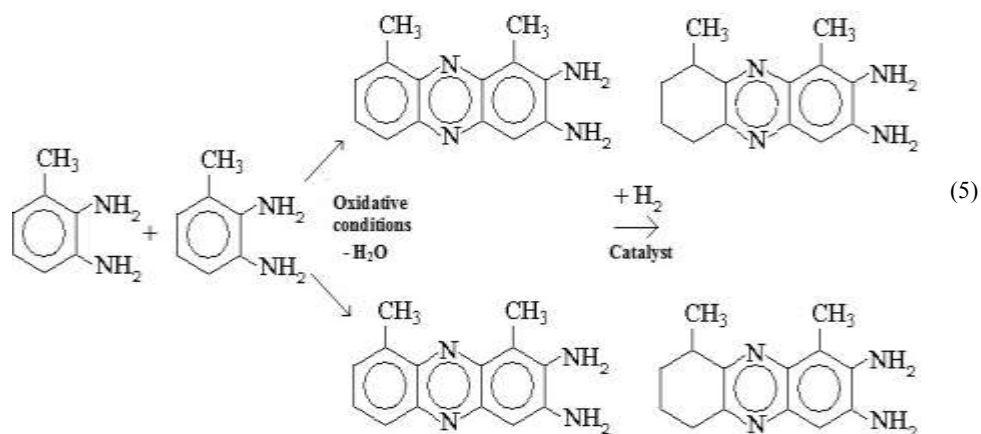


TDA-tar(2,2'-diamino-4,4'-azotoluene) TDA-tar(2,2'-diamino-4,4'-hydrazotoluene)

Figure 2. TDA TAR formation reactions

### 1.2. TDA-tar formation from ortho-isomers

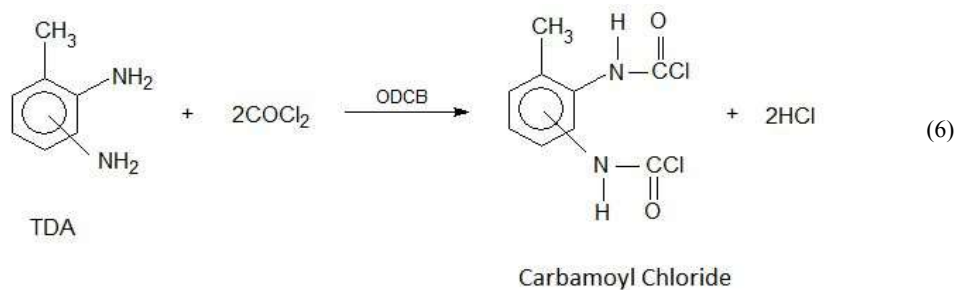
Micro zones of DNT saturated catalyst surface provide oxidative environment so the ortho isomers can react to form diamino-dimethyl-phenazin derivatives giving 80% of TDA-tar components (the aromatic ring can also be hydrogenated) [1]:



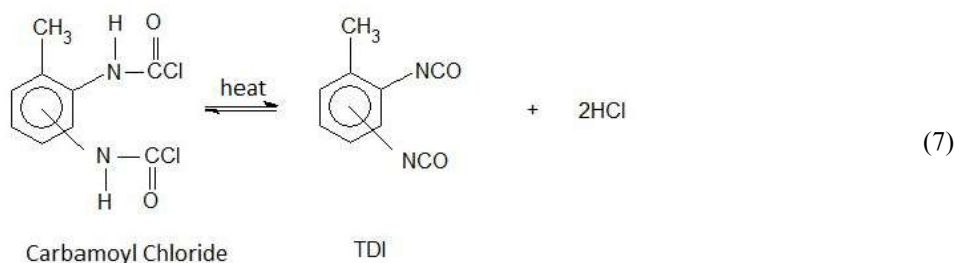
2,3 toluene-diamin (ortho-isomer) diamino-dimethyl-phenazin TAR components

Figure 3. TDA TAR formation from orto isomers of TDA

## 2. Phosgenation reactions of TDA with formation of TDI



TDA – 2,4- and 2,6- toluene-diamine (metha-isomers)



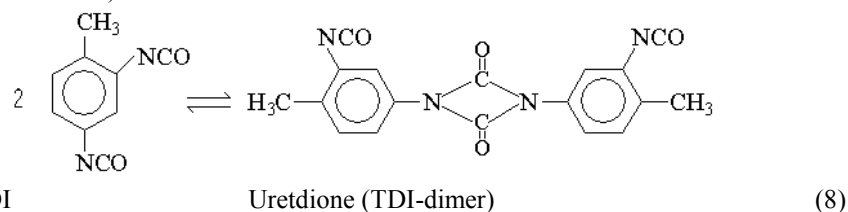
TDI – 2,4- and 2,6- toluene diisocyanate

Figure 4. TDI formation in the phosgenation reaction

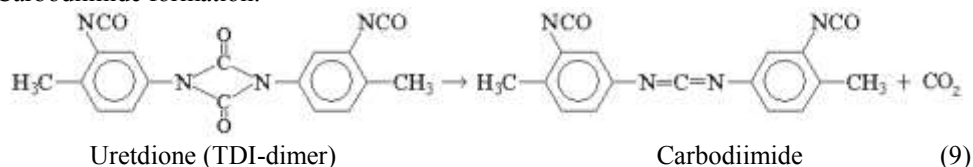
### 3. Reactions of formation of TDI-tar byproducts

During the phosgenation of toluenediamine to toluene diisocyanate followed by distillation of TDI, there are formed relatively high molecular weight by-products containing uretdione, isocyanurate, carbodiimide, uretone imine, urea and/or biuret groups, which will remain in distillation residue as tar byproducts [3,4].

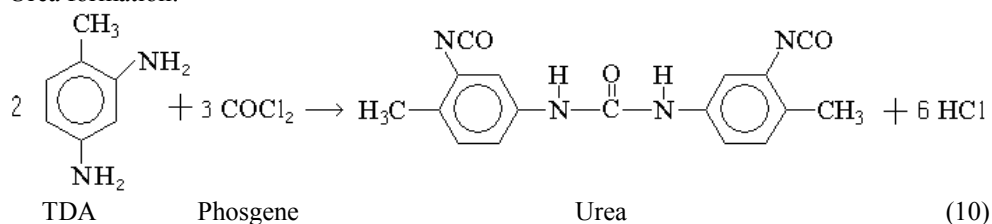
Uretdione (TDI-dimer) formation:



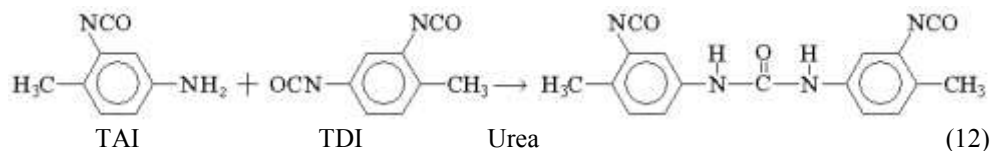
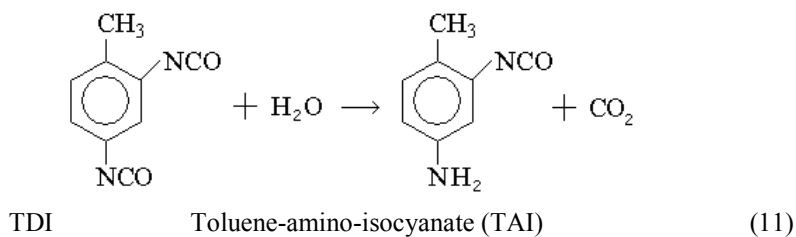
Carbodiimide formation:



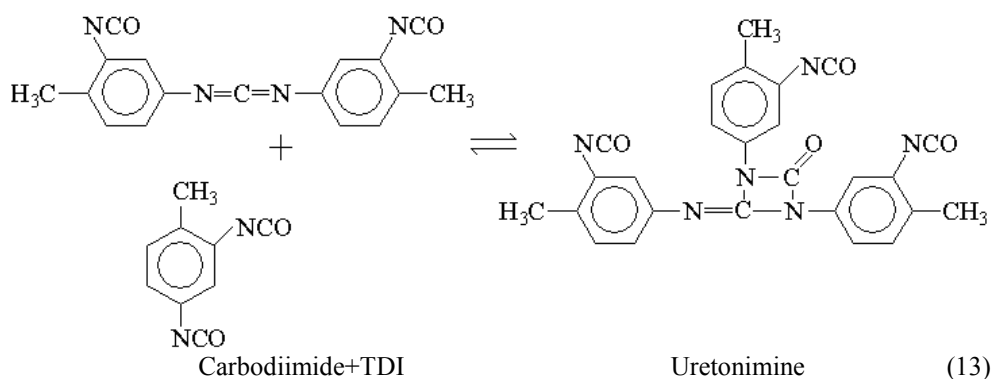
Urea formation:



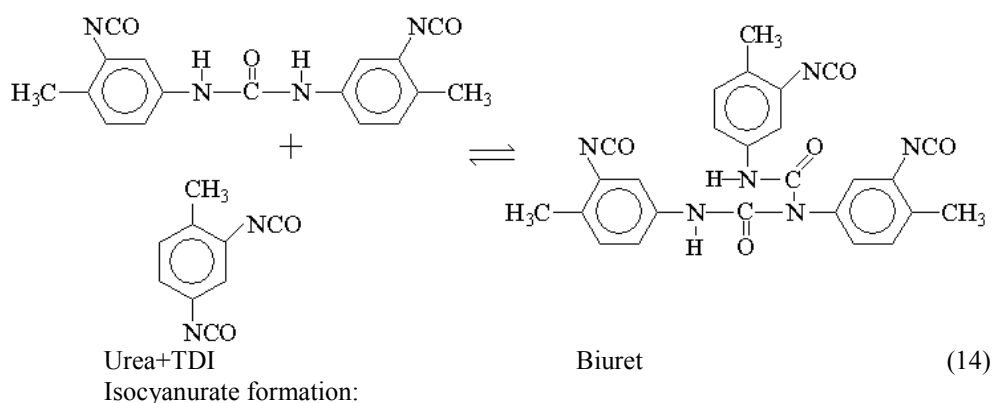
During the phosgenation traces of water in the TDA can result in urea derivatives in two steps:



Uretonimine formation:



Biuret formation:



Isocyanurate formation:

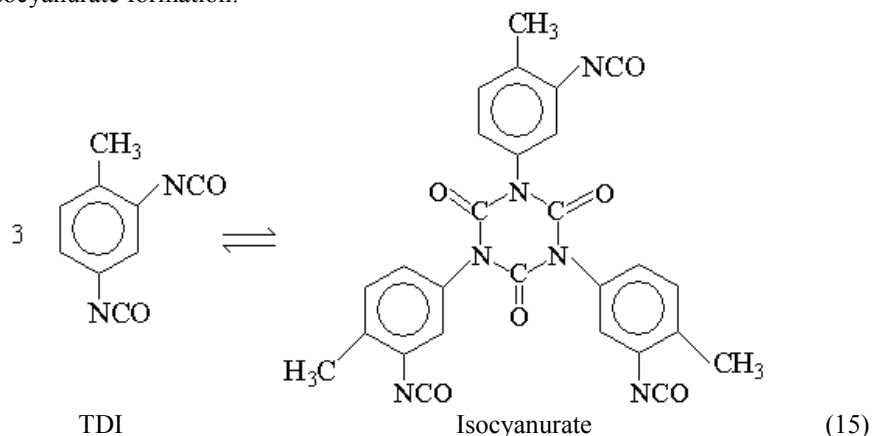
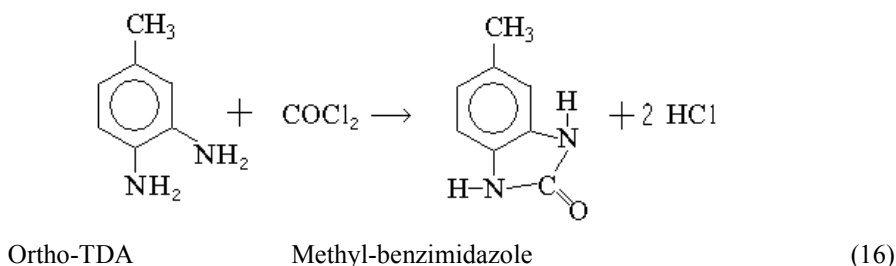


Figure 5. TDI TAR-s as byproduct formation in the phosgenation reaction

Depending upon the ortho-toluene-diamin (OTDA) content of the meta-toluene-diamin (MTDA) starting material, there can also be formed methylbenzimidazoles during phosgenation and with time, they are biuretized with the free isocyanate groups present, with an accompanying formation of cross-linked products.

Methyl-benzimidazole formation:



Biuret formation:

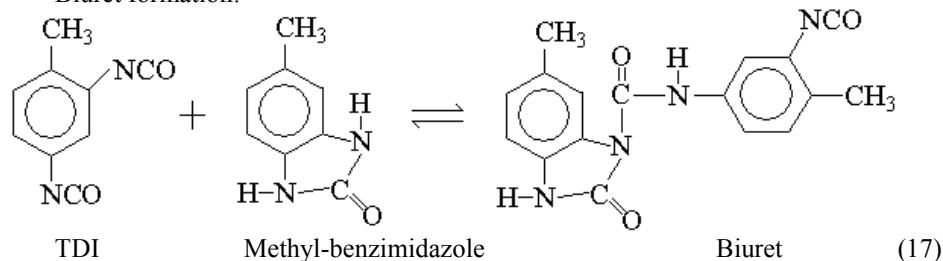


Figure 6. Reaction scheme of biuret formation

During phosgenation the TDA-tar components as azoxy-, azo-, hydroazo-benzene and diamino-dimethyl-phenazine derivatives (2), (3), (4) and (5) form two- or three ringed “heavy” diisocyanates which will remain in distillation residue as tar byproducts.



Where “R” is the azoxy-, azo-, hydroazo-benzene and diamino-dimethyl-phenazine radical.

#### 4. Main tar formation reactions of isocyanates

According to studies performed by L. Cotarca, H. Eckert main phosgenation reactions and functional groups that can be formed were summarized [4], which we further developed with formation of tars by-products as it is shown in the scheme, presented in Figure 5.

In our investigations, we were studying formation of relatively high molecular weight by-products in the TDI synthesis, containing uretdione, isocyanurate, carbodiimide, uretone-imine, urea and/or biuret groups, which will remain in distillation residue as tar byproducts, and furthermore we investigated reactions taking place in the TDI-tar removal and TDI-recovery process from distillation residues.

##### 4.1. Reaction of isocyanates with urea groups

Similarly to allophanate formation, the –NH groups of urea react with isocyanates, to generate biuret, see reaction equation (14).

Also similarly to allophanate formation, the reaction between urea and isocyanates is an equilibrium reaction and needs higher temperatures too (> 110 °C).

The formation of allophanates and biurets in the TDI recovery process, where excess of isocyanate is available, is in fact a source of crosslinking of TDI-tars.

#### 4.2. Reactions of isocyanates with urethanes

Urethane groups may be considered hydrogen active compounds, due to the hydrogen atom linked to the nitrogen atom. By reaction of an isocyanate with urethane group an allophanate is formed:

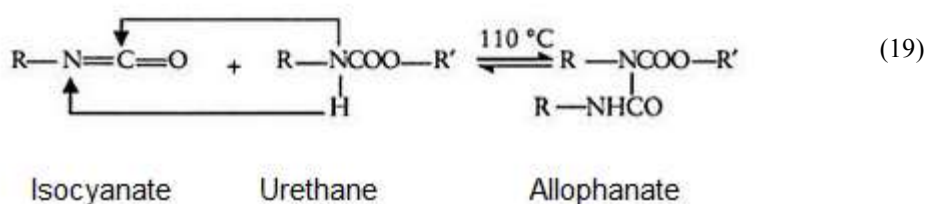
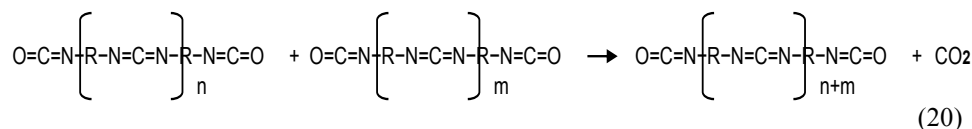


Figure 7. Reaction scheme of allophanate formation

Due to the electron withdrawing effect of the carbonyl groups, the urethane group has a much lower reactivity than the aminic –N–H groups; and in order to promote the allophanate formation higher temperatures are necessary: greater than 110 °C. Figure 7. It is important to mention that the allophanate formation is a reversible reaction [6].

#### 4.3. Reactions of Carbodiimide formations

Carbodiimide can react with another TDI or CDI to form bigger CDI molecule (carbodiimide oligomer / polymer / p-CDI/) while CO<sub>2</sub> is released.



where: n, m = 0, 1, 2, ... "∞"

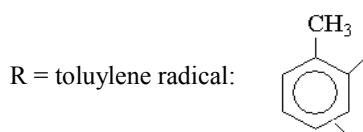


Figure 8. Reaction scheme of carbodiimide formation

This reaction Figure 8 is the main process resulting in the final solid tar powder in the TDI recovery process.

Summarizing our theoretical study, we conclude that tars formation chemical reactions in TDA and TDI synthesis are unavoidable by-product formation reactions, which have large influence on realization of industrial technology of TDA and TDI manufacturing.

The main TDI tar formation process in TDI synthesis is the phosgenation of TDA-tar components: as nitroso-, azo-, hydroazo- and diamino-dimethyl-phenazine derivatives (2), (3), (4) and (5) form two- or three ringed "heavy" diisocyanates. This is followed by

formation of relatively highmolecular weightby-products in the TDI synthesis, containing uretdione, isocyanurate, carbodiimide, uretone-imine, urea and/or biuret groups, which will remain in distillation residue as tar byproducts.

## 5. Experimental Part

In our investigations, we focused on the TDI-tar removal during the TDI-recovery process from TDI distillation residues.

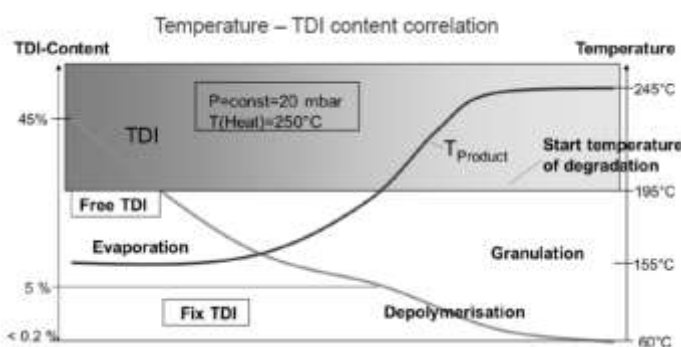
### 5.1. TDI-tar concentrating and removal by evaporation of TDI with Continuous Vacuum Evaporation/Drying system

The experimental study has been performed on LIST AP6300 and AP4000 Type Continuous Vacuum Evaporation/Drying equipment of BorsodChem's TDI Plants.

The feed stream of the TDI distillation residue has usually a temperature of 150–160 °C and composition of 45–55 m/m% TDI and 55–45 m/m% tar. The operating pressure in continuous vacuum evaporator/dryer lies in the 20–25 mbar abs range. The operating temperatures of five zones of vacuum evaporator/dryer increases continuously from 170 °C up to 230–245 °C. Under these operating conditions, a flash evaporation takes place as soon as the stream of the distillation residue enters into the process chamber of the vacuum evaporator/dryer. Further TDI evaporation and subsequent drying take place along the vacuum evaporator/dryer. During the course of the evaporation/drying process the consistency of the distillation residue changes from liquid, through a highly viscous, paste phase to a final free flowing granular residue material. This change of phase consistency is shown in Figure 10. The vacuum evaporator/dryer is heated by thermal oil at the temperature of 240–250 °C. The TDI vapor is withdrawn through the heated dome, which is mounted on top of the vacuum evaporator/dryer. The final free flowing granular dry TAR residue is continuously discharged into a vacuum tight lock system.

The free-flowing granular final residue remaining after TDI evaporation has a TDI content less than or equal to 0.5 m/m%. Main processes taking place along with the continuous vacuum evaporation/drying equipment are shown in Figure 9, the equipment characteristics are given at Table1.

#### TDI Recovery by continuous vacuum evaporation/drying



#### Processes taking place along with the continuous vacuum evaporation/drying equipment

Figure 9. Main processes of TDI-tar concentrating and removal by evaporation of TDI with Continuous Vacuum Evaporation/Drying system



The blue curve in Figure 9 shows change of TDI content of product as result of evaporation from 45m/m% to less than 0.2m/m% and formation of final free flowing granular dry tar residue.

The red curve shows change of product temperature from 160 °C to 245 °C along with the continuous vacuum evaporation/drying equipment at constant pressure of 20 mbar (abs) and constant heating oil temperature of 250 °C.

Table 1

*Process requirements and equipment characteristics for TDI Recovery by continuous vacuum evaporation/drying*

Process requirement	Equipment characteristics
During evaporation, the liquid distillation residue passes through a rubbery, viscous, pasty phase with a tendency to foam.	Robust construction, high torque to overcome the viscous phase, large vapor volume, effective foam breaking by agitator action with droplet disengagement space above the surface.
If the final TDI content is less than 17%, then the residue solidifies, and forms a hard crust.	Good self-cleaning of heating surfaces and efficient grinding action.
High level of containment and safety due to toxicity of TDI.	Enclosed, contained construction.
Low personnel requirement.	Continuous automated operation.
Prevention of decomposition reactions.	Operation in vacuum and narrow residence time distribution.

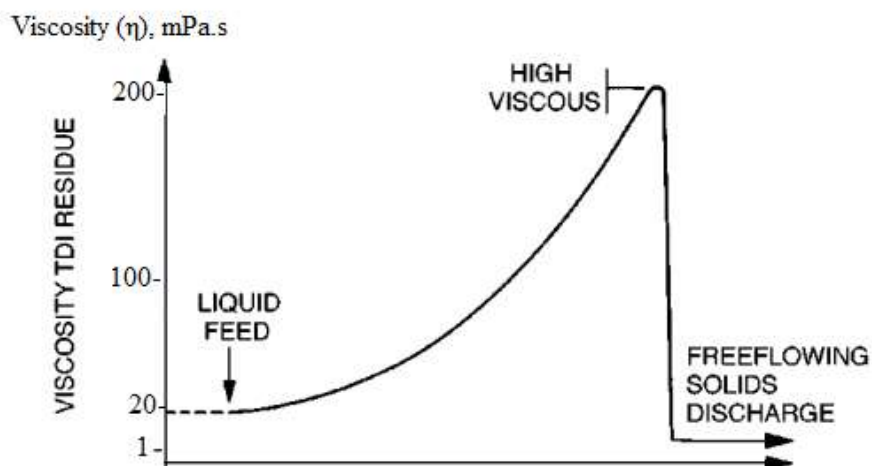
LIST AP6300 and AP4000 Type Continuous Vacuum Evaporation/Drying equipment are well fulfilling process requirements summarized in Table 1.

## **5.2. Chemical reactions and phase transformation, decomposition complex processes of tar removal in the TDI recovery process**

### **5.2.1. Phase transformation of TDI tars in TDI recovery equipment**

Transformation of liquid tars into viscous phase (see Figure 10) and then into free flowing solid granular phase takes place as result of evaporation of free TDI content of liquid tars. Simultaneously, reactions of isocyanate with TDI-tar components occur with formation of viscous, cross-linked products, which contain high molecular weight by-products, such as uretdione, isocyanurate, carbodiimide, uretone imine, urea and/or biuret groups (see former reactions Figures 7–8). However, these condensation reactions take place at moderated temperature (between 100–200°C) in the liquid phase.

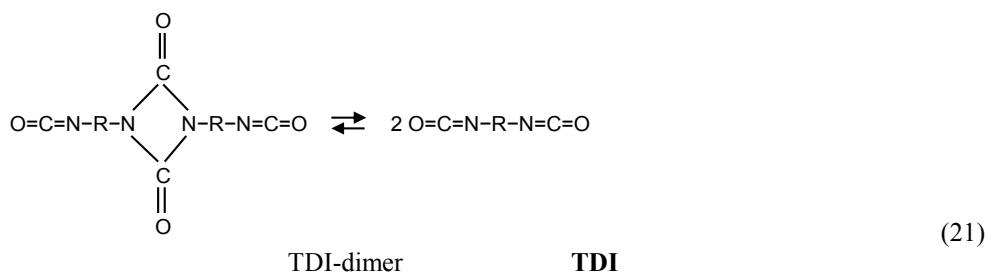
In the final step of the TDI recovery process at the temperature above 200 °C under vacuum, the evaporation (free TDI and small tar molecules evaporate) and gas releasing decomposition reactions are dominating. Urettdione-, uretonimine- and biuret molecules decompose releasing TDI and even the carbodiimide polymerization is going on releasing CO<sub>2</sub> and resulting in the final solid tar powder (see equation Figure 8).



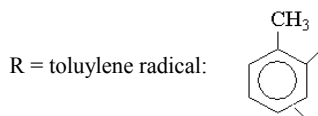
**Viscosity profile of TDI distillation residue vs. evaporator-dryer length**

*Figure 10. Phase transformation of TDI tars in TDI recovery equipment*

TDI-dimer decomposes and evaporates as “pure TDI”, however the molecule “remembers” that it was a “dimer” so it immediately forms a new dimer when condensates in the recovered TDI. Figure 11.

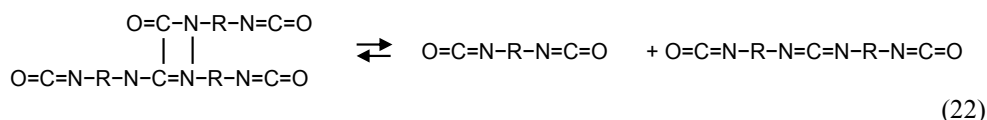


Where:



*Figure 11. Dimerization of TDI*

Uretonimines decompose releasing TDI.



(22)

Uretonimine

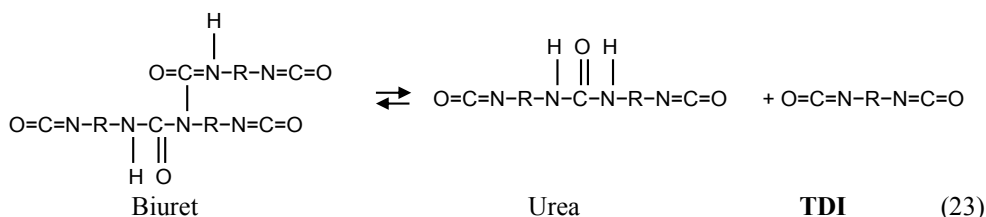
TDI

Carbodiimide (CDI)

Figure 12. Decomposition of TAR- components during distillation process

Carbodiimide can react with another TDI or CDI to form bigger CDI molecule (carbodiimideoligomer / polymer /p-CDI/) while CO<sub>2</sub> is released, as shown in equation (21). According to our experiences, this reaction is the main process resulting in the final solid tar powder in TDI recovery process.

Biurets also decompose releasing TDI.



Biuret

Urea

TDI

(23)

Figure 13. Decomposition of TAR-components during distillation process

### 5.2.2. Effects of residues of catalyst, oxygen and water on TDI recovery process

In our investigations, we were studying based on experiences gained in operation of continuous vacuum evaporation/drying TDI recovery process, effect of various process disturbance factors, such as presence of residues of catalyst in the feed material, or ingress of oxygen and water to the process chamber of TDI recovery equipment and arrived to the following conclusions:

- Residues of catalyst can cause polymerization reaction, with generation of heat, which will result in increase of zone temperatures of TDI recovery equipment.
- Ingress of oxygen can cause decomposition reaction with generation of CO<sub>2</sub>, which will cause foaming problem in the TDI recovery equipment.
- Ingress of water can cause decomposition reaction with generation of CO<sub>2</sub>, which will cause foaming problem in the TDI recovery equipment.

## Conclusions

Summarizing our theoretical study, we conclude that tars formation chemical reactions in TDA and TDI synthesis are unavoidable by-product formation reactions, which have large influence on realization of industrial technology of TDA and TDI manufacturing. In this study, we systematically reviewed most important chemical reaction steps of formation of pre-tars, TDA-tar formation from ortho-isomers, phosgenation reactions of TDA with formation of TDI, reactions of formation of TDI-tar byproducts and further developed main

phosgenation reactions with formation of tar by-products, discussed reaction of isocyanates with urea groups, and reactions of carbodiimid formation.

Furthermore we studied chemical reactions and phase transformation, decomposition complex processes of tar removal in the TDI recovery process. It was discussed the effect of various process disturbance factors, such as presence of residues of catalyst in the feed material, ingress of oxygen and water into the process chamber of TDI recovery equipment, with analysis of background chemical processes of phase transformation of TDI-tars in TDI recovery equipment.

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