

DETERMINATION OF TDA-TAR AND TDI-TAR CONTENT AND QUANTITY IN TDI SYNTHESIS

MAGYARI MIKLÓS¹–ÁBRAHÁM JÓZSEF²–LAKATOS JÁNOS³

Based on experimental investigations into toluene-diamine (TDA) and toluene-diisocyanate (TDI) synthesis and on theoretical considerations about the chemical reactions of tar formation, a gas chromatographic method is described in the way it was used for the determination of TDA-tar and TDI-tar content produced from the synthesis process. Some practical remarks and suggestions are provided for the modification of the ASTM Standard Test Method¹ for unreacted Toluene diisocyanates in prepolymers and coating solutions², using gas chromatography to quantify TDA- and TDI-tars.

Keywords: formation of tars, chemical reactions, oligomer formation, polymerization, decomposition, gas chromatography

Introduction

In our former publications [1–3], the potential recovery of toluene-diamine (TDA) from TDA-tar mixtures and the method of tar disposal has been discussed, as well as the miscibility of TDA-tar with ortho-toluene-diamine (OTDA) liquid streams. TDA-tars are obtained as a byproduct of TDA synthesis. In this paper, first the reaction scheme of the TDA-tar formation process is analyzed. In the subsequent steps, the phosgenation reactions of TDA are considered, leading to the formation of toluene diisocyanate (TDI). The aim of this study is to establish a reliable and applicable method for the determination of tar content in the reaction mixtures.

Besides the main product that can be TDA or TDI, the byproduct in the reaction mixture is considered as tar. The principle of analysis is based on the determination of the TDA or TDI content of the reacted sample, with the tar content obtained as the difference. In order to better understand the chemistry of tars, the reaction schemes below help defining the chemical forms of the molecules that are formed stepwise in a series of complex reactions and appear as byproducts by the end of the synthesis process. Using these reaction schemes, it is possible to identify those different compounds the cumulative data of which can be quantified as the total amount of tar.

¹ BorsodChem Zrt.
Kazincbarcika 3700, Hungary
miklos.magyar@borsodchem.eu

² University of Miskolc, Institute of Chemistry
Miskolc-Egyetemváros 3515, Hungary
abraham.jozsef@upcm.hu

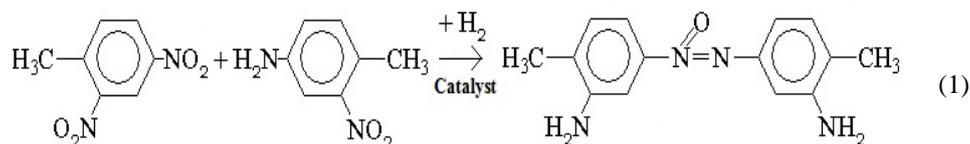
³ University of Miskolc, Institute of Chemistry
Miskolc-Egyetemváros 3515, Hungary
mtasotak@uni-miskolc.hu

1. TDA tars formation reactions

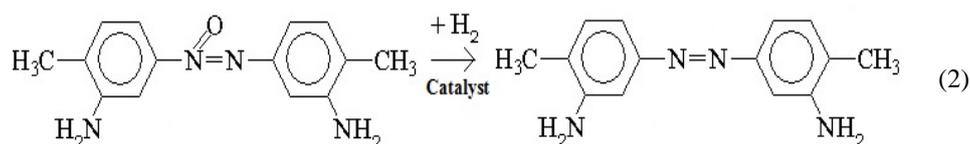
1.1. TDA tars formation as byproduct of TDA synthesis

During dimerization reactions, azoxy-, azo-, and hydrazo-benzene derivatives are formed. Approximately 20% of the tar components are produced by these reactions. Different combinations of pre-tars will produce TDA-tars as it is illustrated in Figure 1 below:

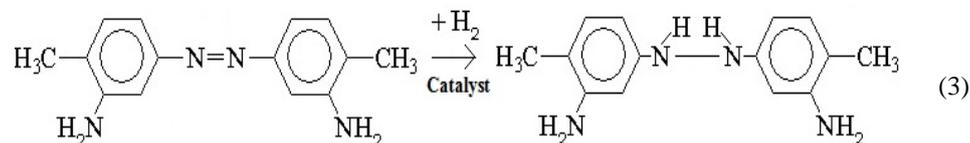
1.1. TDA-tar formation from Pre-tars



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)

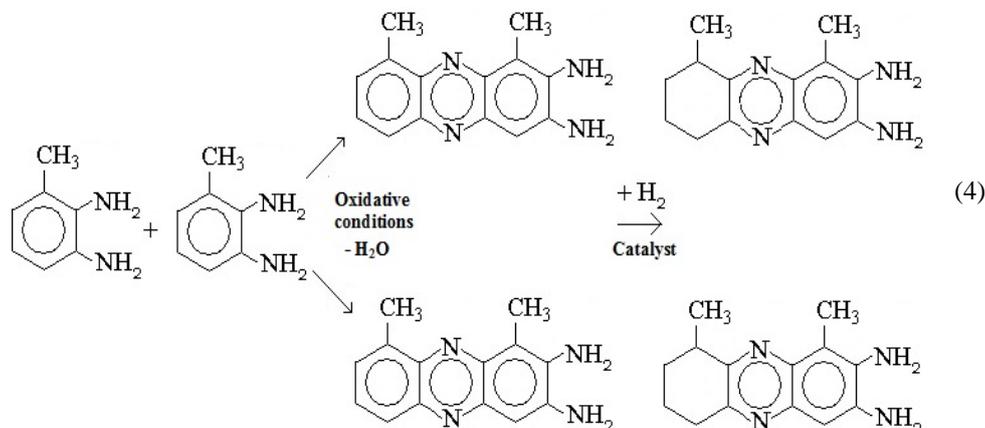


TDA-tar(2,2'-diamino-4,4'-azotoluene) TDA-tar(2,2'-diamino-4,4'-hydrazotoluene)

Figure 1. Reaction scheme of TDA-tar formations

1.2. TDA-tar formation from ortho-isomers

80% of the TDA-tar components are formed from the reactions of ortho-isomers, and the generated tar components are diamino- dimethyl- phenazin derivatives, respectively [1]:



2,3-toluene-diamine (ortho-isomer) diamino-dimethyl-phenazine TAR components

Figure 2. TDA-tar formation from 2,3-toluene-diamine

1.3. Formation reactions of TDI-tar byproducts

- During the phosgenation of toluenediamine to toluene diisocyanate followed by the distillation of TDI, by-products of relatively high molecular weight are formed containing uretdione, isocyanurate, carbodiimide, uretone imine, urea and biuret groups, which will remain in the distillation residues as tar byproducts [3] [4].
- Depending upon the ortho-toluene-diamine (OTDA) content of the meta-toluene-diamine (MTDA) starting material, methylbenzimidazoles might as well be formed during phosgenation and with time, these are biuretized with the free isocyanate groups present, with an accompanying formation of cross-linked products.
- During phosgenation the TDA-tar components as azoxy-, azo-, hydrazo- and diamino-dimethyl-phenazine derivatives (1), (2), (3) and (4) form two- or three ringed “heavy” diisocyanates which will remain in the distillation residue as tar byproducts.

1.4. Main tar formation reactions of isocyanates

In a research performed by L. Cotarca, H. Eckert [4], the main phosgenation reactions were summarized, together with the description of the functional groups that might be formed during the process. Hereby we present an advanced version of their scheme, which we complemented with the formation of tar by-products as it is shown in the following Figure (Figure 3).

As seen, the resulting high molecular weight reaction by-products contain uretdione, isocyanurate, carbodiimide, uretone-imine, urea and biuret groups, which will remain in distillation residue as tars.

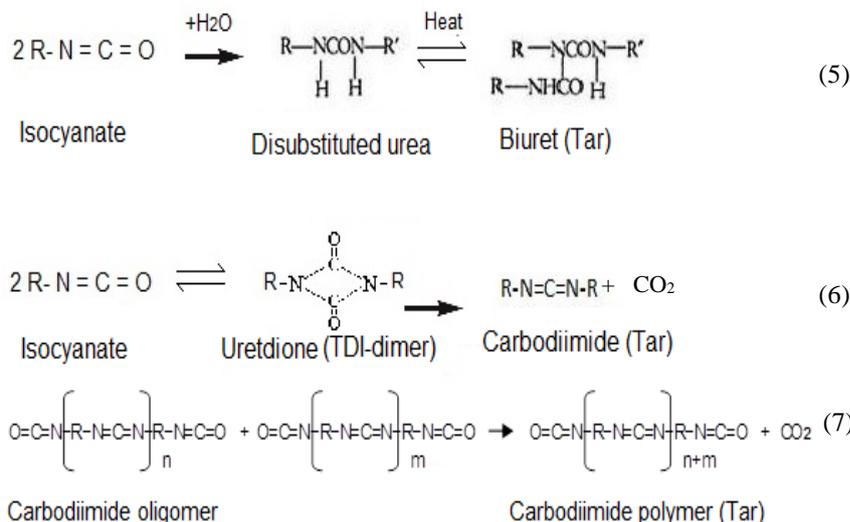


Figure 3. Main reactions of isocyanate-tar by-products formation

Summarizing our theoretical study, we conclude that the chemical reactions which lead to the formation of tar by-products inevitably occur in the TDA and TDI synthesis process and have a considerable influence on the large-scale application of TDA and TDI synthesis in industrial manufacturing.

The determination and quantification of TDA-tar and TDI-tar content produced from TDI synthesis was performed by gas chromatographic method, which is described below.

2. Experimental Part

2.1. Determination of TDA-tar and TDI-tar by gas chromatographic method

According to our experiences, the easiest and most reliable way to determine either TDA- or TDI-tars (in high tar-containing TDA or TDI) is the application of a capillary GC method using an internal standard technique.

In this method, we determine the exact concentration of the TDA and TDI isomers (“TDA%” in the case of TDA-TAR mixtures and “TDI%” in the case of TDI-TAR mixtures, respectively) by using an appropriate internal standard compound.

The concentration of the tar components is then calculated as follows: TAR% = 100% – TDA% (in case of TDA-TAR mixtures) and TAR% = 100% – TDI% (in case of TDI-TAR mixtures).

This is a widely used analytical method in gas chromatography in cases when there are “nondetectable” components in the mixtures.

Some TAR components constitute such large molecules (especially the polymeric carbodiimides in TDI-TAR mixtures) that they cannot be detected by GC (they do not even evaporate in the injector of the GC), therefore, the use of an internal standard method for the determination of componential tar concentration is justified.

With some modification, the international ASTM D3432-89 “Standard Test Method for Unreacted Toluene Diisocyanates in Prepolymers and Coating Solutions by Gas Chromatography” [7] seems suitable for that type of analysis.

Any modern capillary GC instrument with FID detector can be used for this method. Any capillary column that can withstand a final temperature of 300 °C and has the proper resolution range between the internal standard 1,2,4 trichlorobenzene (TCB) and the TDA or TDI peaks can also be used in this method.

High injector temperature (e.g. 300 °C) is rather important in the determination of both TDA-tar and TDI-tar. Given, for example, a crude TDI with high tar content, if the injector temperature is not high enough, part of the free TDI will not be able to evaporate, and the uretdione (TDI-dimer), uretonimines and biurets will not decompose to release TDI. In this case, the tar content will be overestimated (the so-called “recoverable TDI” will be underestimated).

In our investigations, the following gas chromatographic method was applied:

Apparatus:

- Capillary gas chromatograph with flame ionization detector (FID) and auto-injector
- Analytical column of medium polarity (100% dimethyl-polysiloxane stationary phase), dimensions: (30 m x 0.32 mm x 0.1 µm),

Reagents:

- Gases for GC: He (4.6) as carrier gas, N₂ (5.0) as auxiliary gas, H₂ (3.8) fuel gas, synthetic air (N₂/O₂: 80/20% v/v) for the flame
- Dried acetone for TDI-tar analysis (analytical grade)
- Methanol for TDA-tar analysis (analytical grade)
- TCB as internal standard (analytical grade)
- TDI-80 product for TDI-tar analysis (analytical grade)
- 2,4 TDA for TDA-tar analysis (analytical grade)

GC operating conditions:

- *Injectortemperature:* 300 °C
- *Linear Velocity:* 40 cm/s
- *Split Ratio:* 100:1
- *Detectortemperature:* 310 °C

Table 1

The GC oven program

Program steps	Rate [°C/min]	Temperature [°C]	Hold Time [min]
0	–	90.0	0.0
1	20.0	220.0	0.0
2	5.0	300	10

Procedure:

For the chromatographic analysis of TDI-tar, 1.0 ± 0.1 g of the sample and 0.5 ± 0.05 g of TCB should be accurately weighed into the 10 ml standard flask and diluted to 10 ml with dried acetone. Proper mixing can be aided with an ultrasonic bath to enhance dissolution.

For TDA-tar analysis, 1.0 ± 0.1 g of the sample and 0.5 ± 0.05 g of TCB should be accurately weighed into the 10 ml standard flask and diluted to 10 ml with methanol. Proper mixing can be aided with an ultrasonic bath to enhance dissolution.

In both cases, about 1.5 ml solution should be poured into the vial with septa (using a syringe filter if the sample has solid impurities!), then put in the rack of the auto injector. Upon injection of 1.0 μ l of the respective sample into the device, the gas chromatogram under the conditions given in “*GC operating conditions*” should be recorded.

Calculations:

Calibration: For the calibration of TDI-tar analysis, about 1.0 ± 0.05 g TDI-80 and 0.5 ± 0.05 g TCB should be accurately weighed into the 10 ml standard flask, diluted to 10 ml with dried acetone and mixed well.

For the calibration of TDA-tar, about 1.0 ± 0.05 g 2,4 TDA isomer and 0.5 ± 0.05 g TCB should be accurately weighed into the 10 ml standard flask and diluted to 10 ml with methanol, then mixed well.

About 1.5 ml of either solution should be poured in the vial with septa, then put in the rack of the auto injector.

Upon injection of 1.0 μ l of the sample into the device, the gas chromatogram under the conditions given in “*GC operating conditions*” should be recorded.

The response factor (RF) is calculated as follows:

$$RF = (W_i \times A_{TCB}) / (W_{TCB} \times A_i)$$

where:

- W_i = mass of TDI-80 (or 2,4 TDA)
- W_{TCB} = mass of TCB
- A_i = Area of TDI isomer peak(s) (or 2,4 TDA peak)
- A_{TCB} = Area of TCB peak

Sample analysis result:

$$\text{TDI (or TDA) (m/m\%)} = 100 \times RF \times (W_{TCB} \times A_S) / (W_S \times A_{TCB})$$

where:

- TDI (or TDA) (m/m%) = mass percent of the free TDI (or TDA) isomers in the sample
- RF = Response factor calculated in the calibration
- W_{TCB} = mass of TCB
- A_S = Area of TDI (or TDA) isomer peak(s) of the sample
- W_S = mass of the sample
- A_{TCB} = Area of TCB peak

Although this method can be used either for TDI-tar analysis or TDA-tar analysis but not in the same time.

TDI and TDA are potential reaction partner to each other forming urea derivatives quickly in exothermic reaction. When we change from a TDI-tar to TDA-tar analysis (or vice versa) the syringe of the auto injector must be rinsed thoroughly otherwise traces of TDI will react with the TDA sample causing plugging in the injector. Frequent replacement of the silica wool in the injector liner is also needed in this case.

Example of the determination of TDA-tars by gas chromatographic method

The TDA-content of a high tar-containing TDA sample was determined with the described gas chromatographic method. In the first run, the mixture of a 2,4 TDA isomer and the TCB internal standard was analyzed (Table 2) and the TDA/TCB response factor (RF) was calculated. In the second run, the mixture of the TDA sample and the TCB internal standard was analyzed (Table 3 and Figure 4) and the TDA content of the sample (TDA)(m/m%) was determined.

Table 2

Determination of the TDA/TCB response factor (RF)

Component	Retention Time (min.)	Peak area	Component mass (g)	Response factor (RF)
TCB	1.733	3955986	0.4910	0.639534
2,4 TDA isomer	4.285	12439496	0.9874	

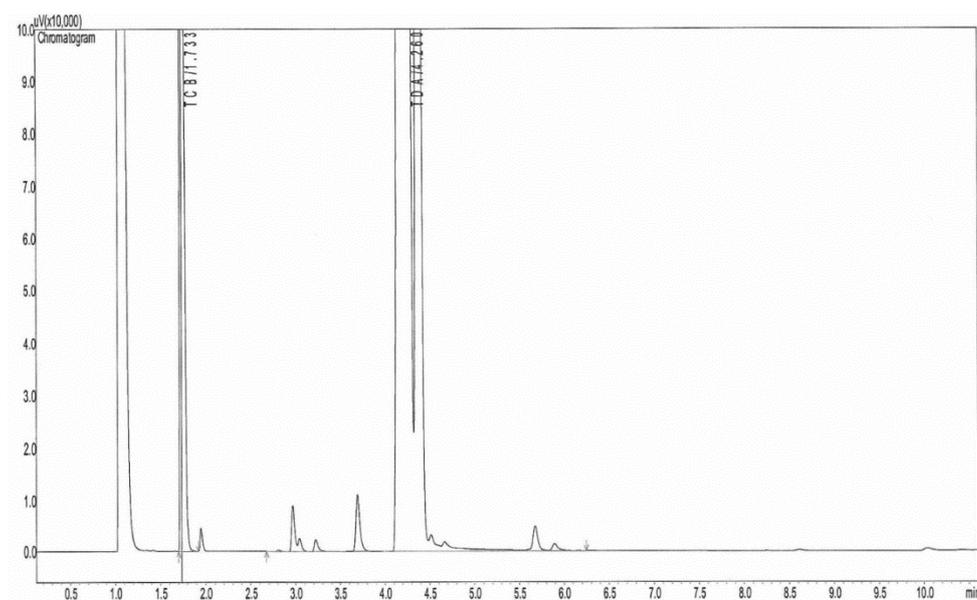


Figure 4. Chromatogram of the TDA sample

Table 3

Determination of the TDA content of the sample

Component	Retention Time (min.)	Peak area	Component mass (g)	TDA content (m/m%)
TCB	1.733	4292922	0.5146	71.03
TDA sample	4.260	9357698	1.0100	

Example of determination of TDI-tars by gas chromatographic methods

The TDI content of a crude-TDI sample with high tar-content was determined by this gas chromatographic method.

In the first run, the mixture of the TDI-80 standard and the TCB internal standard was analyzed (Table 4) and the TDI/TCB response factor (RF) was calculated.

Table 4

Determination of the TDI/TCB response factor (RF)

Component	Retention Time (min.)	Peak area	Component mass (g)	Response factor (RF)
TCB	4.58	2067903	0.5192	0.893005
TDI-80 standard	5.57	4656314	1.0440	

In the second run, the mixture of the crude-TDI sample and the TCB internal standard was analyzed (Table 5 and Figure 5) and the TDI content of the sample (TDI)(m/m%) was determined.

Table 5

Determination of the TDI content of the crude-TDI sample

Component	Retention Time (min.)	Peak area	Component mass (g)	TDI content (m/m%)
TCB	4.58	1884390	0.5175	39.31
Crude-TDI sample	5.56	1662117	1.0370	

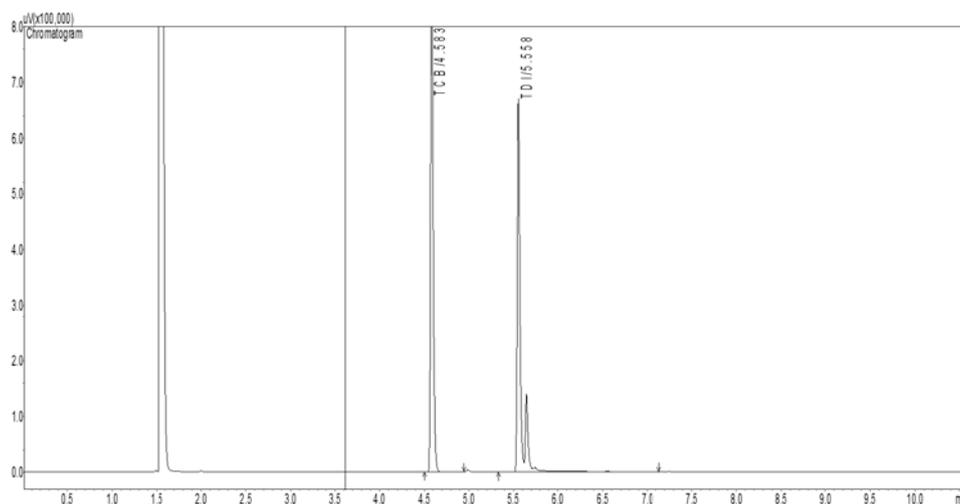


Figure 5. Chromatogram of TDI – TDI-tar mixture

Conclusions

Summarizing our theoretical study, we conclude that the chemical reactions that lead to the formation of tars as by-products in the TDA and TDI synthesis process is unavoidable and have a large influence on the implementation of TDA and TDI manufacturing as an industrial technology. In this study we summarized the most important chemical reaction steps of TDA-tar formation from pre-tars and ortho-isomers, the formation reactions of TDI-tar byproducts and further developed the main phosgenation reactions by describing the formation of tar by-products.

In the study, we described the determination of TDA-tars and TDI-tars by experimentally validated gas chromatographic method, and suggested some practical modifications to the ASTM Standard Test Method for unreacted Toluene diisocyanates in prepolymers and coating solutions by gas chromatography, to make it applicable for the determination of TDA-tars and TDI-tars.

Acknowledgement

The research work presented in this paper based on the results achieved within the TÁMOP-4.2.1.B-10/2/KONV-2010-0001 project and carried out as part of the TÁMOP-4.2.2.A-11/1/KONV-2012-0019 project in the framework of the New Széchenyi Plan. The realization of this project is supported by the European Union, and co-financed by the European Social Fund.

References

- [1] ÁBRAHÁM József–MAGYARI Miklós–RÁCZ Lajos–HUTKAINÉ GÖNDÖR Zsuzsanna–LAKATOS János: Laboratóriumi és félüzemi kísérletek TDA-TAR-elegy TDA-tartalma visszanyerési technológiájának és a TAR ártalmatlanítási módszerének kifejlesztéséhez. *Miskolci Egyetem Közleményei. Anyagmérnöki Tudományok*, Vol. 38, 1, 2013, 7–18.
- [2] HUTKAINÉ GÖNDÖR Zsuzsanna–ÁBRAHÁM József–RÁCZ Lajos–MAGYARI Miklós–LAKATOS János: TDA-TAR és OTDA folyadékáramok elegyíthetőségének vizsgálata. *Miskolci Egyetem Közleményei. Anyagmérnöki Tudományok*, Vol. 37, 1, 2012, 147–152.
- [3] LENGYEL Attila–MOGYORÓDY Ferenc–ÁBRAHÁM József–MAGYARI Miklós–FEHÉR Tamás: Meta-toluilén-diamin (TDA)-kátrány (TAR) koncentrátum előállítása vákuum desztillációval, a koncentrátum viszkozitás hőmérséklet és koncentráció függésének modellezése. *Miskolci Egyetem Közleményei – 2. sorozat, Anyag- és Kohómérnöki Tudományok*, Vol. 35, 1, 2010, 27–38.
- [4] COTARCA, L.–ECKERT, H.: *A Phosgenations – Handbook*. WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim, 2003.
- [5] *ASTM D3432-89: Standard Test Method for Unreacted Toluene Diisocyanates in Urethane Prepolymers and Coating Solutions by Gas Chromatography*. ASTM International, West Conshohocken, PA, 1996.