

AN APPROACH FOR ELIMINATING PHENYL ISOCYANATE FROM SOLVENT USED IN ISOCYANATE PRODUCTION

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Methylene diphenyl diisocyanate (MDI) is one of the most important raw materials of polyurethane industry. During its synthesis unwanted by-products might be formed such as phenyl isocyanate (PI). In this laboratory work, a separation method has been developed and tested for the the elimination of phenyl isocyanate from the ortho-dichlorobenzene solvent purified after MDI production. This method is based on conversion of phenyl isocyanate by MDI precursor methylene diphenyl diamine (MDA). The formed carbamide compounds were separated from the solvent by either distillation or filtration. As a result, the initial phenyl isocyanate content of 9,000 ppm was successfully reduced to 30 ppm by distillation and less efficiently to 231 ppm by filtration.

Keywords: methylene diphenyl diisocyanate, ortho-dichlorobenzene, phenyl isocyanate, distillation, filtration

INTRODUCTION

Polyurethanes are the most versatile class of polymers, used in a surprising array of commercial applications such as flexible- and rigid foams, solid elastomers, thermoplastic polyurethanes, coatings, adhesives, sealants and elastomers used on floors and automotive interiors [1]. They are formed by the exothermic reaction between alcohols with two or more reactive hydroxyl and isocyanates that have more than one reactive isocyanate group. Methylene diphenyl diisocyanate (MDI) is one of the most significant raw material of polyurethane industry [2]. Production of MDI occurs via phosgenation of the appropriate diamine, namely methylene diphenyl diamine (MDA), in a solvent such as dichlorobenzene which is removed from the product by distillation and is reused [3]. MDA is synthesized from the reaction between aniline and formalin. In the case of MDA synthesis some aniline could be remained in the system which might be converted to phenyl isocyanate via phosgenation (*Figure 1*). In MDI synthesis phenyl isocyanate might be a possible source of several by-product due to its reactivity [4]. The reactivity of aniline derivatives with phosgene have been studied by Ulrich et al. [5]. The aromatic diamines such as the MDA are much more reactive amines than others. The reactivity of different aromatic amines with diisocyanates have been measured [6]. Beside the phenyl isocyanate formation, numerous other side-reactions can occur via the MDI synthesis producing several unwanted by-products which might cause problems. For instance, the isocyanates can easily react with amines forming carbamides due to the high reactivity of isocyanate group. Callison et al. investigated the reactions between carbamides and phosgene producing precursor to chlorine radicals, which could form

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conjugated systems with the MDI backbone promoting discoloration [7]. The formation of the by-products is substantial. The elimination of them encounters difficulties.

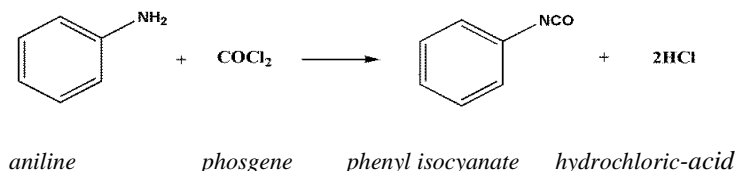


Figure 1
Phenyl-isocyanate formation via phosgenation of aniline

This study focusses only on one possible by-product, phenyl isocyanate. The aim of this research was to find out an appropriate method for phenyl isocyanate removal. Our exploration was based on the reaction of phenyl isocyanates with amines [8]. The phenyl isocyanate was converted to carbamide (*Figure 2*) and then eliminated from the solvent.

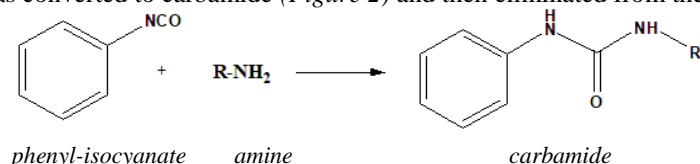


Figure 2
Reaction of phenyl-isocyanate with amine

1. APPLIED METHODS AND REAGENTS

Distillations were carried out using distillation apparatus set up in the laboratory. Three-necked, round-bottom 250 ml of glass flask was used as reaction vessel while a 100 ml of one-necked round-bottom glass flask was used as volumetric flask for the distillate. The flasks were connected by a distillation head and a Liebig-cooler. Heating was provided by melted metal bath heated by laboratory heater. The head- and bottom temperatures were controlled using thermometers. In the case of vacuum distillation, the reduced pressure was set up by oil-ring pump produced by Leybold. About 100 ml of ODCB sample – arisen from the plant – was used mixed with phenyl isocyanate purchased by Sigma Aldrich. For the filtration Whatman glass vacuum membrane filtration device was applied. The vacuum was adjusted using water suction pump. The grain size of the filter was 1.4 μm .

The phenyl isocyanate content of the samples was analyzed by Agilent 6890N gas chromatograph applying Zebtron Inferno capillary column, using flame ionization detector (FID). Scanning electron microscopy (Joel T220 SEM) was used for mapping the structure of the formed carbamides.

2. RESULTS AND DISCUSSION

Distillation was the first type of phenyl isocyanate removal method which was tried. The first idea was that the ortho-dichlorobenzene will be purified this by-product via simple

distillation. The phenyl isocyanate content was measured before and after the distillation. The results are summarized in *Table 1*.

Table 1
Phenyl isocyanate content before and after distillation

PI content (ppm)	
Before distillation	After distillation
1,800	2,979
1,800	2,870
1,800	2,596

The initial 1,800 ppm was not decreased but increased after the distillation without using any reagent. Due to the similar boiling points of the ortho-dichlorobenzene (180 °C) and phenyl-isocyanate (166 °C) the separation of the compounds is difficult. The accumulation of the isocyanate in the distillate can be explained by the lower boiling point, although the difference in boiling points are not large enough to ensure complete separation.

MDA was tested as a reagent for converting phenyl isocyanate into a non-volatile compound before the distillation. Samples with different phenyl isocyanate content was reacted with MDA and then distilled. The starting phenyl isocyanate content was greatly reduced (<100 ppm). The results are summarized in *Table 2*. The amino group of the MDA was reacted with the isocyanate group of the phenyl isocyanate producing carbamide bond. The product carbamide was remained in the bottom of the flask while the ortho-dichlorobenzene was distilled. The phenyl isocyanate content was reduced efficiently.

Table 2
Phenyl isocyanate content before and after distillation using MDA as reactant

PI content (ppm)	
Before distillation	After distillation (using MDA as reagent before)
1,800	89
700	20
500	10

The other main advantage of using MDA as reactant is that it is a familiar material in MDI synthesis. Any MDA residues in the solvent will never cause problems because it can be easily eliminated from the system. In addition, MDA is one of the raw materials produced so that using it will be obvious.

Vacuum distillation – performed under reduced pressure – was also tested for solvent purification after MDA was added to the solvent to react with the phenyl isocyanate. The efficiency of the simple and vacuum distillation is compared in *Table 3*. The initial phenyl isocyanate content was 9,000 ppm. The final phenyl isocyanate content was <40 ppm. The vacuum distillation seemed to be more effective than the simple distillation, although the difference in removal efficiency is minimal. This phenomenon could be explained by the fact that at higher temperature carbamides can be decomposed into amine and isocyanate. In the

case of the simple distillation higher temperature was used which was favorable for the decomposition of the product facilitating phenyl isocyanate formation, while in the case of vacuum distillation lower temperature resulted in less isocyanate release.

Table 3
Phenyl isocyanate content before and after simple- and vacuum distillation

Type of distillation	PI content (ppm)	
	Before distillation	After distillation
simple	9,000	29
		30
		29
vacuum		18
		17
		19

Filtration of impurities is a frequently used method in the industry for purification. The applicability of it was tested for phenyl isocyanate elimination, too. Ortho-dichlorobenzene samples with high phenyl isocyanate content were mixed with the appropriate amount of MDA at room temperature and at higher temperatures as well. Beside the influence of the temperature the effect of the stirring was also studied.

The results are summarized in *Table 4*.

Table 4
Phenyl isocyanate content before and after filtration using MDA as reagent

Sample	Temperature [°C]	Stirring	PI content (ppm)	
			Before filtration	After filtration
1	25–30	No	9,000	58
2	25–30	Yes		57
3	70–90	Yes		110
4	110–120	Yes		128
5	120–130	Yes		231

The starting 9,000 ppm was significantly decreased <300 ppm. It was surprising that without stirring (for 1 hour) and at room temperature the phenyl isocyanate was reduced from 9,000 ppm to 58 ppm. As the temperature was higher the phenyl isocyanate reduction efficiency of the MDA was lower. The structures of the filtrated solid sediments were different. They were examined by scanning electron microscopy. According to the microscopic views (*Figure 3*) the particle sizes of the formed carbamides are different.

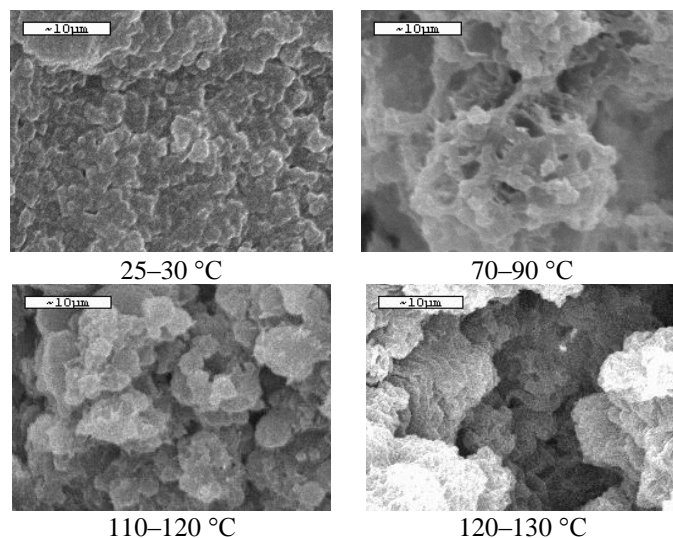


Figure 3
Microscopic views of the filtrated carbamide compounds

At lower temperature the reaction between the MDA and phenyl isocyanate resulted smaller particle sized ($<10\mu\text{m}$) carbamide sediment, while at higher temperature bigger sized ($>10\mu\text{m}$) particles were formed. At higher temperature the decomposition of the carbamide into phenyl isocyanate and amine could also occur such as in the case of the simple distillation. Therefore, more phenyl isocyanate was found in the solvent after the filtration at higher temperature. Considering the filtration method, the phenyl isocyanate content can be reduced significantly. The efficiency of the filtration is as adequate as the distillation's. This procedure can be feasible even in the technology. The filtrate was also examined and it was found that it has a little MDA content. If this method will be applied for phenyl isocyanate removing, it is necessary to take care about this MDA content of the ortho-dichlorobenzene as well.

CONCLUSION

This study was focused on removing of a possible by-product – *phenyl isocyanate* – of MDI synthesis from the solvent. Useful methods were found for phenyl isocyanate elimination: distillation or filtration.

Simple distillation of the ortho-dichlorobenzene was not effective because the phenyl isocyanate co-distilled with ortho-dichlorobenzene. It was essential to convert this isocyanate into another compound which is easier to separate from the solvent. The idea was to find a reactant which can easily react with the phenyl isocyanate. Using MDA as a reagent appeared to be obvious as it is the precursor of MDI synthesis. Applying it as a reagent will never cause any problems even if it remains in the system. The results confirmed that phenyl isocyanate can be reduced significantly from the ortho-dichlorobenzene using MDA.

Filtration seemed to be also a quite good method for a possible phenyl isocyanate reduction. MDA was used as a reagent in this way, too. The efficiency of this method is lower than the distillation, however it is effective enough.

Considering the experimental results, it could be said that both distillation and filtration could be suggested for a possible technological application after MDA was used as a reagent for converting phenyl isocyanate to carbamide. Some disadvantages need to be noted as well such as during the filtration the filter packages must be cleaned frequently causing some difficulties and in the case of distillation high energy is required for evaporation of the solvent.

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