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Investigation of Gas Concentrations Emitted From Chemical Reagents Used in Polyurethane Production

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Abstract:

This study investigates the composition and concentration of gases generated during the heating, polycondensation, curing, crystallization, and recycling processes of liquid diisocyanates, polyether polyols, and chain extenders used in polyurethane synthesis within the temperature range of 60–120 °C. The polycondensation kinetics and thermochemical transformations of both virgin and recycled polyurethane formulations were examined. The concentrations of volatile organic compounds (VOCs), isocyanate vapors, and other gaseous emissions released into the workplace atmosphere during the technological process were determined using ANT-3M and GC-8000 gas analyzers. The measured gas concentrations were compared with the maximum permissible concentrations (MPCs) established for workplace air, and their hazard classes were determined in accordance with GOST 12.1.007–76. Based on the experimental findings, an innovative technological approach and a multi-stage gas purification system were developed to capture, neutralize, and minimize the release of hazardous gaseous emissions into the atmosphere during polyurethane synthesis and recycling. The proposed technology is expected to improve the environmental safety of polyurethane production, ensure compliance of workplace air quality with occupational safety standards, reduce harmful emissions, and significantly enhance the environmental and technological efficiency of polyurethane manufacturing processes.

Keywords: Polyurethane, Recycled Polyurethane, Diisocyanate, Polyether Polyol, Chain Extender, Polycondensation, Gaseous Emissions, Volatile Organic Compounds (VOCs), Isocyanate Vapors, Gas Analyzer, ANT-3M, GC-8000, Workplace Air, Environmental Safety, Gas Neutralization, Gas Purification System, Hazard Classification.

Introduction

Polyurethane (PU) materials are among the most widely used classes of polymers owing to their excellent mechanical strength, abrasion resistance, chemical stability, elasticity, and ability to maintain performance over a wide temperature range. These properties have enabled their extensive application in the automotive, aerospace, mining and metallurgical, oil and gas, machinery manufacturing, construction, electrical engineering, medical, packaging, furniture, and consumer goods industries. The continuous increase in global demand for polyurethane products has resulted in a significant expansion of production capacity, accompanied by growing environmental concerns associated with gaseous emissions generated during polyurethane synthesis and recycling processes.

Polyurethane is generally synthesized through the polyaddition reaction between aromatic or aliphatic diisocyanates, such as 4,4′-methylene diphenyl diisocyanate (MDI), toluene diisocyanate (TDI), hexamethylene diisocyanate (HDI), and isophorone diisocyanate (IPDI), together with polyether or polyester polyols and chain extenders. During polymerization, elevated temperatures, the high reactivity of isocyanate groups, and secondary reactions with moisture can lead to the formation of hazardous gaseous products, including isocyanate vapors, volatile organic compounds (VOCs), amines, aldehydes, carbon dioxide (CO_2), carbon monoxide (CO), nitrogen oxides (NO_x), and, under specific thermal degradation conditions, hydrogen cyanide (HCN). These emissions deteriorate workplace air quality, adversely affect process safety, contribute to atmospheric pollution, and pose significant occupational health risks.

Recent international studies have identified airborne isocyanates as one of the principal environmental and occupational hazards associated with polyurethane manufacturing. Investigations conducted in Germany, the United States, Japan, South Korea, and China have demonstrated that continuous monitoring of MDI and TDI concentrations, combined with local exhaust ventilation, multistage adsorption–filtration systems, and catalytic oxidation technologies, substantially reduces worker exposure and improves industrial safety. In addition, European industrial emission regulations require strict monitoring and control of airborne isocyanate concentrations in workplaces where polyurethane products are manufactured or processed.

Another important environmental issue is the management of polyurethane waste generated at the end of the service life of polymer products. Current industrial recycling technologies include mechanical grinding, glycolysis, hydrolysis, aminolysis, alcoholysis, thermochemical depolymerization, pyrolysis, and energy recovery. Chemical recycling has recently attracted considerable attention because it enables the recovery of valuable polyols that can be reused as secondary raw materials in new polyurethane formulations. Germany, the Netherlands, and Belgium have achieved significant progress in polyol recovery technologies, whereas China and South Korea have successfully implemented glycolysis-based recycling processes at an industrial scale.

Despite these advances, relatively limited information is available regarding the composition and concentration of gaseous emissions generated during polyurethane polycondensation under moderate processing temperatures and during the recycling of polyurethane materials. In particular, the influence of temperature on the evolution of gaseous emissions from MDI-based diisocyanates, polyether polyols, and chain extenders within the range of 60–120 °C has not been comprehensively investigated. Therefore, the present study aims to determine the concentrations of gaseous emissions released into workplace air during the polycondensation of MDI-based polyurethane-forming reagents at temperatures between 60 and 120 °C using ANT-3M and GC-8000 gas analyzers. The measured concentrations are evaluated against the maximum permissible concentrations (MPCs) established for occupational environments and classified according to GOST 12.1.007–76. Furthermore, based on the experimental findings, an innovative multistage gas purification system is proposed to capture and neutralize hazardous gaseous emissions, thereby improving occupational safety, reducing atmospheric pollution, and enhancing the environmental sustainability of polyurethane manufacturing and recycling processes.

Materials and Methods

The concentrations of gaseous components released into the workplace atmosphere were determined using an ANT-3M portable gas analyzer and a GC-8000 gas chromatograph, enabling both qualitative

and quantitative characterization of gaseous emissions. The measured concentrations were compared with the maximum permissible concentrations (MPCs) established for workplace air, and the detected compounds were classified according to the hazard classification specified in GOST 12.1.007–76. All measurements were performed in triplicate, and the average values together with the corresponding experimental errors were calculated. Based on the experimental results, a technological approach for reducing and neutralizing gaseous emissions generated during polyurethane synthesis and thermal recycling was developed. The technical characteristics of the virgin polyurethane material used in this study are presented in Table 1.

Table 1. Optimal technological parameters for the synthesis of virgin polyurethane oligomers.

№	Component	Content (wt.%)	Processing temperature (°C)	Operating pressure (MPa)
1	Desmodur® MS 70 (MDI diisocyanate)	70	90	2,0
2	Desmophen® 2001 KS (polyether polyol)	25,2	75	1,5
3	Baytec® XL (chain extender/polyol)	4,8	25	0,5

Table 1 presents the principal technological parameters employed for the synthesis of virgin polyurethane based on polyurethane-forming oligomers. The polyurethane formulation consisted of MDI-based diisocyanate, Desmophen® 2001 KS polyether polyol, and Baytec® XL chain extender (polyol). The components were incorporated at mass fractions of 70.0, 25.2, and 4.8 wt.%, respectively. The polyurethane synthesis was carried out under controlled processing conditions, with the reaction temperature maintained at 90 °C. During the process, the operating pressures of the MDI, polyether polyol, and chain extender streams were maintained at 2.0, 1.5, and 0.5 MPa, respectively. These processing parameters were selected to ensure a stable reaction between isocyanate and hydroxyl functional groups, thereby promoting complete polymerization and the formation of a homogeneous, high-molecular-weight polyurethane with improved physicochemical properties.

Table 2. Optimal technological parameters for polyurethane waste recycling.

№	Component	Content (wt.%)	Processing temperature (°C)	Operating pressure (MPa)
1	Molten polyurethane waste	85-80	115-120	1,0
2	Desmodur® MS 70 (MDI diisocyanate)	15-20	90-95	2,0
3	Desmophen® 2001 KS (polyether polyol)	-	-	-
4	Baytec® XL (chain extender/polyol)	-	-	-

The technological parameters employed for the recycling of MDI-based polyurethane waste are presented in Table 2. Based on these processing conditions, the chemical composition of gaseous emissions generated during thermal recycling was investigated, and effective approaches for their capture and neutralization were evaluated [1].

Results and Discussion

The experimental results demonstrated that both the composition and concentration of gaseous emissions generated during the synthesis of MDI-based polyurethane and the thermal recycling of polyurethane waste were strongly influenced by processing temperature. Within the temperature range of 60–80 °C, gaseous emissions were primarily associated with the evaporation of residual moisture and the release of trace amounts of volatile organic compounds (VOCs). As the temperature increased to 90–100 °C, the evolution of carbon dioxide (CO_2) became more pronounced owing to secondary

reactions involving isocyanate groups and residual moisture. At 110–120 °C, partial thermal degradation of polyurethane chains resulted in a substantial increase in gaseous emissions, including CO_2, carbon monoxide (CO), aromatic amine vapours, and free isocyanate vapours [2].

A comparison between virgin and recycled polyurethane revealed that the total volume of gaseous emissions generated during the synthesis of virgin polyurethane was consistently lower than that produced during the thermal processing of recycled polyurethane. This difference is primarily attributed to the presence of residual moisture, oxidized polymer segments, and low-molecular-weight degradation products remaining in the recycled polyurethane, which promote additional gas evolution during heating [3], [4].

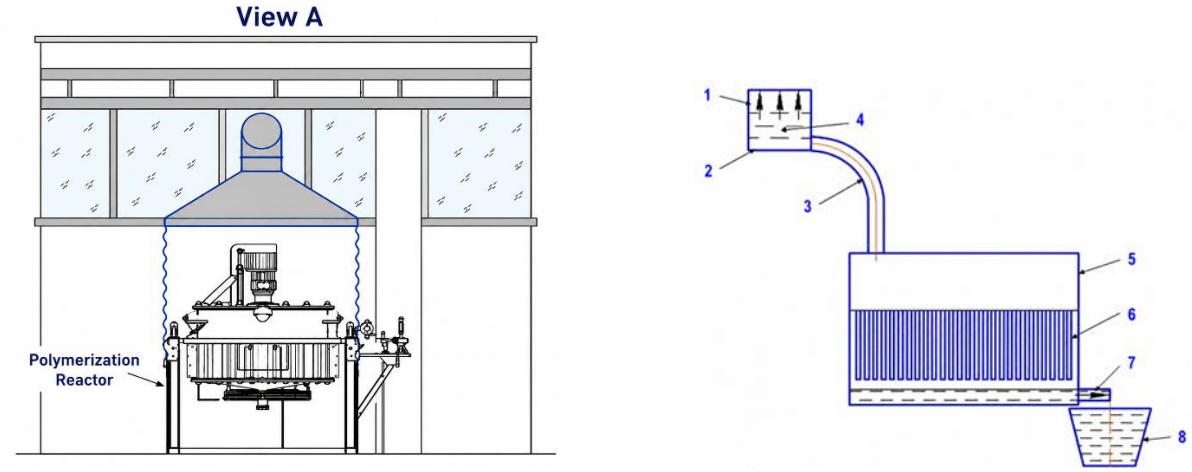
The experimental data further showed that, at 120 °C, the total volume of gaseous emissions released from recycled polyurethane was approximately 30–35% higher than that of the corresponding virgin polyurethane sample. These findings indicate that thermal recycling of polyurethane waste significantly increases gaseous emissions and highlight the necessity for efficient gas collection and purification systems to ensure occupational safety and minimize environmental pollution.

Table 3. Concentrations of volatile chemical compounds detected during polyurethane synthesis at different processing temperatures.

№	Chemical compound	(GOST 12.1.007–76)		Polyurethane-forming reagents								
				1 Desmodur® MS 70 (MDI)			2 Desmophen® 2001 KS			3 Baytec^R XL B		
				Workplace temperature (°C)								
		MPC (mg/m³)	Hazard class	Concentration in workplace air (mg/m³)								
				I 60-80	II 80-100	III 100-120	I 60-80	II 80-100	III 100-120	I 60-80	II 80-100	III 100-120
1	1,4-Diazabicyclooctane	1	II	0,20	0,60	0,80	0,60	0,75	0,86	0,65	0,80	0,90
2	Dichloroethane	10	II	0,20	0,65	0,82	0,65	0,80	0,88	0,65	0,85	0,93
3	Dimethylsiloxane	10	III	0,50	0,70	0,85	0,70	0,85	0,90	0,70	0,86	0,95
4	Gasoline hydrocarbons (AI-92 equivalent)	100	IV	0,60	0,80	0,85	0,75	0,85	0,95	0,78	0,90	0,98

The results presented in Table 3 indicate that the concentrations of volatile chemical compounds released into the workplace atmosphere during the handling of polyurethane-forming chemical reagents increased progressively with increasing processing temperature. The highest concentrations of 1,4-diazabicyclooctane, dichloroethane, and dimethylsiloxane vapours were observed within the temperature range of 100–120 °C. Nevertheless, all measured concentrations remained below the

maximum permissible concentrations (MPCs) specified by GOST 12.1.007–76, indicating that the operating conditions complied with the established occupational safety requirements [5].
Based on the experimental findings, a technological gas filtration system was designed and incorporated into the recycling process to reduce gaseous emissions. The proposed filtration system decreased the concentration of emitted gases from approximately 35% to 25%, thereby improving workplace air quality and reducing the environmental impact of the process [6]. The technological scheme of the developed gas capture and neutralization system is presented in Figure 1.



a) b)

Figure 1. (a) Polyurethane waste recycling reactor; **(b)** Adsorption-based gas filtration system used during polyurethane waste recycling. Figure labels: (1) gaseous emissions; (2) molten polyurethane; (3) gas transfer pipeline; (4, 8) condensate collector; (5) filter housing; (6) adsorbent/filter media; (7) purified gas outlet.

During the thermal recycling of polyurethane waste, the gaseous emissions generated inside the reactor are transferred through a gas pipeline to the adsorption column for purification. As the gas stream passes through the adsorbent bed, hazardous components, including isocyanate vapours, volatile organic compounds (VOCs), aromatic amines, and other gaseous pollutants, are effectively retained by adsorption. The purified gas is subsequently discharged into the atmosphere in compliance with environmental requirements, whereas the condensate produced during adsorbent regeneration is collected in a dedicated condensate vessel for further handling and disposal. The proposed gas treatment system is designed to reduce the release of hazardous gaseous emissions, improve workplace air quality, and enhance the environmental safety of the polyurethane recycling process [7].
The quantitative comparison of gaseous emissions generated during the synthesis of virgin polyurethane, the thermal recycling of polyurethane waste, and after gas filtration is presented in Table 4. The obtained results demonstrate the effectiveness of the proposed adsorption-based filtration system in reducing the concentration and total volume of gaseous emissions released during the recycling process.

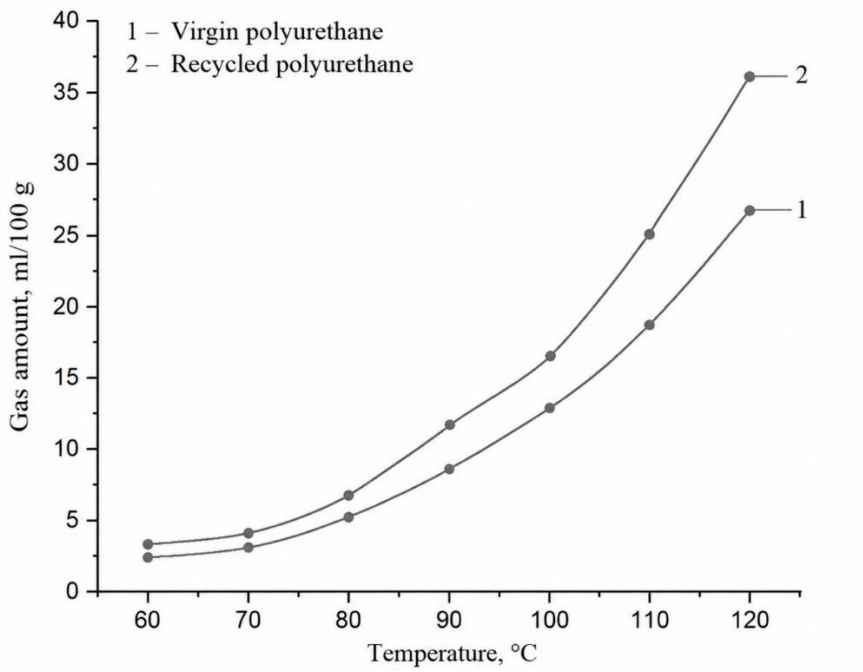


Figure 2. Temperature dependence of gaseous emissions.

Figure 2 illustrates the variation in gaseous emissions released from virgin and recycled polyurethane samples at different processing temperatures. The experimental results demonstrate that increasing the temperature from 60 to 120 °C resulted in a progressive increase in gaseous emissions for both materials. Throughout the investigated temperature range, recycled polyurethane consistently generated higher gas volumes than virgin polyurethane. This behavior can be attributed to the presence of residual moisture, low-molecular-weight degradation products, and residual reactive functional groups formed during the recycling process, which promote additional gas evolution upon heating.

A pronounced increase in gaseous emissions was observed at temperatures above 100 °C, indicating the onset of accelerated thermo-oxidative degradation and partial scission of polyurethane macromolecular chains. These degradation processes contributed to the formation of larger quantities of gaseous products, including carbon dioxide, carbon monoxide, volatile organic compounds, aromatic amines, and residual isocyanate vapours [8], [9].

The obtained results demonstrate that processing temperature is one of the key factors governing gaseous emissions during polyurethane synthesis and thermal recycling. Consequently, the implementation of efficient gas collection and purification systems is essential for maintaining workplace air quality, reducing atmospheric emissions, and improving the environmental safety of polyurethane manufacturing and recycling technologies [10], [11].

Table 4. Quantitative comparison of gaseous emissions released at different processing temperatures.

№	Temperature (°C)	Virgin polyurethane (mL/100 g)	Recycled polyurethane (mL/100 g)	Filtered gases		Gaseous products detected
1	60	2.40	3.24	2.80	-	H_2O vapour
2	70	3.12	4.03	3.65	-	H_2O vapour
3	80	5.24	6.7	6.15	H_2O, CO_2	H_2O vapour, CO_2
4	90	8.60	11.61	8.75	-	CO_2

5	100	12.82	16.64	14.93	-	CO_2, isocyanate vapours (R–N=C=O)
6	110	18.71	25.24	21.98	CO_2	CO_2, CO, aromatic amine vapours
7	120	26.90	36.31	29.37	CO_2, CO,	CO_2, CO, aromatic amines, isocyanate vapours (R–N=C=O)

Increasing the processing temperature from 60 to 120 °C during polyurethane synthesis resulted in a continuous increase in the rate of gaseous emission. For the virgin polyurethane sample, the total gas volume increased from 2.40 mL/100 g at 60 °C to 26.90 mL/100 g at 120 °C, corresponding to an approximately 11.2-fold increase. In contrast, recycled polyurethane exhibited higher gaseous emissions throughout the entire temperature range. The gas volume increased from 3.24 mL/100 g at 60 °C to 36.31 mL/100 g at 120 °C, representing approximately 35% greater gaseous emissions than those of the virgin polyurethane under identical processing conditions [12].

The higher gas evolution observed for recycled polyurethane is attributed to the presence of residual moisture, partially degraded urethane linkages, oxidized polymer segments, and low-molecular-weight volatile degradation products retained within the recycled material. Upon heating, these species undergo secondary reactions and thermal decomposition, thereby promoting additional gaseous emissions [13].

Following treatment with the proposed adsorption–filtration system, the total volume of emitted gases decreased substantially. The filtered gas volumes were 2.80, 3.65, 6.15, 8.75, 14.93, 21.98, and 29.37 mL/100 g at 60, 70, 80, 90, 100, 110, and 120 °C, respectively. Compared with untreated recycled polyurethane, the filtration system reduced the total gaseous emissions by 13.6%, 9.4%, 8.2%, 24.6%, 10.3%, 12.9%, and 19.1%, respectively, demonstrating its effectiveness in mitigating gaseous emissions over the investigated temperature range [14].

A marked increase in gaseous emissions was observed at temperatures exceeding 100 °C, indicating accelerated thermo-oxidative degradation of the polyurethane matrix and progressive scission of urethane macromolecular chains. In particular, processing at 110–120 °C significantly increased the probability of generating toxic gaseous species, including carbon monoxide (CO), aromatic amine vapours, and free isocyanate vapours (R–N=C=O). These findings emphasize the importance of implementing effective gas collection and purification technologies during polyurethane synthesis and recycling to ensure occupational safety and minimize environmental emissions [15].

Conclusion

The experimental results demonstrated that processing temperature is one of the dominant factors influencing gaseous emissions during polyurethane synthesis and thermal recycling. Increasing the processing temperature from 60 to 120 °C resulted in more than an 11-fold increase in the volume of gaseous emissions from virgin polyurethane, whereas recycled polyurethane generated approximately 35% higher gaseous emissions under identical processing conditions. The increased gas evolution from recycled polyurethane was attributed to the presence of residual moisture, partially degraded urethane linkages, and low-molecular-weight volatile degradation products, which accelerated thermal decomposition during heating.

The proposed adsorption–filtration system effectively reduced gaseous emissions by 8.2–24.6%, demonstrating high removal efficiency for carbon monoxide (CO), carbon dioxide (CO_2), aromatic amine vapours, and free isocyanate vapours (R–N=C=O). These findings confirm that the developed gas purification technology can substantially reduce hazardous emissions generated during polyurethane processing while improving workplace air quality and environmental protection.

Overall, the proposed technological approach provides a practical and environmentally sustainable solution for controlling gaseous emissions during polyurethane synthesis and recycling. The developed system has considerable potential for industrial implementation, contributing to improved occupational safety, compliance with environmental regulations, reduced atmospheric pollution, and enhanced resource efficiency in polyurethane manufacturing and recycling processes.

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