

## Chemical Recycling of Polyurethane Foam Waste Via Glycolysis

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The purpose of the glycolysis of flexible polyurethane foams is to recover the polyol. In the process, three phases are obtained: an upper phase which contains the polyol, a bottom phase which has the subproducts of the reaction and the excess of glycol, and a third phase which is in the middle and it is formed by the polyurethane unreacted. Several factors that affect the reaction have been studied to optimize the yield of polyol obtained. These factors are the temperature of reaction, the time of reaction, the catalyst (diethanolamine, DEA) to solvent (diethyleneglycol, DEG) mass ratio, and the catalyst +solvent to polyurethane mass ratio. The recovered polyol is compared to a virgin polyol by a GPC chromatogram in order to verify its quality.

### 1. Introduction

Flexible polyurethane foams (PU) are one of the most widely used cushion materials in the automobile or furniture sector. In the last years, polyurethane foams have been developed strongly and they are one of the most versatile polymers. The majority of the polyurethane waste are incinerated. Due to this fact, PU recycling is nowadays an urgent task to obtain high quality polyols reducing postconsumer PU waste.

Chemical (or tertiary) recycling, involves the use of polymer waste as a feedstock for any of the chemolytic, hydrocracking or pyrolytic processes used to break down polymeric waste into simpler substances to produce virgin materials or to obtain products with a high value such as fuel, monomers or chemicals. In the case of glycolysis of polyurethane, the urethane bonds are broken down releasing the polyol of the polymer chain using glycol as solvent and a catalyst to improve the reaction (Wu CH. et al., 2003; Watando H. et al., 2006).

The election of catalyst is an important factor because it decreases drastically the time to complete the reaction. The catalysts more used are bases like amines, hydroxides and alkoxides and Lewis acids (Bauer G., 1996). In this work, the catalyst used is diethanolamine (DEA) because it is the most active catalyst studied (Molero C. et al., 2006b). Molero C. et al. (2006a) studied the use of different glycols as solvent and the diethyleneglycol (DEG) proved to be the most suitable one to obtain a high purity in the polyol phase.

## 2. Experimental

### 2.1 Methods

When an experiment has several factors that are interesting, the factorial experimental design should be used. Factorial experiments are the way to identify interactions between variables. Because of this, the glycolysis of polyurethane foam experiments were carried out using the Taguchi's parameter design methodology. The operation variables (or control factors) considered more influential are:

- Factor 1: Reaction temperature: Excessively high reaction temperatures (above 220 °C) cause the appearance of secondary products that are not of interest for the process. On the other hand, the process temperature affects the reaction kinetics, taking into account that the application of excessively low temperatures (below 170 °C) can decrease the yield of the reaction. So, the three levels chosen were: 170, 190 and 210°C.

- Factor 2: Reaction time: The percentage of oligomers remaining in the upper phase after 20 minutes of reaction is less than 10%. In fact, the kinetic of the reaction is very fast in the first minutes, but it takes more than 120 minutes to reach an inappreciable amount of oligomers. For this reason, the influence of reaction time over the polyol obtained has been studied. The three levels selected were: 30, 90 and 120 minutes.

- Factor 3: Catalyst /Solvent mass ratio: Uncatalyzed reaction involves the appearance of around 50% of polyol after 150 minutes of reaction; while with the use of a catalyst, the reaction reaches nearly 70% of polyol after 25 minutes. So, the amount of catalyst proves to be a very important process factor. The three mass ratio levels chosen were: 1:9, 1:6 and 1:3.

- Factor 4: (Catalyst+Solvent)/Polymer mass ratio: The type of reaction and purification methods require that the amount of solvent used in the reaction has to be significantly higher than the stoichiometric one. Due to this excess, the reaction mass is separated into two phases, being able to collect almost all the polyol in the upper phase. It is important to obtain an appropriate relation between the mass of solvent and polyurethane. The three mass ratio levels taken were: 1.25:1, 1.5:1 and 2:1.

In Table 1 appears the orthogonal array  $L_9$  used to perform the nine experiments combining the different selected levels of each control factor considered.

Table 1:  $L_9$  Orthogonal Array.

Experiment	Temperature (°C)	Time (min)	DEA/DEG (w:w)	(DEG+DEA)/PU (w:w)
L1	170	30	1:9	1.25:1
L2	170	90	1:6	1.5:1
L3	170	120	1:3	2:1
L4	190	30	1:6	2:1
L5	190	90	1:3	1.25:1
L6	190	120	1:9	1.5:1
L7	210	30	1:3	1:5:1
L8	210	90	1:9	2:1
L9	210	120	1:6	1.25:1

According to the experimental planning aforementioned, Table 2 shows the quantities of solvent, catalyst and polymer used.

Table 2: Quantities of reactant, catalyst and solvent used.

	L1	L2	L3	L4	L5	L6	L7	L8	L9
Polymer PU, (g)	75.00	67.50	56.25	56.25	75.00	67.50	67.50	56.25	75.00
Catalyst DEA, (g)	9.38	14.46	28.13	16.07	23.44	10.13	25.31	11.25	13.39
Solvent DEG, (g)	84.39	86.79	84.38	96.43	70.31	91.13	75.94	101.25	80.36

## 2.2 Materials

The postconsumer flexible PU foam waste used come from car seats out of use. The car seat is made up of synthetic fabric and flexible PU foam. The synthetic material was separated and thrown away, and the foam was crushed to 2 mm diameter particles.

The diethanolamine was selected as catalyst due to its suitable catalytic activity reported by several authors (Borda J. et al., 2000; Molero C. et al., 2006b). The diethylenglycol was chosen as solvent because it has been reported as the most favorable one in the literature (Molero C. et al., 2006a).

All of these substances were placed in a three-necked flask of 1 L volume where the experiments were carried out. The system was equipped with a set refrigerant, an initial purge of nitrogen to prevent possible oxidation of the reaction products, and a temperature control system with magnetic stirring system. The starting time for the reaction was taken into account when the temperature was the desired. Temperature was maintained constant during the whole reaction. Once reaction time was attained, the mixture was cooled to room temperature and poured into a funnel where the phase separation was accomplished. The polyol was retained in the upper phase, while isocyanates were found in the heavy fraction with the excess of solvent, in the form of amine. The two phases were separated and labeled for later analysis.

## 2.3 Characterization

The glycolysis products were separated and analyzed.

The polyol (upper phase) was analyzed by a gel permeation chromatograph (GPC) to determine the molecular weight distribution. The samples were dissolved in tetrahydrofuran (THF) at a concentration of 2 mg/mL and then filtered with a pore size of 0.45  $\mu$ m. The THF was used as eluent at 40 °C and 1 mL/min.

Virgin polyol and pure DEG were used for calibration purposes, in order to compare the chromatogram of the virgin and recovered polyols.

## 3. Results and discussion

In the glycolysis of polyurethane foams, three phases are obtained. The upper phase contains the recovered polyol, the bottom phase is composed of the excess of glycol and the reaction by-products, and the third phase is in the middle and it is formed by a solid product (unreacted polyurethane).

As it has been said before, the influence of several factors has been studied: the reaction temperature, the reaction time, and the amount of catalyst and solvent used. All these

factors have been studied together using the parameter design methodology developed by Taguchi®.

All the experiments were replicated three times. In Table 3 the average values of mass of polyol obtained per mass of PU used as reactant is shown for each experimental condition.

Table 3: Results obtained in the experimental design (Average values).

Experiment	Polyol to PU mass ratio
L1	$1.100 \pm 0.233$
L2	$0.573 \pm 0.021$
L3	$0.630 \pm 0.001$
L4	$0.440 \pm 0.001$
L5	$1.008 \pm 0.129$
L6	$0.722 \pm 0.115$
L7	$0.962 \pm 0.069$
L8	$0.926 \pm 0.120$
L9	$0.924 \pm 0.057$

GPC chromatograms of the virgin and the recovered polyols obtained at different conditions can be seen in Figure 1.

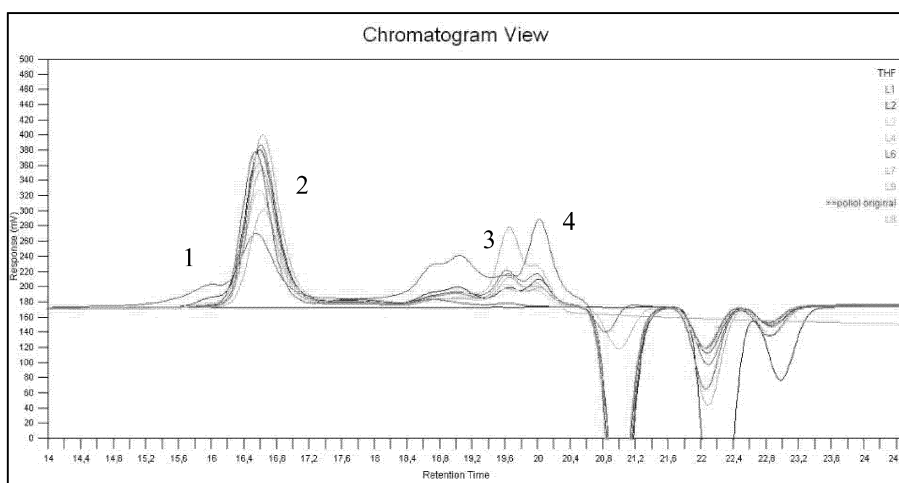


Figure 1: GPC chromatograms of the virgin polyol and the recovered polyols.

The reaction time has an influence on the polyurethane structure. The glycol action breaks down the polyurethane structure into smaller fragments. If the reaction is not complete, it can be seen a first peak in the chromatogram (see experiment L1 where the lowest reaction time was applied, 30 min).

The second peak shows the complete recovery of the polyol.

The third and fourth peaks are correlated with the subproducts of the reaction. These peaks are higher than the corresponding ones in the virgin polyol. The bottom liquid phase of reaction is formed by the excess of DEG and the aromatic by-products derived from the initial isocyanates. A little quantity of the bottom phase is dissolved in the upper phase decreasing its purity and forming these peaks.

The last peaks correspond to the glycol and THF respectively.

### 3.1 Analysis of variance: ANOVA

An analysis of variance using the ANOVA<sup>®</sup> commercial software was realized to obtain the contribution of the factors and their interactions over the response variable (polyol yield), and to determine the levels that maximize the polyol production.

In this ANOVA, the contributions of all no significant factors have been pooled of according to the significance test of Fisher with a confidence level of 99%. The analysis results are shown in Table 4.

According to the results showed in Table 4, it is observed that the catalyst+solvent to polyurethane mass ratio is the most significant factor with an influence of 39.66%. The catalyst to solvent mass ratio is the second one with an influence of 24.65% and finally, the temperature has an influence of the 14.36%. The contribution of the experimental and analysis errors is 21.33%. The response table of the polyol to PU mass ratio is shown in Table 5.

It can be seen how the level 3 is the optimum for the temperature factor (210 °C). For DEA/DEG and (DEA+DEG)/PU mass ratios, the best levels are the first ones (1:9 and 1.25:1 respectively). The time does not have a considerable influence in the quantity of polyol obtained (in the range tested). The time chosen is 90 minutes (level 2) to assure a complete reaction, as it has been seen in Figure 1. According to Taguchi's methodology if these levels of control factors are used, a maximum polyol to polyurethane mass ratio would be obtained whose value would be  $1.271 \pm 0.100$ .

Table 4: ANOVA of the polyol production values.

Variation source	Mixed	Degrees of freedom	S	V	F	S'	P%
Temperature	[N]	2	763.55	381.78	7.73	664.79	14.36
Time	[Y]	2	115.08	57.54			
DEA/DEG	[N]	2	1240.12	620.06	12.56	1141.35	24.65
(DEA+DEG)/PU	[N]	2	1934.75	967.38	19.59	1835.99	39.66
e1	[N]	0	0				
e2	[Y]	12	576.27	48.02			
<e>		14	691.35	49.38		987.64	21.33

Table 5: Response table of polyol to PU mass ratio.

Level	Temperature			Time			DEA/DEG			(DEA+DEG)/PU		
	1	2	3	1	2	3	1	2	3	1	2	3
Polyol/PU	0.768	0.723	0.937	0.834	0.835	0.759	0.915	0.646	0.867	1.010	0.752	0.665

#### 4. Conclusions

The obtained results show that the glycolysis of the polyurethane foams is very efficient to achieve a high polyol to PU ratio mass. The chromatograms show (Figure 1) that the recovered polyol is similar to the virgin polyol with a very close molecular weight.

Following the Taguchi's methodology, lower temperatures provide too slow degradation rates, so the best temperature is 210 °C because an increase in the reaction temperature speeds the degradation up markedly.

The catalyst reduces the reaction time and allows the complete breakdown of the polyurethane chain against the process with a lower quantity of DEA. So, this quantity has been studied due to economic reasons. Table 5 shows that using the fewest quantity of DEA (DEA/DEG=1:9) has a higher yield than using higher quantities, being this factor the most important one. Also, a high catalyst concentration affects negatively the process because the secondary reactions and the contamination of the polyol phase occur. Therefore, the best operational option is also the most economic one.

Increasing the relative amount of glycol does not provide any additional improvement in the yield of polyol and affects negatively to the economy of the process. So, the best (DEA+DEG)/PU mass ratio is 1.25:1.

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