UNIVERSIDAD SAN FRANCISCO DE QUITO USFQ

Colegio de Ciencias e Ingenierías

Chemical recycling of polyurethane foam by methanolysis with the use of an aluminum-based catalyst

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Ingeniería Química

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HOJA DE CALIFICACIÓN
DE TRABAJO DE FIN DE CARRERA

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RESUMEN

El poliuretano (PU) es un polímero utilizado en una variedad de industrias, como muebles, aislamiento, piezas automotrices, artículos de limpieza, etc. Su versatilidad ha llevado a una gran producción de este material, causando contaminación no deseada en ciertas zonas. El poliuretano está compuesto principalmente de polioles e isocianatos, y se añaden otros compuestos clave, como agentes espumantes y catalizadores para ayudar con su producción. El reciclaje de este material puede darse por diversos métodos, un ejemplo de estos es el reciclaje químico. La metanólisis es un tipo de reciclaje químico que se ha estudiado en el poliuretano, sin embargo, la investigación realizada no es tan extensa, además, no se ha registrado en la literatura el uso de un catalizador para facilitar la despolimerización de este material. En el presente estudio se realizó la metanólisis del PU utilizando un catalizador de basado en Aluminio, para entender como este afecta a la reacción. Se realizaron cálculos en donde se descubrió que el catalizador incrementó la conversión del PU. Tras analizar los residuos sólidos de reacción, se logró graficar los espectros IR de diferentes porcentajes de conversión y del poliuretano puro. Utilizando un equipo GC-MS se pudieron obtener los cromatogramas, con los que se identificaron posibles residuos líquidos de la reacción, su distribución y cómo el catalizador afectaba a estos productos.

Palabras clave: Poliuretano, polímero, reciclaje químico, metanólisis, despolimerización, catalizador.

ABSTRACT

Polyurethane (PU) is an important polymer used in a wide variety of industries, like furniture, insulation, automotive parts, cleaning gear, etc. Due to its high versatility, a high amount of this material is produced worldwide, leading to unwanted contamination in some areas. Polyurethane is composed of polyols and isocyanates, other key compounds are added to help finish its production, like foaming agents and catalysts. PU recycling can be achieved through various methods, one of them being chemical recycling. Methanolysis is an example of a chemical recycling technique, however, research on this topic is not extensive, furthermore, no current studies show the use of a catalyst to help with the depolymerization of this material. In the present study, methanolysis of PU was carried out using an Aluminum-based catalyst, to understand how it affects the reaction. Calculations discovered that the catalyst increased conversion of the PU foam. After analyzing solid residues from the reaction, IR spectrums were obtained at different conversion values and for pure PU. With the help of a GC-MS, chromatograms were obtained, which helped identify possible liquid residues, their distribution, and how the catalyst affected these products.

Key words: Polyurethane, polymer, chemical recycling, methanolysis, depolymerization, catalyst.

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1. INTRODUCTION

Poluyrethane (PU) is an important polymer used in a wide variety of industries, like furniture, insulation, automotive parts, cleaning gear, etc [1]. Due to its high versatility, a large amount of this material is manufactured. According to Asociación Ecuatoriana de Plásticos (ASEPLAS), around 348,984 tons of PU were produced in 2017 only in Ecuador [2]. Additionally, 24.72 million tons of PU were produced in 2021 worldwide, and a projected estimate of 29.9 million tons by 2029 [3]. With the massive manufacturing of this material, unwanted contamination is a problem in certain areas. For instance, H. Mu *et al.* conducted a study consisting of sampling five different water sites in the Jiaodong Peninsula in China, where they found contamination by several microplastics, including polyurethane [4]. Furthermore, microplastics were also found in the Brazilian Amazon Continental Shelf, with cellulose fibers, polyamides, and polyurethane being the most abundant [5].

Polyurethane is composed mainly of isocyanates and polyols, with some additives to help increase strength and overall properties of the material. It contains approximately 30% polyols by weight and 50% isocyanates, the remaining composition is divided predominantly by a foaming agent (10% wt) in the case of PU foams, also a 4-5% of catalysts and finally a 5-10% of non-combustible molecules such as phosphate ester compounds [6].

The recycling of this material has become a far-reaching investigation topic, due to the different methods that can be applied. The main types of recycling include chemical, thermal, and physical recycling. Nowadays, the latter of the mentioned methods is the most popular, specifically regrinding. Nevertheless, performance of the recovered product has an inferior quality in comparison to the original, which limits the market size [1]. Thermal recycling includes processes such as pyrolysis, gasification, and hydrogenation. These methods have been studied, some in a smaller scale, and provided good results, but some require certain conditions to be met to be a viable option [7]. Chemical recycling of polyurethane is an alternative that has been studied with different solvents. Glycolysis is the favored method, and has been proven to be economically acceptable, however, further investigation is required for this process to fully enter the industry [8]. Another example of chemical recycling is methanolysis, in which the material is depolymerized using methanol as a solvent.

Methanolysis is a reaction that has not been studied to its full extent, it is known that the resulting monomers from the reaction are mainly polyols and carbamates [6]. Nonetheless, chemical recycling investigation of polymers aims to provide an effective alternative solution to the already existing ones, which is why obtaining high degradation methods is a desired result in this area. A computational study was able to determine the reaction mechanism as well as satisfactorily estimate kinetic parameters of the degradation of polyurethane and proposing as future work the addition of a catalyst to analyze the impact it has on the reaction [9]. Moreover, there is no report of an effective catalytic system regarding methanolysis of polyurethane, which is why, in the case of this study, the catalyst used will be an Aluminum-based compound.

In this work, the methanolysis of a commercial PU sponge, with and without the addition of a catalysts will be developed. Catalyst effect onto the conversion will be tested by varying reaction time and temperature. Characterization of the reaction’s products will be carried out to get insights about the depolymerization products. FTIR, Uv-Vis, and GC-MS will be used.

2. EXPERIMENTAL METHOD

2.1 Materials

• Methanol • PU foam • Filter Paper • 500ml glass vessel• Scale • 250ml flask • Funnel • Spatula • Aluminum-Based Catalyst • Nitrogen • HPLC Grade Acetone

2.2 Catalyst synthesis

A precipitation method was used to prepare the Aluminum-Based catalyst [10].

2.3 PU foam methanolysis with catalyst application

2.3.1 Time variation.

PU foam flakes (see figure 1.a) were depolymerized in a mixture of an alcoholyzing agent (methanol, PU mass to volume ratio of 1:200). Reactions were performed in a parr reactor (see figure 1.b) equipped with an automatic stirrer and a 500ml vessel. Nitrogen was pumped into the reactor to remove air particles stuck inside. Time was varied in steps of 1h (from 1 to 5h) at a constant temperature of 150˚C.

Figure 1: a) Pictures of PU foams and flakes used for depolymerization process, and b) reactor setup used for PU methanolysis

2.3.2 Temperature variation.

Sample and reactor procedure are the were carried out identically as stated in the time variation section, only this time varying temperature in steps of 10˚C (from 110 to 150˚C) at a constant time of 130min.

2.3.3 Conversion.

The reaction products were filtered, with the filter paper's initial weight being measured prior to being in contact with the products. The final weight was taken and the initial one was subtracted from it, to be able to obtain the reaction's conversion. Which was calculated with the following equation:

$$X = \frac{W_f}{W_i}$$

Where,

W_f = Final weight

W_i = Initial weight

2.4 Product characterization

2.4.1 UV-vis.

UV-Vis was used to analyze the change in possible compounds throughout the reaction. From 200 to 625 nm. A small sample of 5ml was extracted from the reactor and diluted in methanol (1:100, 1:200, depending on absorbance read on UV).

2.4.2 Fourier transfer infrared spectroscopy (FTIR).

FTIR was employed to identify the solid compound remaining after the reaction was filtered, from 650 to 4000 cm-1. A mortar as pestle was used to grind the powder for its analysis.

2.4.3 Gas chromatography-mass spectrometry (GC-MS).

The liquid residue was evaporated using a rotary evaporator (40rpm, 40˚C for 25min), the remaining product was then diluted with 5ml of HPLC grade acetone, with an oven temperature of 320˚C. This sample was further diluted in HPLC grade acetone (1:20) and injected in the GC-MS, the column used was TG-5MS (Length: 30m, ID:0.25mm, Film: 0.25 μm).

2.4.4 Statistical analysis

An ANOVA variance analysis was carried out to examine if the Aluminum-Based catalyst had a significative impact on PU conversion in the methanolysis process.

3. RESULTS AND DISCUSSION

3.1 Overall review of methanolysis reaction

Figure 2 shows the IR spectra of solid products after complete (X=100%) and partial conversion (X< 100%) of PU during the methanolysis process. Pure PU spectra and solid products after incomplete reaction appear to be identical, showing the presence of not depolymerized PU in the solid residue. Three representative peaks for PU are observable at 1100, 2860, and 3340 cm^{-1}, which represent the C-O-C, CH_2, and N-H bond respectively [11]. On the other hand, for fully converted PU, there is still the presence of solid residues, with a different IR spectrum than PU. These residues might be related to the presence of additives, colorants, catalysts, and other compounds necessary for the PU production.

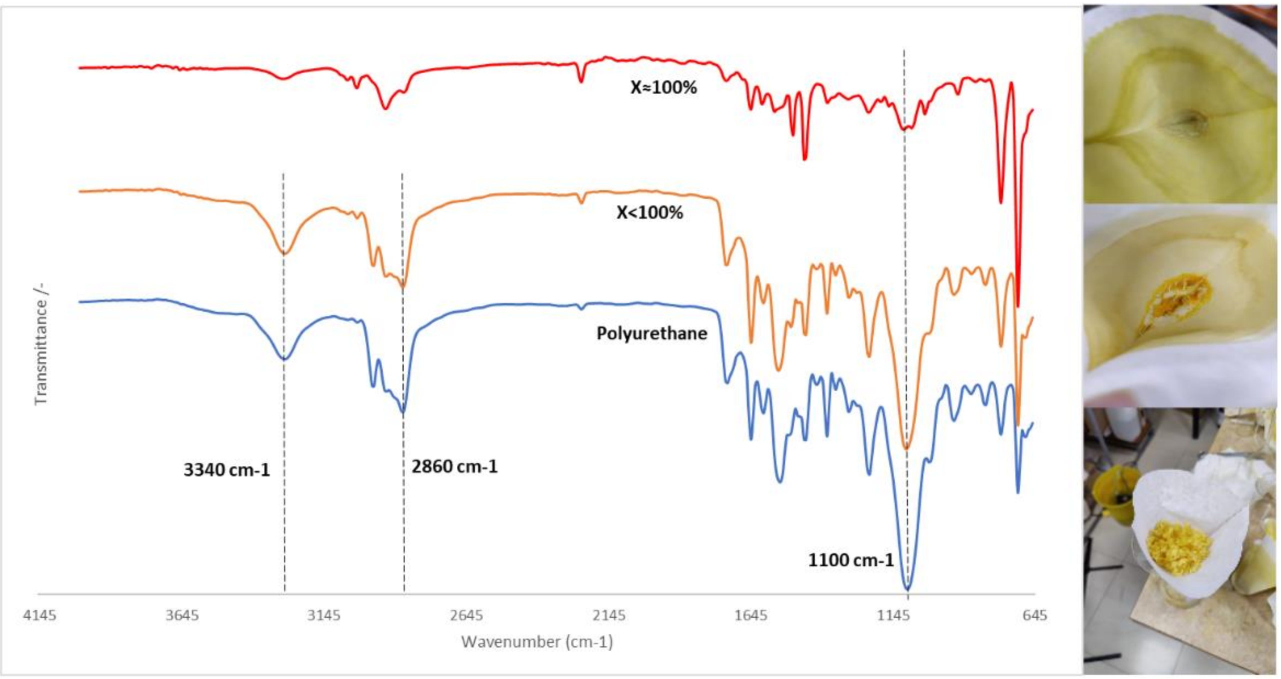

Figure 2: Exemplary FTIR: Spectra of solid residues after finished methanolysis reactions when partial and full conversion is achieved, and when it’s not

3.2 Conversion results

Figure 3 shows the values of PU conversion at different temperatures with and without the presence of the Al-based catalyst. The overall trend in this graph shows that catalyst does improve conversion when it is applied to the reaction. For instance, at 110˚C, it is visible that it provided about a 5% increment. For reaction temperatures of 120˚C and 130˚C the catalyst increased the conversion by 10%, boosting it from 65 up to 75%. It is also noticeable that 140 and 150˚C temperatures were not carried out with catalyst application. At these temperatures, conversion rate was already reaching 100%, in fact, a full conversion was obtained when the reaction was set to 150˚C, and 95% for 140˚C, when the residence time was 130 minutes. Unfortunately, catalyst application seems to not be active enough for PU depolymerization by methanolysis. 5 to 10% increments are not that significant for justifying the use of a catalyst. Additionally, an ANOVA statistical analysis was carried to back up the claim stating that catalyst has no significant effect on PU conversion (see Annex C for variance tables).

Results lead to believe that this reaction is more dependent on temperature, and that catalyst application will only have a small impact upon it. Furthermore, depolymerization reactions nowadays can be carried out at much higher temperatures, ranging from 450 to 800˚C, which would accelerate PU methanolysis with little to no effort, rendering the use of a catalyst as pointless [12].

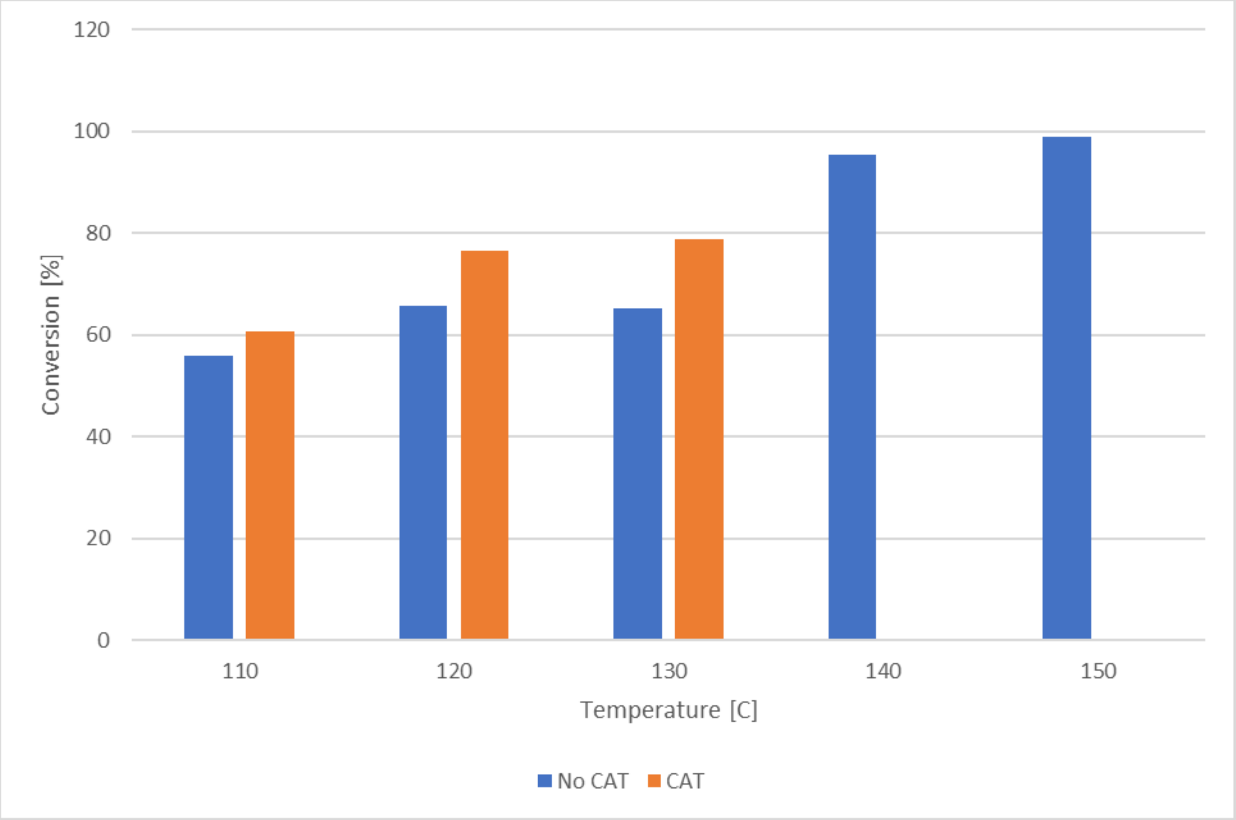

Figure 3: PU conversion after methanolysis reaction at different temperatures with and without catalyst. Residence time: 130 min

3.3 Product characterization

3.3.1 UV-vis.

Once conversion analysis was finished, the liquid-products were studied. Figure 4 depicts the UV-Vis spectra of a diluted reaction liquid-product. As it can be seen from the figure below, a consistent spectrum was obtained for PU methanolysis reactions. At different times, the reaction shows the same pattern only increasing its absorbance values. Two peaks are clearly present at 210 and 290 nm. In figure 4, the only peak that shows a clear and visual change is the one at 210 nm, which can be used to make certain statements about the reaction. It is noticeable that the peak absorbance is increasing as time goes on, which indicates an increase in concentration of a compound. According to Beer’s Law, absorbance is proportional to the concentration of a substance, which reaffirms the claim made about a molecule changing its concentration during the course of the reaction [13]. Both peaks were analyzed along time, as depicted in figure 5. Figure 4.a shows a linear increment in absorbance, until reaching a plateau, suggesting that the reaction has finished. Figure 5.b shows no indication on the progression of the PU methanolysis throughout time, absorbance values fluctuate at random which justifies the use of the 210nm peak as the main source for data. The peak value reached in the first plot (figure 5.a) is just below two, the difference in absorbance between the maximum value and minimum value is 1.536. A slight fluctuation can be observed from minute 40 to 90, which could be considered an anomaly, and could have been caused by an error on the equipment used. As for figure 5.b, the maximum value nears 1.4, with the lowest value being just above one. As mentioned previously, no observable trend can be analyzed in this graph.

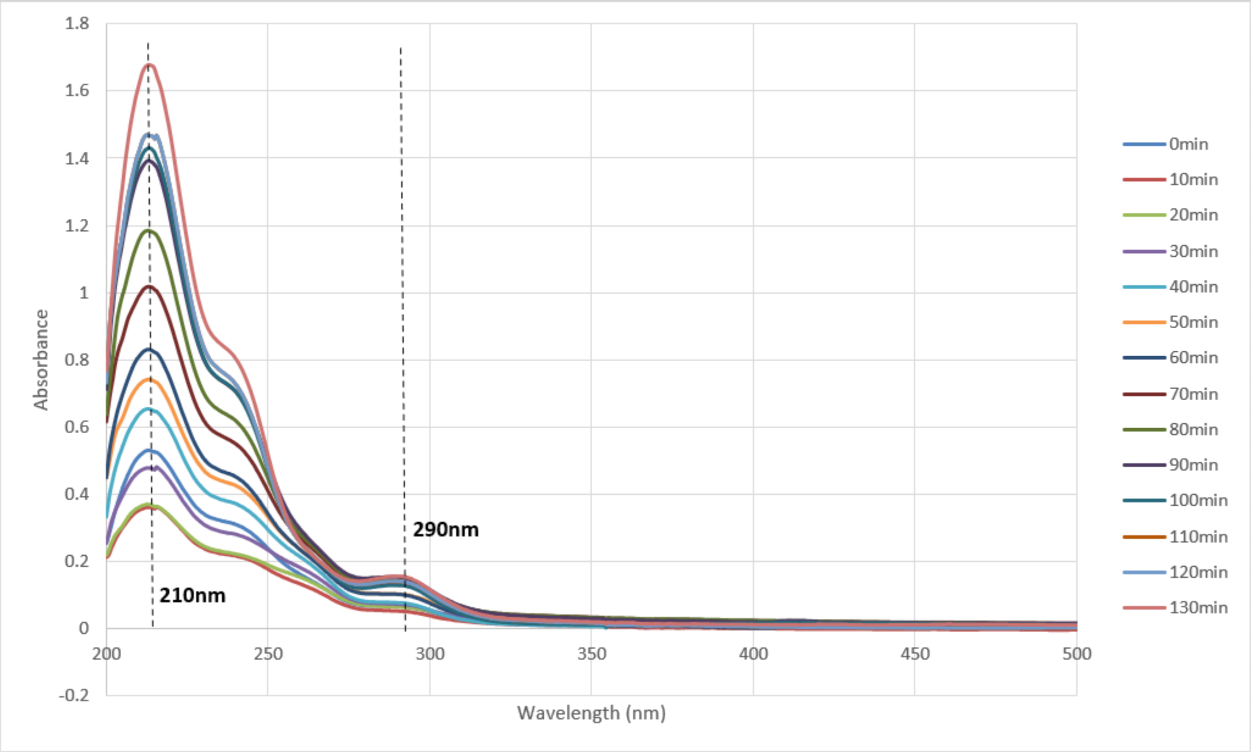

Figure 4: Exemplary UV-Vis spectrums of methanolysis PU reaction at different reaction times. (Reaction conditions: Polyurethane as raw material · 1g, Methanol as solvent · 200ml, Temperature: 120◦C, Residence Time: 130 minutes)

Figure 6 shows an example reaction at a temperature of 120°C, where peak values at the 210nm peak were taken. In general, absorbance tends to increase with time, it is also noticeable that there is a minimum present at the start of the reaction, however, it can be said that there is a strong increasing correlation between absorbance and time for PU methanolysis. Absorbance starts to increase at the 20-minute mark, reaching a value of 1.4 once it reaches 100 minutes.

The minimum present at the start is an important part of this plot, as its behavior can provide information about the reaction. Polyurethane foams are made in a wide variety of ways, it is known that PU foam is manufactured using polyols and isocyanates as the main reactants, however, these molecules come in numerous forms. For example, the polyol used for the reaction can be ester based or ether based, furthermore, catalyst and additives are used to complete the formation of this foam [14]. The initial decrease in absorbance could indicate the existence of another compound which absorbs light at the same wavelength as the one that increases afterwards, which could possibly be a form of polyol. S. Nam *et al* studied different behaviors of polyethylene glycol and obtained UV absorption spectra for them. The obtained results show a similar behavior to the peak at 290nm, showed in figure 2. Even though this was not the peak analyzed, it provides enough insight to infer that the change present in figure 5 could be related to a polyol type molecule [15].

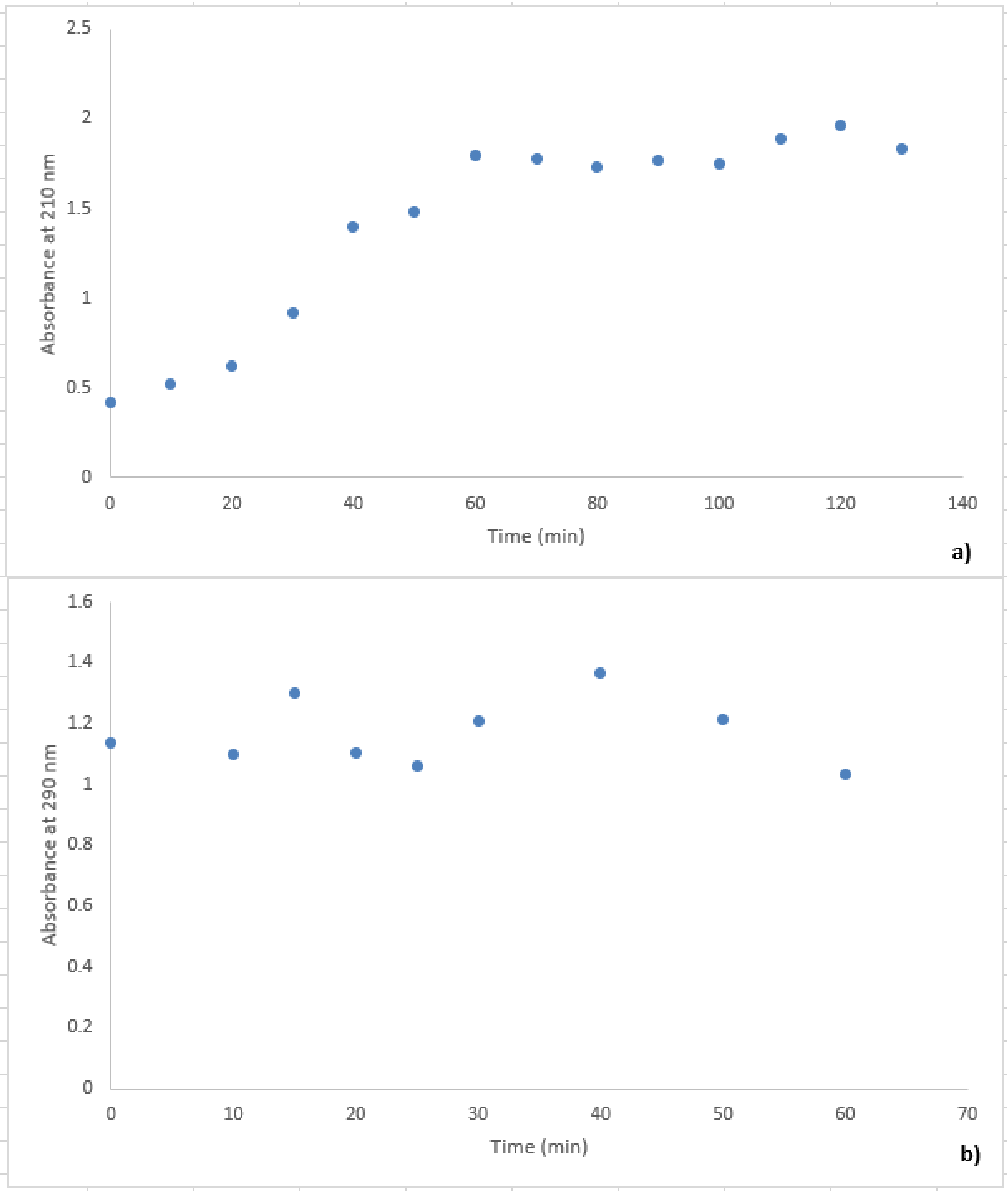

Figure 5: Comparison of peak values when different peaks are analyzed; a) Values at 210nm peak; b) Values at 290nm peak (Reaction Conditions: Polyurethane as raw material · 1g, methanol · 200ml, Temperature= 150◦C, Residence Time: a) 130 minutes, b) 60 minutes)

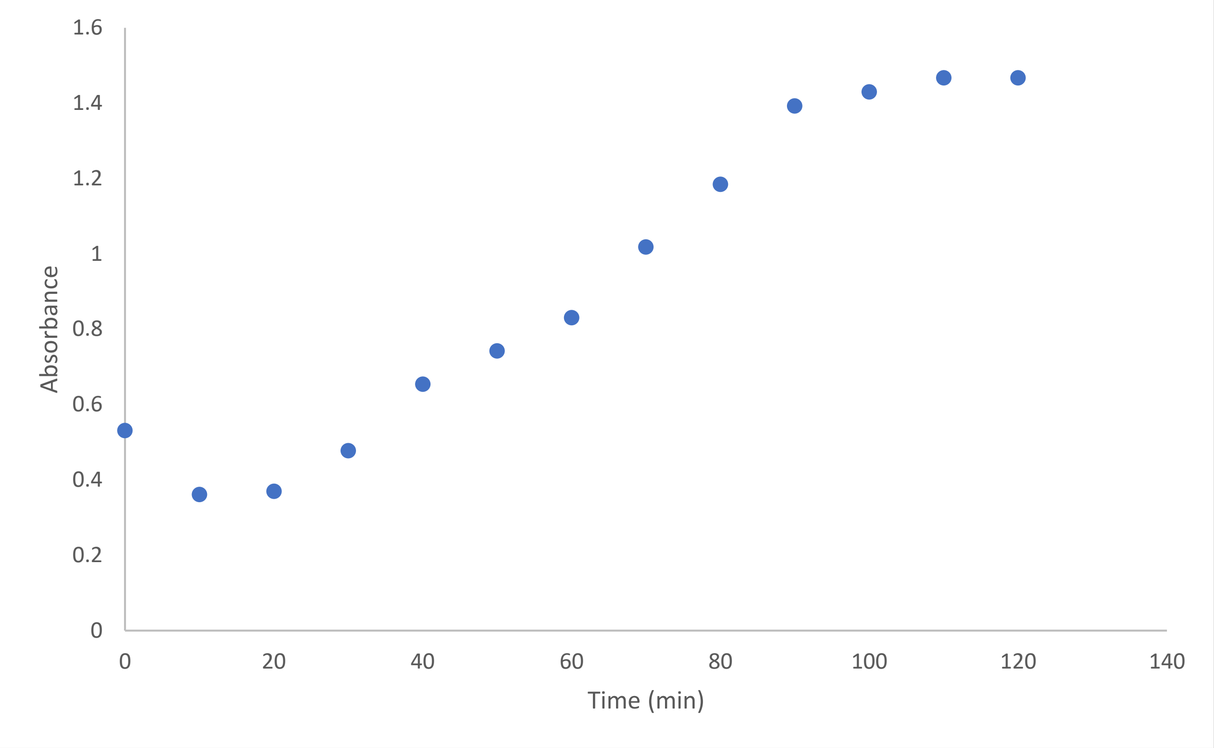

Figure 6: Exemplary of low temperature reaction where an initial minimum is present in the peak values. (Reaction conditions: Polyurethane as raw material · 1g, Methanol as solvent · 200ml, Temperature: 120◦C, Residence Time: 130 minutes)

As seen in previous figures, absorbance tends to increase with time. However, in this example there is no minimum present in the reaction. After minute 80, a slight decrease in absorbance can be observed, nevertheless, after that, absorbance starts increasing and surpasses the previous maximum value. The difference between reactions shown in figure 6 and 7, is that the latter was carried out at a higher temperature (140˚C). It can be inferred that due to the high temperature, the initial decomposition of the unknown compound already took place before the first absorbance value was recorded. It also leads to believe that PU foam methanolysis is heavily temperature dependent.

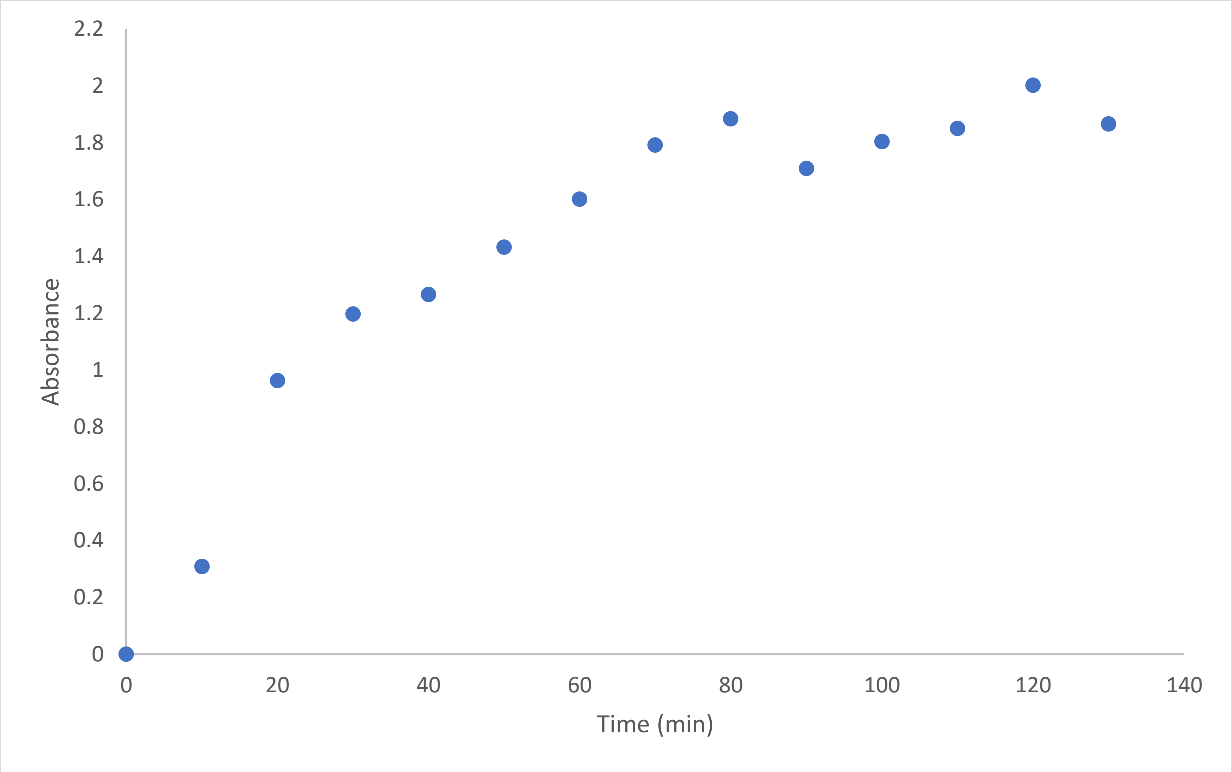

Figure 7: Exemplary of PU methanolysis reaction where there is no initial minimum present in the peak values. (Reaction conditions: Polyurethane as raw material · 1g, Methanol as solvent · 200ml, Temperature: 140◦C, Residence Time: 130 minutes)

3.3.2 GC-MS.

To get further insights, GC-MS chromatograms were taken for liquid products. Figure 8 shows the complete chromatogram of a liquid product from PU methanolysis at 30- and 60-min reaction time. In general, in both chromatograms' product distribution looks similar, the main difference being a clear increase in the intensity of peak 1, which indicates polyol formation in PU methanolysis. Peaks formed at 3 minutes indicate the presence of alcohol molecules, which would be the polyols present in PU foams. In the first 30 minutes of the reaction, these molecules are starting to be formed due to depolymerization. The fact that the peak 1 dramatically increases its abundance, demonstrates the correct depolymerization of the material, as more of its composing molecules are being formed. Another key difference is the change in the intensity of peak 2, showing higher abundance for a reaction time of 30 minutes. Peaks 2 to 9 indicate the presence of isocyanates, this same pattern was found in a study investigating methanolysis of commercially available PU foam [6].

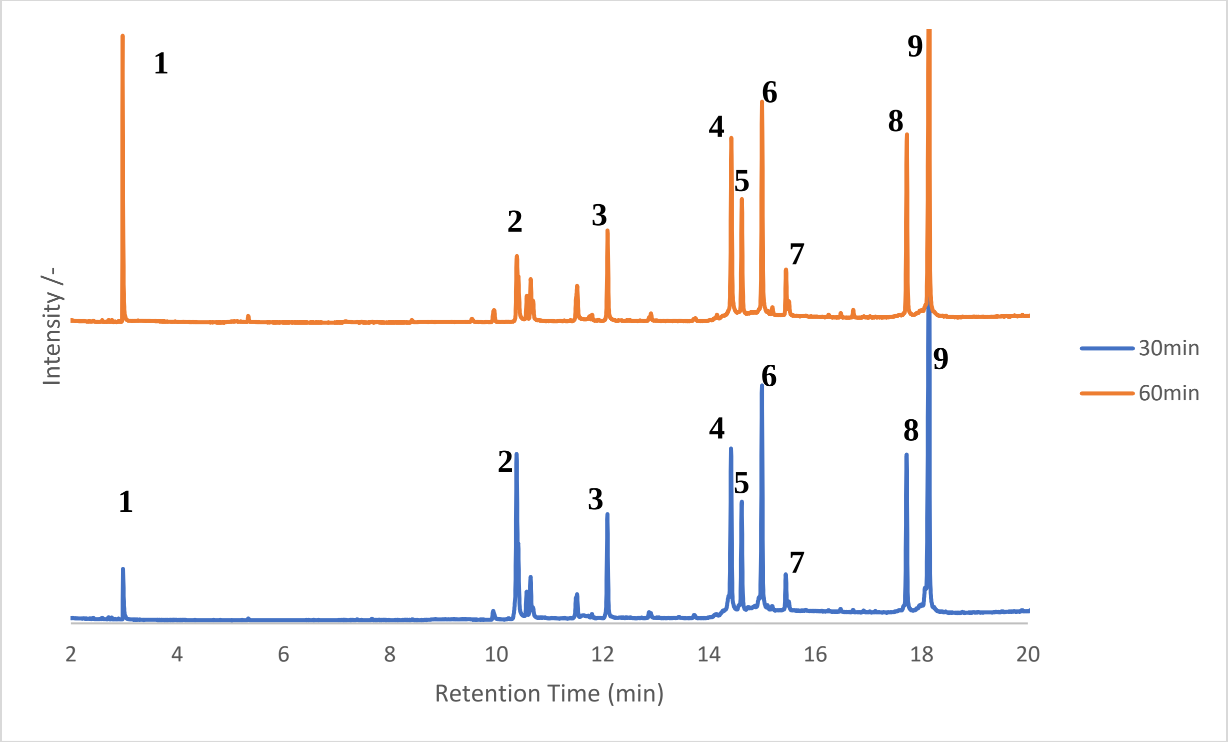

Figure 8: Complete chromatograms for PU reactions at different times when no catalyst is applied

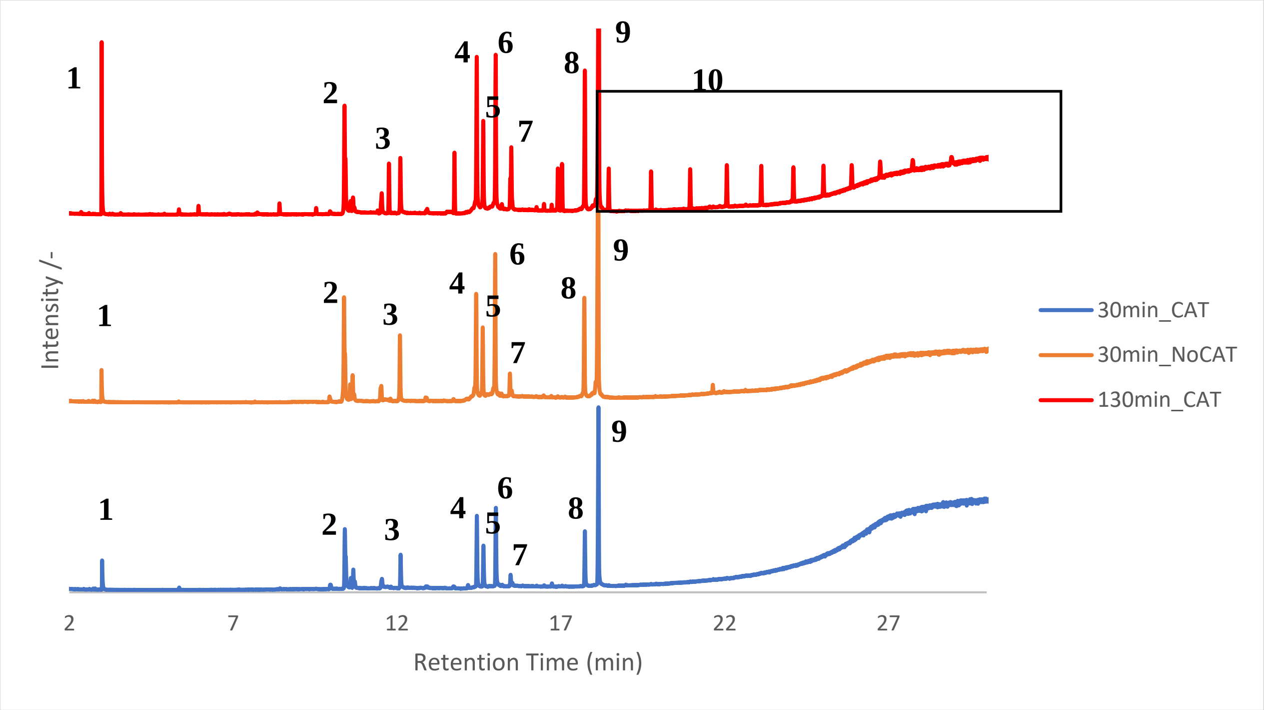

Figure 9: Complete chromatograms for PU reaction when catalyst is applied

Figure 9 shows product distribution when catalyst is applied to the reaction. In general, the peaks shown in chromatograms when catalyst is applied and when its not, look mostly similar. The 130-minute reaction presents all the peaks shown in the other two reaction, however, more peaks can be observed in this reaction, shown in box 10. GC-MS provided an aid with possible identification of molecules present in liquid products of PU reaction.

Table 1: Shows peaks present in figure 8, their retention time, and possible functional groups and compounds for each one

Peak	**Retention time (min)**	**Possible functional group**	**Possible Compound**
1	3	-OH	Polyol
2	10	R-N=C=O	Isocyanate
3	12	R-N=C=O	Isocyanate
4	14	R-N=C=O	Isocyanate
5	14	R-N=C=O	Isocyanate
6	15	R-N=C=O	Isocyanate
7	15.5	R-N=C=O	Isocyanate
8	18	R-N=C=O	Isocyanate
9	19	R-N=C=O	Isocyanate
10 (box)	20+	SiH-O-Si	Octasiloxane

Most of the molecules shown in box 10 in the 130-minute chromatogram show a structure similar or exactly like the one shown in figure 10. It is known that the main composition of PU foam comes from polyols and isocyanates, which have no presence of silicon in them. However, it was also mentioned that additives are a common substance in the manufacturing of this material. Silicone has been an important compound involved in the synthesis of polymer additives, and many of these are sold separately, and are bought by polymer manufacturers. Dow Inc is an example of a company which sells silicone base additives, offering a list of them [16]. Furthermore, during an industrial visit carried out to Colchones Paraiso, a retailer and mattress manufacturer, it was discovered that silicone is used in the synthesis of their PU foam [17]. This would suggest that the catalyst used in PU foam methanolysis participated in dissolving silicone-based molecules, which appeared in the liquid residual products, rather than in the solid ones.

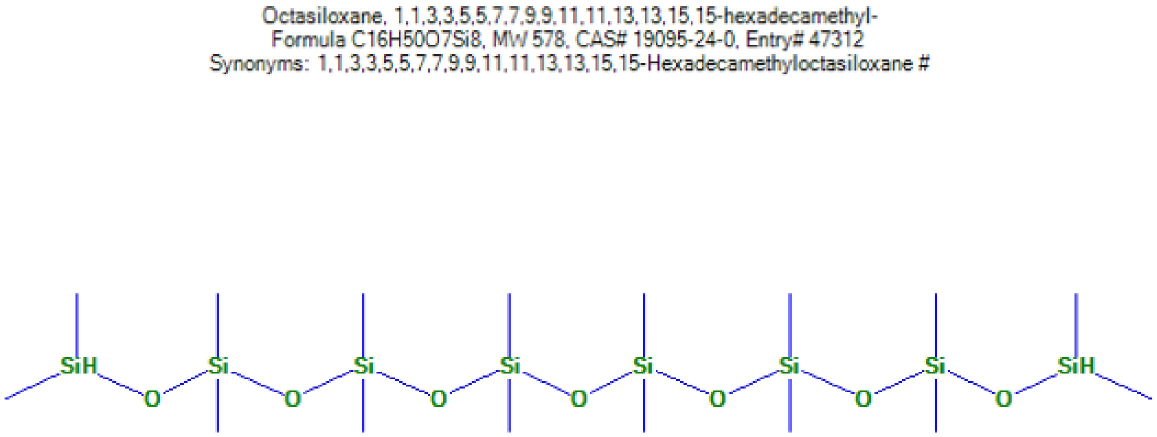

Figure 10: Shows structure of peaks appearing after 20-minute retention time on 130-minute PU methanolysis reaction with catalyst applied

4. CONCLUSION

The aim of this investigation was to provide insight into PU foam methanolysis reaction, and how a catalyst would affect its overall process. In order to measure the effectiveness of the catalyst, conversion calculations were performed. The Aluminum-Based catalyst proved that it does increase overall conversion of the reaction, however, the difference between results when catalyst was used and when not, was not too significant, managing to increase conversion by only 10%, in the case of the 120˚C and 130˚C reactions. Characterization of the reaction through several methods was also carried out, UV-Vis spectrums aided in the understanding of how the reaction was progressing over time, and provided insight on the reaction's overall behavior. With the help of FTIR, the solid residues were identified, and proved that there was a complete conversion of the PU at certain temperatures, only showing additives left in IR spectrums. With the use of GC-MS technique, it was possible to graph complete chromatograms for PU methanolysis at different times, and with application of catalyst. It was discovered that the reaction was following its natural course, since the abundance of polyols was increasing overtime. The addition of Aluminum based catalyst also brought up an interesting result: silicone-based molecules appeared in the chromatogram at 130-minutes into the reaction, only when catalyst was applied. PU methanolysis still has room for further investigation, for example, another catalyst could be used to see if it would aid in conversion results. Also, a different solvent could be used to evaluate if the reaction still decomposes into polyols and isocyanates, and no other compounds. The exact composition of the PU foam used in this investigation was unknown, using a pure PU foam would be an interesting extension to the work carried out in this research. In conclusion, this investigation helped deepen the understanding of PU foam methanolysis and the effect the Aluminum-Based catalyst has on it, using conversion calculations and different characterization techniques.

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ANNEX A: TIME VS ABSORBANCE FOR PU METHANOLYSIS REACTIONS

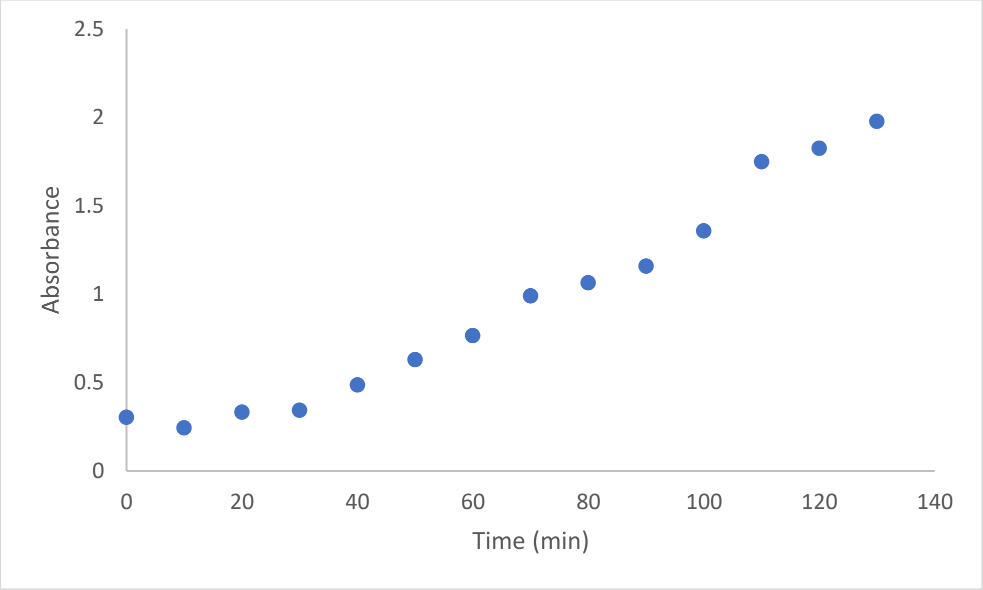


Figure a.1: Shows PU methanolysis reaction progression (Reaction conditions: Polyurethane as raw material · 1g, Methanol as solvent · 200ml, Temperature: 110°C, Residence Time: 130 minutes, Catalyst: Applied)

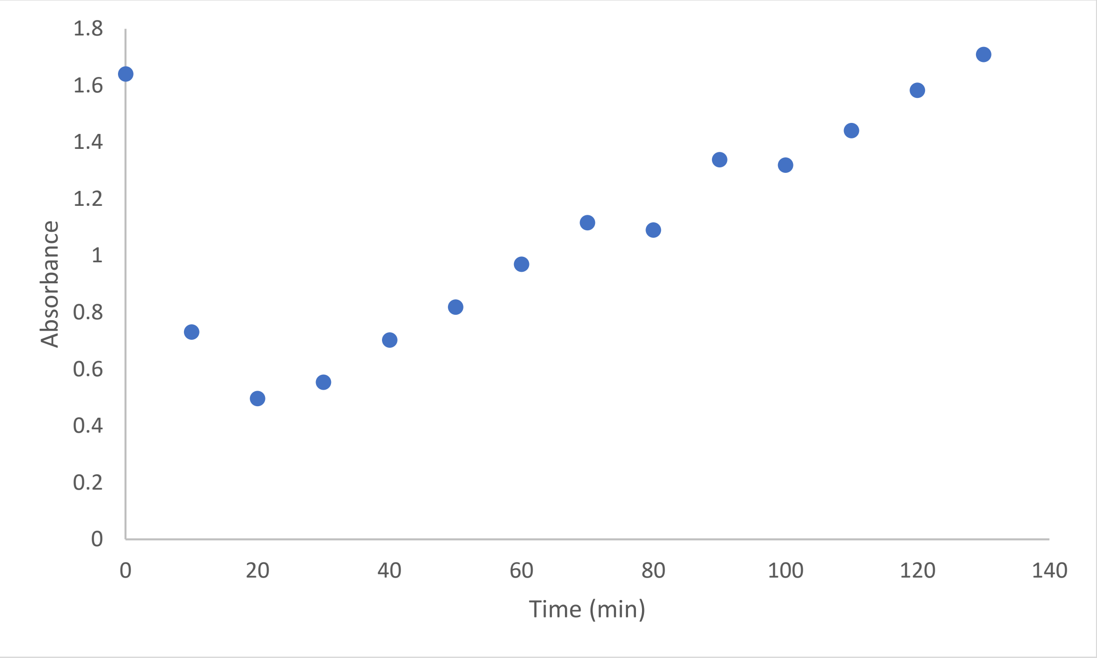


Figure a.2: Shows PU methanolysis reaction progression (Reaction conditions: Polyurethane as raw material · 1g, Methanol as solvent · 200ml, Temperature: 120°C, Residence Time: 130 minutes, Catalyst: Applied)

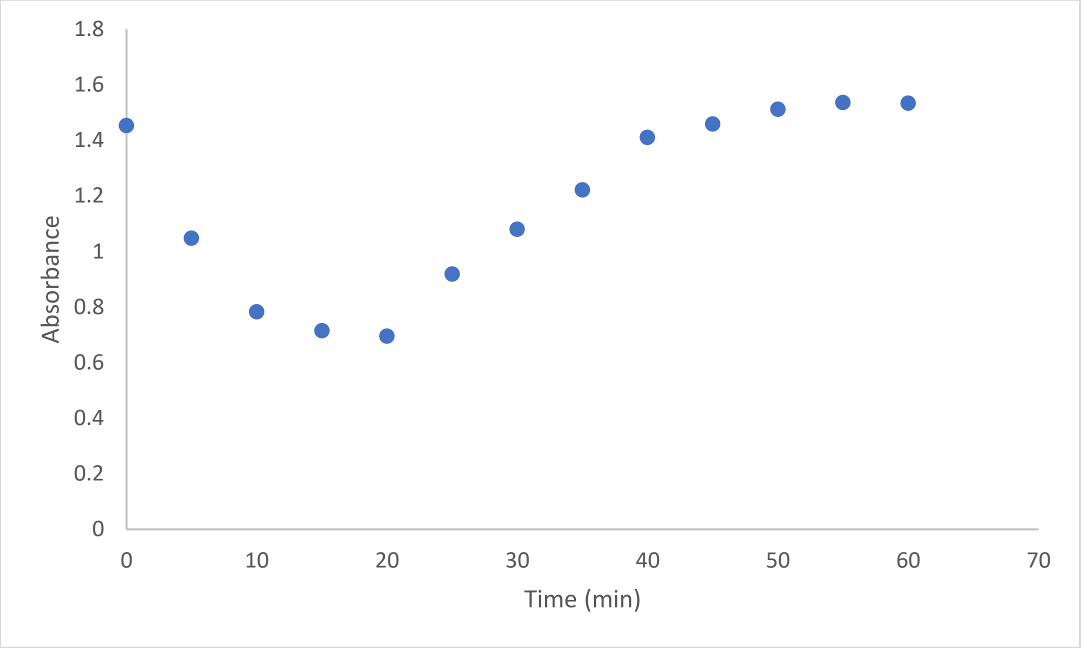


Figure a.3: Shows PU methanolysis reaction progression (Reaction conditions: Polyurethane as raw material · 1g, Methanol as solvent · 200ml, Temperature: 130°C, Residence Time: 60 minutes, Catalyst: Not Applied)

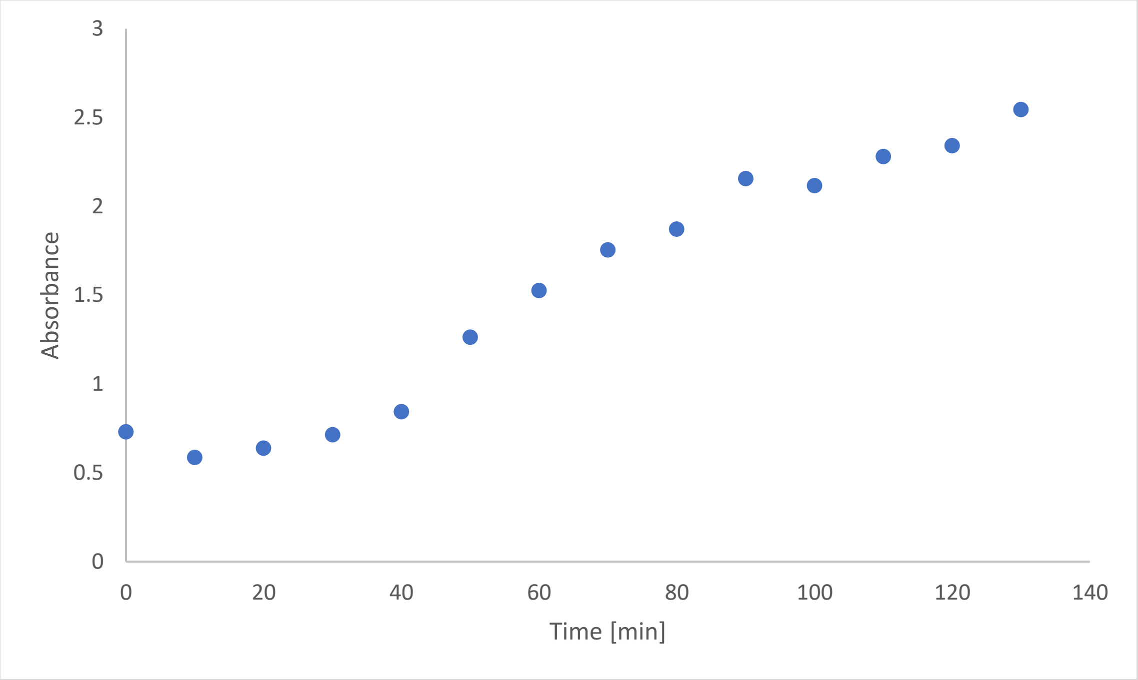


Figure a.4: Shows PU methanolysis reaction progression (Reaction conditions: Polyurethane as raw material · 1g, Methanol as solvent · 200ml, Temperature: 130°C, Residence Time: 130 minutes, Catalyst: Applied)

ANNEX B: CONVERSION TABLES FOR PU METHANOLYSIS

Table b.1. Shows conversion values at different temperatures for PU methanolysis when no catalyst is applied.

No CAT						
Temperatura (°C)	**Pi**	**Pf**	**dP**	**1-dP**	**Conversion**	**Conv Corrected**
110	1.5978	2.1454	0.5476	0.4524	45.24%	55.80%
120	1.5871	2.055	0.4679	0.5321	53.21%	65.63%
130	1.6303	2.1013	0.471	0.529	52.90%	65.25%
140	1.5877	1.8149	0.2272	0.7728	77.28%	95.33%
150	1.5844	1.7824	0.198	0.802	80.20%	98.93%

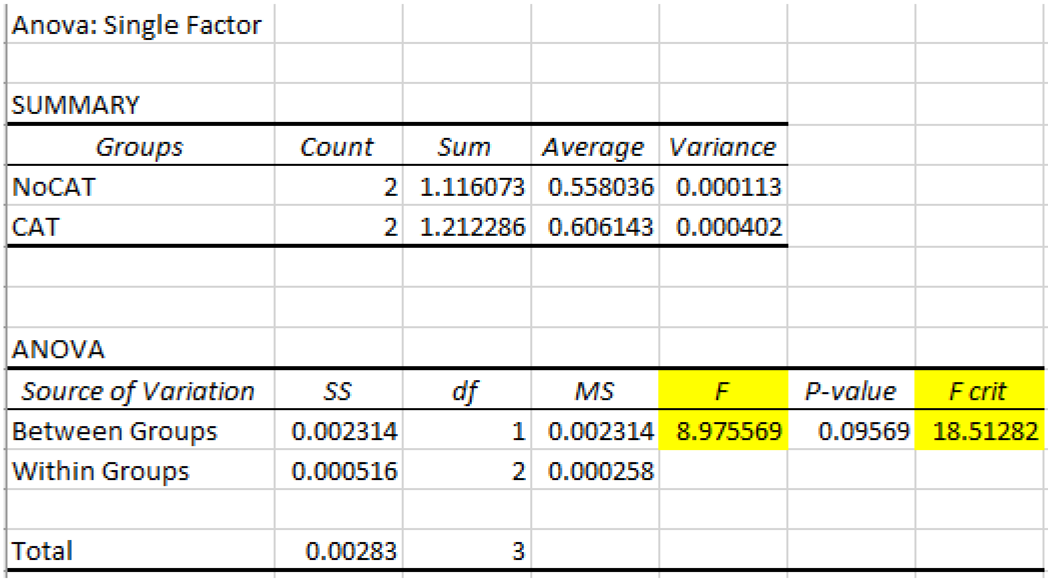
Table b.2. Shows conversion values at different temperatures for PU methanolysis when catalyst is applied.

CAT						
Temperatura (˚C)	**Pi**	**Pf**	**dP**	**1-dP**	**Conversion**	**Conv Corrected**
110	1.5933	2.1019	0.5086	0.4914	49.14%	60.61%
120	1.6191	1.9985	0.3794	0.6206	62.06%	76.55%
130	1.62615	1.9874	0.36125	0.63875	63.88%	78.79%
140	N/A	N/A	N/A	N/A	N/A	N/A
150	N/A	N/A	N/A	N/A	N/A	N/A

Table b.3. Shows percentage difference in conversion between reaction when catalyst is applied and when it’s not.

Temp (˚C)	**No CAT**	**CAT**	**% dif**
110	55.80363	60.61428	4.810657
120	65.63464	76.55113	10.91649
130	65.25225	78.78993	13.53768
140	95.40741	N/A	N/A
150	98.92685	N/A	N/A

ANNEX C: ANOVA ANALYSIS FOR CATALYST IMPACT ON PU METHANOYSIS



Anova: Single Factor

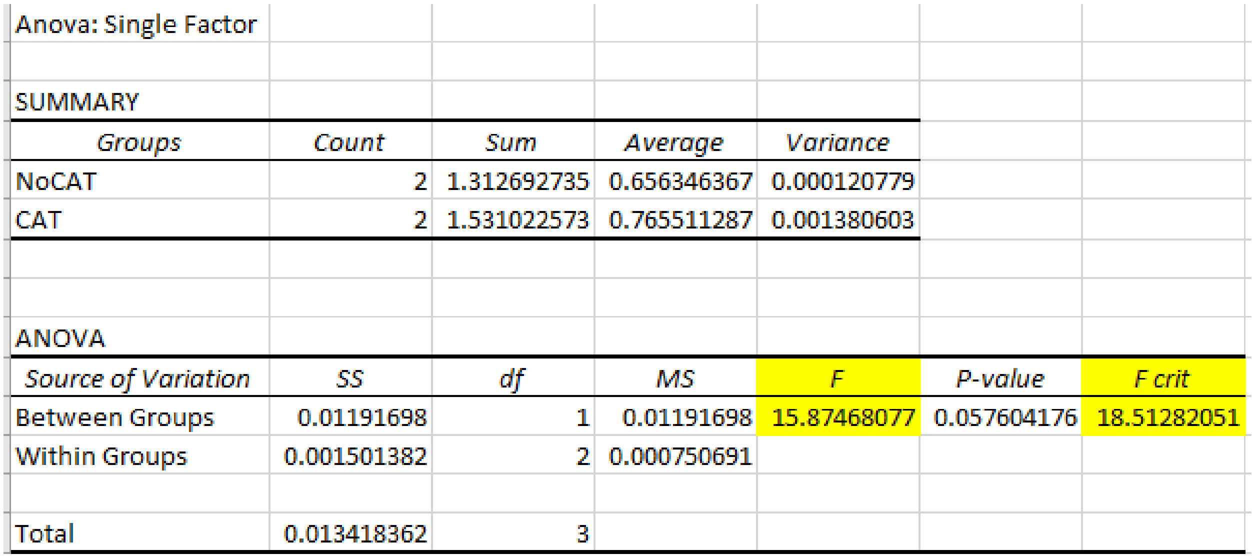
SUMMARY

Groups	Count	Sum	Average	Variance
NoCAT	2	1.116073	0.558036	0.000113
CAT	2	1.212286	0.606143	0.000402

ANOVA

Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	0.002314	1	0.002314	8.975569	0.09569	18.51282
Within Groups	0.000516	2	0.000258			
Total	0.00283	3				

Figure c.1. Shows ANOVA analysis for 110 °C



Anova: Single Factor

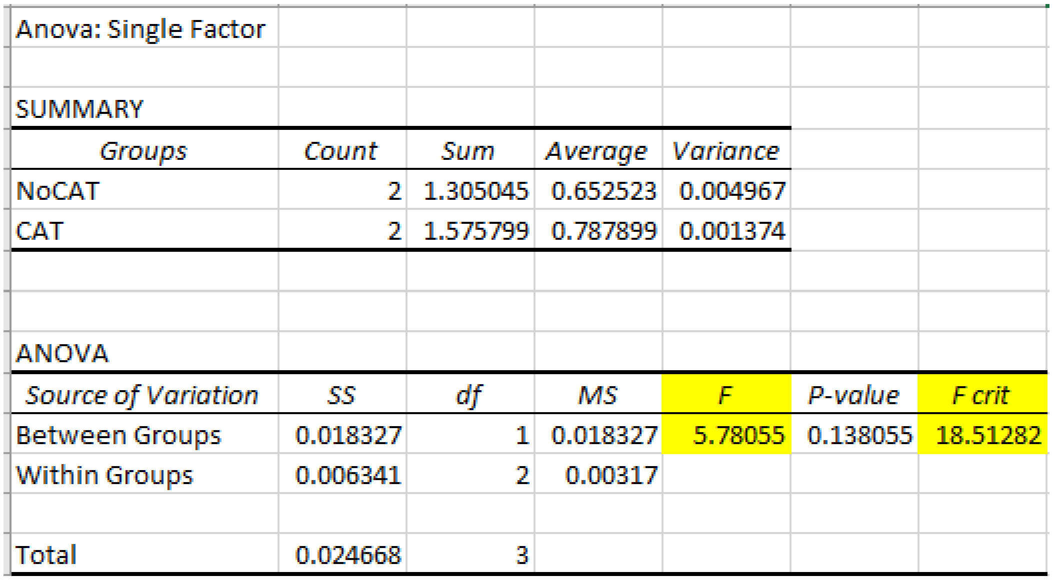
SUMMARY

Groups	Count	Sum	Average	Variance
NoCAT	2	1.312692735	0.656346367	0.000120779
CAT	2	1.531022573	0.765511287	0.001380603

ANOVA

Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	0.01191698	1	0.01191698	15.87468077	0.057604176	18.51282051
Within Groups	0.001501382	2	0.000750691			
Total	0.013418362	3				

Figure c.2. Shows ANOVA analysis for 120 °C



Anova: Single Factor

SUMMARY

Groups	Count	Sum	Average	Variance
NoCAT	2	1.305045	0.652523	0.004967
CAT	2	1.575799	0.787899	0.001374

ANOVA

Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	0.018327	1	0.018327	5.78055	0.138055	18.51282
Within Groups	0.006341	2	0.00317			
Total	0.024668	3				

Figure c.3. Shows ANOVA analysis for 130 °C