Master Thesis

Chemical Recycling of post-consumer Mattress Materials

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THESIS TOPIC

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DISCLAIMER

This thesis is submitted in partial fulfilment of the requirements for the degree of The International Master of Science Air Quality Control, Solid Waste and Waste Water Process Engineering (WASTE) at The University of Stuttgart, Germany. This thesis has never been submitted for any degree or examination to any other University/program. I confirm that this thesis is original work except where stated. This declaration constitutes an assertion that full and accurate references and citations have been included for all material, directly included or indirectly contributing to the thesis.

22nd February, 2018   Savina Padumane Yogish

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ABSTRACT

Chemical recycling of post-consumer foam waste is a comprehensive investigation. The principal aim of chemical recycling of flexible polyurethane foam is the recovery of polyol, which can be consecutively used in the synthesis of new polyurethane materials. In this work, glycolysis of the foam has been adopted as the experimental technique to achieve this aim. The post-consumer foam was initially examined and prepared with regard to different properties. This was subsequently subjected to glycolysis, with the use of a glycolysis agent and a suitable catalyst. The reaction conditions, such as glycol, catalyst, flexible foam, temperature, ratios of glycol-foam and glycol-catalyst were varied and these products were assessed qualitatively and partially quantitative using various analytical methods. The results from analysis were compared to the standard values from literature and based on the type of foam. The most efficient reaction was scaled-up and from the secondary polyol thus obtained, the foam synthesis was carried out and optimised.

Das chemische Recycling von post-consumer Schaumstoffabfällen erfordert eine umfassende Untersuchung. Das Hauptziel des chemischen Recycling von Weichschaumpolyurethan ist die Rückgewinnung von Polyolen, die für die Synthese neuer Polyurethanschaumstoffe eingesetzt werden können. In dieser Arbeit wurde Glykolyse des Schaums als Methode des chemischen Recycling verwendet, um dieses Ziel zu erreichen. Der Schaumstoff aus Sperrmüllabfällen wurde zunächst auf verschiedene Eigenschaften untersucht und aufbereitet. Dieser wurde anschließend einer Glykolyse unter Verwendung geeigneter Glykole und geeigneter Katalysatoren unterzogen. Die Reaktionsbedingungen wie z.B. Glykol, Katalysator, Weichschaum, Temperatur, Verhältnis von Glykol : Schaum und Glykol : Katalysator wurden variiert und diese Produkte mit verschiedenen analytischen Methoden qualitativ und teilweise quantitativ bewertet. Die Analyseergebnisse wurden mit den Werten aus der Literatur verglichen und auf der Grundlage der Schaumart evaluiert. Die vielversprechendste Reaktion wurde hochskaliert und aus dem so gewonnenen Sekundärpolyol die Schaumherstellung durchgeführt und optimiert.

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Abbreviations

BDO	*Butanediol*
CHGP	*Catalytic Hydro-Gasification with Plasma*
DEA	*Diethanolamine*
DEG	*Diethylene Glycol*
DPG	*Dipropylene Glycol*
EG	*Ethylene Glycol*
EU	*European Union*
FGI	*Functional Group Interconversion*
FTIR-ATR	*Fourier Transform Infrared-Attenuated Total Reflectance*
GC-MS	*Gas Chromatography coupled with Mass Spectrometry*
HDO	*Hexanediol*
ICT	*Institut für Chemische Technologie*
KAc	*Potassium Acetate*
MDA	*Methylene diphenyl diamine*
MDI	*Methylene diphenyl diisocyanate*
MPG	*Monopropylene Glycol*
ºSh A	*Shore A (unit of hardness for elastomers and soft materials)*
PCS FF	*Post-consumer Schaum Flexible Foam*
PEBA	*Poly (ethylene-butylene adipate)*
PER	*Pentaerythritol*
PEP	*Polyetherpolyol*
PU	*Polyurethane*
PUF	*Flexible Polyurethane Foam*
PUR	*Rigid Polyurethane Foam*
RI	*Refractive Index*
RID	*Refractive Index Detector*
RIM	*Reaction Injection Moulding*
TDA	*Toluenediamine*
TDI	*Toluenediisocyanate*
THF	*Tetrahydrofuran*
URBANREC	*New approaches for the valorisation of URBAN bulky waste into high added value RECycled products This project has received funding from the European Union's Horizon 2020 research and innovation program under grant agreement N° 690103..*
UVD	*UV Detector*
WPC	*Wood Plastic Composites*

1 URBANREC

Cities need energy and resources to sustain life and consequently they generate waste and residues, imposing environmental pressures far beyond their borders into the surrounding areas and eventually to the global environment. Almost 75 % of the European Union citizens live in cities and in their urban areas and this data is projected to reach 82 % in 2050. Therefore an adequate global waste management system is necessary to avoid further environmental and social problems, allowing a sustainable growth in the urban areas worldwide.

Despite some of the current urban municipal waste streams being conveniently managed and properly valorised, there are still several waste streams, such as *Bulky Waste*, that have limited opportunities to positively contribute to generate value. Bulky waste is defined as *"solid waste that may require special handling and management and which by reason of its bulkiness, shape or weight cannot be placed in a container or bundled."* This waste includes furniture, mattresses, upholstery, appliances, textile etc. Currently, the European generation of bulky waste is at 19 Mt/a, of which 60% is being landfilled due to lack of specific global EU legislation and cost-effective valorisation methods. *URBANREC* aims to be the base to develop a global EU framework, collaborating in the definition and support of future EU legislation in urban bulky waste management (Figure 1).

Figure 1: The integral system employed in the URBANREC project

For this purpose, URBANREC will implement an eco-innovative and integral bulky waste management system by enhancing the prevention and reuse, improving logistics and allowing new waste treatments to obtain high added value recycled products and demonstrate its effectiveness in different Spain, Belgium, Poland and Turkey.

From the global management point of view, URBANREC aims to improve the logistics - implementing collection and reuse, separation and disassembling processes of bulky waste and to obtain high quality raw materials, i.e. metal, plastics, wood, textile, foams and promoting innovative valorisation routes for those which are considered more problematic. URBANREC focusses on the following raw materials streams: Polyurethane (PU) foam, mixed hard plastics and mixed textiles and wood and aims for the reduction of approximately 50 % of bulky waste landfilling at local levels.

The waste treatment considered in this project include

- Rebonding and solvolysis for the PU materials, in order to prepare recycled adhesives and foam
- Textile unravelling and short controlled fragmentation to obtain needle-felt and fibre reinforced composites from textiles
- Wood plastic composites (WPC) from mixed textiles, mixed hard plastics and wood and
- Catalytic hydro-gasification with plasma (CHGP) mainly from mixed hard plastics and wood, in order to obtain chemicals (solvent) or additives

These treatments will be optimised and implemented at industrial level with the help of URBANREC partners which are the top research institutes at EU level and companies interested in obtaining novel eco-friendly products from waste, under a circular economy approach. In general terms, URBANREC targets to achieve a potential valorisation of 82 % of all European bulky waste (11.5 M ton) landfilled, with an economic positive net profit of 225.6 €/ton [1].

In order to realise the goals of the URBANREC project, several research facilities and industrial associates have become involved and each of them have their own share of objectives that needs to be fulfilled. Fraunhofer Institute for Chemical Technology (Germany) necessitates the chemical recycling of the waste mattress foam by virtue of solvolysis.

2   MOTIVATION

The increasing use of plastic by consumers and industries requires cost-effective and environmentally safe recycling techniques in order to reduce the growing pressure on the environment. The possibilities for plastic recycling are primary or in-plant recycling, secondary or mechanical recycling and tertiary or chemical recycling. All these possibilities have advantages and disadvantages but chemical recycling could be one of the most interesting because it can achieve the recovery of high-value raw materials used in the production of new plastic products. The incentive of this work and the approach needed to fulfil the same has been discussed in this chapter.

2.1   Polyurethane - Market Research and Trends

Polyurethanes are one of the major consumer plastic material, alongside polyethylene, polypropylene etc., with an annual production capacity of nearly 12 million tons worldwide [2]. In the last years, polyurethane foams have been developed strongly and they are one of the most versatile polymers [3]. Polyurethanes play a crucial role in preserving the natural resources of our planet. Durable polyurethane coatings ensure that the lifetime of many products is extended well beyond what would be achieved without the coating. Polyurethanes help to save energy sustainably. They help architects to insulate buildings better which reduces the consumption of gas, oil and electricity, which would otherwise be needed to heat and cool them. Thanks to polyurethanes, automotive producers can design their vehicles more attractively and construct lighter frames which save on fuel consumption and emissions. Moreover, polyurethane foams used to insulate refrigerators mean that food is preserved longer and saves it from going to waste. There is now increased focus on ensuring that polyurethane products are not simply discarded or disposed of when they reach the end of their natural life [4]. Due to this fact, PU recycling is nowadays an urgent task to obtain high quality polyols reducing post-consumer PU waste [3].

The worldwide PU consumption by region in 2000 is shown in Figure 2 [5].
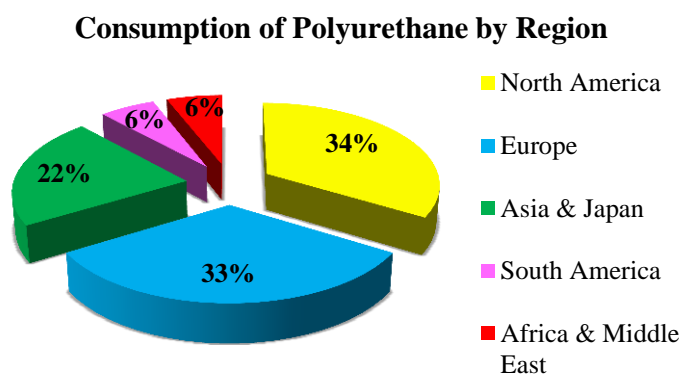
Figure 2: Worldwide PU consumption by region in 2000

According to Transparency Market Research, the global polyurethane foam market is likely to rise from 51.4 Billion USD to 74 Billion USD over the period of 2017-2022. The strong growth prospects of the polyurethane foam market between 2017 and 2022 are illustrated in its robust 7.6 % CAGR therein. The global polyurethane foam market is segmented by product type into flexible and rigid polyurethane foam. Of these, flexible polyurethane foam is the dominant contributor to the global polyurethane foam market. The flexible polyurethane foam segment accounted for 50.2 % of the global market in 2017, with a valuation of 25.5 Billion USD, and is likely to rise to a valuation of 36 Billion USD by 2022. The flexible polyurethane foam segment is expected to account for 50.6 % of the global market by 2022 [6].

Szycher [7] lists seven main categories of PU applications and gives product examples:

- Flexible slabstock foams: furniture, bedding, automobiles, carpets
- Flexible moulded foams: automobile seatings, bedding
- Rigid foams: refrigerators, insulation board
- Solid elastomers: elastomers, footwear, adhesives, medical
- Reaction injection moulding (RIM): automobiles (bumpers, side panels)
- Carpet backing: carpets
- Two-component applications: casting, sealants

The distribution of PU in Europe into different field of applications is shown in Figure 3 [5].
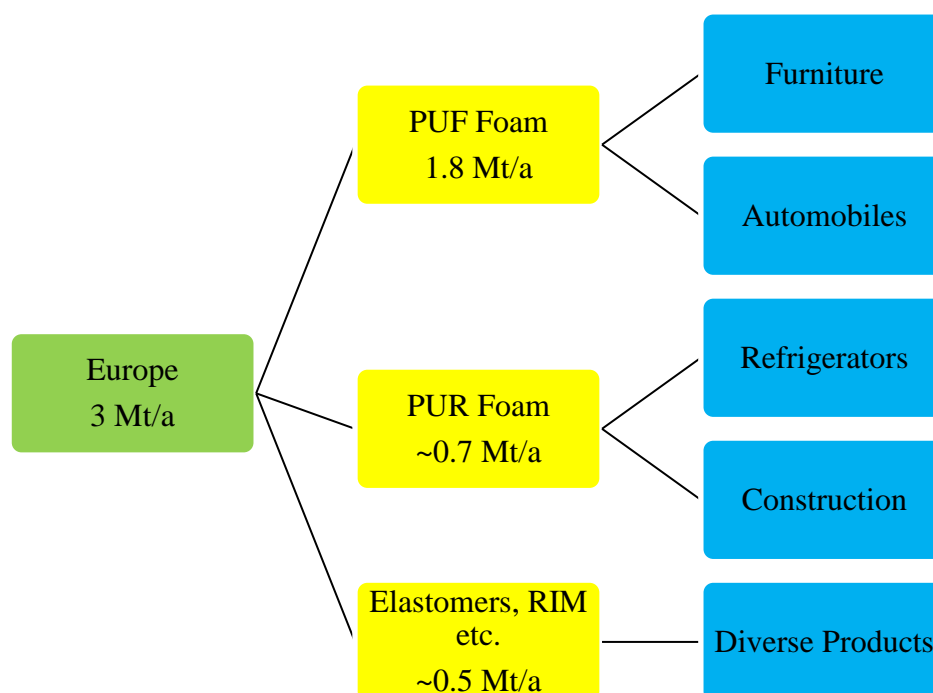
Figure 3: Distribution of PU in Europe based on application.

90 % of the post-consumer polyurethane materials are disposed in landfills and only 10 % is either incinerated or recycled, which amounts to 150 kt/a. Probing further into the lifecycle of PU

consumption in Europe, Figure 4 [8] can be mapped. This figure shows the worldwide distribution of PU consumption as of 2013 and it is clearly seen that flexible foams used for mattresses and for vehicular seatings are the most commonly used type of polyurethanes.

Distribution of polyurethane consumption worldwide
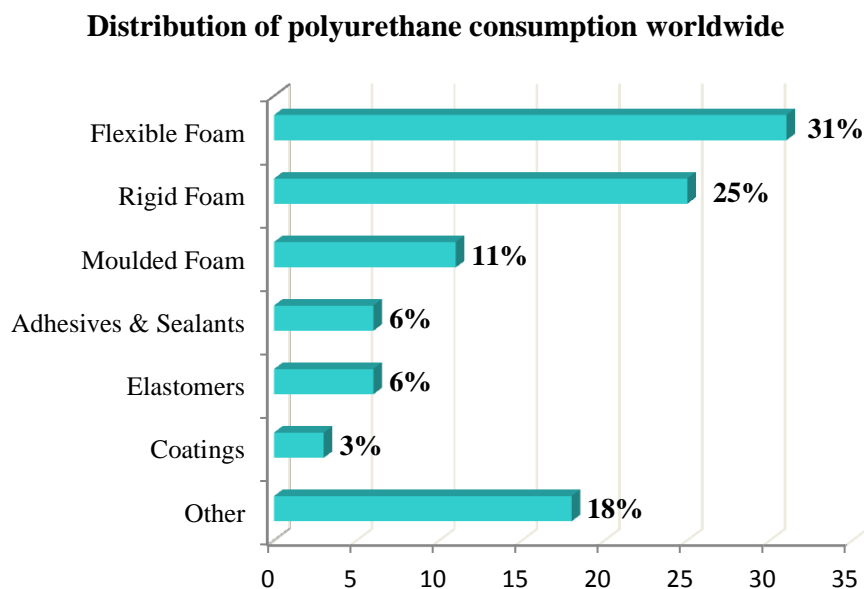
Figure 4: Consumption of PU in the year 2013

By weight, approximately 1.3 million tons of PU waste is generated each year in the USA alone. The largest market is for flexible polyurethane foam (PUF) (47 % flexible and 28 % rigid), followed by PU elastomers (8 %). For the US, this added up to around 1640 million ton in 1995. North America represents around 30–35 % of the world's total consumption, with the remainder in Western Europe (around 40 %), the Far East (around 15 %) and the rest of the world (around 10–15 %) [9].

2.2   Chemical Recycling of Polyurethane Foam Waste

Polyurethanes are among the most important class of specialty polymers. But, ironically, the term *polyurethane* leads to a great deal of confusion. The term is more of convenience than of accuracy because polyurethanes are not derived from polymerizing a methane monomer, nor are they polymers containing primarily urethane groups. The polyurethanes include those polymers containing a plurality of urethane groups in the molecular backbone, regardless of the chemical composition of the rest of the chain. Thus, typical polyurethane may contain, in addition to the urethane linkages, aliphatic and aromatic hydrocarbons, esters, ethers, amides, urea, isocyanurate groups etc. [7].

There are different chemical recycling treatments, depending on the nature of the polymeric material. Polyurethanes are in the class of compounds called reaction polymers, which include epoxies, unsaturated polyesters and phenolics. The properties of polyurethane are greatly influenced by the types of isocyanates and polyols used to make it. Long, flexible segments, contributed by the polyol, give soft,

elastic polymer. High amounts of crosslinking give tough or rigid polymers. Long chains and low crosslinking give a polymer that is very stretchy, short chains with lots of crosslinks produce a hard polymer while long chains and intermediate crosslinking give a polymer useful for making foam. The crosslinking present in polyurethanes means that the polymer consists of a three-dimensional network and molecular weight is very high [10].

In order to fulfil the requirements of the European Directive 2008/98/EC on end-of-life vehicles, it is necessary to increase the recycling rate of PU. This report includes the description and operation of glycolysis technique for the chemical treatment of post-consumer flexible PU foam waste. The details on experimentation procedures and optimisation of operation process parameters will be explained in the chapters that follow [11].

2.3   Work Definition

As stated previously, the main objective of the URBANREC project is to effectively manage the bulky waste produced in the EU region and this work conducted at Fraunhofer Gesellschaft ICT (Pfinztal, Germany) is to realise this objective in the scope of PU foam. Since the central focus of this work is the chemical recycling of post-consumer polyurethane foam and the experiments have been focussed on the solvolysis of post-consumer polyurethane foam waste, the primary aim has been the development and optimisation of the chemical recycling processes, feasible from a technological and environmental point of view as well as cost-effective from an economic point of view, for obtaining high valued raw material in the preparation of recycled foam or adhesives. The parameters that will be compared for the solvolysis are time, temperature, type of glycol, type of foam and the type of catalyst. By performing these experiments, an optimised reaction condition will be governed and scaled-up to obtain the secondary polyols. Subsequently, foam synthesis will be carried out from the secondary polyols, under optimised conditions.

3 LITERATURE REVIEW

In order to support the experimental procedure, literature review was conducted regarding the various possibilities for recycling PU foam, parameters and technology employed for the processes was made.

Polyurethane is the sixth most used polymer with a production of approximately 12 million tons per year. As a direct consequence of their commercial success, a lot of waste is generated and their treatment is an environmental challenge. In the past, landfilling was the solution to the problem. However, there is little information about the behaviour of PU in landfills due to the large life period of the polyurethanes (>10 years). This fact, joined to the new environmental laws, is essential to develop environmental sustainable recycling processes. According to the standard ASTM D 7209-06 [12], recycling processes can be classified in this way:

- *Primary recycling* is the processing of scrap plastic product into a product with characteristic similar to those of the original product.
- *Secondary recycling* is the processing of scrap plastic product into a product that has characteristics different from those of the original product.
- *Tertiary recycling* is the production of basic chemicals or fuels from segregated plastic scrap or plastic material that is part of a municipal waste stream of other source.
- *Quaternary recycling* is the useful retrieval of the energy content of scrap plastic by its use as a fuel to produce products such as steam, electricity and so forth.

Mechanical recycling processes include the primary and the secondary recycling. These kinds of processes do not modify polymer internal structure. On the other hand, through secondary recycling, the chemical recycling processes help to obtain basic hydrocarbon units known as monomers (tertiary recycling) that are able to be used as synthesis materials in chemical and petrochemical industry. This way, it is possible to achieve high value added products [13]. And quaternary recycling methods are those processes which help retrieve energy from the polyurethane waste. For example, municipal waste combustion, rotary kiln, two-stage incineration processes etc. (as listed in Figure 5).

Recycling of Polyurethanes		
Mechanical recycling •Adhesive Pressing •Particle Bonding •Regrind •Injection Moulding •Compression Moulding	**Feedstock Recycling** •Glycolysis •Hydrolysis •Pyrolysis •Hydrogenation •Gas production	**Energy Recovery** •Municipal Waste Combustion •Fluidised Bed Kiln •Rotary Kiln •Two-stage Incineration •Metallurgical Recycling
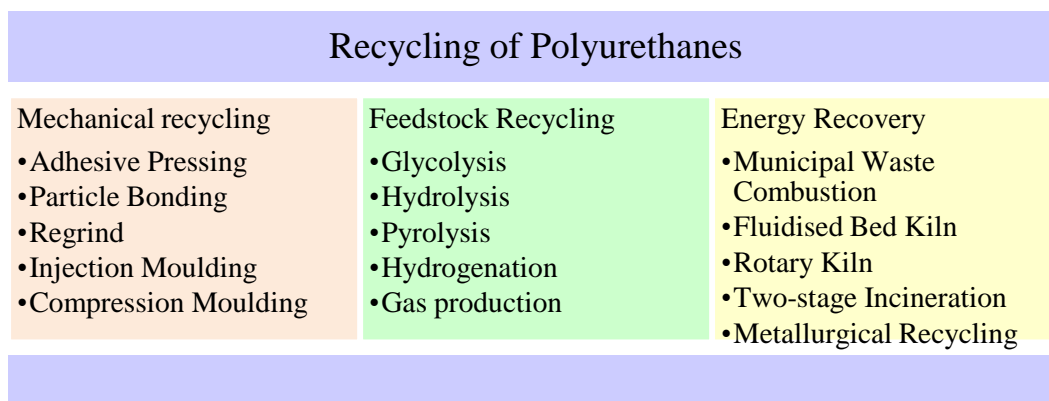
Figure 5: Different types of PU recycling processes

Therefore, an in-depth description of the main polyurethane chemical/feedstock recycling processes (glycolysis and hydrolysis) conducted previously is given below.

Glycolysis of PU is the degradation of material, which causes disintegration of urethane and urea groups, occurring under the influence of a glycols or amines mixture. The product of PU waste glycolysis (glycolysate) can be homogenous mixture or it can be divided into two or three separated phases. The upper phase consists mainly of polyols, which are similar to virgin polyols, and the bottom phase consists of aromatic carbamates, urea, unreacted glycol, and amines. The products of PU waste glycolysis should be purified. The common methods of purification are extraction, distillation and removal of amine groups [14].

$$-R\text{-}N(H)\text{-}C(OO)\text{-}O\text{-}R' + OH\text{-}R''\text{-}OH \longrightarrow -R\text{-}N(H)\text{-}C(OO)\text{-}O\text{-}R'' + HO\text{-}R' \qquad \text{Equation 1}$$
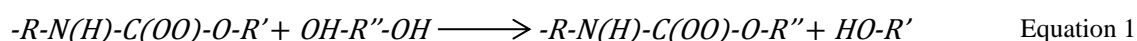
According to Molero et al. [15], glycolysis was conducted in a jacketed flask with refluxing condenser under nitrogen atmosphere to avoid oxidation in the temperature range 175-195 ºC, where DEG was used as the glycolysis agent and the reaction temperature maintained at 190 ºC. The DEG:PU ratio was kept at 1.5 and in order to obtain high quality secondary polyol 2.2 wt.% of catalyst (related to DEG) was considered optimum. At extreme conditions, carbamate is not formed but yields and aromatic structure and glycol and this was confirmed using IR spectra.

Simon et al. [16] performed glycolysis of flexible foams containing polymeric polyols concluding that it is possible to do so using similar reaction conditions as the glycolysis of conventional foams synthesized with flexible polyether polyol. The secondary polyol had a hydroxyl number of around 60 mg KOH/g.

Borda et al. [17] conducted glycolysis of flexible polyurethane foams and elastomers based on polyether polyols using aliphatic glycols, DEG or EG and DEA mixture. Glycolysis ran fastest when the agent is DEG, but produced a highly viscous glycolysate. To solve this, DEA and EG mixture in the ratio 1:1 to

1:9 was used and the results showed that the reaction time decreased with the increasing quantity of DEA.

From the glycolysis of car PU car waste at atmospheric pressure and isothermal conditions (220 ºC) carried out by Wu et al. [18] using DEG and KAc, the adequate reaction time was found to be 90 min and the optimum concentration of DEG and KAc was 1:1.5 and 100:1 with respect to the mass of PU. The polyol was purified by distillation.

According to Nikje and Mohammadi [19], PU glycolysis using sorbitol/glycerine/water mixture as a destroying agent and sodium hydroxide as catalyst was conducted in order to compare the mechanical properties of secondary polyol with that of virgin polyol. The experiment resulted in the conclusion that increasing content of secondary polyol in flexible foam caused decrease in elongation at break and increase in storage modulus of PU foam.

Datta and Rohn [20] performed glycolysis of PU foam using 1,6-hexanediol. Glycolysates with the molecular weight 670 and 600 g/mol were used for the PU elastomers synthesis. PU elastomers were formed by prepolymer method using MDI and various chain extenders: butanediol (BDO), EG and hexanediol (HDO). The resulting elastomers had the tensile strength in the range 13.4-15.6 MPa, hardness in the range 85-94 ºSh A, density in the range 1.016-1.053 g/cm^3 and glass transition temperature at 0.5 and 0.8 ºC.

The various parameters, temperature, time, type of glycol, catalyst etc., compared in the glycolysis from previous studies are summed up in Table 1.

Table 1: Various reaction conditions as studied from the literature

Glycol	Temperature [ºC]	Time [h]	Catalyst	Catalyst:Glycol	Foam:Glycol	Additional	Citations
DEG	210	1.5	DEA	1:9	(DEA+DEG):PU=1.25:1		[3]
DEG	200	4	NaOH			Pentaerythritol (PER) DEG:PER=9:1	[21]
DEG	190		Stannous octoate		1:1.5	H$_2$O with 37% HCl	[22]
EG	197.85	2	NaOH	PU:NaOH=1:0.01	1:1		[23]
DEG	220	2	KAc	PU:KAc=1:0.02	1:1		[23]
MEG DEG MPG DPG	190, 198		DEA/ Titanium n-butoxide		1:0.75-1:1.5	Potassium octoate/ Calcium octoate	[24]
DEG	190		Carboxylate	2.2%	1:1.5		[14]
EG			DEA	1:1 to 1:9			[14]
DEG	220 1 atm	1.5	KAc	1:1	1:1.5		[14]
Sorbitol/ Glycerine/ Water mixture			NaOH				[14]

True to any real process, glycolysis also has its own advantages and disadvantages. The advantages and disadvantages of glycolysis of PU is show in Figure 6.
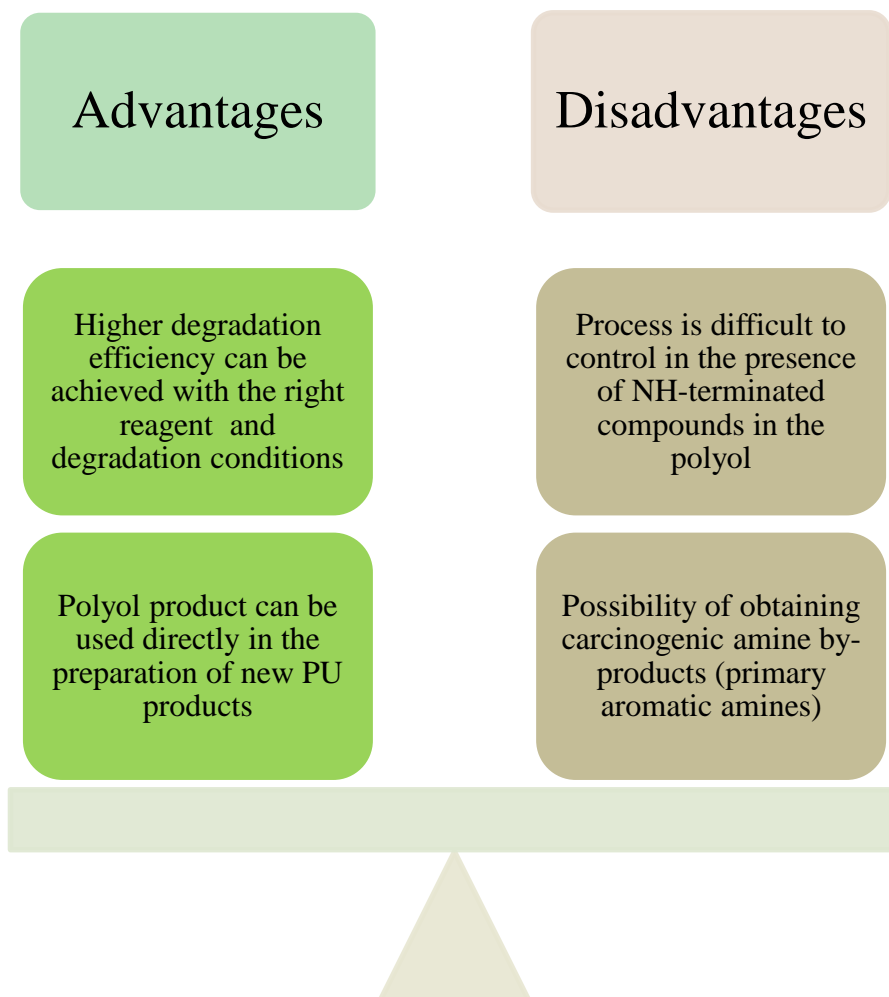
Figure 6: Main advantages and disadvantages of glycolysis of PU.

Calvo-Correas et.al. successfully synthesised thermoplastic polyurethanes with glycolysate polyol from recycled waste. Elastomers were obtained with replacing PEBA macrodiol with recycled one up to 25 wt. % over the whole polyol mass. It showed that glycolysate polyol could be a valuable component in polyurethane production and at the same time it allowed for the management of polyurethane waste. FTIR spectra confirmed the total polymerization reaction for all samples and their chemical structures were similar to each other. The thermomechanical stability was higher as glycolysate polyol content increased. Moreover, the storage moduli of polyurethanes with glycolysate are higher in all temperature range than for reference PU. Static mechanical properties of polyurethanes indicated that with the addition of glycolysate polyol the Young modulus and the tensile strength were improved. All polyurethanes containing glycolysate polyol showed higher percentages of elongation at break than the reference [25].

Kraitape and Thongpin synthesised flexible PU foam by using secondary PU foam polyol (functionality- 4) obtained from glycolysis wasted PU foam, as a polyol. PU foam is prepared by incorporation of secondary PU foam polyol 2, 4, 6, 8 and 10 wt. % in a petrochemical polyol (CARADOL.SA34-05, functionality-2). Triethlylenediamine was used as the gelling catalyst. A polyether modified polysiloxane was used as the surfactant. Distilled water was used as a blowing agent to generate foam. Polymeric MDI with an average functionality of 2.7 was used to generate urethane linkage and carbon dioxide. The parameters investigated were characteristic time, cell structure and cell morphology, tensile properties, compressive properties and compression set were compared with petrochemical based PU foam. The higher contents of recycled PU foam polyol caused acceleration of foaming reaction. The results indicated that the tensile and compressive properties of PU foam are enhanced by incorporation of recycled PU foam polyol and concluded that modification of polyurethane foam with recycled PU foam polyol was able to improve mechanical properties which are suitable for automotive seat application [26].

4   EXPERIMENTAL METHODOLOGY

In this chapter, the methodology adopted to degrade the post-consumer mattresses foam will be elaborately discussed. The task begins by grinding the foam to a required size, carrying out glycolysis by varying the parameters, purification of the obtained phases by vacuum distillation (optional) and then analytically testing the purified product.

4.1   Analysis of Foam

The waste mattresses material obtained from the project partner has to be analysed for its water content. IR and Raman spectrometric analysis has to be performed to learn about the functional groups present in the foam, in order to know if the foam is MDI or TDI based. Figure 7 shows the sample of the 170710 PCS FF foam as received from the project-partner.

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Figure 7 : 170710 PCS FF foam sample before shredding

4.1.1   Water Content

A sample of foam is randomly taken from the lot, weighed and dried under vacuum conditions. The change in the weight of the foam indicates the amount of water present in the foam. Water is undesired mainly because it favours the formation of primary amines in the product, which consequently affects

the glycolysis reaction and so it must be as low as 1.5%. Figure 8 shows the vacuum dryer that was used for drying the foam.

Figure 8: Vacuum Dryer – Binder VDL 115

4.1.2 FTIR-ATR Spectrometry

Infrared spectroscopy is the most commonly used spectroscopic method as it provides results quickly, even though not the most accurate [27]. Applications of modern FT-IR spectrometry include simple, routine identity and purity examinations (quality control) as well as quantitative analysis, process measurements, the identification of unknown compounds and the investigation of biological materials [28]. An important advantage of the ATR technique is its applicability to turbid solutions, aqueous solutions included [27]. Figure 9 shows the IR spectrometer used during the analysis of this work.

Figure 9: FT-IR Spectrometer 6700 with ATR-Durascope unit from Thermo Fischer Scientific

4.1.3   Raman Spectroscopy

Raman spectrometers are used to analyse light scattered by molecules. A major advantage of Raman spectroscopy is the high spatial resolution that can be obtained, typically of the order of 1 meter (compared to approx. 10 meter with FT-IR) [27]. This is conducted for the qualitative assessment of the polyols. Figure 10 shows the Raman spectrometer used to aid this work.

Figure 10: RFS 100/S FT-Raman Spectrometer from Bruker Optics

4.2   Size Reduction

The waste mattress material is usually larger than the required size needed to perform the chemical recycling processes. The preferred size range of the foam for the experiment is <4 mm (Figure 12) and hence, it is ground to the required size using Retsch SM 2000 cutting mill. Figure 11 shows the cutting mill employed to shred the foam.
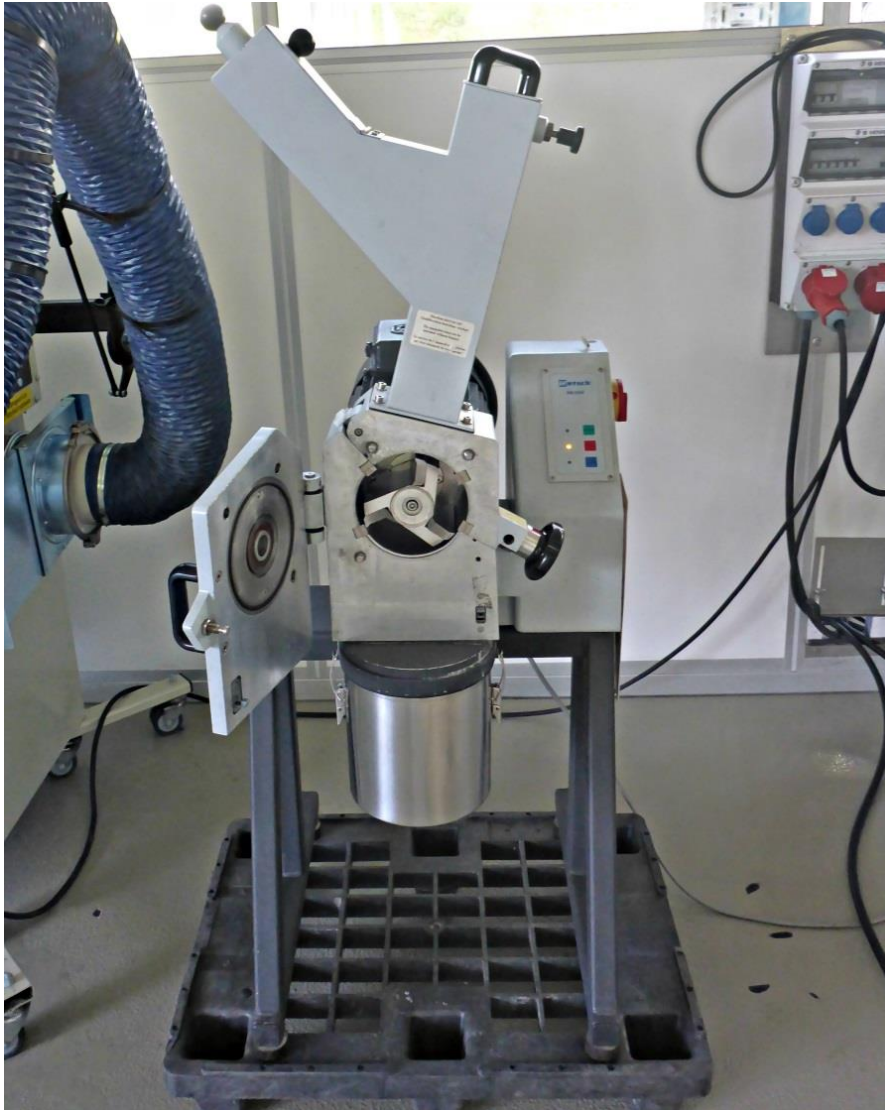
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Figure 11: Retsch SM 2000 Cutting Mill

The SM 2000 cutting mill crushes by cutting and shearing. The feed material is taken up by the rotor mounted on both sides and is crushed by the stainless steel cutting strips inserted in the housing. With the disc and cutting roller rotor, helically arranged reversible cutting plates of hard metal operate by successive cutting. It is because of an additional flywheel mass on the motor shaft that the unusual driving power typical of the SM 2000 is obtained, although it is otherwise only achieved in motors with

double the drive power. The mill casing is made of aluminium. The hopper, rotor, motor flange, door insert, 5 L collecting vessel and bottom sieve are of stainless steel [29].

Figure 12: 170710 PCS FF foam sample after shredding

4.3   Glycolysis

Glycolysis, conducted as the solvolysis method, was performed by varying certain parameters. It was carried out using the different batches of foam received from the project partners. These batches were named based on their date of arrival at Fraunhofer Institute viz. 170621 PCS FF, 170710 PCS FF, 170808 Week 29 and so on. The temperature was maintained constant either at 200 or 220 °C with the help of a Mohr & Co ST-48 Senstherm thermal element attached to the heating mantle and the glycol to foam ratio (mass) was regulated either as 1:1 or 1:2. The catalyst was always weighed as 1% of the glycol mass. Figure 13 shows the glycolysis setup built up to perform the reaction. A three-necked round-bottom flask of apposite capacity was connected to a stirrer (Heidolph RZR 2021), the thermal element as mentioned above and a reflux condenser with a molecular sieve, which prevented the moisture from entering the system. A heating mantle, mounted on an adjustable platform, held the bottom of the flask through which the contents of the flask were heated. The required amount of glycolysis agent and catalyst were fed to the reactor and the heating commenced. The foam was added

batch-wise to the system once the reactor has obtained the stipulated temperature. Once the entire lot of foam had been fed, the reaction proceeded for 6 hours. Consecutively, it was cooled, weighed and stored for carrying out the analysis. These results are discussed in the following chapter.
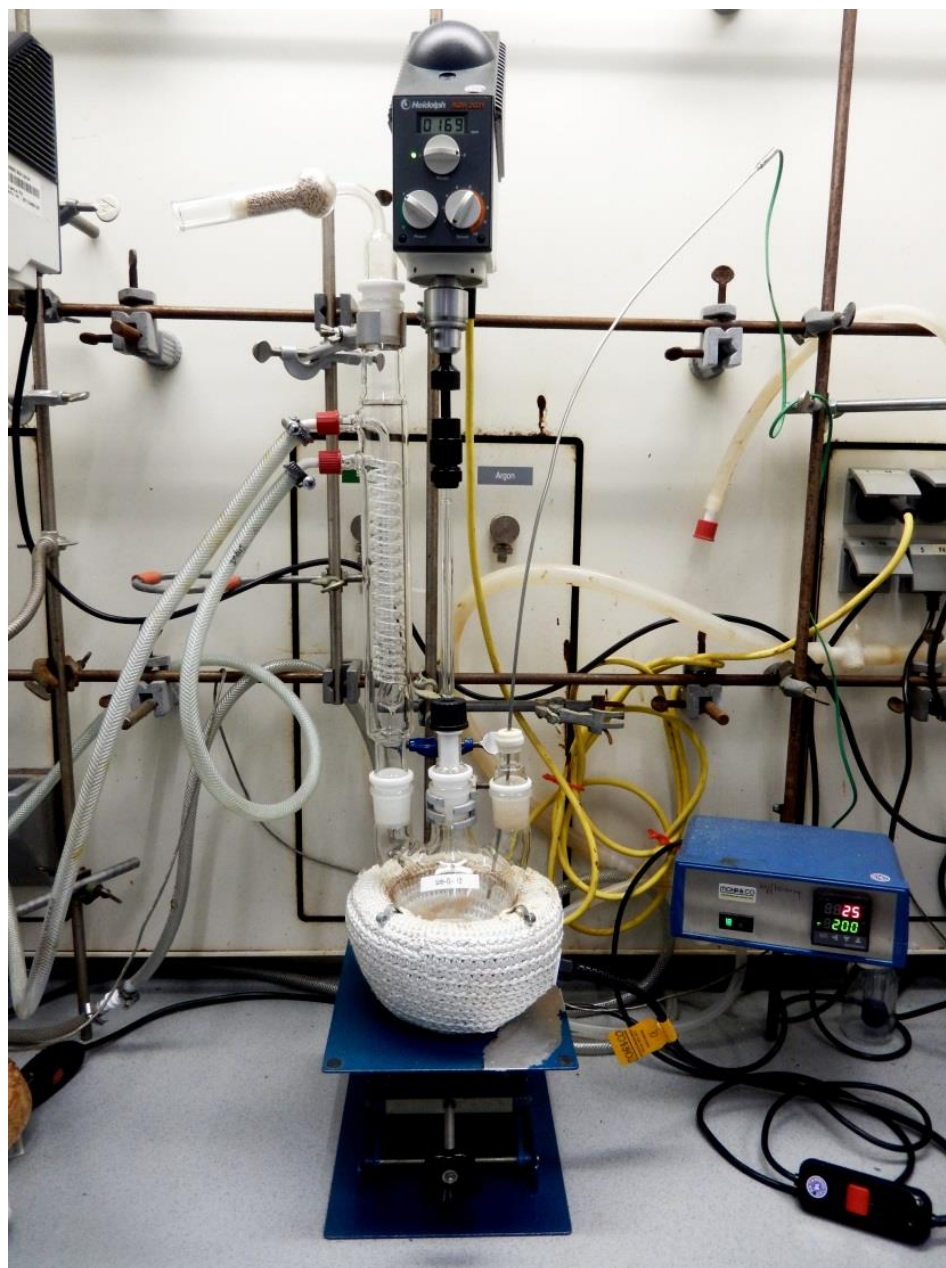
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Figure 13: Experimental setup for glycolysis reaction.

The glycolysis trials which were analysed to having relatively low concentration of 2,4-TDA, along with their respective reaction parameters have been presented in Table 2.

Table 2: Parameters compared for the glycolysis reaction

Trial Name	Glycol	Catalyst	Foam	Glycol:Foam [wt.%]	Temperature [°C]	Duration [h]
Urb-G-013	DEG	DEA	170710 PCS FF	1:1	200	6
Urb-G-023	LUPRANOL 2074	DEA	170731 PCS FF	1:1	200	6
Urb-G-025	LUPRANOL 2074	DEA	170808 PCS FF Week 29	1:1	200	6
Urb-G-031	LUPRANOL 2074	DEA	170808 PCS FF Week 31	1:1	220	6
Urb-G-035	DEG	DEA	170808 PCS FF Week 31	1:1	220	6
Urb-G-036	DEG	KOH	170808 PCS FF Week 31	1:1	220	6
Urb-G-047	DEG	DEA	170808 PCS FF Week 29 & 170731 PCS FF	1:2	220	6

The *scaling up* of the reaction was done as Urb-G-047 with the parameters mentioned in Table 2. During the glycolysis of 170621 foam (pre-trial), with DEG and DEA as the reagents, the temperature failed to reach 200 ºC and there was rapid condensation taking place. It was observed that the DEG used for this trail was previously kept exposed to the atmosphere in an open beaker. Assuming this as the reason for the temperature inconsistency, the refractive index of this DEG samples was obtained in comparison with various DEG-Water samples. This is explained in the following chapter.

4.4   Vacuum Distillation

During glycolysis, generally, three phases are obtained: an upper phase which contains the polyol, a bottom phase which has the sub-products of the reaction and the excess of glycol and a third phase which is in the middle and it is formed by the unreacted polyurethane (as seen in Figure 26). It is sometimes necessary to purify the glycolysis product and during the course of this work vacuum distillation was used to separate the impurities. Also, the bottom product was subjected to vacuum distillation in order to learn the types of by-products obtained. Vacuum distillation (as seen in Figure 14) is performed at a pressure lower than 50 mbar using a vacuum pump and so, a liquid nitrogen atmosphere, created in a Dewar bottle as a cooling trap, is used in order to prevent the contamination of the vacuum pump by the by-products. The polyol retained is then analysed using IR and/or Raman spectroscopic techniques.

Figure 14: Vacuum distillation setup

4.5   Analysis of the Glycolysis Product

The polyols retained from vacuum distillation were analysed using several analytical methods, which are discussed in the following section.

4.5.1   Refractometry

As mentioned earlier, refractometry was employed in order to assess the water content of the faulty DEG sample, which had failed to attain the required temperature. The refractive indices (RI) of several mixtures of DEG, LUPRANOL 2074 and water at different mass ratios was determined using A Krüss Optronic AR4D refractometer (Figure 15 a). The mixtures were maintained at 20 ºC using a Huber ministat 125 cc2 type thermostat (Figure 15 b) with isopropanol as the fluid. The knowledge of refractive indices is required as it aids in evaluating the identity of the compound and to assess the purity of the required chemicals and compare the refractive indices of the mixtures with that of the pure chemicals.
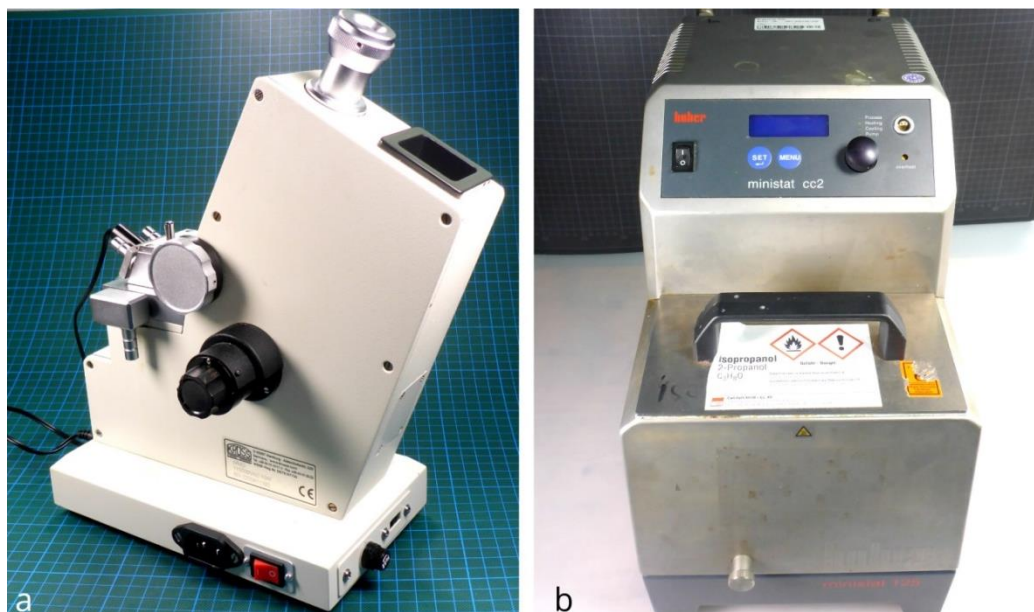
Figure 15: Refractometry Setup- A Krüss Optronic ARD4 Model (a); Huber Ministat cc2 Model (b)

4.5.2   Hydroxyl Value

Hydroxyl value is a number arising from a wet analytical method for the hydroxyl content of a polyol; it is the milligrams of potassium hydroxide equivalent to the hydroxyl content in one gram of polyol or other hydroxyl compound. The OH number for each lot of polyol is provided by the manufacturer. Polyols are sometimes characterized by quoting the weight percentage of hydroxyl groups [30]. The OH number was determined according to DIN 53240-2 using Metrohm Titrando 836 device (Figure 16).

Figure 16: Metrohm Titrando 836 OH Number measuring device

The OH Number can be formulated as,

$$OH\ Number = \frac{56.1 * 1000}{Equivalent\ Weight}$$

<div align="right">Equation 2</div>

where, 56.1 is the atomic weight of potassium hydroxide, 1000 is the number of milligrams in one gram of sample and the equivalent weight is expressed as,

$$Equivalent\ Weight = \frac{Molecular\ Weight}{Functionality}$$

<div align="right">Equation 3</div>

4.5.3 Centrifugation

A centrifuge is laboratory equipment, driven by a motor, which spins liquid samples at high speed. There are various types of centrifuges, depending on the size and the sample capacity. Centrifuges work by the sedimentation principle, where the centripetal acceleration is used to separate substances of greater and lesser density [31]. Figure 17 shows the centrifugation device used to separate the undesired solids from Urb-G-014 and 015 glycolysis products. This was conducted at 5000 rpm for the above mentioned samples for about 1 hour.

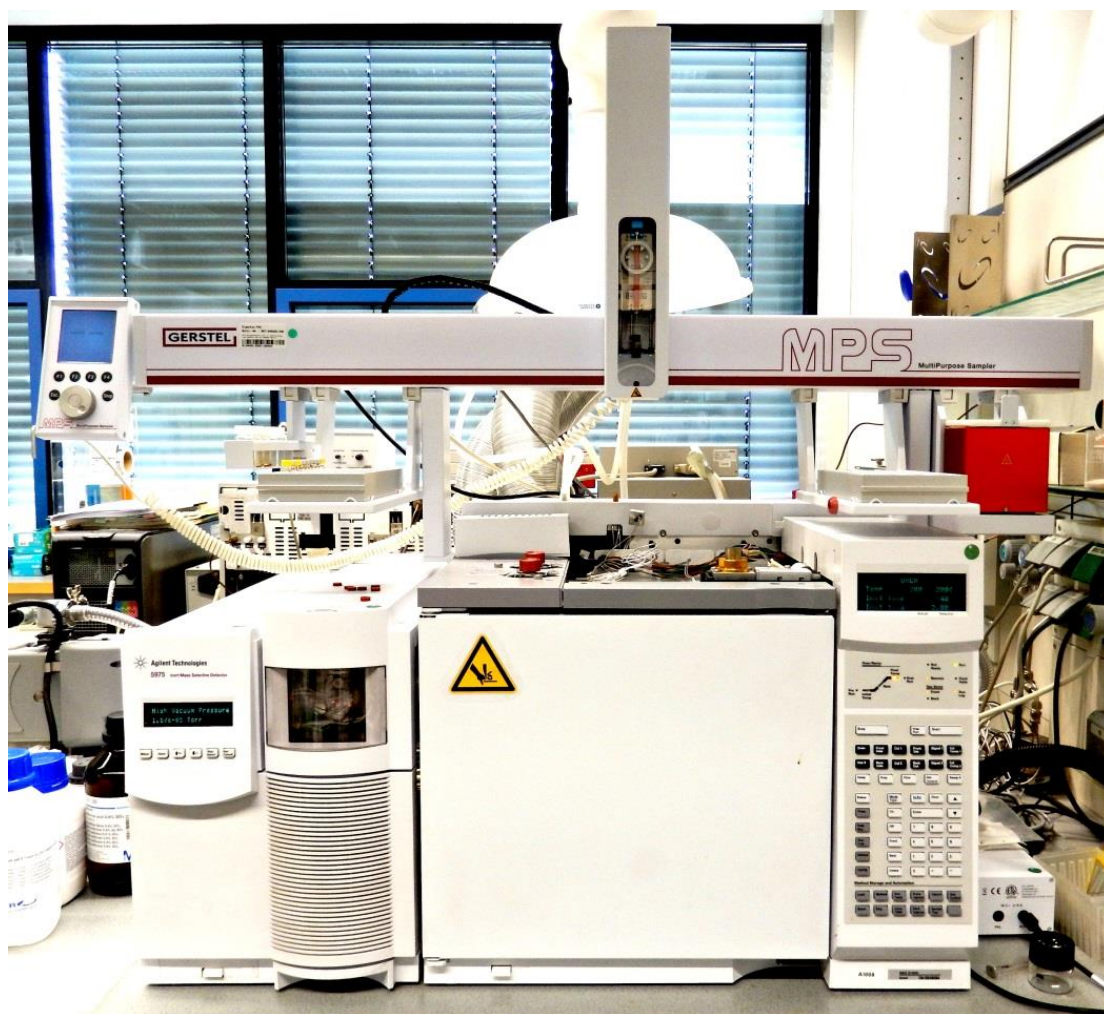<div align="right">©Fraunhofer Gesellschaft ICT Pfinztal</div>

Figure 17: Hettich Universal 320 Centrifuge

4.5.4   FTIR-ATR Spectrometry

Once the polyols from different trials of glycolysis have been obtained, FTIR-ATR analysis was conducted again, in order to obtain the information regarding the various functional groups present in the polyol-rich phase based on its capability to stimulate different intensity of IR radiation at different wavelengths. The instrument used for this purpose is the same as already shown in Figure 9. The results of the IR analysis are discussed in the following chapter (4.5.4).

4.5.5   Gas Chromatography coupled with Mass Spectrometry

Gas chromatography mass spectrometry (GC-MS) is an instrumental technique, comprising of a gas chromatograph (GC) coupled with a mass spectrometer (MS), by which complex mixtures of chemicals may be separated, identified and quantified [32]. Figure 18 shows the GC-MS device used to qualitatively and quantitatively assess the glycolysis products and to deliver information about the type of diisocyanate, based on the amine detected, that was used for the manufacture of the foam.

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Figure 18: Agilent Technologies 5975 Inert Mass Selective Detector coupled with Gerstel Multi-Purpose Sampler

4.5.6 Size Exclusion (Gel Permeation) Chromatography

Gel permeation chromatography (GPC) is a type of size exclusion chromatography (SEC) that separates analytes on the basis of size (Figure 19). The technique is often used for the analysis of polymers. GPC separates based on the size or hydrodynamic volume (radius of gyration) of the analytes. This differs from other separation techniques which depend upon chemical or physical interactions to separate analytes. Separation occurs via the use of porous beads packed in a column [33].

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Figure 19: Agilent Technologies 1100 Series coupled with PSS ETA-2010 detector used for Gel Permeation Chromatography

4.6 Synthesis of Secondary Polyurethane Foam

The synthesis of secondary polyurethane foam is to be carried out using standard and secondary polyol (obtained from glycolysis) in various mass ratios aided by the use of catalyst mixture. The parameters such as height, temperature, pressure and the dielectric constant are monitored and recorded using FOAMAT Type 281 from Format Messtechnik GmbH. The data recording starts with the 10 s stirring step after isocyanate is added to the polyol mixture. This pre-mixture is then transferred immediately on to the cardboard cylinder (radius: 75 mm, height: 230 mm), where the foaming occurred and all measurements were performed. The secondary foams thus obtained are allowed to cure for a period of 24 hours before being tested for their densities. Once the foam had cured, it was cut as show in Figure

20. The base (3 cm from the bottom) was discarded; the top (T) and the bottom (B) sections were used for air permeability measurements and the 5 cm cube from the centre was used to determine the foam density.
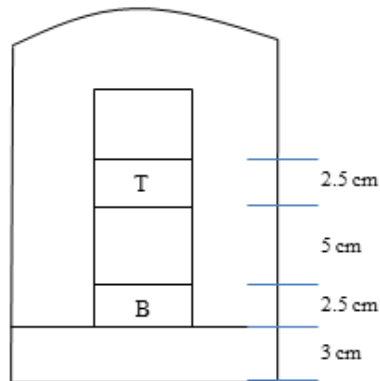

Figure 20: Sections cut from the standard and secondary foams for density and air permeability tests

4.6.1   Density

Density is a key flexible polyurethane foam specification. It is an important indicator of foam performance with regard to comfort, support and durability. Flexible PU foams are commonly available in density of 13-80 kg/m^3. The PU foam density was measured with an SI-234 balance from Denver Instruments (USA) on foam cubes (50 x 50 x 50 mm^3).

4.6.2   Air Permeability

Flexible PU foams are open cell materials that allow free movement of air between the foam cavities and this is determined by air permeability measurements. The air permeability test was carried out by a Textest Instruments FX3300 system from Textest AG, Schwerzenbach (Switzerland) (Figure 21) according to DIN EN ISO 7231, 125 Pa and 125 dm^3/s air flow on 50 x 50 x 25 mm^3 cuboids.

Figure 21: Textest Instruments FX3300 system from Textest AG, Schwerzenbach (Switzerland)

5 RESULTS AND DISCUSSIONS

This chapter discusses the results and inferences made during the course of this work.

5.1 Analysis of Foam

The results from the analysis of the foam are discussed below.

5.1.1 Water Content

The water content of the various foam-lots is given below in Table 3.

Table 3: Water content of the various foams used for the reactions

Sl. No.	Foam	Water Content (%)
1	170621 PCS FF	1.00
2	170710 PCS FF	*1.53*
3	170731 PCS FF	1.30
4	170808 PCS FF Week 29	0.84
5	170808 PCS FF Week 31	0.93

The water content in the foams was low enough (recommended to be below 1.5 %) to perform glycolysis reactions.

5.1.2 FTIR-ATR Spectrometry

The IR spectrum obtained from the analysis of 170710 PCS flexible foam is as shown in Figure 22. It can be observed that all the three graphs of white, green and yellow samples have similar trend and show very low transmittance around 1080 cm^{-1}, which infers the presence of C-O-C stretch of alcohols and possibly even C-N stretch of aliphatic amines. The peak at 1500 cm^{-1} denotes the C=C stretching and the smaller peaks between 1200 cm^{-1} and 1300 cm^{-1} represents the Amide III deformation stretching. The peaks between 1680 cm^{-1} and 1740 cm^{-1} show the presence of CO in urethanes. Between the peaks of 2850 cm^{-1} and 2960 cm^{-1}, CH$_2$ stretching could be expected. The small peak at 3250 cm^{-1} represents the presence of OH in strong concentration. This is the expected functional group from a flexible polyurethane foam [34].
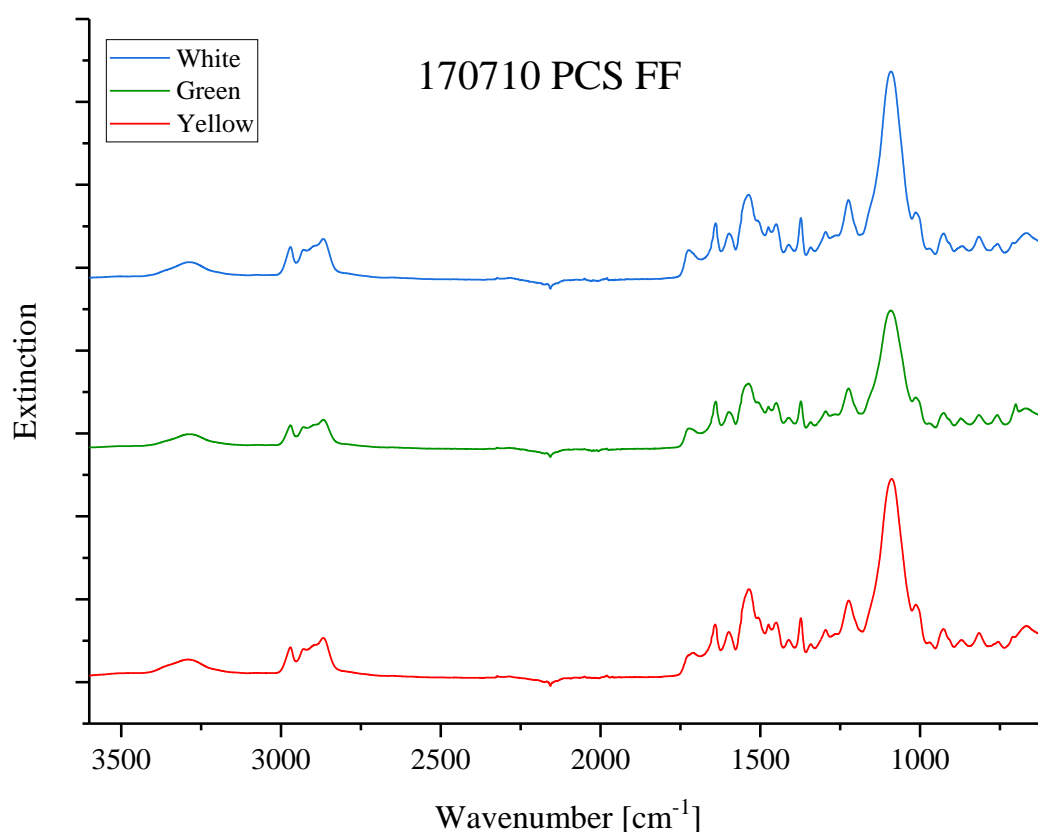
Figure 22: FTIR-ATR spectra of the 170710 PCS FF foam sample

5.1.3   Raman Spectroscopy

The Raman spectra obtained from the analysis of 170710 PCS flexible foam is as shown in Figure 23. It can be observed that all the three graphs of white, green and yellow samples have the same trend, where the peak is observed between 2850 cm^{-1} and 2950 cm^{-1} which confirms the presence of sp^3 C-H stretch and the absorption around 1500 cm^{-1} confirms the presence of C=C stretch. Above 3000 cm^{-1}, NH groups are present.
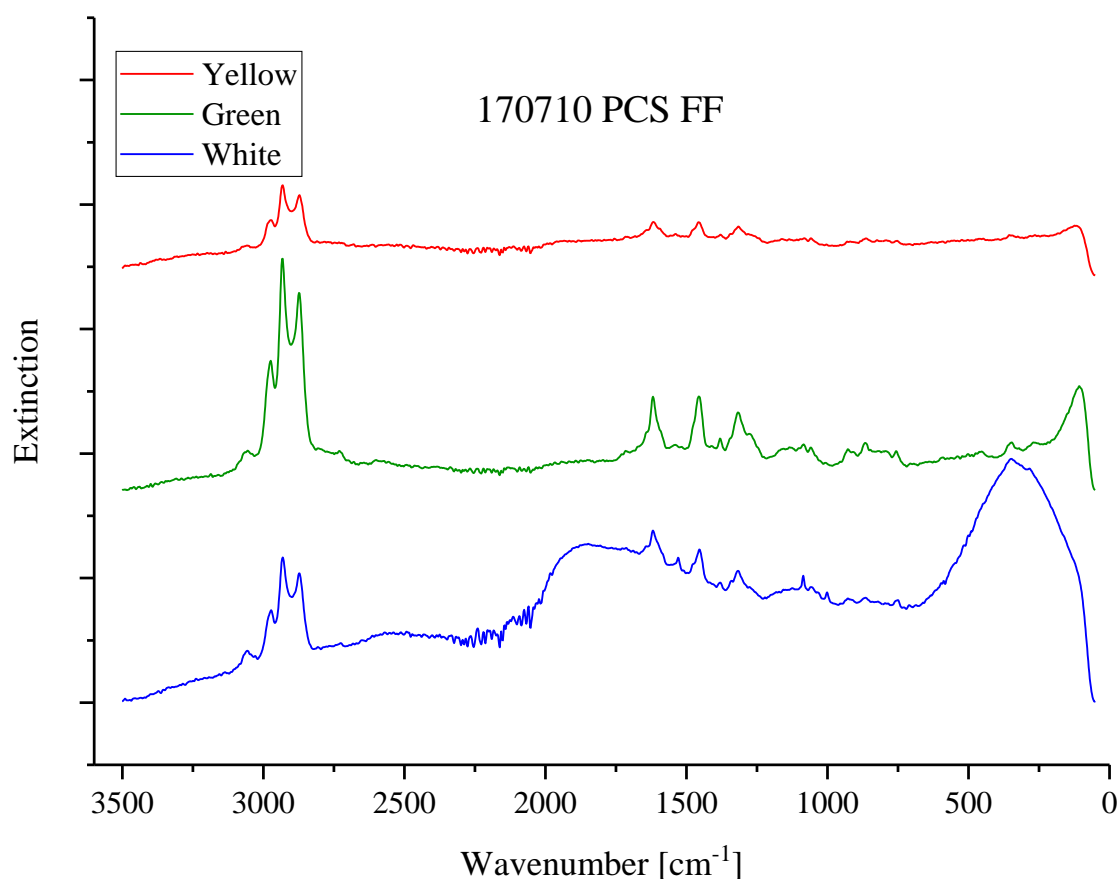
Figure 23: Raman spectra of the 170710 PCS FF foam sample

5.2 Analysis of the Glycolysis Product

The analysis of the glycolysis products are described below.

5.2.1 Refractometry

Table 4 - Table 6 lists the refractive indices that were obtained from the instrument reading.

Table 4: Refractive indices for mixtures of DEG and water

DEG [g]	Water [g]	RI
10	0	1.4470
8	2	1.4270
6	4	1.4040
4	6	1.3805
2	8	1.3560
0	10	1.3335

Figure 24 shows a graph, which was plotted to check the water content in the faulty DEG that was used for the glycolysis of 170621 foam with DEA as the catalyst. The refractive index of this DEG was

measured to be 1.4455 at 20 ºC. From the graph, it can be determined that the DEG contained 3 % of water and confirmed the assumption.
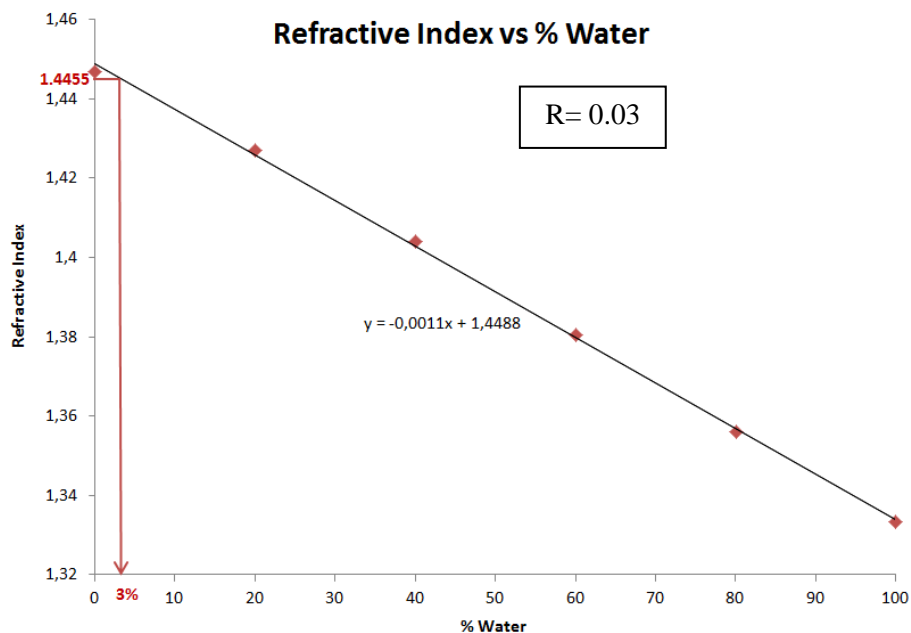

Figure 24: Graph to determine the quantity of water present in the erroneous DEG sample

LUPRANOL 2074 was mixed in different ratios with water and tested to check if the LUPRANOL 2074 used in the experiments was completely dry (Table 5). The RI of the pure LUPRANOL 2074 verified with that of water-free LUPRANOL 2074, which inferred that the LUPRANOL 2074 used for glycolysis was completely dry.

Table 5: Refractive indices for mixtures of LUPRANOL 2074 and water

LUPRANOL 2074 [g]	Water [g]	RI
10	0	1.4545
8	2	1.4500
6	4	1.4500
4	6	1.4505
2	8	1.3545
0	10	1.3335

DEG and LUPRANOL 2074 was also mixed in various proportions in order to test its miscibility (Table 6). It was observed that the mixtures were not completely miscible and as the quantity of LUPRANOL 2074 increased, the cloud-like formation in the mixture was more intense and after 60% LUPRANOL 2074, the mixture showed the value of RI same as that of pure LUPRANOL 2074.

Table 6: Refractive indices for mixtures of DEG and LUPRANOL 2074

DEG [g]	LUPRANOL 2074 [g]	RI
10	0	1.4470
8	2	1.4475
6	4	1.4465
4	6	1.4545
2	8	1.4545
0	10	1.4545

5.2.2 Hydroxyl Value

The commonly used polyol for mattress foam manufacturing is LUPRANOL 2074. We compare the OH value of DEG and LUPRANOL 2074 with the glycolysis products. Table 7 shows the hydroxyl values detected for the samples. The values that are marked * shows the inconsistent results due to the presence of solids (similar to the observations as seen in Figure 25) in the sample leading to inhomogeneity of the mixture. So the * trials were proposed to be repeated after the sample has been treated to centrifugation.

Table 7: OH values determined for the various samples of glycolysis products

Trial	Avg. OH value [mg KOH/ g Polyol]	Std. Deviation [mg KOH/ g Polyol]
DEG	956.10	13.5
LUPRANOL 2074	46.45	0.45
Urb-G-013	133.75	0.65
Urb-G-023	44.45	2.85
Urb-G-025	42.60	0.60
Urb-G-031	53.70	3.30
Urb-G-035	101.60	13.40
Urb-G-036	102.08	15.08
Urb-G-047	87.30[§]	0.50
	56.70[#]	0.90

§: before vacuum distillation
#: after vacuum distillation

Solving Equation 2 and Equation 3 from the information provided by the product data sheet for LUPRANOL 2074 i.e. functionality – 3 and the molecular weight – 3500 g/mol, the equivalent weight of LUPRANOL 2074 is,

$$Equivalent\ Weight = \frac{3500\frac{g}{mol}}{3} = 1166.67\ g/mol$$

And hence the OH Number of LUPRANOL is,

$$OH\ Number = \frac{56.1 * 1000}{Equivalent\ Weight} = \frac{56.1 * 1000}{1166.67} = \sim\mathbf{48\ mg\ KOH/g}$$

calculated to be approx. 48 mg KOH/g.

Table 8: Polyol fractions in the glycolysis product

Trial	Average OH Number mg KOH/ g Polyol	Polyol (wt. %)	
		LUPRANOL 2074 [%]	DEG [%]
Urb-G-013	133.75	91.5	8.5
Urb-G-023	44.45	100.35	*-0.35*
Urb-G-025	42.6	100.53	*-0.53*
Urb-G-031	53.7	99.44	0.56
Urb-G-035	101.6	94.69	5.31
Urb-G-036	102.1	94.64	5.36
Urb-G-047	87.3	96.11	3.89
	56.7	99.14	0.86

Table 8 presents the polyol fractions of LUPRANOL 2074 and DEG found in the glycolysis product. The assumption made here is that the glycolysis product contains only the glycolysis agent (LUPRANOL 2074 or DEG in the course of this work) and the secondary polyol (LUPRANOL 2074). Considering that LUPRANOL 2074 is the most customary polyol for the manufacture of mattress, the following assumptions were made. While all the trials have high fractions of LUPRANOL 2074, trials Urb-G-023 and 25 have negative fractions of DEG; it must be noted that the two particular trials utilised LUPRANOL 2074 as the glycolysis agent and had fairly high quantity of solid residue in the product, which have no contribution to the OH value determination. This solid residue can assumed to be

composed of oligomers which further reduce the OH value of the sample and thus causing the negative values to appear. Additionally, trials Urb-G-014 and 15 showed erratic values of OH number because of its inhomogeneity (Figure 25) and so, these samples were subjected to centrifugation.
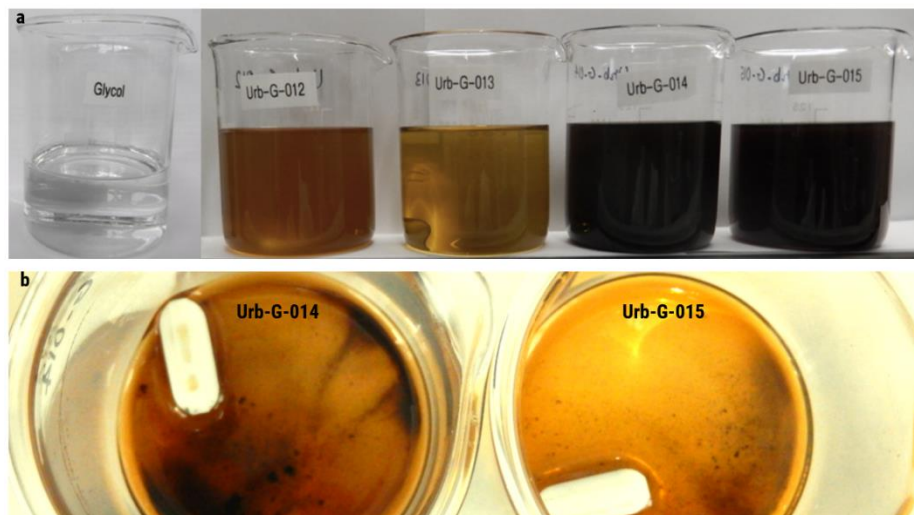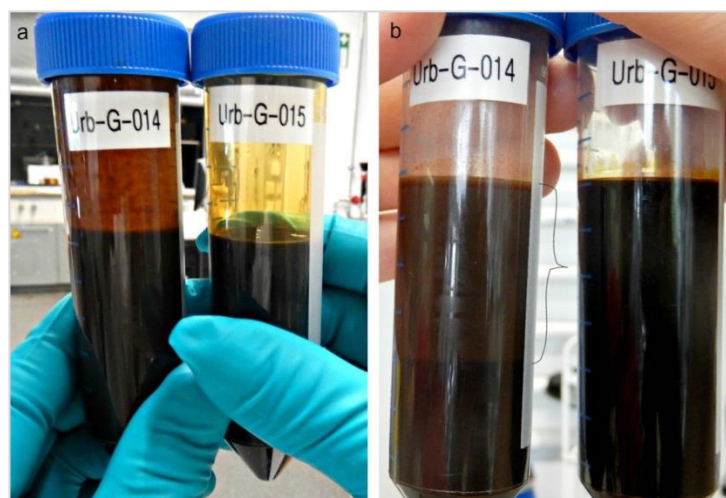

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Figure 25: Secondary polyols for Hydroxyl value determination (a); Presence of solids in trials Urb-G-014 and 015 (b)

5.2.3   Centrifugation

The products of Urb-G-014, 015 and 047 were subjected to centrifugation in order to separate the solids and obtain a homogenous mixture. Undeterred by centrifuging, the samples Urb-G-014 and 015 (as seen in Figure 26) showed minimal separation in the sample Urb-G-015 and some visible separation in Urb-G-014. However, the scaled-up trail Urb-G-047 was effectively centrifuged; as a result of which a considerable portion of the polyol was separated from the solid residue and this secondary polyol was vacuum distilled.

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Figure 26: Inhomogeneous samples before (a) and after (b) centrifugation

5.2.4   FTIR-ATR Spectrometry

The FTIR-ATR spectra of the glycolysis agents and products and 2,4-TDA are seen in Figure 27 and Figure 28 shows the spectra of the polyols before and after distillation. It can be noticed that spectra of glycolysis products showed minute peaks for the stable urethane groups around 1700 cm^{-1}. Furthermore, the peaks around 3400 cm^{-1} represent the OH group of the alcohols. The sharp peak seen in the region of 1000-1250 cm^{-1} is due to the C-O-C stretching consistent with ether groups. The other bands are attributed to stretching (2800-3000 cm^{-1}) and bending (1350 cm^{-1}, 1450 cm^{-1}) of CH$_3$ and CH$_2$ groups [35]. Comparing the spectra of the products with that of 2,4-TDA (NH$_2$ vibrations between 1600-1650 cm^{-1}, it can be concluded that the products contain negligible traces of the amine. As the FTIR-ATR analysis technique is beneficial to obtain rapid results as opposed to accuracy, GPC and GC-MS measurements were conducted to overcome this drawback and have been discussed in the subsequent sections.
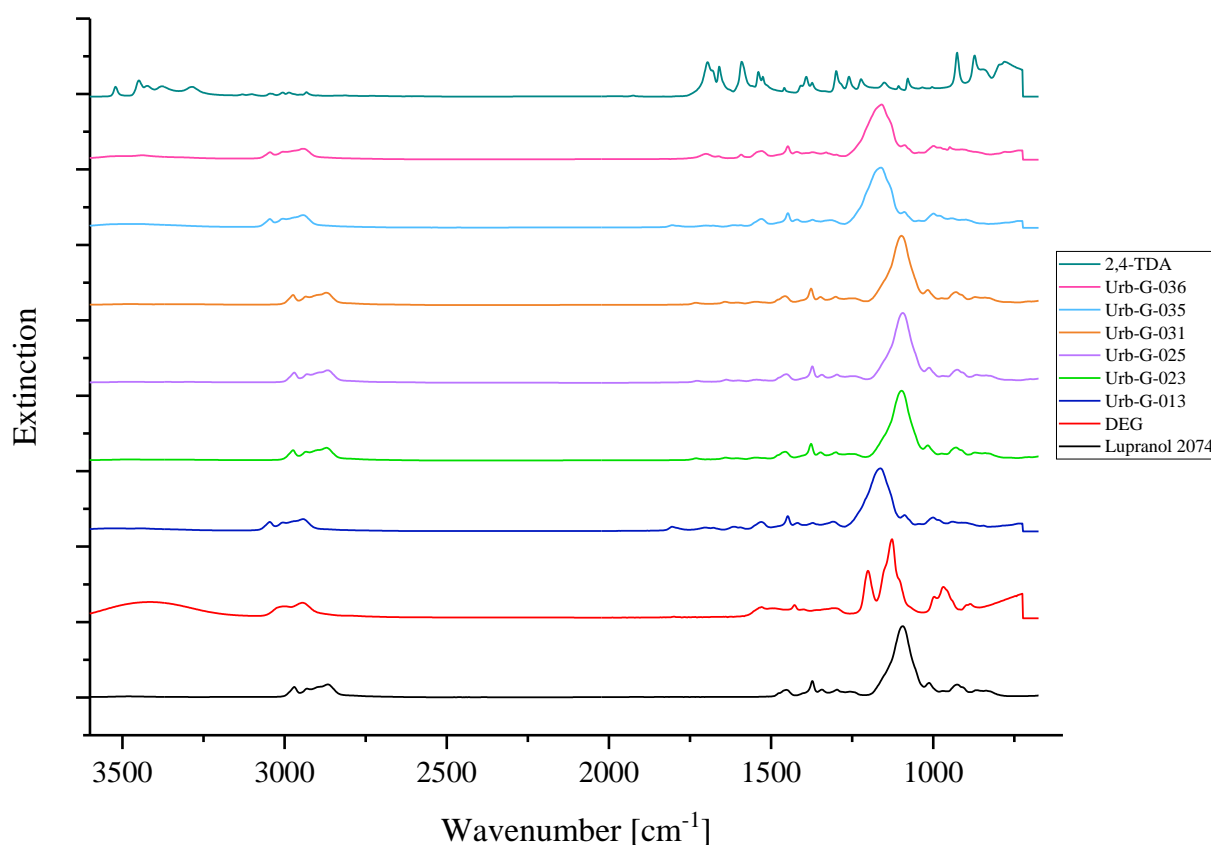
Figure 27: IR Spectra of the products of glycolysis
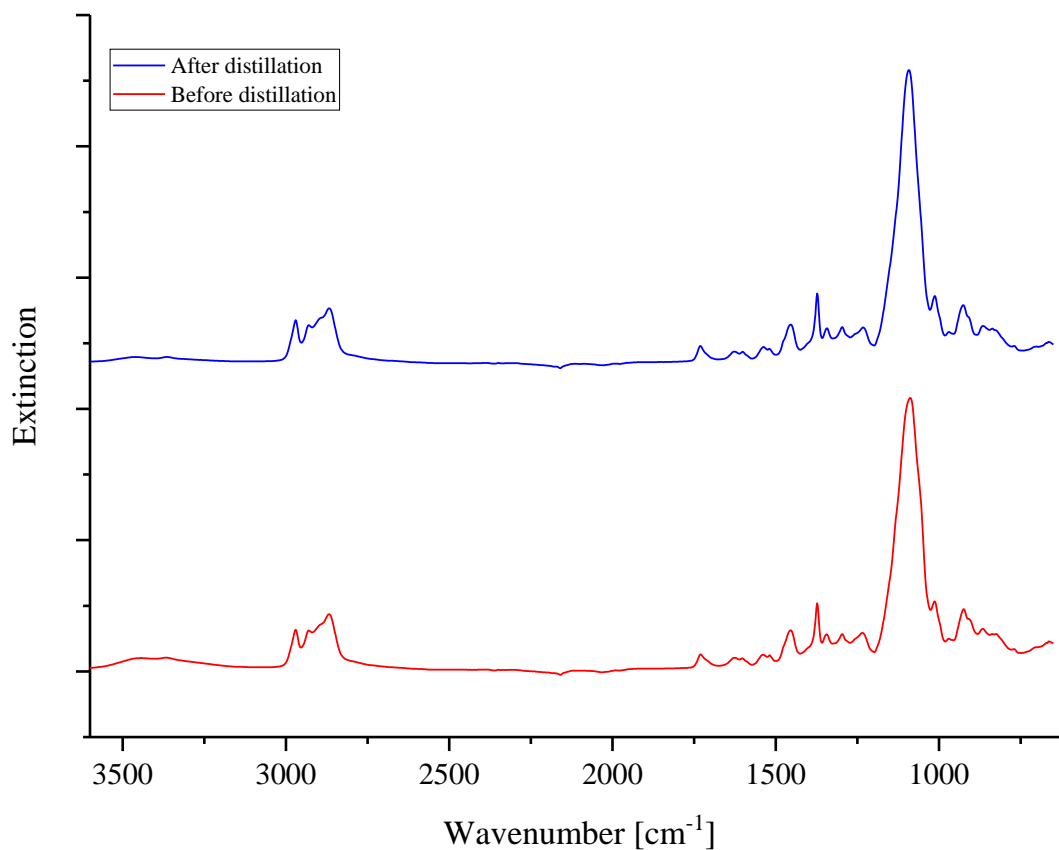
Figure 28: IR Spectrum of the scaled-up glycolysis process Urb-G-047 (after vacuum distillation)

5.2.5 Gas Chromatography coupled with Mass Spectrometry

The results of the GC-MS analysis are shown in Table 9. It was observed that some of the samples on mixing the solvent THF (Tetrahydrofuran), the samples were not completely miscible. So a portion of the sample had to be filtered and measured. The detection limit of the measurement is 0.075 mg/mL.

Table 9: Concentration of 2,4-TDA from the GC-MS measurements

Trial	Glycol	Glycol:Foam	Concentration of 2,4-TDA [mg/mL]
Urb-G-013	DEG	1:1	0.07
Urb-G-023	LUPRANOL 2074	1:1	0.14
Urb-G-025	LUPRANOL 2074	1:1	0.18
Urb-G-031	LUPRANOL 2074	1:1	0.24
Urb-G-035	DEG	1:1	-
Urb-G-036	DEG	1:2	4.51
Urb-G-047	DEG	1.2	0.46

The suggested concentration of TDA in the glycolysis product is approx. 0.1 mg/mL [36] and the values seen in Table 9 hovered roughly around the suggested value. Ergo, it can be inferred that these products, excluding Urb-G-036, were suitable for the synthesis of the recycled foam.

5.2.6 Size Exclusion Chromatography

Given below are the Size Exclusion Chromatograms of the glycolysis reactions for the above-mentioned trials. The chromatograms display the graph from the Refractive Index Detector (RID, shown in red) and the UV Detector (shown in green). The UV Detector enables the identification of the UV-active compounds which are otherwise extremely low in concentration to be detected by an RID. The UV stabilisers (stabilisers for polymers are used to prevent the various effects such as oxidation, chain scission and uncontrolled re-combinations and cross-linking reactions that are caused by photo-oxidation of polymers) added to the polyol facilitates the UV activeness in the sample.
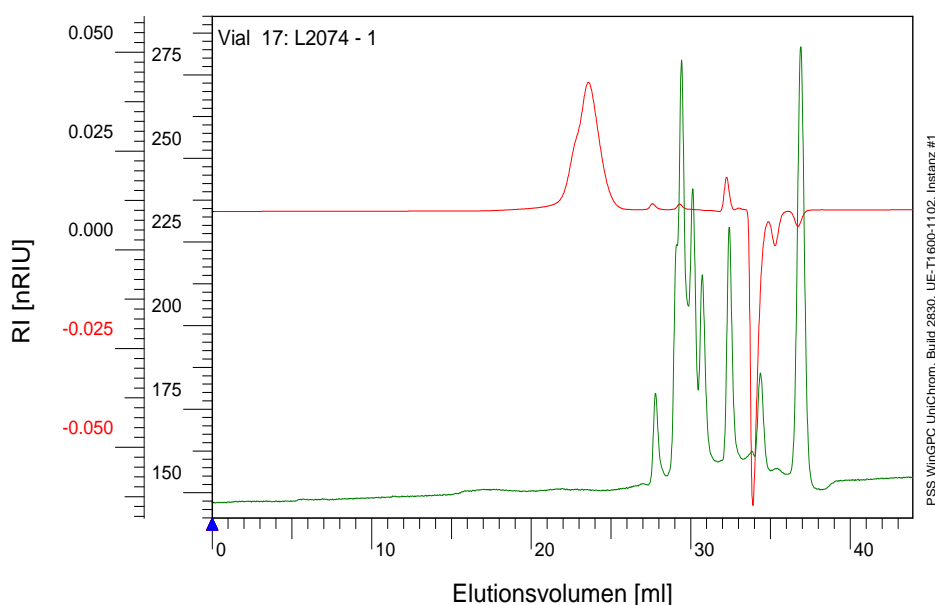
Figure 29: Reference chromatogram for LUPRANOL 2074

Figure 29 shows the presence of high molecular weight polyols at the 24th min in pure LUPRANOL 2074 in the RID. Peaks between 28th min and 32nd minute in the UVD could be attributed to the presence of urethane oligomers and the stabilisers in LUPRANOL 2074. The UV-active substances are mostly anti-oxidants which are added to the polyols during its manufacture in order to prevent the discolouration of the foam core.
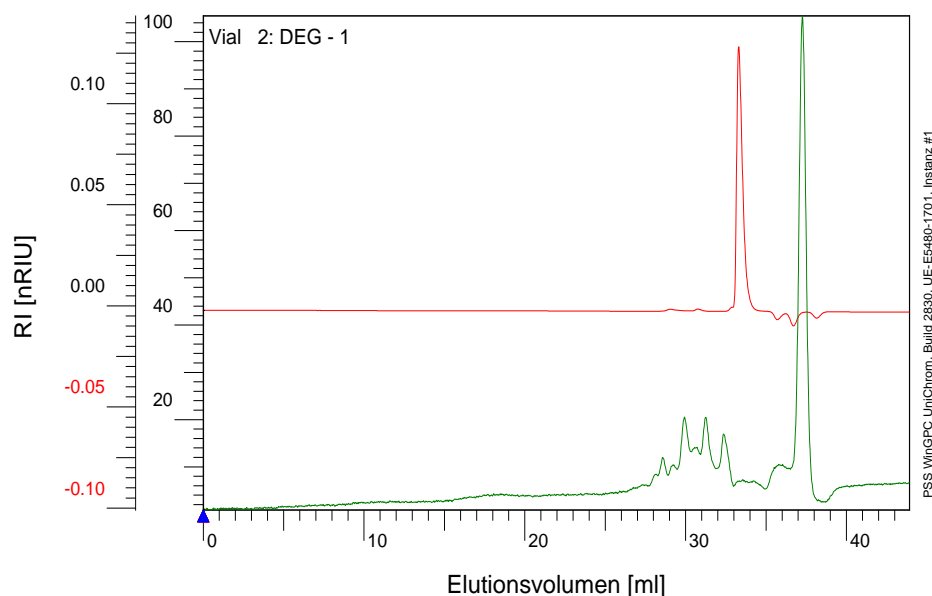
Figure 30: Reference chromatogram for DEG

Similarly, Figure 30 shows the OH groups of the DEG at the 32nd minute in the RID and in Figure 31, the chromatogram for 2,4-TDA shows a large peak at the 34th minute.
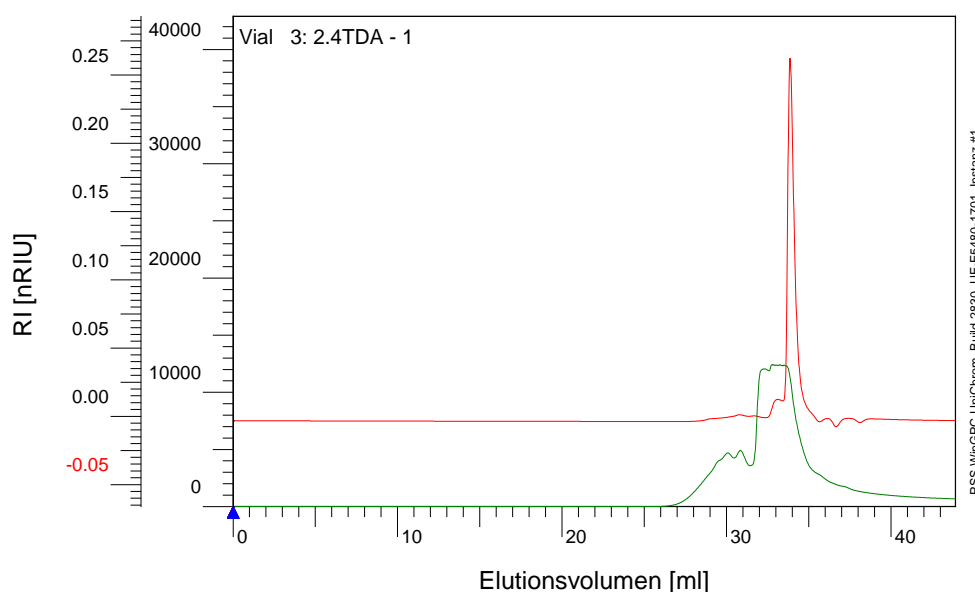
Figure 31: Reference chromatogram for 2,4-TDA

Figure 32 shows the chromatogram of Urb-G-023. Comparing this with Figure 29 (LUPRANOL 2074 being the glycolysis used for this trial), it can be observed in Figure 32 that the first peak in RID represents the high molecular weight polyols ($\sim 24^{th}$ min) and its bulge on the left indicates the presence of the isocyanate groups (in UVD), subsequent smaller peaks represent the by-products (inclusive of the stabilisers, between 28th and 31st min in RID) and the final peak represents the unreacted glycol ($\sim 33^{rd}$ min in RID), in this case LUPRANOL 2074.
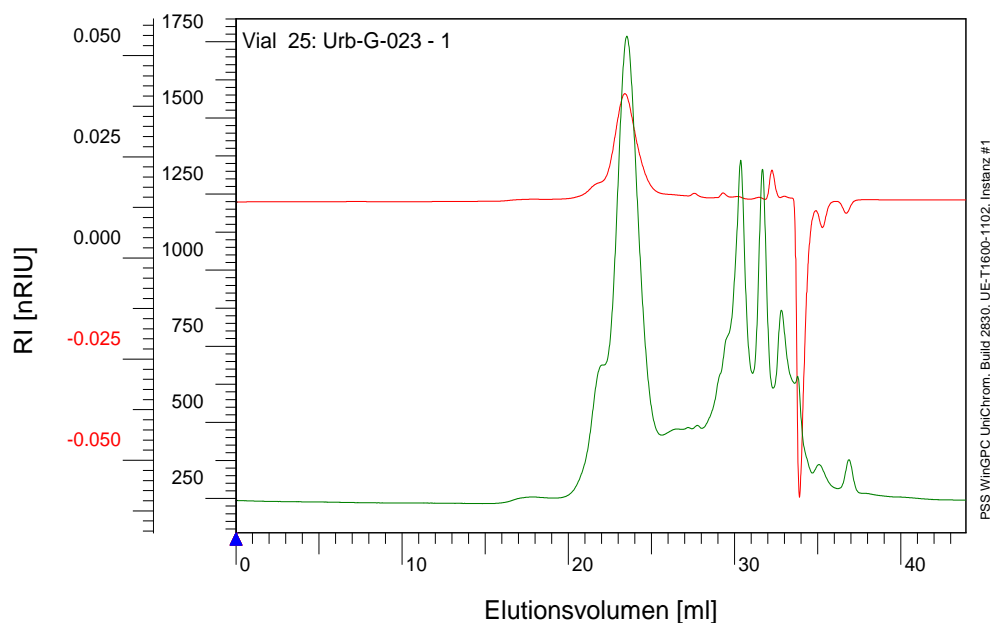
Figure 32: Chromatogram for Urb-G-023
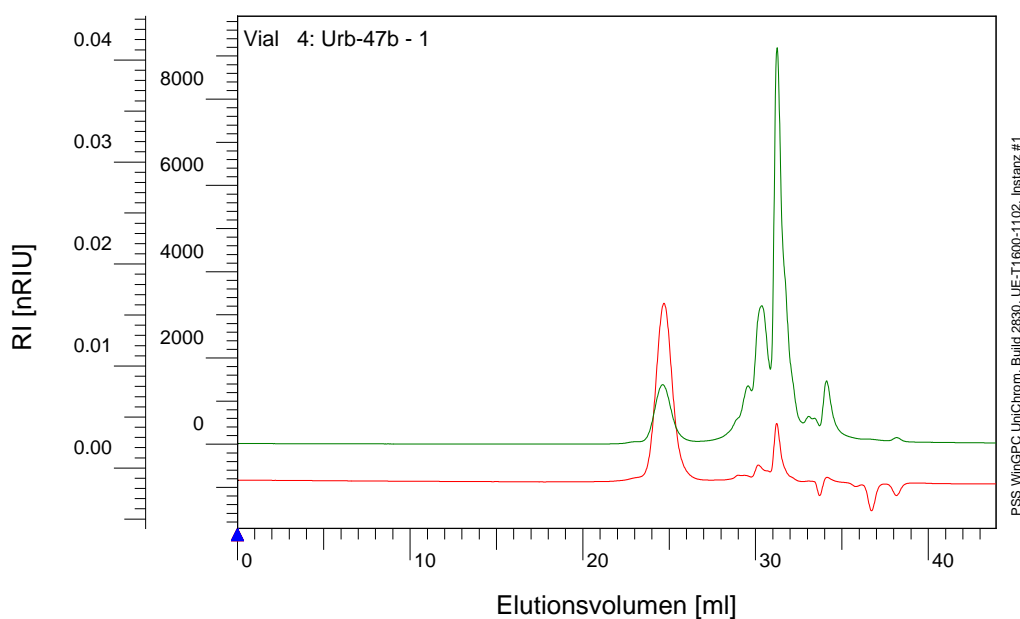
Figure 33: Chromatogram for Urb-G-047 (after purification)

Similarly in Figure 33, first peak in RID represents the high molecular weight polyols (~25th min) and it can also be observed that there is no visible determination of the isocyanate peaks in the secondary polyol. The chromatograms of the other products are enclosed in Appendix F.

5.3   Synthesis of Secondary Polyurethane Foam

Table 10 shows the formulations used for the manufacture of the secondary foam.

Table 10: Formulations used for the manufacture of the secondary foam

Trial	Lupranol 2074 [g]	Secondary Polyol [g]	Water [g]	Tegostab BF 2370 [g]	TEDA 33LV [g]	Niax A1 [g]	Kosmos29 [g]	TDI 80 – Bedarf [g]
Urb-F-01	100	0	3.83	1	0.083	0.035	0.215	50.30
Urb-F-02	90	10	3.83	1	0.083	0.035	0.215	50.48
Urb-F-03	80	20	3.83	1	0.083	0.035	0.215	50.66
Urb-F-04	70	30	3.83	1	0.083	0.035	0.215	50.84
Urb-F-05	50	50	3.83	1	0.083	0.035	0.215	51.20
Urb-F-06	100	0	3.83	1	0.083	0.035	0.215	50.30
Urb-F-07	50	50	3.83	0.5	0.042	0.018	0.108	51.2

The characteristic features observed for standard foam formulation and Urb-F-04 from the FOAMAT Type 281 device are presented in Figure 34 and Figure 35. The foam height immediately increased to its maximum within the first 100 s (approx.) and then stabilised between 235-240 mm. The pressure profile is seen gradually decreasing through the foaming process.
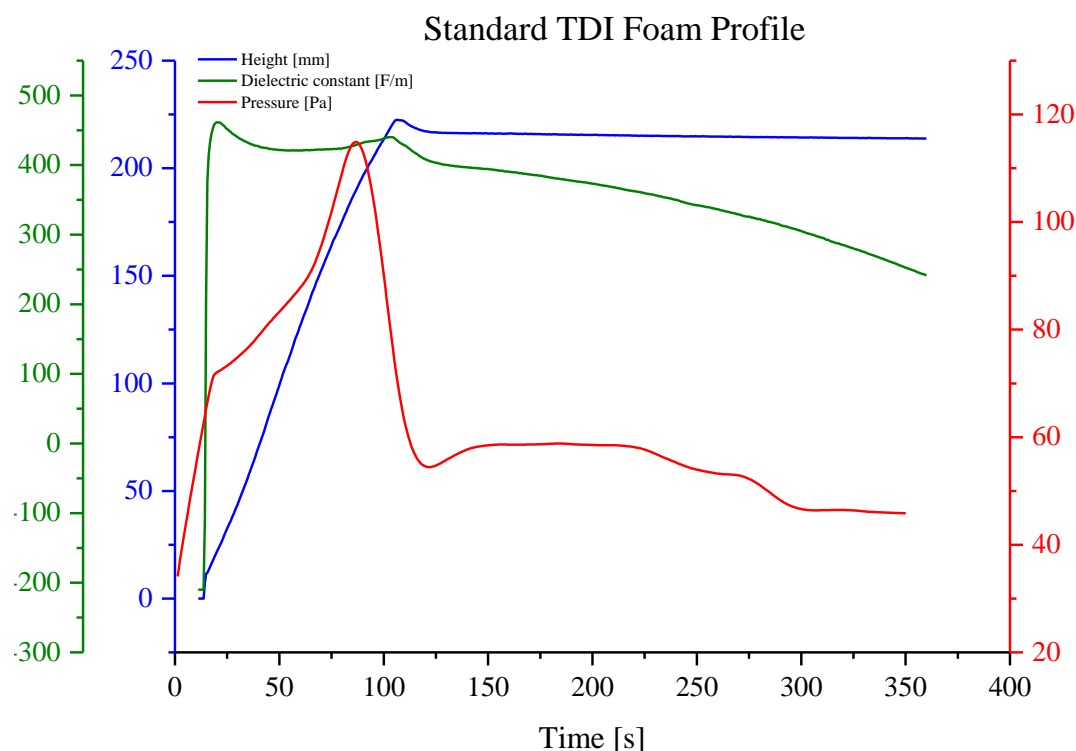
Figure 34: Height, Pressure and Dielectric constant v/s Time curves for standard foam formulations
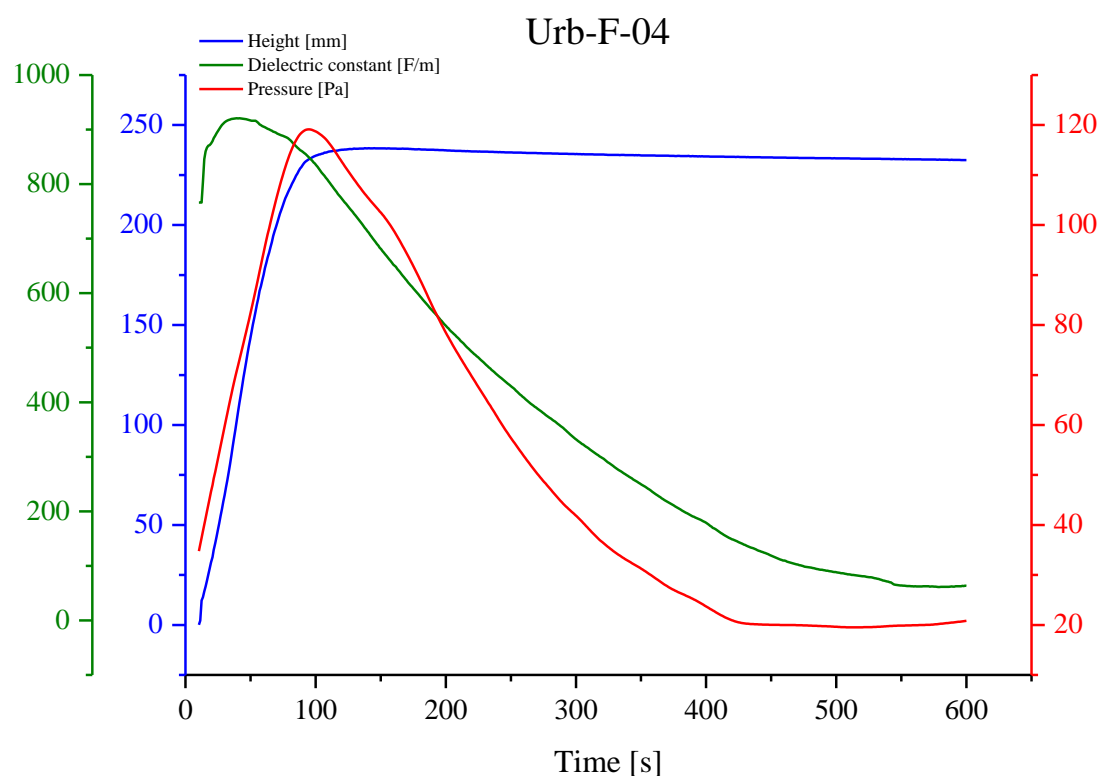
Figure 35: Height, Pressure and Dielectric constant v/s Time curves for 30 phpp secondary polyol-foam formulations

As the quantity of secondary polyol was increased in the foaming mixture, the reaction took place at an accelerated rate. The maximum velocity of the trial Urb-F-05 was calculated by the FOAMAT Type 281 device as 194 mm/s whereas trails Urb-F-02, -03 and -04 had 21, 77 and 5 mm/s as their maximum velocity. Also, since the trial Urb-F-01 had an error in the measurement of its rise profile and trials Urb-F-05, -06 and -07 collapsed and failed to rise to a substantial height (Table 11), these foams cannot be considered for density and air permeability measurements.

Table 11: Velocity and Height measurements from FOAMAT Type 281 device

Trial	Maximum Velocity [mm/s]	Final Height [mm]
Urb-F-01	2.14	231.80
Urb-F-02	21.34	251.20
Urb-F-03	77.23	233.40
Urb-F-04	4.91	232.50
Urb-F-05	193.83	180.70
Urb-F-06	2.81	190.39
Urb-F-07	120.62	122.75

The foams obtained from secondary polyols are seen in Figure 36.
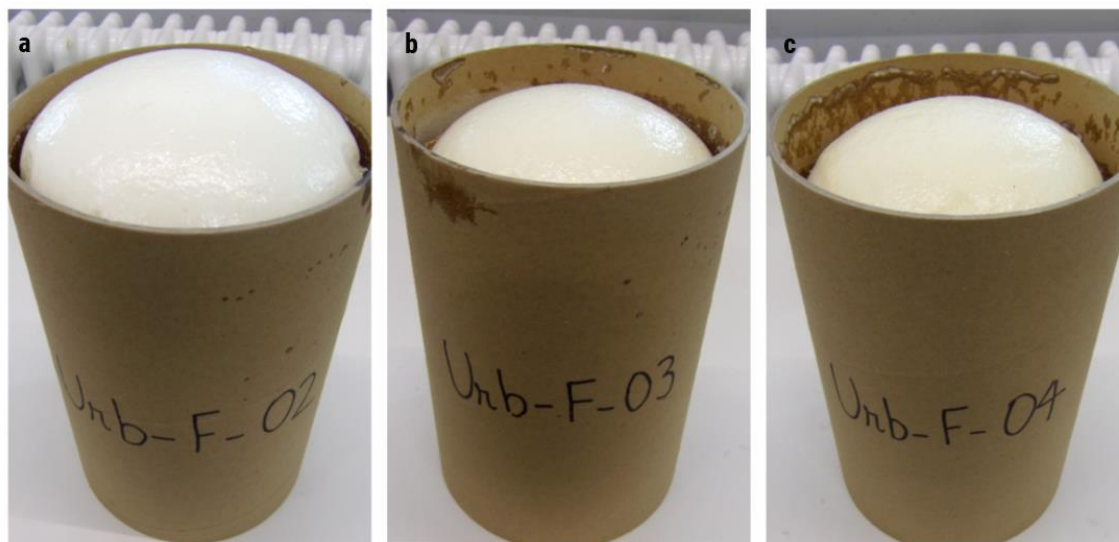
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Figure 36: PU foams obtained using various ratios of secondary polyol (a) 10 phpp, (b) 20 phpp and (c) 30 phpp

From Figure 37, the height (rise) profiles of all the foaming trials can be observed. Trials Urb-F-02, -03, -04 and the standard TDI Foam profile shows a good stability in height maintenance. However, trial Urb-F-07 failed to stabilise and consequently, collapsed (as seen in Figure 37).
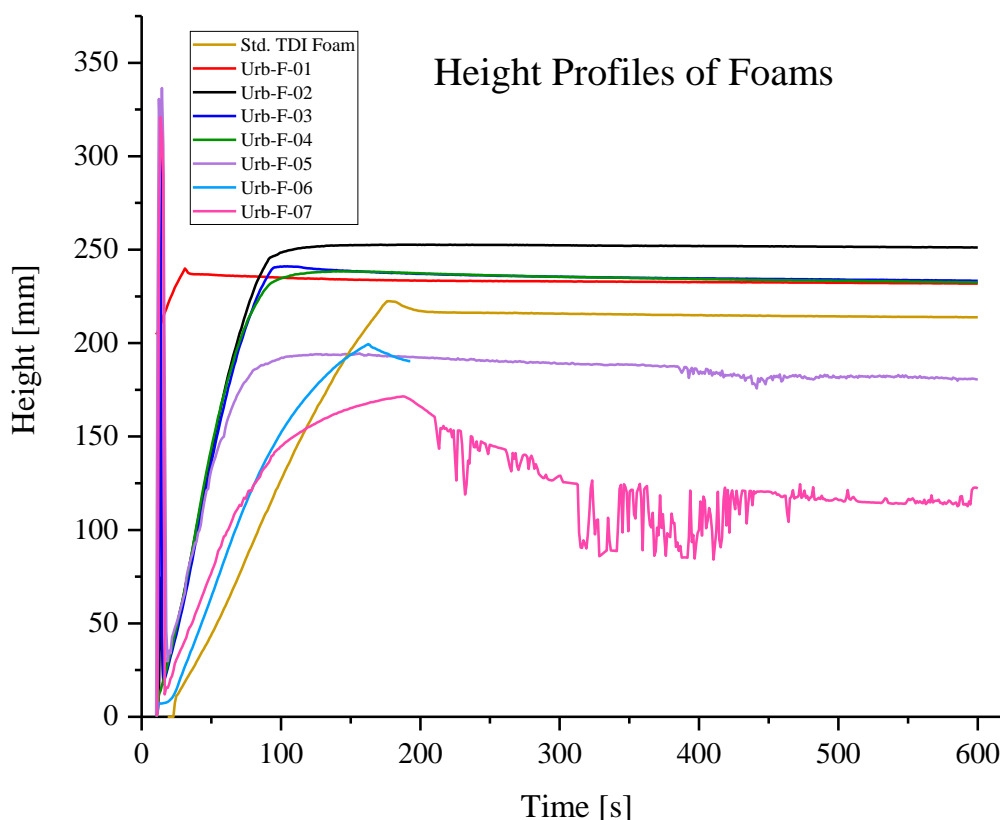
Figure 37: Height profiles for the various foaming trials

The trail Urb-F-05 (50 phpp secondary polyol) reacted at an extremely high velocity (one probable reason could be that the quantity of catalyst deemed too high as the quantity of secondary polyols

increased) because of which it was not possible to empty the pre-mixture completely on to the foaming cylinder. As a result, inhomogeneous foam was obtained (as seen in Figure 38).

Figure 38: Foam obtained from 50 phpp secondary polyol (Urb-F-05)
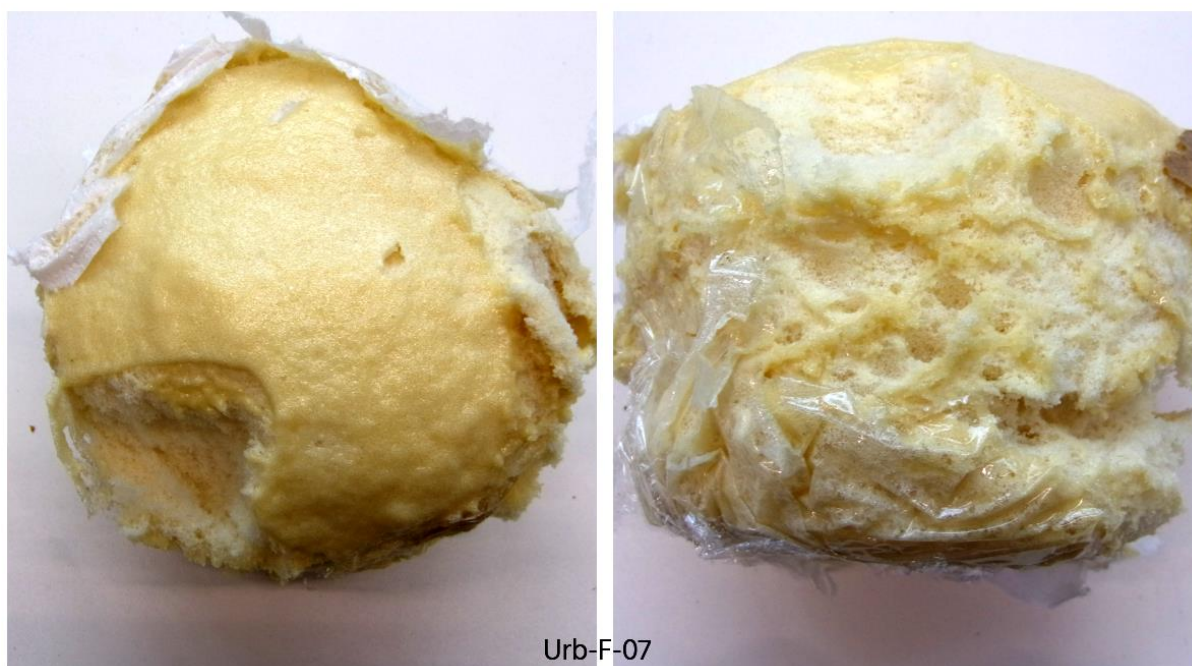
Figure 39: Secondary foam from Urb-F-07 trial

5.3.1   Density

The density of the standard TDI foam and foams obtained from secondary polyols are listed in Table 12.

Table 12: Densities calculated for the standard TDI foam and various secondary foams

Trial	Dimensions cm x cm x cm	Weight [g]	Density [kg/m^3]
Standard TDI Foam	5 x 4.9 x 5	3.828	31.25
Urb-F-02	5 x 5.1 x 5	3.603	28.26
Urb-F-03	5 x 5 x 5.1	3.687	28.92
Urb-F-04	5 x 5.1 5.1	3.373	25.94

5.3.2 Air Permeability

The average of the air permeability values and its standard variance are mention in Table 13.

Table 13: Average value and standard variance determined from the air permeability tests

Trial		Average Air Permeability [dm^3/s]	Standard Variance
Standard TDI Foam	Top	0.128	0.011
	Bottom	0.312	0.006
Urb-F-02	Top	0.085	0.008
	Bottom	0.055	0.003
Urb-F-03	Top	0.159	0.014
	Bottom	0.091	0.005
Urb-F-04	Top	0.135	0.016
	Bottom	0.043	0.009

6 CONCLUSIONS AND RECOMMENDATIONS

The glycolysis reactions were carried out for different post-consumer PU foams using various glycolysis agents and catalysts at different temperatures and different mass ratios of the educts. Several observations were made based on the nature of the product obtained after analysis.

The glycolysis reactions established that trials with DEG as the glycolysis agent and DEA as the catalyst produced a secondary polyol which had relatively low concentration of 2,4-TDA and furthermore, had substantially low stable urethane groups.

One of the hindrances that were encountered during this study was the presence of solid residue in the product i.e. inhomogeneous fraction. This was primarily observed in the reactions that used LUPRANOL 2074 with DEA as the educts in the glycolysis reaction. Partial reasoning would be the stability of urethane groups and oligomers in the product owing to the fact that the reaction did not run to completion. In order to overcome this drawback, filtration is recommended in the products which are highly viscous.

Since the reaction time was six hours, which is relatively a longer span of time, microwave-assisted glycolysis can be proposed in this regard. This enables the reaction to take place using the microwave radiation as the source of thermal energy for the reaction and this being a faster operation, the reaction time can be immensely reduced.

The third recommendation would be with respect to the 'Design for Recycling'. Generally, the manufacture of PU foam, especially in the case of aircraft seating and moulded foams, involves the use of a mixture of several polyols. Keeping in mind the scope for recycling the foam, reduction of the number of polyols used during the manufacture of the foam could be minimised.

Additionally, since the foam failed to stabilise after increasing the quantity of secondary polyols above 30 phpp, it is advisable to reduce the amount of catalyst in order to optimise the foaming process and as a result of which, collapsing of the foam can be avoided.

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Appendix A: FTIR-ATR and Raman spectra of the various foam samples

FTIR-ATR spectra of the various foam samples
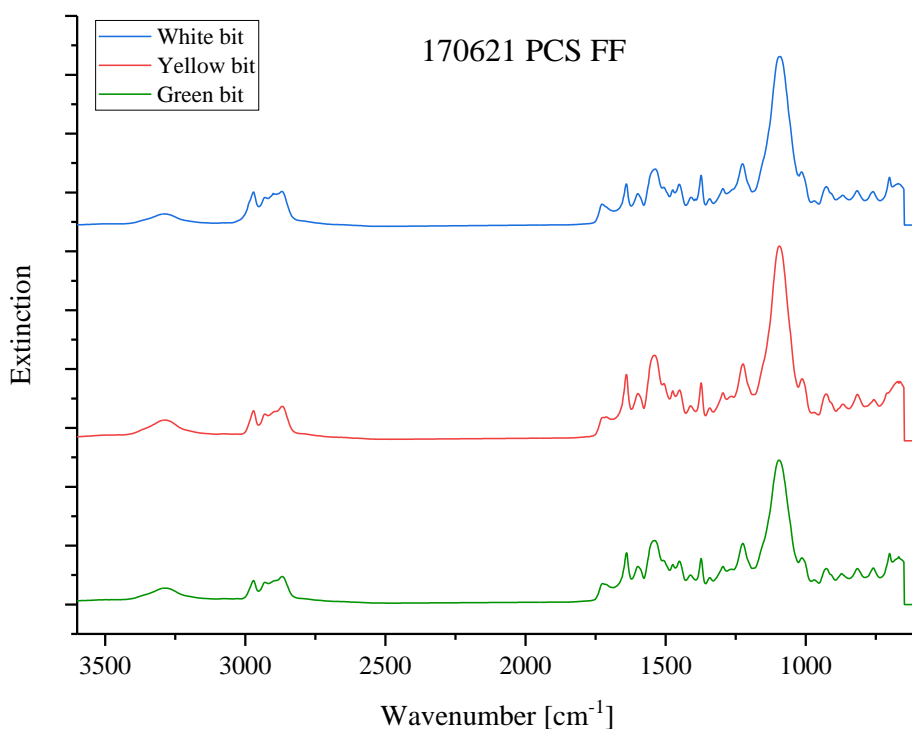
Figure A.1: FTIR-ATR spectra of the 170621 PCS FF foam sample
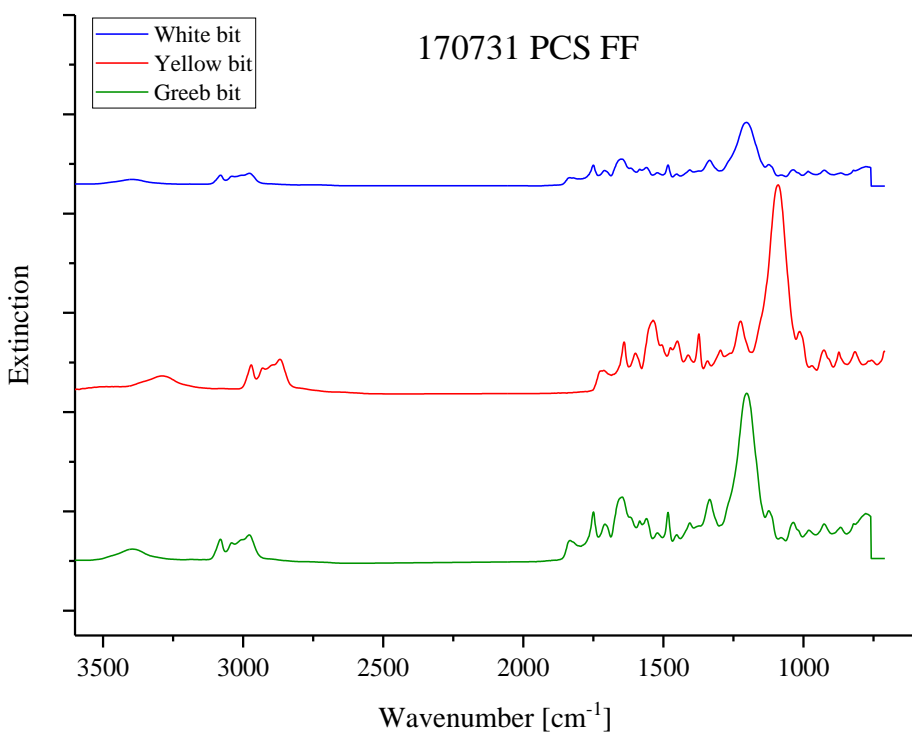
Figure A.2: FTIR-ATR spectra of the 170731 PCS FF foam sample
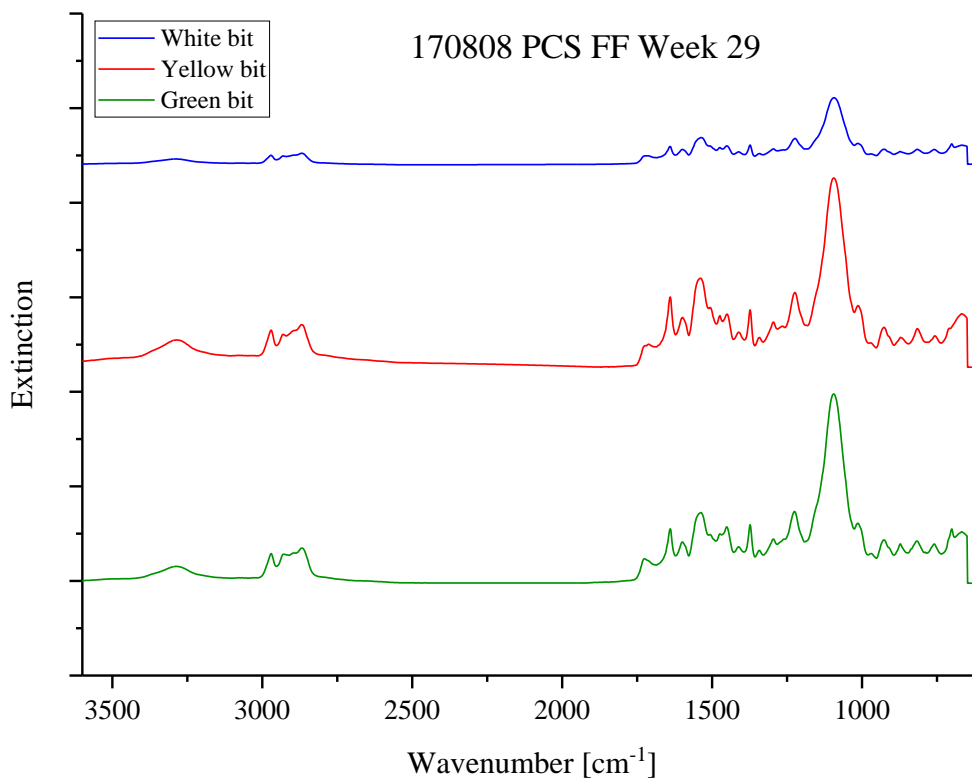
Figure A.3: FTIR-ATR spectra of the 170808 Week 29 PCS FF foam sample
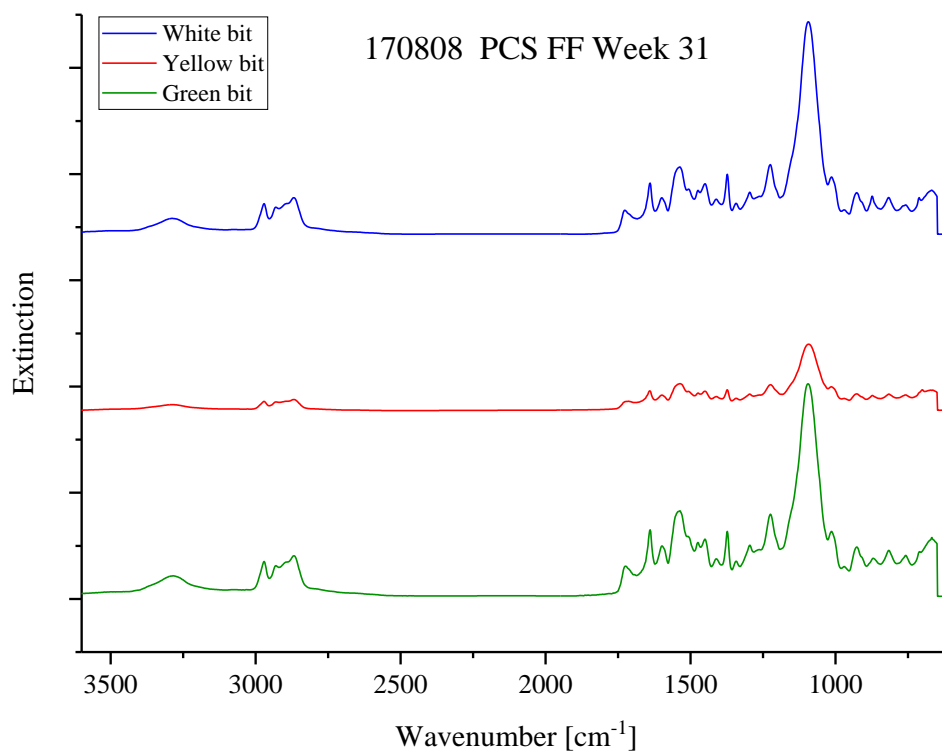
Figure A.4: FTIR-ATR spectra of the 170808 Week 31 PCS FF foam sample

Raman spectra of the various foam samples
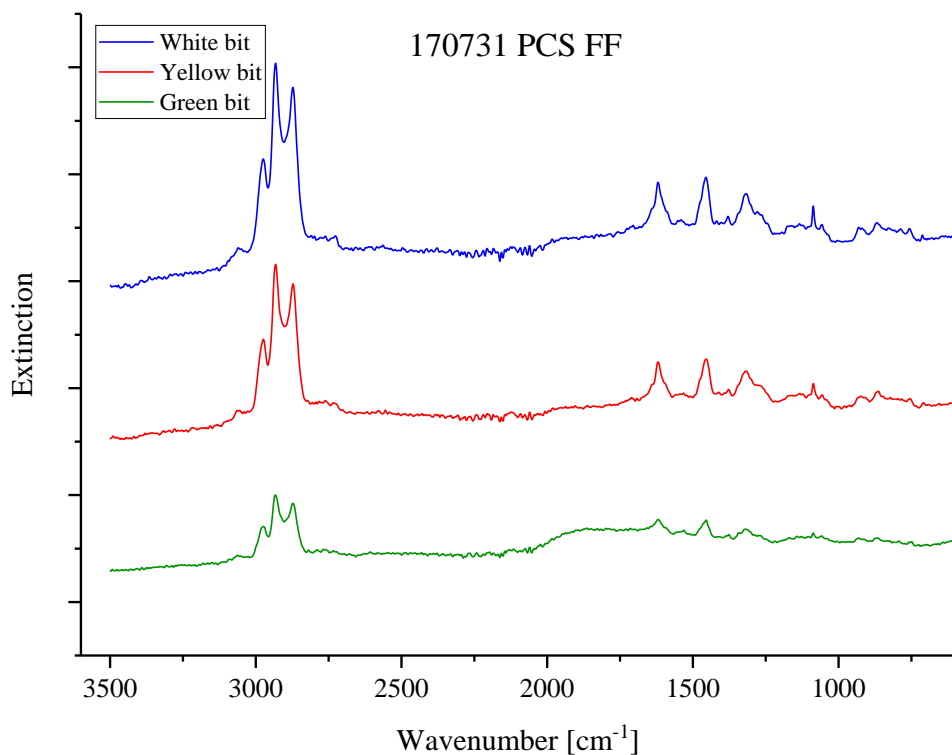
Figure A.5: Raman spectra of the 170731 PCS FF foam sample
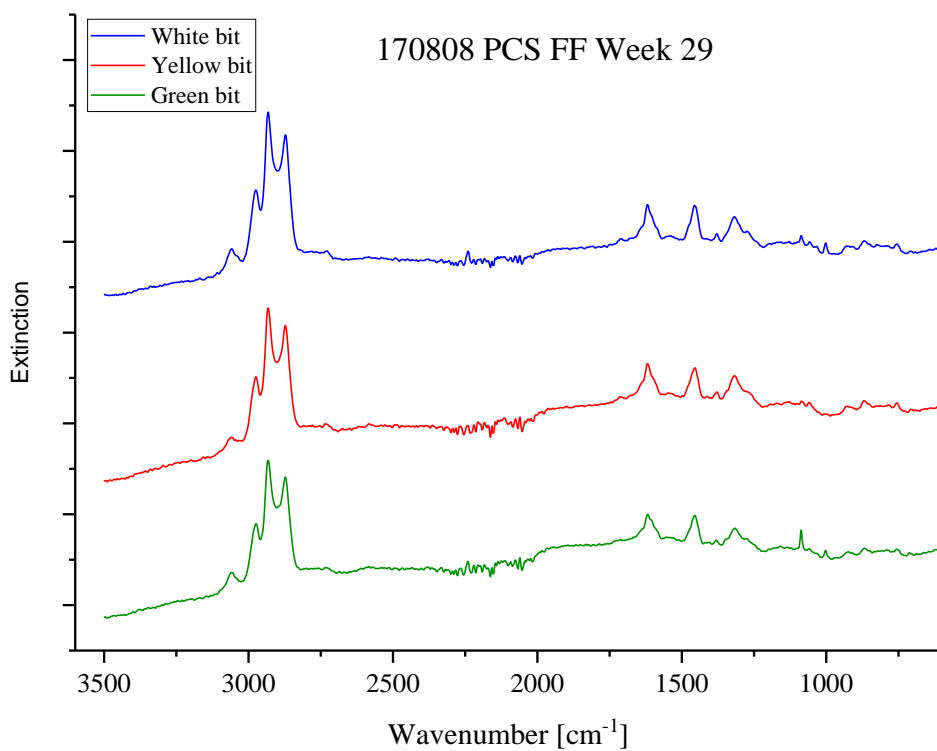
Figure A.6: Raman spectra of the 170808 Week 29 PCS FF foam sample
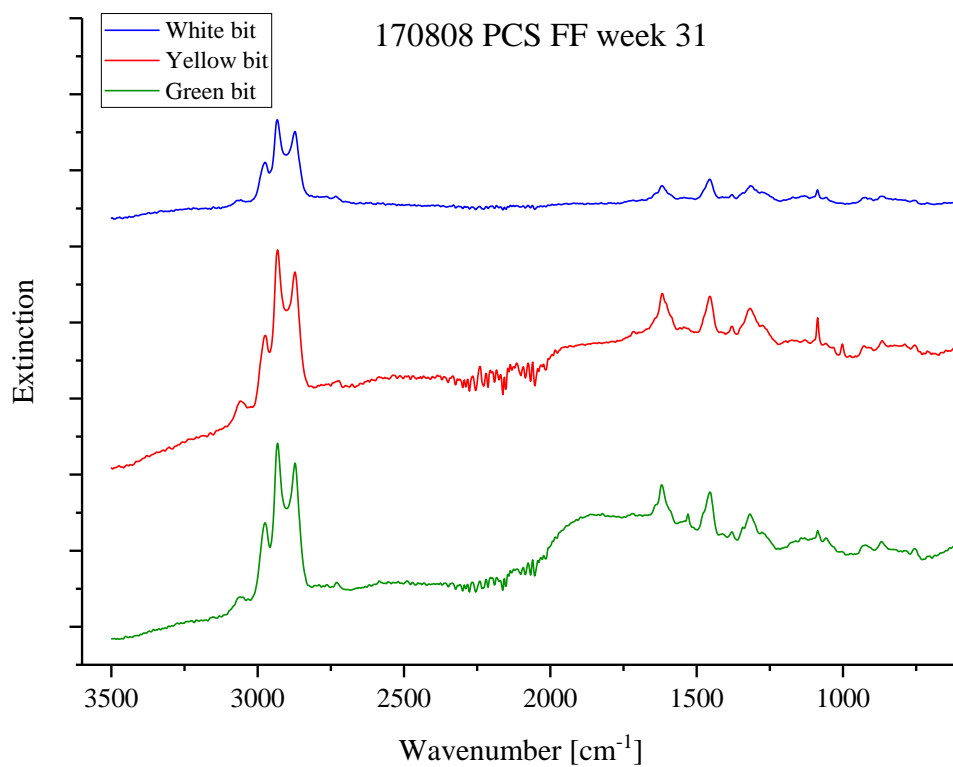
Figure A.7: Raman spectra of the 170808 Week 31 PCS FF foam sample

Appendix B: Glycolysis trials conducted for various parameters

Table B.1: Parameters compared for the glycolysis reaction

Trial	Glycol	Catalyst	Glycol:Catalyst	Mass of Glycol [g]	Mass of Catalyst [g]	Foam	Glycol:Foam	Mass of Foam [g]	Temperature [ºC]	Duration [h]
Urb-G-012	DEG	KOH	100:1	198.2	2.010	170710 PCS FF	1:1	201.1	200	6
Urb-G-014	LUPRANOL 2074	KOH	100:1	108.7	1.076	170710 PCS FF	1:1	101.6	200	6
Urb-G-015	LUPRANOL 2074	DEA	100:1	98.5	1.044	170710 PCS FF	1:1	100.1	200	6
Urb-G-016	DEG	KOH	100:1	199.6	2.031	170731 PCS FF	1:1	201.4	200	6
Urb-G-017	DEG	DEA	100:1	203.9	1.725	170731 PCS FF	1:1	201.4	200	6
Urb-G-018	DEG	KOH	100:1	200.2	2.100	170808 PCS FF Week 29	1:1	201.2	200	6
Urb-G-019	DEG	DEA	100:1	201.8	2.058	170808 PCS FF Week 29	1:1	200.3	200	6
Urb-G-020	DEG	KOH	100:1	200.4	2.080	170808 PCS FF Week 31	1:1	201.3	200	6
Urb-G-021	DEG	DEA	100:1	200.1	2.028	170808 PCS FF Week 31	1:1	200.7	200	6
Urb-G-022	LUPRANOL 2074	KOH	100:1	199.9	2.100	170731 PCS FF	1:1	201.5	200	6
Urb-G-024	LUPRANOL 2074	KOH	100:1	99.9	1.023	170808 PCS FF Week 29	1:1	100.3	200	6
Urb-G-026	LUPRANOL 2074	KOH	100:1	99.9	1.035	170808 PCS FF Week 31	1:1	100.8	200	6
Urb-G-027	LUPRANOL 2074	DEA	100:1	109.0	1.125	170808 PCS FF Week 31	1:1	101.6	200	6
Urb-G-028	LUPRANOL 2074	KOH	100:1	101.2	1.029	170710 PCS FF	1:1	101.2	220	6
Urb-G-029	LUPRANOL 2074	DEA	100:1	99.8	1.071	170731 PCS FF	1:1	100.6	220	6
Urb-G-030	LUPRANOL 2074	DEA	100:1	100.7	1.065	170808 PCS FF Week 29	1:1	100.5	220	6

Appendix B: Glycolysis trials conducted for various parameters

Trial	Glycol	Catalyst	Glycol:Catalyst	Mass of Glycol [g]	Mass of Catalyst [g]	Foam	Glycol:Foam	Mass of Foam [g]	Temperature [°C]	Duration [h]
Urb-G-032	LUPRANOL 2074	KOH	100:1	102.7	1.030	170808 PCS FF Week 31	1:2	200.8	220	6
Urb-G-033	LUPRANOL 2074	DEA	100:1	102.7	1.003	170808 PCS FF Week 31	1:2	200.8	220	6
Urb-G-034	DEG	KOH	100:1	99.7	1.100	170808 PCS FF Week 31	1:1	100.6	220	6
Urb-G-037	DEG	DEA	100:1	100.8	1.140	170808 PCS FF Week 31	1:2	200.4	220	6
Urb-G-038	DEG	Sn (Oct)$_2$	$6 * 10^{-3}$	101.6	0.301	170808 PCS FF Week 31	1:1	100.7	220	6
Urb-G-039	LUPRANOL 2074	Sn (Oct)$_2$	$6 * 10^{-3}$	101.5	0.287	170808 PCS FF Week 31	1:1	101.0	220	6
Urb-G-040	DEG	Sn (Oct)$_2$	$6 * 10^{-3}$	99.7	0.284	170808 PCS FF Week 31	1:2	100.5	220	6
Urb-G-041	DEG	DBTDL	$6 * 10^{-3}$	100.6	0.349	170808 PCS FF Week 31	1:1	101.1	220	6
Urb-G-042	DEG	DBTDL	$6 * 10^{-3}$	101.7	0.360	170808 PCS FF Week 31	1:1	101.2	220	6
Urb-G-043	DEG	KOSMOS Pro 1	$6 * 10^{-3}$	100.3	2.500	170808 PCS FF Week 31	1:1	101.1	220	6
Urb-G-044	DEG	KOSMOS Pro 1	$6 * 10^{-3}$	102.3	2.500	170808 PCS FF Week 31	1:2	200.5	220	6
Urb-G-045	DEG	KOSMOS EF	$6 * 10^{-3}$	100.9	0.4	170808 PCS FF Week 31	1:1	100.6	220	6
Urb-G-046	DEG	KOSMOS EF	$6 * 10^{-3}$	99.9	0.4	170808 PCS FF Week 31	1:2	200.4	220	6

Appendix C: Hydroxyl values of the glycolysis products and the mass ratio of their polyol

Table C.1: OH value determined for the various samples of glycolysis products

Trial	Glycolysis Agent	Avg. OH value mg KOH/ g Polyol	Standard Deviation mg KOH/ g Polyol	Polyol (wt. %)*	
				LUPRANOL 2074	DEG
Urb-G-012	DEG	59.95	0.65	98.82	1.18
Urb-G-014	LUPRANOL 2074	66.33	15.51	98.18	1.82
Urb-G-015	LUPRANOL 2074	67.98	9.41	98.02	1.98
Urb-G-016	DEG	101.05	0.85	94.74	5.26
Urb-G-017	DEG	101.75	0.05	94.68	5.32
Urb-G-018	DEG	109.95	3.15	93.86	6.14
Urb-G-019	DEG	140.25	1.35	90.86	9.14
Urb-G-020	DEG	143.90	1.40	90.50	9.50
Urb-G-021	DEG	143	0.50	90.59	9.41
Urb-G-022	LUPRANOL 2074	59.15	3.35	98.90	1.10
Urb-G-024	LUPRANOL 2074	61.35	2.15	98.68	1.32
Urb-G-026	LUPRANOL 2074	70.75	1.55	97.75	2.25
Urb-G-027	LUPRANOL 2074	55.45	0.65	99.26	0.74
Urb-G-028	LUPRANOL 2074	65.05	1.05	98.31	1.69
Urb-G-029	LUPRANOL 2074	51.10	0.50	99.69	0.31
Urb-G-030	LUPRANOL 2074	46.45	0.65	100.15	-0.15[§]

Appendix C: Hydroxyl values of the glycolysis products and the mass ratio of their polyol

Trial	Glycolysis Agent	Avg. OH value mg KOH/ g Polyol	Standard Deviation mg KOH/ g Polyol	Polyol (wt. %)*	
				LUPRANOL 2074	DEG
Urb-G-032	LUPRANOL 2074	110.15	1.25	93.84	6.16
Urb-G-033	LUPRANOL 2074	55.55	1.35	99.25	0.75
Urb-G-034	DEG	93.40	1.50	95.50	4.50
Urb-G-037	DEG	115.25	8.55	93.34	6.66
Urb-G-038	DEG	97.68	13.57	95.08	4.92
Urb-G-039	LUPRANOL 2074	21.5	0.10	102.63	-2.63[§]
Urb-G-040	DEG	89.60	1.20	95.88	4.12
Urb-G-041	DEG	76.25	2.25	97.20	2.80
Urb-G-042	DEG	95.53	20.83	95.29	4.71
Urb-G-043	DEG	95.20	8.70	95.32	4.68
Urb-G-044	DEG	87.80	1.10	96.06	3.94
Urb-G-045-L	DEG	94.05	0.15	95.44	4.56
Urb-G-045-S	DEG	221.5	12.70	82.81	17.19
Urb-G-046	DEG	81.45	13.55	96.69	3.31

*Assumption made here is that the glycolysis product contains only the glycolysis agent (LUPRANOL 2074 or DEG in this case) and the secondary polyol (LUPRANOL 2074).

§ The reasons for the negative values are explained in 5.2.2 Hydroxyl Value.

Appendix D: FTIR-ATR spectra of the glycolysis products
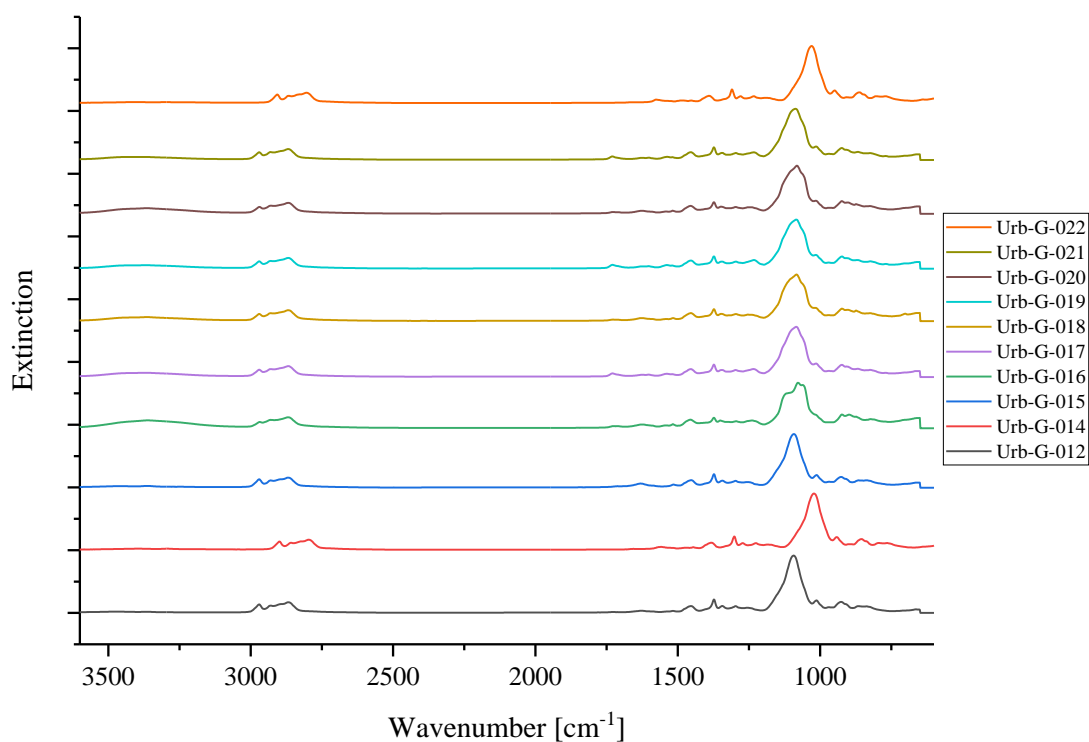
Figure D.1: FTIR-ATR Spectra of the products of glycolysis
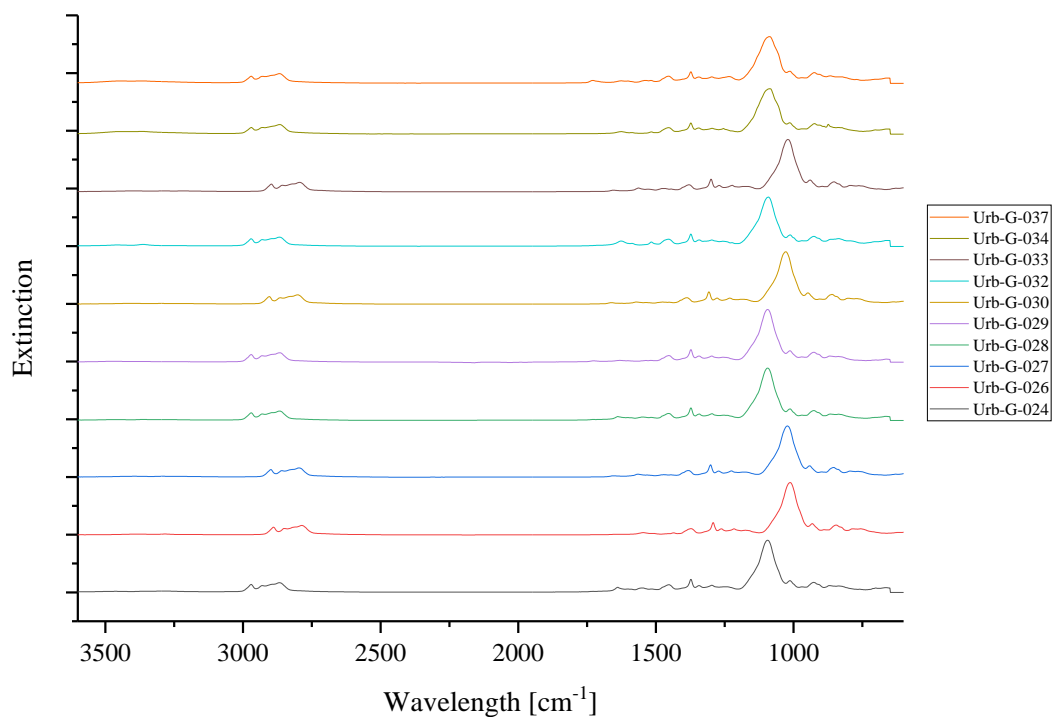
Figure D.2: FTIR-ATR Spectra of the products of glycolysis
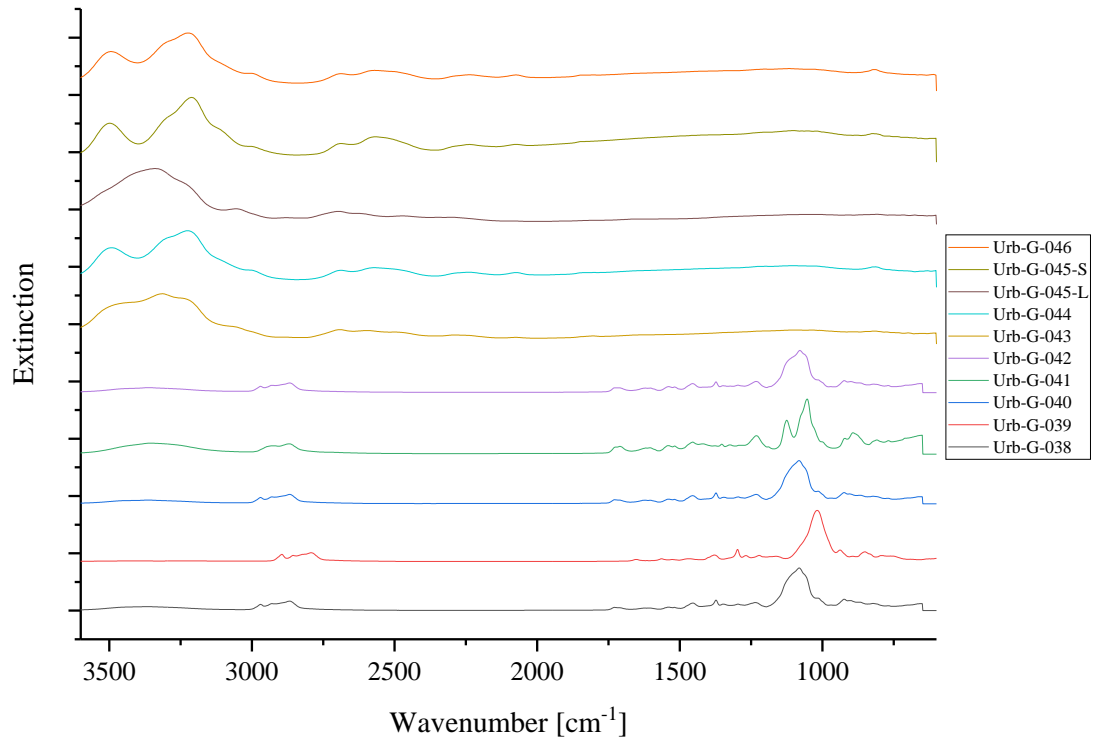
Figure D.3: FTIR-ATR Spectra of the products of glycolysis

Appendix E: Results of the GC-MS analysis for the 2,4-TDA concentration in the glycolysis products

Table E.1: Concentration of 2,4-TDA from the GC-MS measurements

Trial	Glycol	Glycol:Foam	Concentration of 2,4-TDA [mg/mL]
Urb-G-012	DEG	1:1	0.6887
Urb-G-014	Lupranol 2074	1:1	0.3996
Urb-G-015	Lupranol 2074	1:1	0.9032
Urb-G-016	DEG	1:1	1.4525
Urb-G-017	DEG	1:1	-
Urb-G-018	DEG	1:1	2.0115
Urb-G-019	DEG	1:1	-
Urb-G-020	DEG	1:1	1.9701
Urb-G-021	DEG	1:1	-
Urb-G-022	Lupranol 2074	1:1	1.0899
Urb-G-024	Lupranol 2074	1:1	0.9078
Urb-G-026	Lupranol 2074	1:1	1.5521
Urb-G-027	Lupranol 2074	1:1	0.2889
Urb-G-028	Lupranol 2074	1:1	1.074
Urb-G-029	Lupranol 2074	1:1	0.3502
Urb-G-030	Lupranol 2074	1:1	0.4602
Urb-G-032	Lupranol 2074	1:2	3.5656
Urb-G-033	Lupranol 2074	1:2	0.7139
Urb-G-034	DEG	1:1	4.2954
Urb-G-037	DEG	1:2	-
Urb-G-038	DEG	1:1	0.7008
Urb-G-039	Lupranol 2074	1:1	0.0662
Urb-G-040	DEG	1:2	1.1116
Urb-G-041	DEG	1:1	0.9132
Urb-G-042	DEG	1:1	1.1096
Urb-G-043	DEG	1:1	0.7239
Urb-G-044	DEG	1:1	0.7070
Urb-G-045-L	DEG	1:1	0.2112
Urb-G-045-S	DEG	1:1	0.6638
Urb-G-046	DEG	1:1	1.0683

Appendix F: Size exclusion chromatograms of the glycolysis products
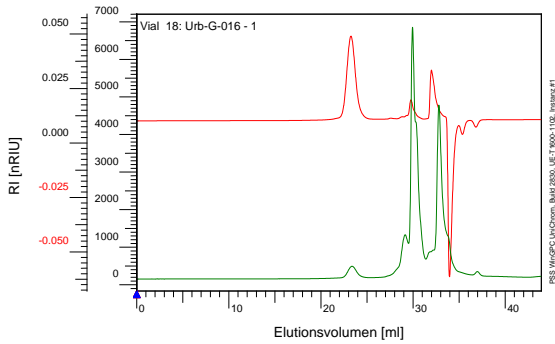
Figure F.1: Chromatogram for Urb-G-016
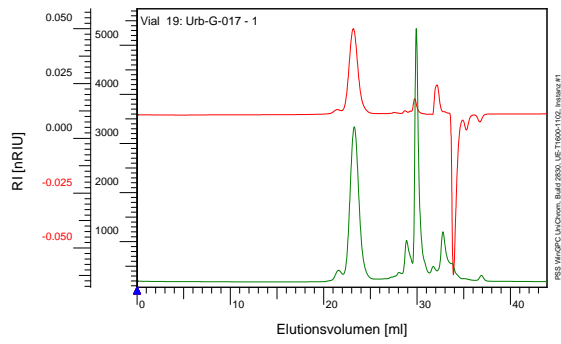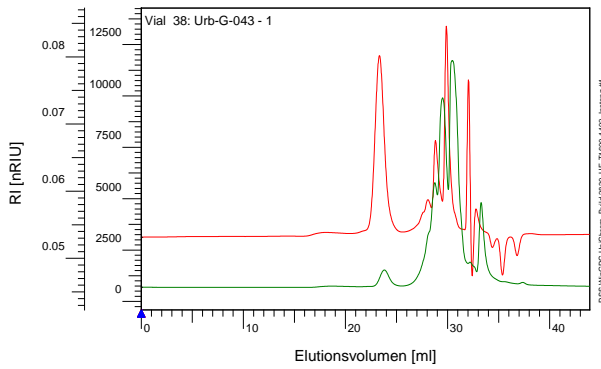
Figure F.2: Chromatogram for Urb-G-017
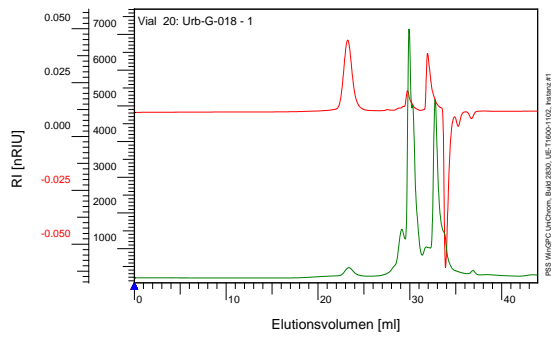
Figure F.3: Chromatogram for Urb-G-018
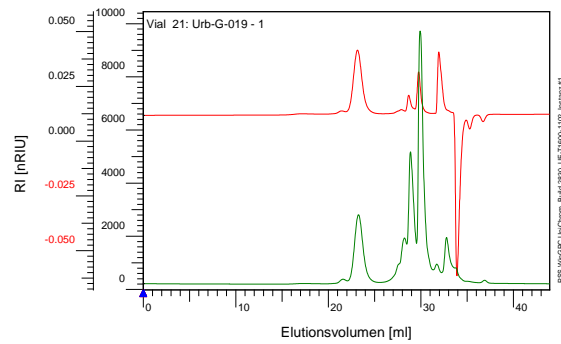
Figure F.4: Chromatogram for Urb-G-019
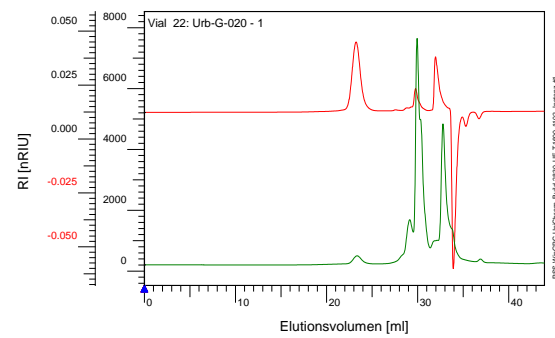
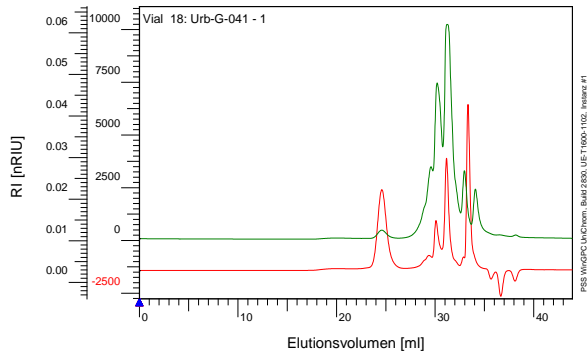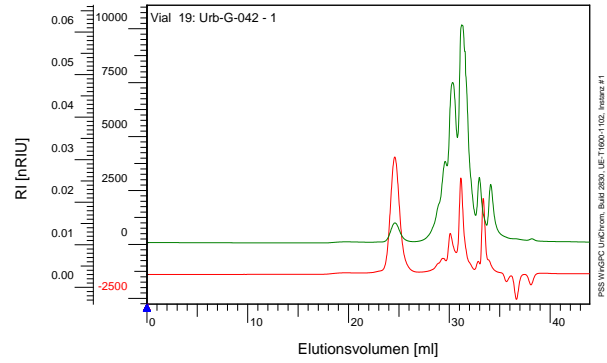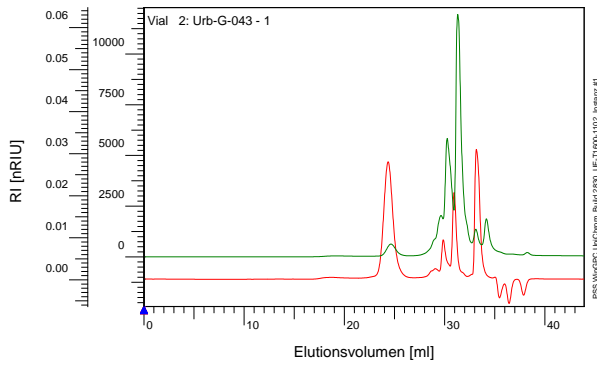**Figure F.5:** Chromatogram for Urb-G-020
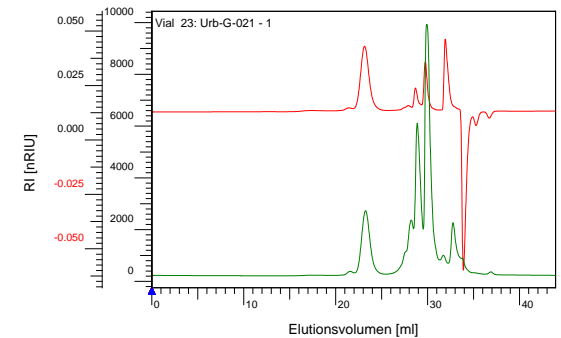
Figure F.6: Chromatogram for Urb-G-021
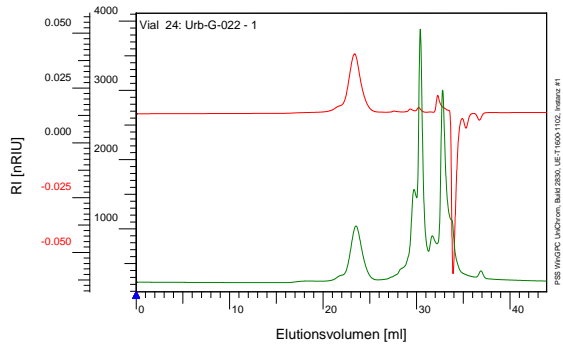
Figure F.7: Chromatogram for Urb-G-022
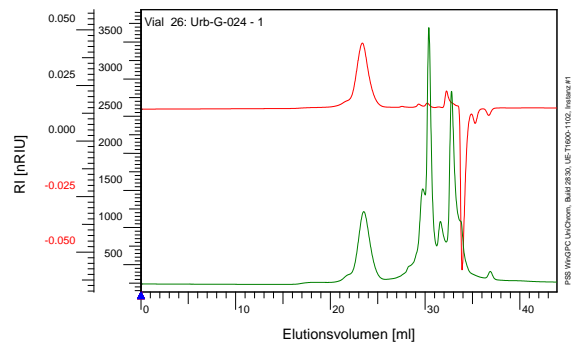
Figure F.8: Chromatogram for Urb-G-024
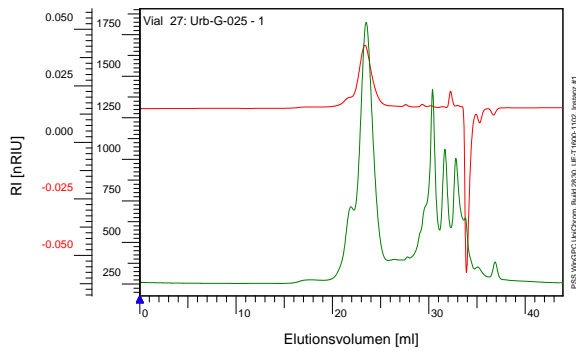
Figure F.9: Chromatogram for Urb-G-025
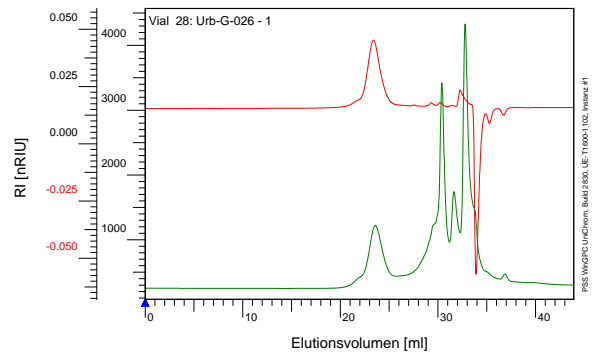
Figure F.10: Chromatogram for Urb-G-026
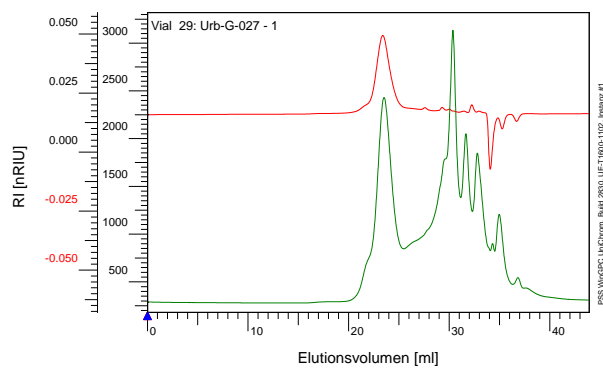
Figure F.11: Chromatogram for Urb-G-027
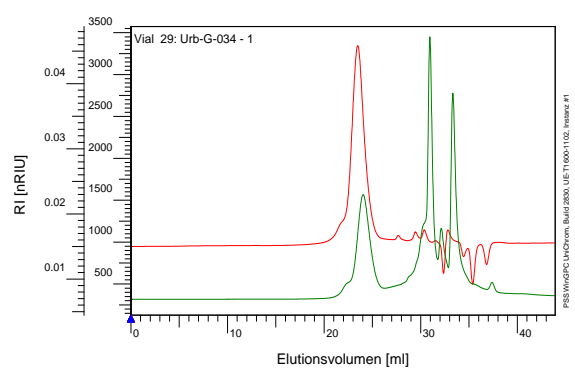
Figure F.12: Chromatogram for Urb-G-028

Figure F.13: Chromatogram for Urb-G-029
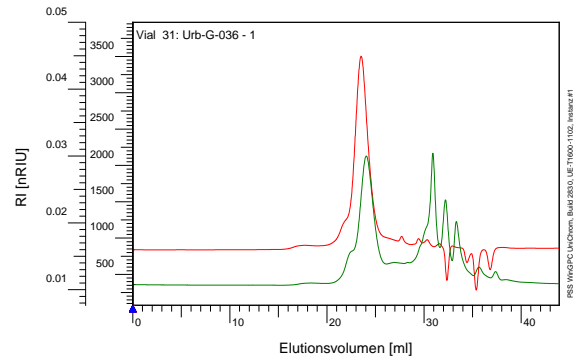
Figure F.14: Chromatogram for Urb-G-030
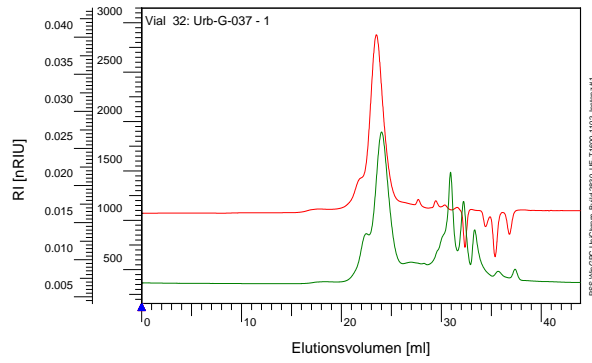
Figure F.15: Chromatogram for Urb-G-031
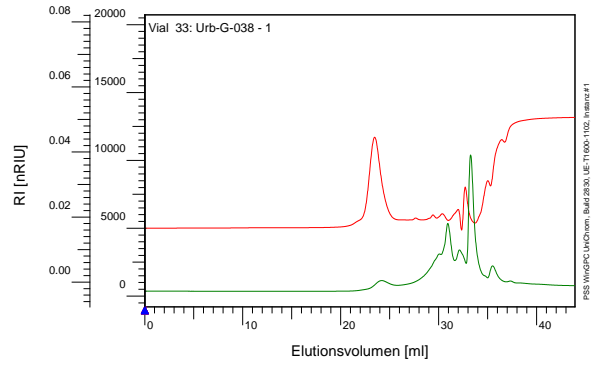
Figure F.16: Chromatogram for Urb-G-032
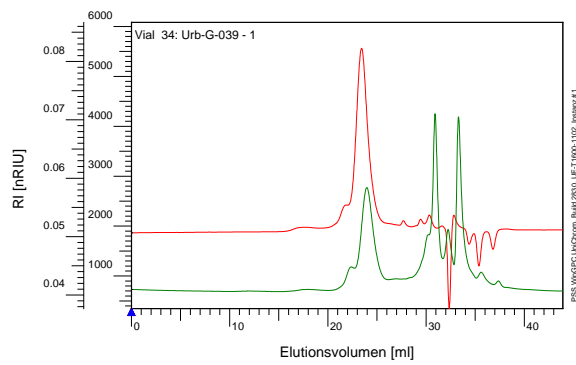
Figure F.17: Chromatogram for Urb-G-033
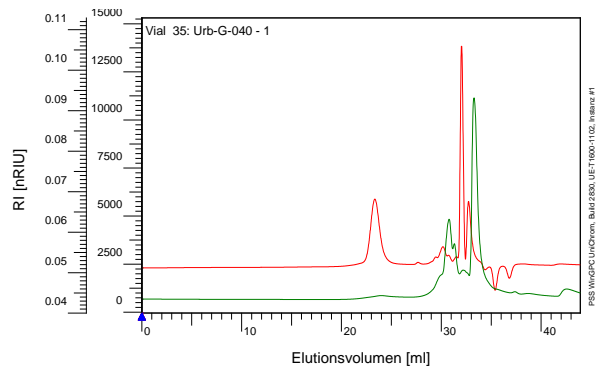
Figure F.18: Chromatogram for Urb-G-034

Figure F.19: Chromatogram for Urb-G-035
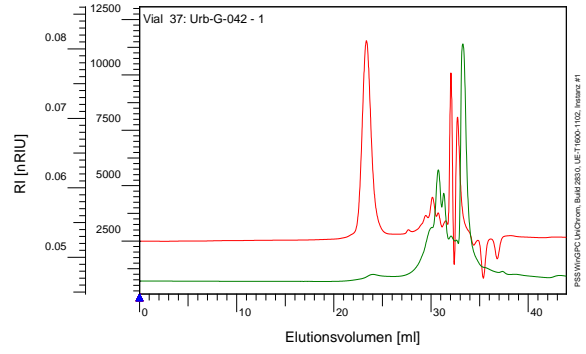
Figure F.20: Chromatogram for Urb-G-036

Figure F.21: Chromatogram for Urb-G-037
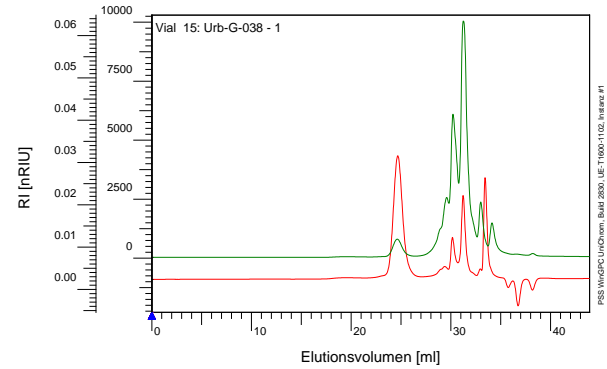
Figure F.22: Chromatogram for Urb-G-038
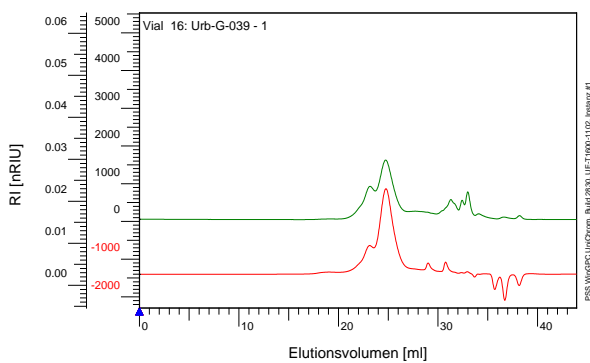
Figure F.23: Chromatogram for Urb-G-039
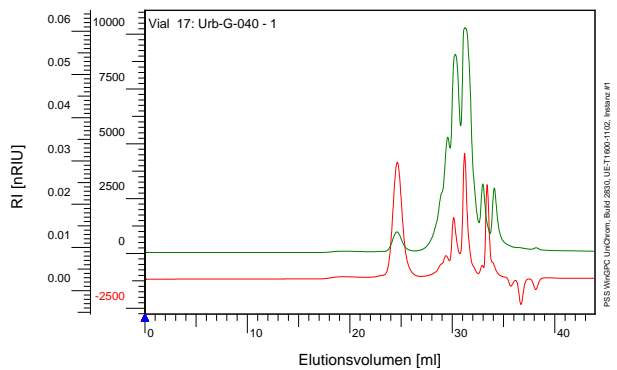
Figure F.24: Chromatogram for Urb-G-040

Figure F.25: Chromatogram for Urb-G-041

Figure F.26: Chromatogram for Urb-G-042

Figure F.27: Chromatogram for Urb-G-043
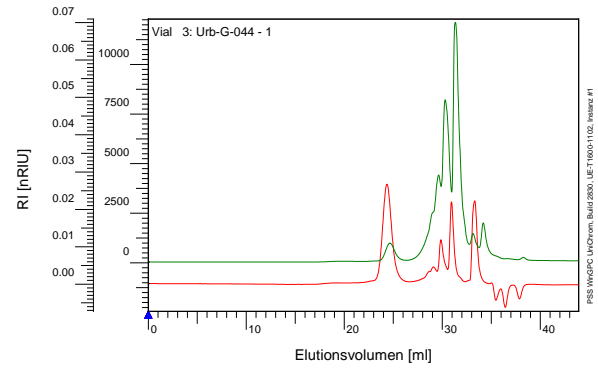
Figure F.28: Chromatogram for Urb-G-044
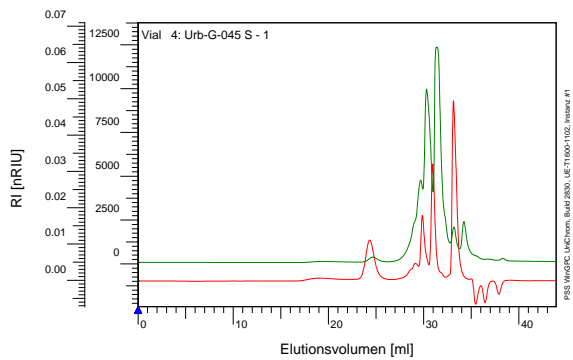
Figure F.29: Chromatogram for Urb-G-045-S
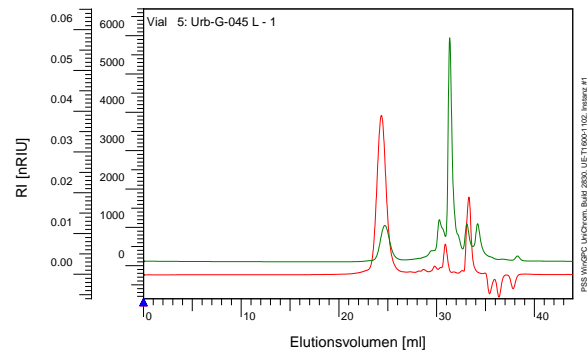
Figure F.30: Chromatogram for Urb-G-045-L

Figure F.31: Chromatogram for Urb-G-046
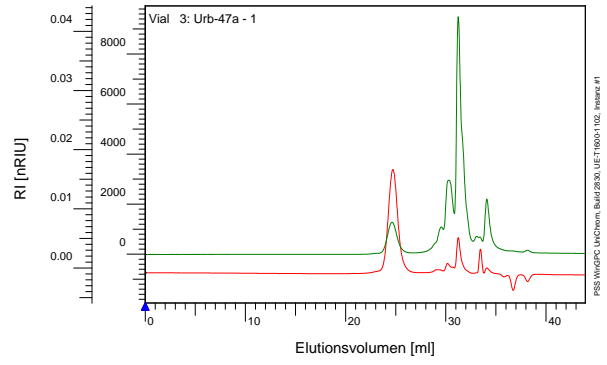
Figure F.32: Chromatogram for Urb-G-047 (before purification)

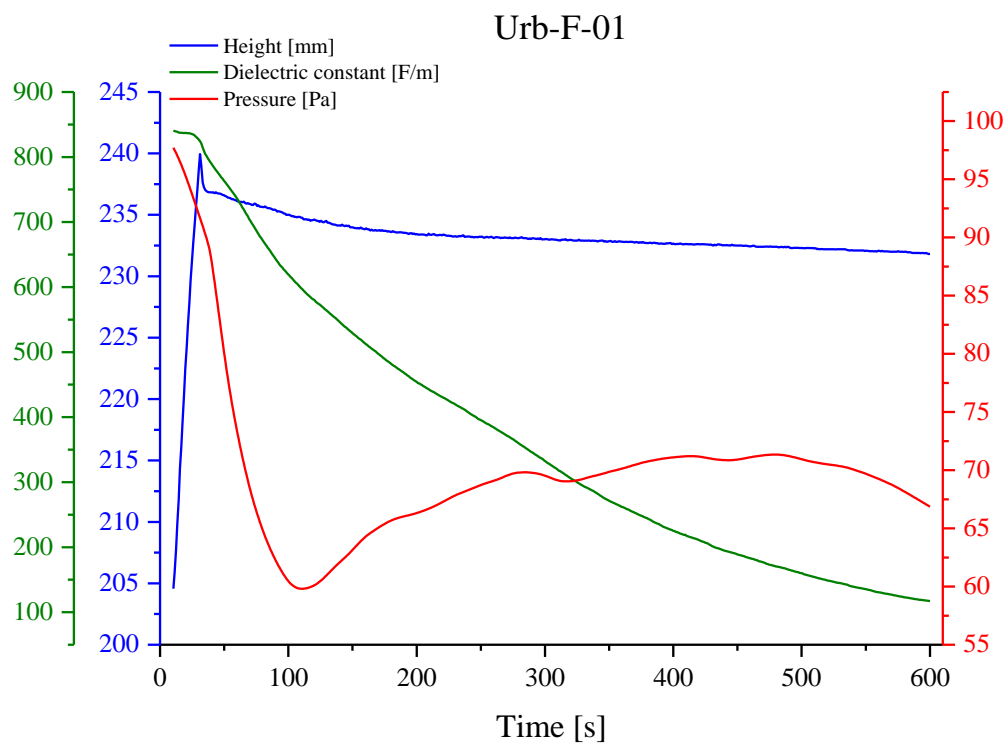# *Appendix G: Height, pressure and dielectric constant v/s time curves for various foam formulations*

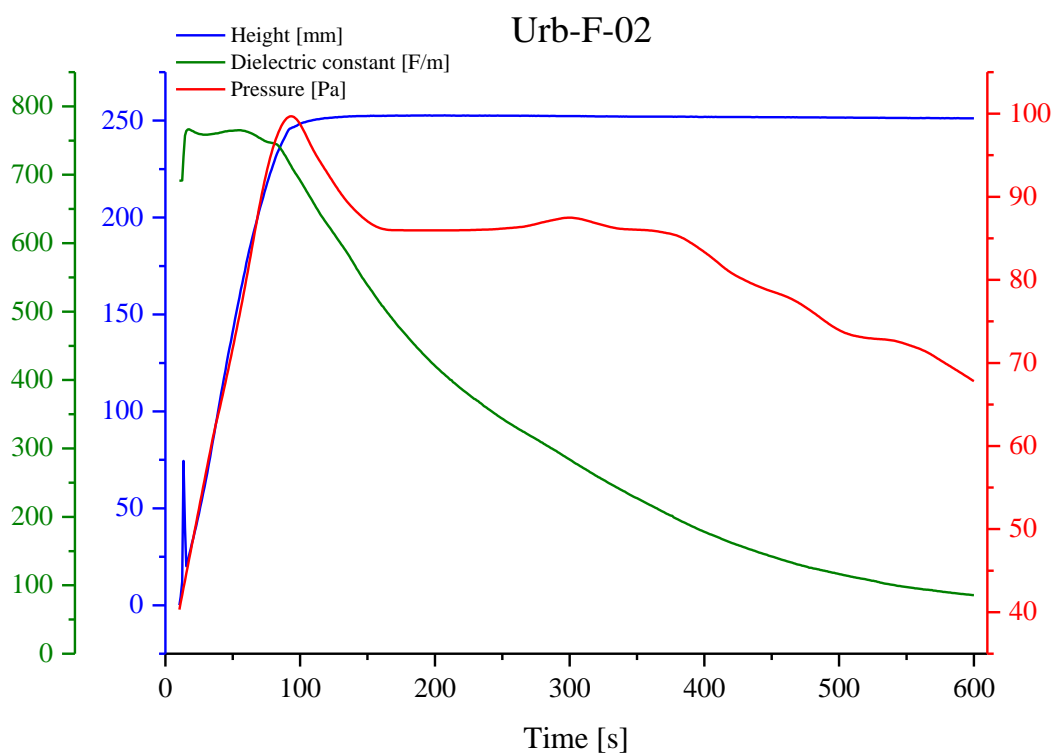**Figure G.1:** Height, Pressure and Dielectric constant v/s Time curves for Urb-F-01

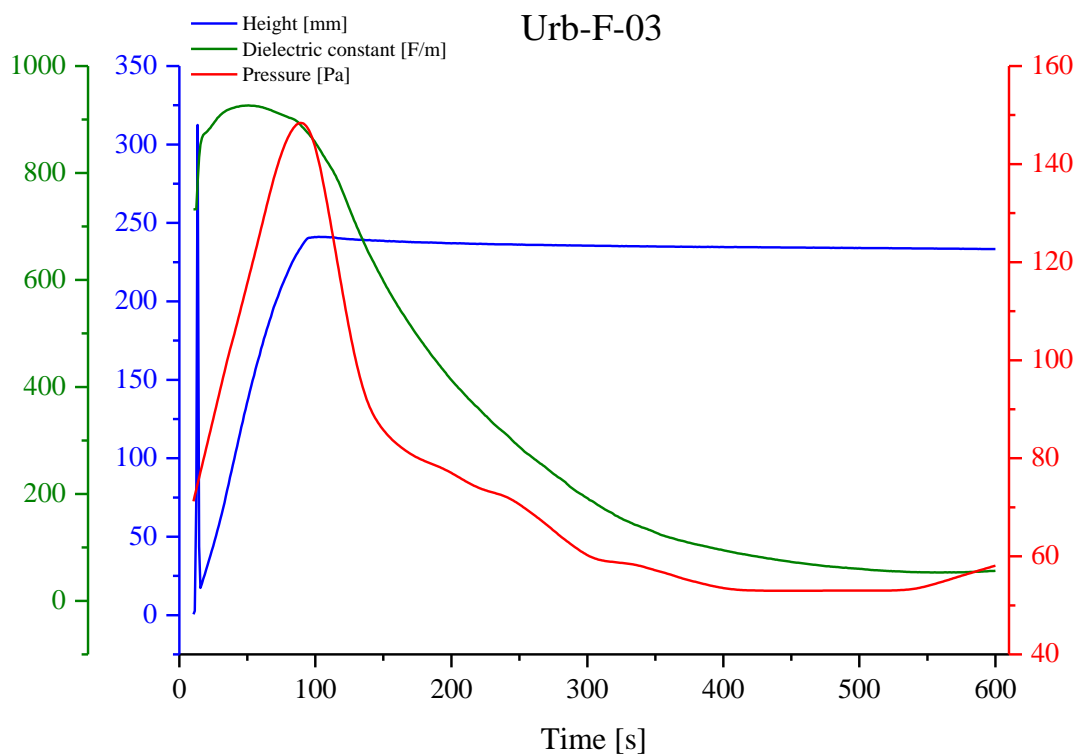**Figure G.2:** Height, Pressure and Dielectric constant v/s Time curves for Urb-F-02

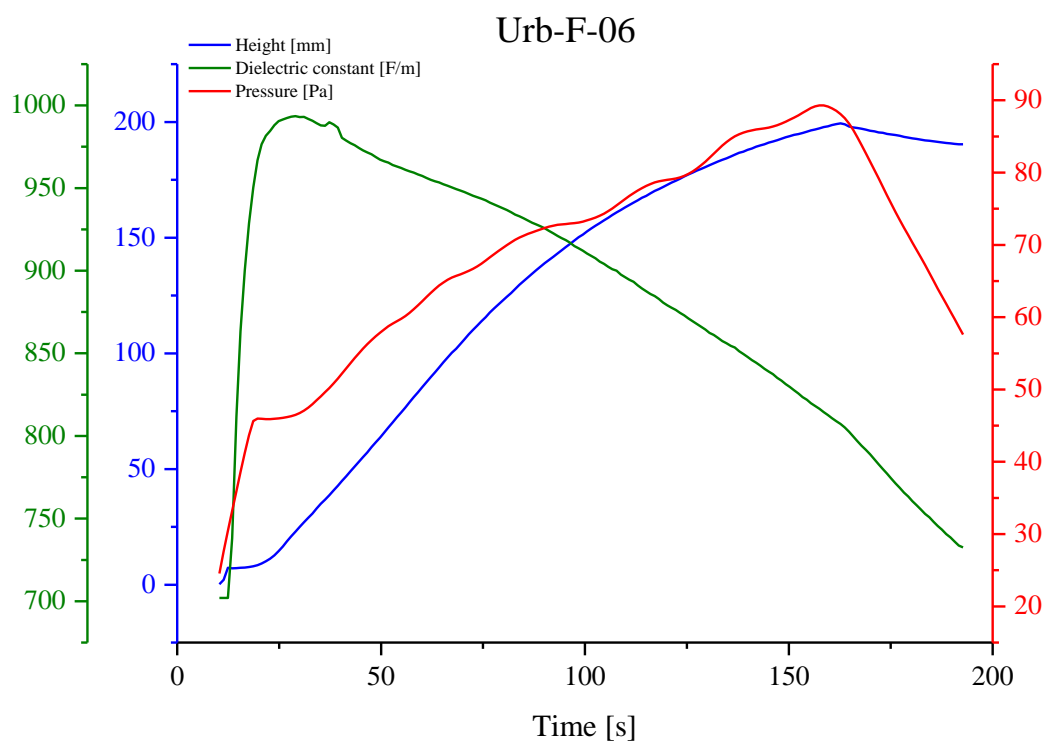**Figure G.3:** Time v/s Height, Pressure and Dielectric constant curves for Urb-F-03

Figure G.4: Height, Pressure and Dielectric constant v/s Time curves for Urb-F-06
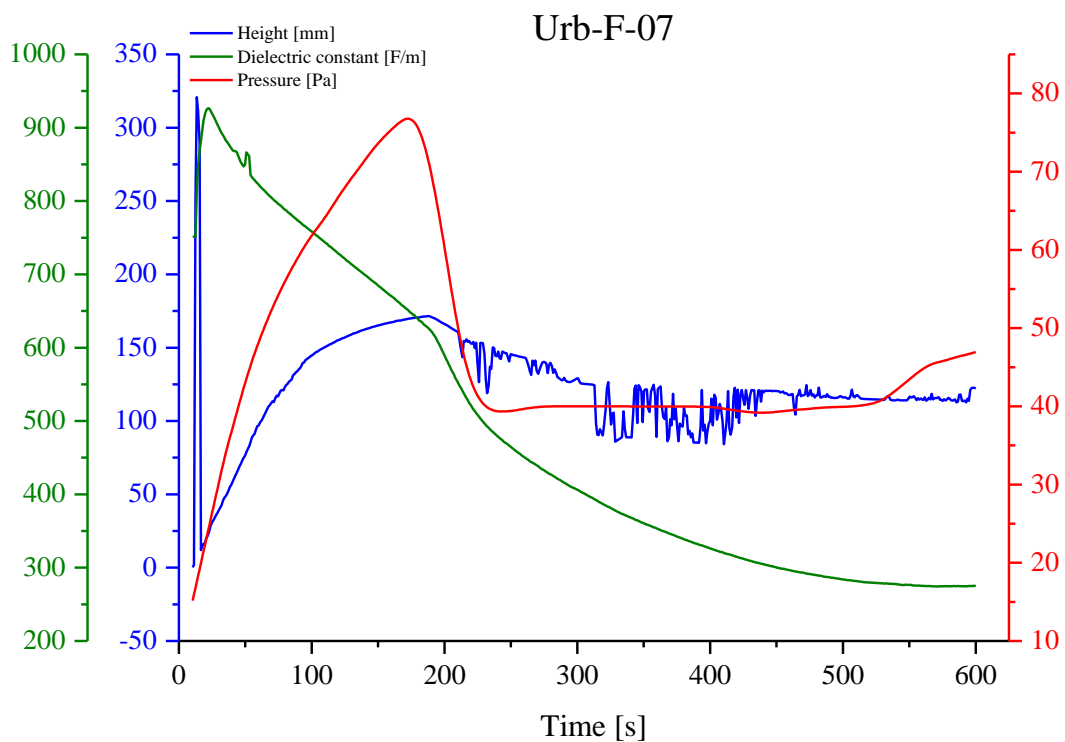
Figure G.5: Height, Pressure and Dielectric constant v/s Time curves for Urb-F-07