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DEPOLYMERIZATION OF FLEXIBLE POLYURETHANE FOAM WASTE VIA "SPLIT PHASE" GLYCOLYSIS USING ZINC ACETATE [$ZN(AC)_2$] FOR ULTIMATE RECOVERY OF POLYOL

By

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ADDIS ABABA UNIVERSITY
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Depolymerization of Flexible Polyurethane Foam Waste Via "Split Phase" Glycolysis using Zinc Acetate catalyst [$Zn(Ac)_2$] for Ultimate Recovery of Polyol

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This thesis has been submitted to the Addis Ababa University with my approval as the University advisor.

Advisor:

Dr. Beteley Tekola _____

Signature

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ABSTRACT

Polyurethanes find wider range of application, in many industrial sectors. This results generation of bulk of waste which affects the environment in many aspects of pollution. Amongst many techniques, chemical recycling is most preferred to carry out the recycling of PU waste scrap because of its ability to yield recycled polyol that can be used as an alternative to the virgin polyol. For this study one of chemical recycling approach, which is glycolysis specifically "split phase glycolysis" was chosen as a method that allows recovering a polyol with related quality and property of the virgin polyol. The recovery process goes through on by using ethylene glycol as a solvent and zinc acetate Zn $(Ac)_2$ as a catalyst by considering parameters like, temperature, catalyst loading and decomposition time. Then, two phases are obtained: an upper phase which contains the recovered polyol and, a bottom phase which includes sub-products of the reaction with the excess of glycol. Finally, properties such us hydroxyl value, viscosity, amine value, acid value and water content of the recovered polyol were analyzed in considering of "ASTDM" and compared with that of virgin polyol. Based on that hydroxyl value of (144.3mg KOH/g), viscosity of (276.208cps), total amine value (10.878mg KOH/g), then moisture content (1.74%) and acid value of (0.012mg KOH/g); at a temperature 190 ^{0}c, catalyst load of 2% and reaction time of 2hr were found as best result of the recovered polyol properties lied under the standard range of virgin polyol.

Keywords: Chemical Recycling, Glycolysis, Polyurethane, Polyol

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LIST OF ACRONYM

ASTDM	American standard titration method
CASEs	Coating, Adhesives, Sealants and Elastomers
CFCs	Cloro floro carbons
DEG	Di-ethylene glycol
DMCHA	Dimethyl-cyclohexyl amine
DMEA	Dmethyl-ethnol amine
DPG	Di propylene glycol
EG	Ethylene glycol
FTIR	Fourier transform infrared spectrometry
GPC	Gel permeation chromatography
MDI	Diphenylmethane
MEG	Mono ethylene glycol
MPG	Mono propylene glycol
MW	Molecular weight
PET	Polyethylene teraphitylene
PPG	Poly propylene glycol
PU	Polyurethane
PUF	Polyurethane foam
PUR	PR
TDI	Tolune di-isocyanate
TEDA	Tri-ethylene diamine
VPO	Vapor pressure osmometry

1. INTRODUCTION

1.1. Background

Polyurethanes (PUs) are one of the most common families of polymers. Polyurethane foam is an innovation by Otto Bayer in 1937 G.C. Now a day, it is found to be the best substitute for the rubber because of its versatile properties (Ron, 2004). In fact, polyurethane is the 6th most used polymer all over the world with production of approximately 18million tons per year (Ortel.G, 1985). They are essentially different from most other plastics in that there is no urethane monomer and the polymer is almost invariably created by the exothermic reactions between alcohols with two or more reactive hydroxyls (-OH) groups per molecule (diols, triols, polyols) and isocyanates that have more than one reactive isocyanate group -NCO- per molecule (diisocyanates, polyisocyanates) (Bayer.AG &Yantai Wanhua, 2015).

The variety of polyurethane products reaches from flexible and rigid foams over thermoplastic elastomers to adhesives, paints, and varnishes which are produced with different formulations depending on practical considerations (Mohammadi, 2009). Flexible polyurethane foams make up roughly 37% of the global consumption of such products. The global market outlook forecasts that their use is expected to increase by 10 million tons by the coming years. The main characteristic of flexible PUs is their open cell microstructure that results in densities ranging from 13 to 80kg.m^{-3} (Lucas, 2005).

There is the extensive industrial use of polyurethane polymers due to their commercial success. The production thereof is accompanied by a considerable accumulation of waste or scrap polyurethane polymer, particularly polyurethane foams. A very large quantity of polyurethane foam scrap is generated by slab stock manufacturing or industrial plants involved in the manufacture of articles which employ foam as cushioning element (Aguado et al., 2005). These scraped polymers are generally disposed by techniques including incineration or landfill. However, such disposal techniques, besides representing an environmental pollution problem, have an economic loss associated with the land required for

landfill and due to their non-bio-degradable nature and the costly materials used in the preparation of the foam (Borda J, 2000).

It is therefore of interest to consider the recovery and eventual recycling of such materials. Many scientists have dedicated their research to finding the most sustainable route of recycling of polyurethane foam waste mainly includes physical as well as chemical methods. The physical recycling of polyurethane is mainly working on the principle of rebonding and regrinding technologies (Modesti, M., 1998), but the resultant recycler leads to an adverse change in mechanical properties of new products, so chemical recycling of method was a preferable approach on previous works. Chemical depolymerization of polyurethanes may be achieved by processes like hydrolysis, aminolysis, and glycolysis (Datta & Janusz, 2010).

Among all available techniques, a route of glycolysis the most advantageous chemical recycling method, involves mixing polyurethanes and/or polyurea-polyurethane products with compounds containing at least two reactive hydroxyl groups and reaction facilitating catalysts (Chao-Hsiung Wua et al., 2003). In glycolysis, substances reacted to produce a liquid product comprising a mixture of compounds containing hydroxyl end groups, i.e. a recyclate polyol. The recyclate polyol can be employed alone or in combination with virgin polyols to prepare polyurethane compounds preferably foams but may also be used in various polyurethane, polyurea-polyurethane and poly-isocyanurate applications (Behrend &Naber, 2009).

1.2. Statement of the Problem

Polyurethanes are used in so many diverse applications and industrial uses. Unfortunately, as like the other man-made synthetics, the darker side of this glowing industry is the saturation of several hundred tons of polyurethane waste daily across the world, includes post-consumer wastes such as used in car cushioning, outdated panels and as an insulator for refrigerators. (ZOPE, 2010). Similarly, a huge volume is accumulated during the production period. For instance, 10-30% by weight of total polyurethane foam production is disposed of as a scrap during block production, which requires subsequent cutting (Haghshenas, 2006). This not only represents an economic loss but also poses an environmental pollution problem.

Incineration and landfilling mechanisms were taken as common disposal techniques for a long period of time to dispose such wastes. But because of small polyurethane foam plastic pile-up density, the spatial volume to weight requirements is accordingly enormous (Nikje, 2011). So, the disposal of the wasted foam scrap carried out in a land-fill type operation is a serious waste of land resources. And which also affects adversely the ecology of surroundings (Ron, 2004). Similarly, the options of burning polyurethane scrap could not be accepted, it may release oxides of nitrogen, hydrocyanic acid, carbon dioxide and other toxic materials into the atmosphere (Alavi Nikje, 2011). In addition to this, polyurethane materials are derived from natural resources like petroleum, they are scarce and not easily replaceable (Ramesh & Lee, 2004).

The physical recycling of polyurethane mainly involves rebonding and regrinding technologies, but the resultant recycler leads to an adverse change in mechanical properties of new products (JADHAV, 2010). As compared to hydrolysis and aminolysis, glycolysis is the most advantageous and commonly recommended chemical recycling method due to process simplicity, high polyol yield, applicability for many types of polyurethanes, robustness and tolerance too many impurities, etc. Different types of catalysts have been tested aiming for high PU conversion and recovery of a polyol with best properties of which, zinc acetate had shown superior activity and selectivity towards polyol with best properties (Santos & Carone, 2013).

1.3. Objectives

1.3.1. General objective

The general objective of this research is to catalytically de-polymerize flexible polyurethane foam wastes via split-phase glycolysis for ultimate recovery of polyol.

1.3.2. Specific objectives

The specific objectives are:

- To de-polymerize flexible polyurethane foam wastes via glycolysis into polyol in presence of zinc acetate($Zn(Ac)_2$) catalyst
- To investigate the main and interaction effect of important operating conditions (i.e. temperature, time and concentration of catalyst), on the recovered polyol properties.
- To determine the optimal operating conditions that gives a polyol with property similar to virgin polyol.
- to characterize the recovered Polyol by determining; Hydroxyl value, Viscosity, Total amine value, Acid value and moisture content.
- To synthesize a polyurethane foam block using a recovered polyol at optimal operating conditions before and after purification and check its foamability.

1.4. Significance of the Study

The growing demand for polyurethanes in diverse applications ends up in the release of large quantity of waste polyurethane foam in the solid waste stream. This can cause great environmental pollution problem and indirectly contributes for scarcity of natural resources as discussed on problem statement. This fact has brought the polyurethane foam waste treatment as a necessary issue, engaging the attention of the scientific and industrial world.

Generally this paper aims on de-polymerization of flexible polyurethane foam wastes to recover polyol by using one of chemical recycling technique "split-phase glycolysis. The conversion of waste to raw monomers is relatively high. By the end of this work it is expected to that the discoveries/outcomes of this investigation can play a big role in:

- Initiating future researches in the field,
- Awareness creation to government, industries and society about recovery process of this valuable material "polyol" maintaining natural resources and their well binges
- Diminishing the quantity of foam waste disposed in landfill
- Enhancing the sustainability for forthcoming generations.

As it is associated to lowering of the environmental impacts that PU waste could impose and also relieves exploitation of virgin natural resources. The consumption of recovered polyol is a win-win for it is economical and environmentally safe. In Ethiopian context problem related to accumulation of polyurethane foam waste does not seems serious issue currently, because of lower consumption of this product all over the country. But in the near future production and use of PU product becomes higher and higher and it leads to releasing of huge volume of waste. So, adaptation of chemical recycling approach will be necessary and option less because of many reasons discussed earlier.

1.5. Scope of the study

The scope of this study is recycling of flexible polyurethane foam waste through split phase glycolysis methodology using catalyst [Zinc Acetate $Ac(Zn)_2$] and ethylene glycol as a solvent to recover valuable chemical called polyol, which is raw material used for foam production. Beyond this the effects of parameters i.e., temperature, time and catalyst to solvent ratio on the recovered polyol basic property like hydroxyl value, viscosity, total amine value, moisture content and acids value was analyzed. At the final sample foam block was synthesized using the recycled chemical to check the viability of the recovered polyol.

2. LITERATURE REVIEW

2.1. Polymeric Foam

Polymeric foam is a plastic produced by dispersion of a gas in a polymer matrix. It generally consists of a minimum of two phases, a solid polymer matrix and a gaseous phase (blowing agent). Polymeric foams may be either expanded rubbers or cellular elastomers or sponges. Foam is a colloidal suspension of a gas in a liquid created by agitation. Foams are cushiony materials formed by the creation of gas bubbles in a base material such as natural rubber, synthetic rubber or other elastomeric materials (Szycher, M, 2002).

Polymeric foams may be flexible, semi-flexible (or semi-rigid) and rigid, depending on chemical composition and the rigidity of the resin used as a matrix and the type of cross linking that exists between the molecules. The matrix is made up of the base resin and other compounding ingredients that may include plasticizers, stabilizers, surfactants, dyes and pigments, fire retardants and fillers. The composition of the plastic matrix plays an important role in determining foam properties such as chemical resistance, thermal stability, flammability, specific heat, transition temperature and rigidity. With respect to the base resin of the matrix, plastic foams may be either thermoplastic or thermosetting (Ramesh & Lee, 2004).

Thermoplastic foams are based on linear or slightly branched (non-cross-linked) polymers and thus have properties normally associated with thermoplastics. The polymerization of the base resin is generally completed first and they exhibit a definite melting range and are generally susceptible to attack by organic solvents. It is used in thermal insulation for walls, roofs, ceilings and perimeter (Szycher, M, 2002). In contrast, thermosetting foams the matrix of these foams is based on cross-linked polymers so that, like the bulk plastics from which they are derived, they have generally good resistance to solvents and most chemicals. They do not usually exhibit a melting range and can often be used at higher temperatures than thermoplastic foams (there are exceptions). It includes like, Polyurethane has very high thermal resistance for given thickness, low water absorption and low water vapor permeability; good thermal stability and good adhesion (Efstathiou &Kypros, 2014).

2.2. Polyurethanes

Polyurethane (PU) stands for an important group of products within the big family of polymers or plastics. PU is one of the larger polymer product groups within the thermoset plastics family. Polyurethane, usually referred to as PU, is actually another name or generic name for the family of chemicals known as the urethane polymers, which are composed of two principal raw materials: isocyanates and polyols (Oertel. G. 2000).

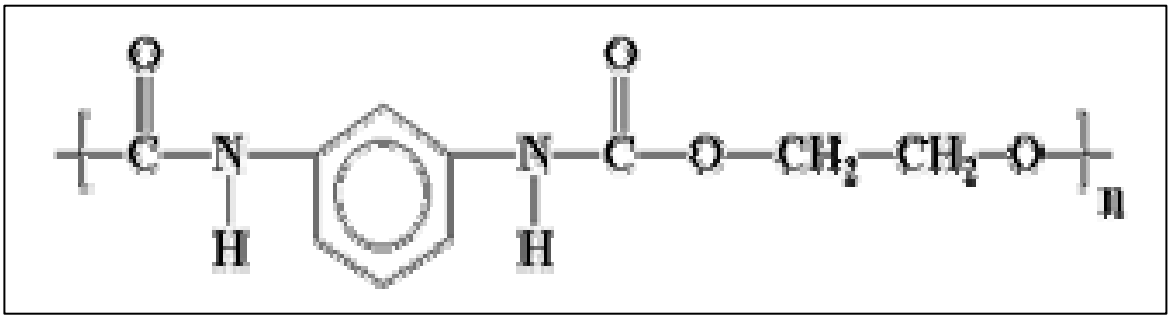


Figure 2.1: Chemical structure of typical polyurethane

It is formed by reacting a polyether or polyester polyol as a hydroxyl-containing monomer (a polymeric alcohol with more than two reactive hydroxyl groups per molecule), such as poly (propylene glycol) (PPG) or poly (tetramethylene glycol) (PTMG), with diisocyanate or a polymeric isocyanate, e.g., diphenylmethane diisocyanate (MDI) or toluene diisocyanate or (TDI), in the presence of suitable catalysts and additives, especially chain extenders (Akindoyo et al., 2016).

R–NCO + OH–R → R–NH–COOR---------- (2.1)

Isocyanate group Alcohol group Urethane form

Source: (Nikje & Nikrah, 2007)

2.2.1. Types of Polyurethanes and their applications

Depending on the polyol and isocyanate employed in the reaction it is possible to obtain a huge variety of PU specialties. From application point of view, polyurethane can be classified in foams (Flexible and Rigid) and in the denominated CASEs (Coatings, Adhesives, Sealants and Elastomers).

2.2.1.1. Flexible polyurethane foam

Among all PU products, flexible foam is the largest product family by quantity covers over 50% of the total world foam production. This foam is formed by the reaction of the di-isocyanate and the long chain diol. They have a low polarity as they have a very low density of urethane groups. Flexible polyurethane foams are of two types' low and high density flexible polyurethane foams (Krueger et al., 2003). The range of density is between 10-80 kg/m ^{3} for low density flexible polyurethane foams. Flexible foams had relatively low load bearing properties but high recovery properties when compared to semi-rigid and rigid foams. Generally, they show higher tensile strength and elongation at break (Akindoyo et al., 2016).

In addition, flexible polyurethane foams can be made in either slab stock or molded form. In slab stock production, large slabs were made in a long and continuously pour lasting for an hour or more. The dimensions of the slab stock foams depend on the end usage. During the foaming operation, the cell walls rupture and the polymer material retracts to form a web of elastic bands creating cell structure. This elastic web structure is what makes flexible polyurethane foams such excellent cushioning materials. Properties of flexible polyurethane foams can be controlled through a series of parameters. Flexibility (elongation) depends on the degree of crosslinking, which can be adjusted via the choice of starting materials (Kirk-Othmer, 2001). Flexible slab stocks are used for upholstered furniture, mattresses, vehicle trims, textiles and other applications.

2.2.1.2. Rigid polyurethane Foam

Rigid polyurethane foams are derived from highly functional starting materials; therefore, they are densely cross linked and have high strength. They consist of a high percent of closed cells and have unique characteristics such as they can be prepared at temperature without heating, adhere to many kinds of materials such as steel, wood, thermosetting resins and foams, and fibers. The foam density can be varied in a wide range. They are resistant to petroleum, oils and other non-polar solvents.

It significantly cuts fuel and construction costs while making commercial and residential properties safer, better utilized and more comfortable around the globe (Akindoyo et al., 2016). The isocyanates used are generally polymeric MDI types (PMDI) with functionalities of 2.6 to 2.8. The main constituents of the polyol component are short-chain polyols with 2 to 8 hydroxyl groups. Their density determines the mechanical property level of rigid polyurethane foams. The flame retardancy of the rigid polymer foams can be considerably improved by increasing the equivalent NCO/OH ratio. (Efstathiou & Kypros, 2014).

Rigid foams can be used inside the metal and plastic walls of most refrigerators and freezers or behind paper, metals and other surface materials in the case of thermal insulation panels in the construction sector. They also have a wide application range in the automotive industries where they are used in dashboards, exterior parts of a car like bumpers and fenders, between the doors of a car etc. They are also used in ship-building and packaging. Versatile rigid PU foam is even used in horticulture, in furniture and sports equipment, in solar technology and also for rock consolidation in mining and civil engineering (Boustead, 2005).

2.2.1.3. Coatings, Adhesives, Sealants and Elastomers

There is a growing range of applications and advantageous markets that may be derived from the use of PUs as coatings, adhesives, sealants or elastomers (CASE). This is because PUs often reveals excellent and versatile mechanical, chemical and physical properties. PU adhesives can offer good bonding properties, whereas very tight seals may be obtained from PU sealants. For a PU to be suitable for coating applications, it needs to possess good adhesive properties, high chemical resistivity, excellent drying, low temperature flexibility and adequate scratch resistivity (Leitsch, 2016).

PU elastomers are another type of important materials, which may be used for a variety of useful application, such as shoe soles, household items, surfboards, goggles and ski boots. They may be fashioned into a wide variety of shapes, colors and design. They are lighter compared to metals, and can provide highly desirable stress recovery properties as well as can withstand several environmental factors. Although they have an elastic property, they also possess some degree of plastic nature (Prisacariu, 2011).

2.2.2. Polyurethane Foam application based on their type

In recent years the PU is one of the most versatile polymers in the modern cellular plastics industry. The majority of PUs is used in the production of flexible foams (≥31%), followed by rigid foams (25%), elastomers (>7.8%) and also used for specialty applications to an extent of 16.2% in the form of coatings, fibers, adhesives, caulks, sealants, etc. Versatility of polyurethanes comes from the unique synthesis of them, which is owned to the reaction of a range of isocyanates as well as a wide range of polyols. With a diverse range of high-performance properties, they are essential to a multitude of end-use applications (Ron, 2004).

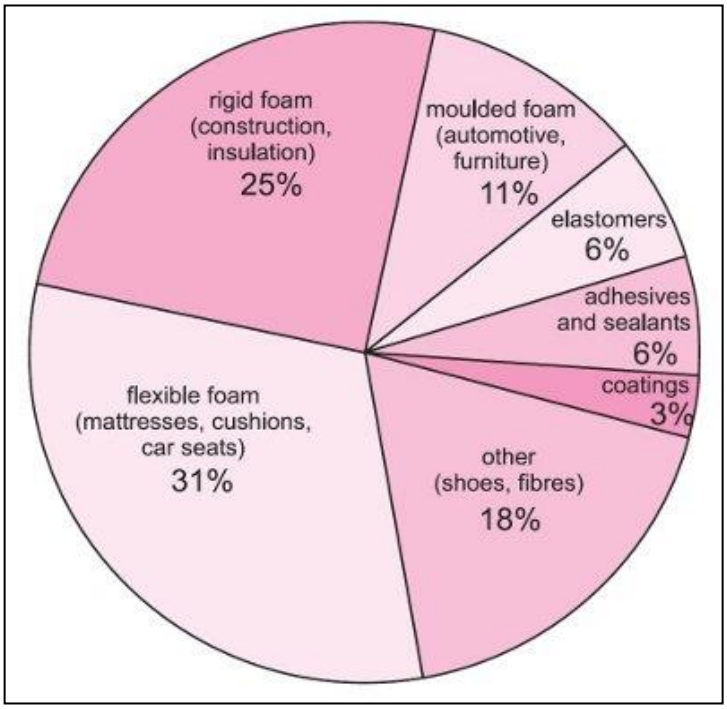


Figure 2.2: PU application based on their type, source (Rodríguez, 2013)

2.2.3. Properties of Polyurethane

Polyurethane properties are mainly depending on the type of PU foam making raw materials, foam formulations and produced foam type. Some of general polyurethane foam properties are discussed here and several physical and chemical properties of PU materials are listed in Table 2.1 and 2.2

Common properties of polyurethane foam

- High Load Bearing Capacity
- Abrasion and Impact Resistance
- Flexibility
- Tear Resistance
- Resistance to Water, Oil & Grease
- Strong Bonding Properties
- Performance in Harsh Environments

Table 2.1: Physical properties of PU

Property	Value	Type of PU	Reference
Density	20 kg/m3 32.2 kg/m3 39.0 kg/m3 1120–1240 kg/m3	PUR foam PUR foam HFC PUR foam HFC PUR elastomers	(Elomaa, 1999)
Specific heat	1400 J/kg K	PUR foam	(Bayer, 2015)
Flash ignition temperature	310 °C	Rigid foam	(Bayer, 2015)
Melting point	204 – 232°C	PUF foam PU elastomers	

Table 2:2: Chemical properties of PU

Property	Value	Type of PU	Reference
C, H, N S, O + ash (diff.)	63.9, 8.3, 1.6 %-wt. 0, 26.2 %-wt.	PU – based adhesive	(Zieliński, 2006)
Moisture (as received) Volatiles (dry) Ash (dry) Fixedcarbon(diff.) (dry)	1.8 % wt. 88.2 % wt. 11.5 % wt. 0.3 % wt.	PUF foam	(Bayer, 2015)

2.3. Polyurethane structure and production chemistry

2.3.1. Micro structure of PU

A broad spectrum of properties gives polyurethanes their versatility. This broad spectrum of properties is achieved by the appropriate selection of polyols and additives. Variations of the chain length and the degree of branching or crosslinking determine the molecular structure of polyurethanes. Crosslinking takes place both chemically (triols, polyfunctional isocyanates) and physically by phase separation into generally amorphous urea rigid segments and flexible polyol segments (Ionescu & Mihail, 2005). This structure is characteristic of flexible polyurethane foams. Rigid and flexible polyurethane foams, they do not only differ in molecular structure but also in the type of foam cell structure (closed cell or open cell).

Open-cell structure foam contains pores, which are connected to each other to form an interconnected network. This kind of foam has a comparatively lower density and a sponge-like appearance. Open cell foams have sound absorbing properties and, when flexible, cushioning characteristics.

Closed-cell structure foam does not have a network of connected cells. It is a solid foam material. Normally this kind of foam has higher compressive strength due to its structure. This kind of foam has a higher dimensional stability, absorbs less moisture and has higher strength when compared to open-cell foam. Its structure makes it have a harder surface feel and makes it better at absorbing impacts (Krol & Piotr, 2007).

2.3.2. Chemistry of PU

The basis of polyurethane chemistry is the high reactivity of isocyanates. The reactivity of the isocyanate group can be contributed to the positive charge of the carbon atom in the cumulated double bond system of its N=C=O group. The electron deficiency on the carbon explains the reactivity of isocyanates towards nucleophilic attack, therefore most reaction take place across the C=N bond. When the isocyanate group (NCO) reacts with alcohols, amines, carboxylic acids and water, urethane, urea and amide linkages are formed. In general, in polymerization reaction of polyurethane foam there are two basic reaction stages these are Blow reaction and Gelation reaction (Randall & Lee, 2002)**.**

Blow reaction

Reaction of Isocyanates with Water

The first step of the blow reaction involves the reaction of an isocyanate group with water to yield a thermally unstable carbamic acid which decomposes to give an amine functionality, carbon dioxide, and heat. And this reaction of isocyanates with water is accelerated by the addition of catalysts such as acids, bases (tertiary amines) and metal complexes (Organo tin compounds).

Carbon in the isocyanate group is sandwiched right between two electronegative atoms, oxygen and nitrogen. The water has two lone pairs of electrons and donates this pair of electrons to carbon. The amine will immediately react with another isocyanate to form symmetric urea. Catalysts are also used for this reaction because water tends to be very insoluble in isocyanates such as MDI and TDI (G).

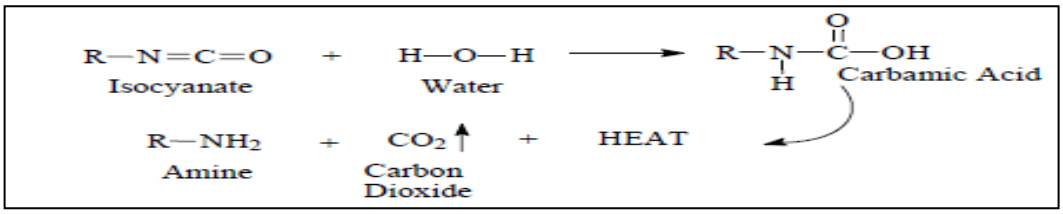


Figure 2.3: First Step of the Blow Reaction. Source (Gist, Double, 2013) .

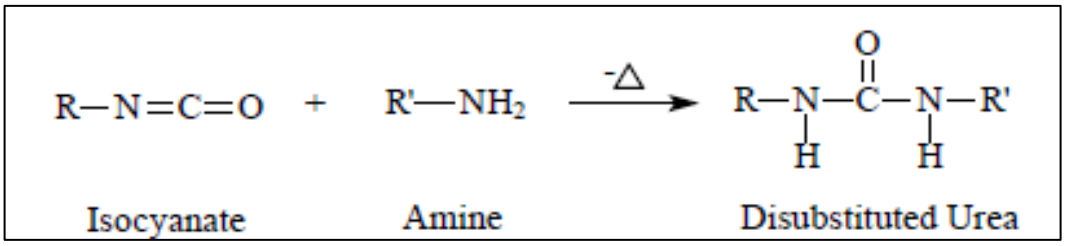


Figure 2.4: Second step of blow reaction.

The newly formed amine group reacts with another isocyanate group to give a di substituted urea and additional heat is generated. The total heat generated from the blow reaction is approximately 47 kcal per mole of water reacted, along with the carbon dioxide released in the first step and serves as the principal source for 'blowing' the foam mixture, though some auxiliary blowing agents are also usually utilized (Randall & Lee, 2002).

The urethane and urea groups, which are formed, contain other "active" hydrogen atoms, which can further react with isocyanate in side reactions to form allophanates and biurets. Isocyanate-biuret reaction is significantly faster than the allophonate reaction and occurs at lower temperature. Iscoyanate-biuret and isocyanate-urethane reactions lead to branching or cross-linking of the polymer chain with significant effects on properties of the polyurethane product (Dounis & Wilkes, 1997).

Gelation Reaction

The gelation reaction, also sometimes called the polymerization reaction, involves the reaction of an isocyanate group with an alcohol group to give a urethane linkage.

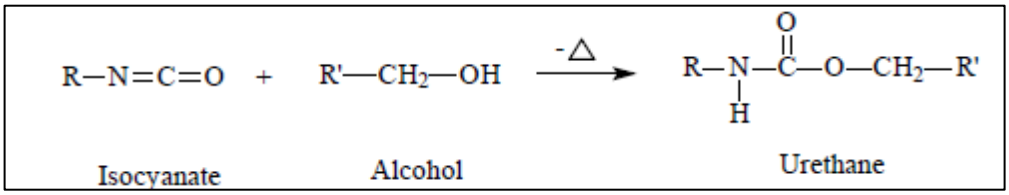


Figure 2.5: Reaction of an isocyanate with alcohol.

Isocyanate alcohol reaction

The most important reaction in production of polyurethane is between isocyanate and hydroxyl groups. The reaction is exothermic and reversible and yields to urethane. Aliphatic primary alcohols are the most reactive and react much faster than secondary and tertiary alcohols due to steric reasons.

R-N=C=C + HO- R' ⟶ R—NHCOO—R' + HEAT ---------- 2.2

Isocyanate Alcohol Urethane Reaction heat

2.4. Raw materials for production of polyurethane foam

A variety of raw materials are used to produce polyurethanes. These include monomers, prepolymers, stabilizers which protect the integrity of the polymer, and colorants. The main chemicals and raw materials used in polyurethane production are Polyol, Toluene Di-Isocyanate (TDI), Blowing Agents, Catalyst, Silicon oil and Water. Polyol and TDI are the two main chemicals for the production of polyurethane foam production (Seymour, 1995).

2.4.1. Polyol

The main reacting species required to produce polyurethanes are compounds that contain multiple alcohol groups (OH), called polyols. Materials often used for this purpose are polyether polyols, which are polymers formed from cyclic ethers. They are typically produced through an alkylene oxide polymerization process (Guo et ail., 2002). They are high molecular weight polymers that have a wide range of viscosity. Various polyether polyols that are used include polyethylene glycol, polypropylene glycol, and polytetramethylene glycol. These materials are generally utilized when the desired polyurethane is going to be used to make flexible foams or thermoset elastomers (Ionescu et al., 2016).

Polyester polyols also used as a reacting species in the production of polyurethanes. They can be obtained as a byproduct of terephthalic acid production. They are typically based on saturated aromatic carboxylic acids and diols. Branched polyester polyols are used for polyurethane foams and coatings. Polyester polyols were the most used reacting species for the production of polyurethanes. However, polyether polyols became significantly less expense and have supplanted polyester polyols (Boustead, 2005).

2.4.2. Isocyanates

Isocyanates with two or more functional groups are the key products required for the formation of polyurethane polymers. Quantitavely aromatic isocyanates account for the vast majority of global diisocyanate production. These compounds are characterized by a (NCO) group, which are highly reactive alcohols (Sonnenschein, 2007). They can be categorized as di-functional or hetero-functional and aromatic or aliphatic in nature.

Among the several available options, the most commonly used ones are methylene di-phenyl diisocyanate (MDI), toluene diisocyanate (TDI) and aliphatic diisocyanates. TDI is produced by chemically adding nitrogen groups on toluene, reacting these with hydrogen to produce a diamine, and separating the undesired isomers (Koeckelberghs, 2001).

2.4.3. Catalysts

The catalysts that are often incorporated into PUs may be grouped into two main categories: metal complexes and amine compounds. Amine catalysts traditionally consist of tertiary amines, such as dimethylcyclohexylamine (DMCHA), dimethyl-ethanolamine (DMEA), 1,4-diazabicyclo octane (DABCO) and triethylenediamine (TEDA). The selection of tertiary amine catalysts is based on their ability to drive either the urea, urethane or isocyanate trimerization reactions. Metal complexes from compounds of bismuth, lead, zinc, tin and mercury may also be used as catalysts for urethanes. For the production of PU sealants, coatings and elastomers and mercury carboxylates have been found to be specifically effective (Guo et al., 2002).

2.4.4. Chain extenders and cross-linkers

Another group of compounds that often play important roles in the polymeric morphology of PU are the chain extenders (f = 2) and cross-linkers (f = 3 or more). These compounds are usually amine and hydroxyl terminated, with low molecular weights. They are highly useful for improving the morphology of PU adhesives, elastomers, fibers and some other important microcellular and skin foams (Sonnenschein, 2014). The elastomeric features of these compounds are obtained from the copolymer interface of the soft and hard segments of the polymer. As such, the domains of the hard segment urethane serve as cross-linkers for the domains of the soft segment amorphous polyester (or polyether) (Krol & Piotr, 2007).

2.4.5. Surfactants

Surfactants are often used to improve the properties of foam as well as non-foam PU polymers. They resemble block polymers of silicone oils and some other organic compounds. In applications that involve foams they are applied for the emulsification of liquid components, the regulation of cell sizes and for stabilization of cell structures to guide against collapse as well as against voids at the sub surface. For non-foam applications, they are applied as anti-foaming and air release agents, and as wetting agents. They may also be used to remove surface imperfections, such as sink marks, orange peels and pin holes (Hill, 1999).

2.5. Manufacturing Process of polyurethane

While polyurethane polymers are used for a vast array of applications, their production method can be broken into three distinct phases. First, the bulk polymer product is made. Next, the polymer is exposed to various processing steps and finally, the polymer is transformed into its final product and shipped. At the start of polyurethane foam production, the reacting raw materials are held as liquids in large, stainless steel tanks. These tanks are equipped with agitators to keep the materials fluid. A metering device is attached to the tanks so that the appropriate amount of reactive material can be pumped out.

The reacting materials are passed through a heat exchanger as they are pumped into pipes. The exchanger adjusts the temperature to the reactive level. Inside the pipes, the polymerization reaction occurs. By the time the polymerizing liquid gets to the end of the pipe, the polyurethane is already formed. On one end of the pipe is a dispensing head for the polymer (Mills, 2007). The dispensing head is hooked up to the processing line. A roll of baking paper is spooled at the start of the processing line. This paper is moved along a conveyor and brought under the dispensing head. As the paper passes under, polyurethane is blown onto it. As the polymer is dispensed, it is mixed with carbon dioxide which causes it to expand. It continues to rise as it moves along the conveyor. After the expansion reaction begins, a second top layer of paper is rolled on. Additionally, side papers may also be rolled into the process. Each layer of paper contains the polyurethane foam giving it shape. The foam is passed through a series of panels that control the width and height of the foam bun. As they travel through this section of the production line, they are typically dried. At the end of the production line, the foam insulation is cut with an automatic saw to the desired length. The foam bun is then conveyed to the final processing steps that include cooling, packaging, stacking, and shipping (Robie, 2011).

2.6. Polyol in polyurethane foam production process

Polymeric compounds with several hydroxyl groups, known as polyols, are essential components in the manufacture of polyurethanes (PU), they are predominant reaction partners of the isocyanates.

Polyols used in polyurethane manufacture are divided from the structural point of view in two groups. In the first group there are the low molecular weight (MW) polyols, having unitary and concrete MW, such as: propylene glycol, ethylene glycol, dipropylene glycol, diethylene glycol, etc. These polyols are currently used in the polyurethane fabrication as chain extenders (the polyols with two hydroxyl groups/mole called diols) or as cross linkers (the polyols with more than two hydroxyl groups/mole such as triols, tetraols, etc.) (Ionescu & Mihail, 2005).

The second group of polyols for polyurethane contains low MW polymers (oligomers with a maximum MW of 10,000 Daltons) with terminal hydroxyl groups (hydroxy telechelic oligomers), called oligo-polyols, characterized by an average molecular weight and having a molecular weight distribution (MWD) of homologous species. An oligo-polyol for polyurethanes, may have two, three, four, five, six, seven or a maximum of hydroxyl groups/mol. Polyols with a higher number of hydroxyl groups/mol are rarely used. The two main classes of polyols are Polyether and Polyester Polyols (Gist & Double, 2013).

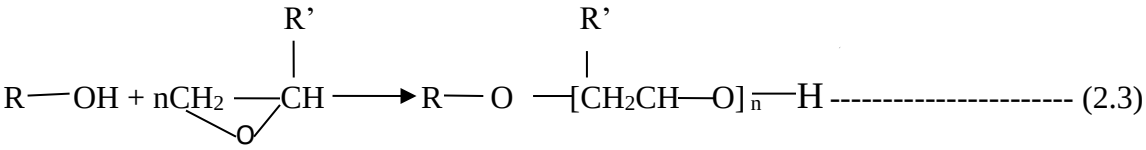
2.6.1. Polyester Polyol

The polyester polyols for urethane include aliphatic and aromatic polyesters. They are used to a much lesser degree than polyether polyols. They are more expensive to produce and much more viscous than polyether with comparable chain lengths. On the other hand, they are far less sensitive to photo-oxidation but susceptible to hydrolysis. Aliphatic Polyesters are prepared by poly-condensation reaction of dibasic acids such as adipic acid, phthalic acid and sebaci acid with glycols such as ethylene glycol, propylene glycol, diethylene glycol, 1,4-butanediol and 1,6-hexanediol. These polyesters have high viscosity, low functionality and are difficult to handle but they offer physical properties not obtainable by polyether polyols. 10% of flexible foam are made from polyester-type polyols (Lee, 2004).

2.6.2. Polyether Polyol

Polyether polyols are the most commonly used products. Polyether-type polyols are used in 90% of the flexible foams produced today. They form the "backbone" of polyurethanes (e.g. polyols with molecular weight of about 500). A wide range of long and short-chained polyether polyols with 2 to 8 OH groups per molecule can be synthesized by the alkali-catalyzed polymerization reaction between low molecular weight di- and polyfunctional

"starting" alcohols (initiators) with epoxides (ethylene and/or propylene oxide) (Kaushiva, 2000). The initiators serve as reaction partners for the alkylene oxides and also engage the ether chain. The structure of the polyols and hence the processing and property profile of the polyurethane products can be controlled within wide limits by selection of the length and composition of the polyether chains and the functionality of the starter molecules (David Randall, 2003).



---------- (2.3)

In comparison with polyester, products based on polyether polyols are more stable to hydrolysis but more sensitive to oxidation. Since functionality and equivalent weight of polyether polyols can be widely varied, polyether polyols are extensively used for producing various polyurethanes such as flexible, semi-flexible and rigid foams as well as elastomers, coatings, adhesives, sealants and resins (Akindoyo et al., 2016). Polyether polyol come in a wide variety of grades based on their end use, but are all constructed in a similar manner. Polyols for flexible applications use low functionality initiators such as dipropylen glycol (f=2) or glycerin (f=3). Polyols for rigid applications use high functionality initiators such sucrose (f=8), sorbitol (f=6), toluene-diamine (f=4).

Advantage(s) of Polyether Polyols over Polyester Polyols

- Various functionality polyols (2 to 8) are available.
- Equivalent weight can be widely changed.
- The viscosities are lower than those of polyesters.
- Production costs are cheaper than those of aliphatic polyesters
- Resulting foams are hydrolysis resistant

2.7. Basic characteristics of Polyol

Irrespective of the chemical structure of the oligomeric chain, the polyols have general and common characteristics and these characteristics are determined by the same analytical methods (Ionescu & Mihail, 2005).

2.7.1. Hydroxyl Number

The first common characteristic of polyols for polyurethanes is the presence of terminal hydroxyl groups. The hydroxyl number is defined as the quantitative value of the amount of hydroxyl groups available for the reaction with isocyanates. The hydroxyl number (or hydroxyl index) is expressed as milligrams of potassium hydroxide equivalent for one gram of the sample (mg KOH/g).

The most important analytical method for hydroxyl number determination (OH#) is the reaction of the terminal hydroxyl groups with organic anhydrides (acetic anhydride or phthalic anhydride). The acidic carboxyl groups resulting from this reaction are neutralized with the equimolecular quantity of potassium hydroxide (Efstathiou & Kypros, 2014).

2.7.2. Functionality

Functionality is the second important characteristic of a polyol and is defined as the number of hydroxyl groups/molecule of polyol. The functionality of a polyol is not very easy to determine. An old method is based on the determination of the conversion at the gel point (p) of a reaction between a polyol and a diisocyanate. The functionality is determined by using the well-known equation of Flory p = 2/f, where p is the conversion at gel point and f is the medium functionality of the reaction system. For polyether polyols an NMR method was elaborated for functionality determination. The most usual and practical method for functionality determination is based on the assessment of the MW of a polyol, by a method applicable to low MW compounds (MW <10,000 Daltons), such as vapor pressure osmometry (VPO) or gel permeation chromatography (GPC), together with hydroxyl number determination (Mills, 2007).

2.7.3. Molecular Weight and Molecular Weight Distribution

The MWD is an important characteristic of oligo-polyols, differentiating the oligo polyols from the unitary low MW polyols of organic chemistry. As in all polymers, the MW distribution of oligo-polyols is given by the ratio between weight average molecular weight MW (Mw) and the number average molecular weight, Mn, both being determined by GPC.

$$\text{MWD} = \frac{M_w}{m_n} \quad (2.4)$$

A broad MWD represents a large number of macromolecules which have a wide distribution of molecular weights and a narrow MWD shows that the majority of molecular species are situated in a very narrow interval of polymerization degree. The extremely narrow MWD polymers, called mono disperse polymers (all the macromolecules have the same molecular weight), are very difficult to obtain by synthetic methods (Krol & Piotr, 2007).

2.7.4. Reactivity

The reactivity of polyols in polyurethane fabrication is a very important practical characteristic and it is a measure of the reaction rate of a polyol with an isocyanate in order to make the final polyurethane polymer. One practical method is the measurement of viscosity, in time. It is observed that the polyols with low reactivity (0% primary hydroxyl, i.e., having only secondary hydroxyls) have the lowest viscosity increase over time (A. Lapprand, 2005). By contrast, the very high reactivity polyols, having 85-100% primary hydroxyl content, have the highest viscosity increase over time. This method of evaluation of viscosity increase in time is a very simple and useful practical method to ascertain the reactivity of polyols.

2.7.5. Viscosity

The viscosity is a special characteristic of all polyols gives an indication of their process ability. Practically all of them are liquid at room temperature. This fact is a really important technological advantage, because the high MW polyurethane polymer is obtained using only low viscosity or medium viscosity liquid intermediates, which are very easy to process. The polyols viscosity is determined using different type of viscometers, especially by Brookfield Viscometer (Ionescu &Mihail, 2005).

2.7.6. Color

Generally, polyols color is determined in to two color scales, the APHA color scale which is used for very light colored or colorless polyols, (e.g., high MW polyether polyols or polyester polyols) and the Gardner color scale, used for polyols having a more intensive color, of yellow to brown color (for example sucrose-based polyether polyols, ortho-toluene diamine based polyols) (Leitsch, 2016). The light color of oligo-polyols increases their commercial value and is an indication that the product was not degraded during the process of synthesis.

2.7.7. Acid Number

The reaction of a polyol with polyisocyanates is catalyzed by tertiary amines. The presence of a residual acidity decreases the catalytic activity of the tertiary amines, by acid-base neutralization. To avoid negatively affecting the reactivity in polyurethane synthesis it is very important to carefully control the acidity of polyols. Thus, the acid number is the amount of acidic groups in an oligo-polyol. The acid number is expressed as the number of milligrams of potassium hydroxide required to neutralize the acidity of one-gram sample (Ionescu & Mihail, 2005).

2.8. Polyurethane Foam Waste and Its Management

Treatment of aged polymeric materials has been a problem all around the world, and trends indicate that the overall amount of solid waste that the human generate continues to increase all over the world. For instance, only in the US, approximately 1.3 million tons, by weight, of waste polyurethanes are generated each year. North America represents around 30–35% of the world total consumption, with the remainder in Western Europe (around 40%), the Far East (around 15%) and the rest of the world (around 10–15%). The darker side of this huge consumption of PU product is the saturation of several hundred tons of polyurethane waste daily. It includes post-consumer wastes and defected products and foam trims during slab stock manufacturing (Kopczynska, 2016).

Majority of this waste, from end-of-life vehicles, scrapped refrigerators, district heating tubes and from many other sources receiving increased attention worldwide as a result of rapidly rising amounts and increasingly tight legislation on its treatment and disposal. But as a general trend there is no any specific use and it simply dumped on landfill sites, but they have proved to be non-biodegradable. Since polyurethanes are generally classified as thermosetting polymers they cannot be melted and reprocessed by extrusion process, without suffering extensive degradation (Garforth, 2004).

Table 2.3: Disposal and recycling process of polyurethane foam waste

Disposal and processing of polyurethane foam waste			
Land filling	**Mechanical recycling**	**Energy recovery**	**Feedstock recycling**
	Rebinding Regrinding Adhesive Pressing Compression molding	Pyrolysis Gasification Incineration	Hydrolysis Aminolysis Glycolysis

2.8.1. Landfilling

In the past most, PU scrap ends up on landfills, for foams often after a compacting step that gives bricks of a density of around 500 kg/m^3 (JADHAV, 2010). And besides end of-life PU also significant amounts of production waste can be disposed, which affects adversely the ecology of surroundings because. It is the least desired option because of small polyurethane foam plastic pile-up density, land fill will be serious waste of land resources. At the same time polyurethane wastes are very difficult to decompose in the natural conditions. Biodegradation of PU varies strongly with PU crystallinity, molecular structure, cross-linking and the length of repeating units. When polyurethanes get buried down the soil, it get broken down by the action of water to give urea (Ron, 2004).

2.8.2. Mechanical Recycling (Physical Recycling)

Physical recycling method is crushing polyurethane foam wastes, only changing physical form. The smashing solid particles have no reactive activity, but directly make new polyurethane products as recovery processing of raw materials. Grinding PU wastes into powders and then reusing these powders in various ways constitutes a mechanical recycling approach. The powdered PU is available as filler in production of PU foams or elastomers. When used as fillers, the powders are usually first added to the polyol component in a PU production process (Zia, 2007).

Molded PU products, such as auto seat cushions can contain up to 20% regrind material without any deterioration in properties or performance. Mechanical recyclers grind PU into powders with various milling and knife-cutting processes. To be used as fillers, PU particles should be less than 200 μm in size, and preferably under 100μm. Shredded PUR foam wastes can be rebounded using heat, pressure and an adhesive binder (Nikje, 2011). Some of mechanical or physical PU recycling methods are:

- Regrinding, (Ron, 2004).
- Adhesive pressing, (Scheirs, 1998).
- Rebinding, (Branderup et al., 1998)
- Compression Molding and Injection Molding.

2.8.3. Thermo chemical processing

In the thermo chemical recycling of PU products, the waste stream as a source of energy, fuel or some value monomers. Energy recovery is the only suitable disposal method for PU wastes with no markets and applications.

Incinerations with energy recovery have an important role to play, viewed within the context of the growing range of recycling and re-use options for plastics, including PUs. With 86% of the world's oil, coal and gas being burnt for energy, there is a strong case for partial substitution of the energy resources with waste plastics. Incineration of a PU foam results in a volume reduction of around 99% which has large implication to reducing the land filling of this material, at the same time destroying CFCs and other harmful foam blowing agents (Zevenhoven et al., 2003).

The common thermo chemical processing are:

- Pyrolysis, (Kaminsky& Scheirs , 2006).
- Gasification, (Weigand, 1998).
- Incineration, (Schoen, 2000)

2.8.4. Chemical recycling

Chemical recycling is the recovery process of monomers as the main products by breaking down of urethane bonds under controlled reaction conditions. This can be achieved using main chemical recycling methods, namely, hydrolysis, aminolysis and glycolysis. The polyurethane polymerization is reversible. Functional groups such as carbamic acid, ester base, ester bond and ether bond will gradually depolymerize to original reactant or other oligomer and even small molecule organic compound under the condition of chemical reagents, catalysts and heating (Wenqing Yanga, 2012). Chemical recycling is following the degradation principle.

Generally, it is used to recover one of constituents which have a particular commercial interest, the polyol, a valuable raw material which can be used to manufacture new foams. There are various possible chemical processes such as hydrolysis, glycolysis, aminolysis, etc. The name for each depolymerization reactions depends on reagent used to affect it and the operating conditions like, temperature, pressure, catalyst type and concentration, decomposition mechanisms and so on (Modesti, 1998).

2.8.4.1. Hydrolysis

Hydrolysis is a method of polyurethane waste recycling by the reaction of polymer with water leading to total depolymerization to monomers. The hydrolysis of a polymer matrix occurs through two processes: water diffusion into polymer and hydrolysis reaction. Using this recycling method polyol and amine intermediates can be produced form PU and it is common for polymers such as PET, PU, and polyamide (Mahoney, 1990). After recycling, the distilled and purified polyol can be uses as a component in the new PU formulations. The recovery and recycling of the polyol showed that superheated steam temperature should be around 288°C, producing a polyol.

The chemistry of a general hydrolysis process is:

$$R' - NCOO-R'' + H2O \longrightarrow R-NH2 + HO-R + CO_2 \text{----------} 2.5$$

$$R'-NH-CO-NH-R''+H2O \longrightarrow 2R-NH2 + CO2 \text{----------} 2.6$$

The main drawback of this method is:

- Use of high temperatures,
- High pressure and
- Long-time needed for complete depolymerization and
- Various components are need to be separated in order to permit their reuse.
- Further chemical treatments can be carried out to separate or eliminate primary amines formed.

2.8.4.2. Aminolysis

Aminolysis is the reaction of PU waste with amines such as dibutylamine, ethanolamine, lactam or lactam adduct under pressure at elevated temperatures. In this process potassium and sodium hydroxide are the main catalysts. There are few studies in the field of amine treatment for PU recycling. Polyols, aromatic amines and carbametes are the main products. Finally, the polyols are separated which can be used in new PUF formulation as virgin polyol (Nikje & Alavi, 2011). The great disadvantage of this aminolysis processes is related to the increased free amine value obtained in the recovered polyol. The amines have an adverse effect in the polyurethane systems formed from the recycled polyols, these amines react with isocyanates to yield polyurea and also greatly accelerate the polyurethane formation reaction. These urea groups can undesirably harm physical properties and reduce the controllability of the polyurethane formation reaction by other catalysts (Carone & Santos, 2013).

2.8.4.3. Glycolysis

Glycolysis is typical a thermo-chemical interaction between polyurethane and hydroxyl containing polyol. It is a depolymerization reaction of condensation polymers such as polyamides (nylons), polyesters, PET, or addition polymers such as PU. It was developed during 1980s (mainly in Italy, Germany, France and the USA), is the most widely used chemical recycling method for PU wastes. The high molecular weight, cross-linked, solid polyurethanes are broken down to lower molecular weight, liquid products and the conversion of waste to raw monomers is relatively high (Garforth, 2004). It is a process of successive trans-esterification reactions of the urethane bond with low molecular weight glycols as a glycolyzing agent by the aid of a catalyst. This kind of depolymerization of PU waste leads to obtaining products such as diols, diamines, diacids, or oligomerols (Wu CH et al., 2003).

Compounds acting as glycolysis agents can be aliphatic compounds or oligomerols contained at least two hydroxyl groups. It is the only chemical route so far adopted for recycling rigid and elastomeric polyurethanes on an industrial scale. Its main advantages are:

- Its applicability for many types of polyurethanes,
- It does not require separation of the products,
- It is simple operation in batch reactors or as a continuous process,
- Its moderate requirements for reaction temperature under ambient pressure,
- Its robustness and tolerance too many impurities.
- Its low requirements in equipment

2.9. Drawbacks of other recycling mechanisms over chemical recycling process.

However, besides of environmental pollution problem, the above two disposal technology have an economic loss associated with both the land required for landfill and the costly materials used in the preparation of the foam disposed in these operations. It is therefore of interest to consider the recovery and eventual reuse of such materials. There for the method is being phased out gradually (Wenqing Yanga, 2012). The physical recycling of polyurethane is mainly working on the principle of rebonding and regrinding technologies, but the resultant recycler leads to adverse change in mechanical properties of new products. Physical processes such as melt-processing methods are successfully applied to thermoplastic, but in the case of PU foams these kinds of processes are not suitable due to PU foam crosslinked structure. Although it seems to be lucrative process of scrap recycling, but there are some drawbacks (JADHAV, 2010).

- The second-generation product made with physical recycling methods is inferior regarding the mechanical stress and strain.
- Due to particle size of grinded polyurethane powder, a superior appearance of surface is not easily achievable.
- Cost for collection and separation of scrap from contaminants as fabric, fiber, metal strips, wire inserts is relatively high

2.10. Overview of Process of Glycolysis

Basically, glycolysis implies the heat-up of pre-grinded PU scrap at a medium high temperature range of 170 to 220 0c and the polyurethane chain is degraded by successive transesterification reactions of the urethane bond in high-boiling point glycols with and without a catalyst. In this transesterification process the ester group joined to the carbonyl group of the urethane is interchanged by the hydroxyl group of the glycol (Chao-Yun Yu & Wen-Jau Lee, 2002). Glycols act as destroying agents by attaching to the urethane functional groups which followed by breaking of ester groups and liberation of the polyols and amines. The transesterification leads to the recovered polyol containing active hydroxyl groups. Chemistry of glycolysis involves the breakdown of urethane bond, in which polymer chain is depolymerized to a mixture of liquid oligomers, which proceeds according to the following reaction.

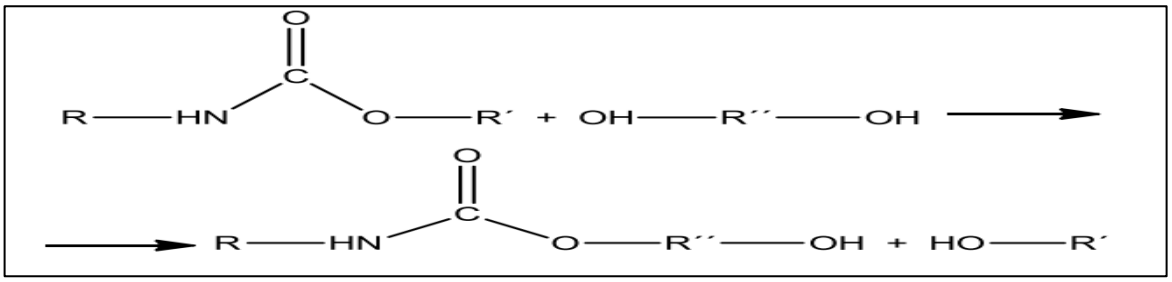


Figure 2.6**:** Chemistry of glycolysis involves the breakdown of urethane bond.

The product of PU waste glycolysis (glycolysate) can be homogenous mixture or it can be divided into two separated phases. The upper phase consists mainly of polyols, which are similar to virgin polyols, and the bottom phase consists of aromatic carbametes, ureas, un-reacted glycol, and amines (Alicia Aguado, Lidia Martínez, Alberto Moral, José Fermoso, Rubén Irusta, 2005). It can be employed alone or in combination with virgin polyols to prepare polyurethane compounds preferably foams but may also be used in various polyurethane, polyurea-polyurethane and poly-isocyanurate applications. It has also been proposed a further purification after the glycolysis which consists of recovering under vacuum the low molecular weight diol solvent used. It is an effective recycling way, due to mild reaction condition and the good performance of product (Alavi Nikje, 2011).

Among all available techniques, route of "split-phase" glycolysis is adapted for this research, which has ability to yield a monophasic product as a trans-esterification reaction involving a breaking of urethane bond (Borda, 2000). In "split-phase" glycolysis better quality products can be achieved from flexible PU foams preferably based on TDI by reacting with the glycolyzing solvent producing a two product phases in the reactor. The lighter layer contains the flexible polyol and the heavier layer contains TDI derived compounds, can be converted in to a polyol used to make rigid polyurethane foam.

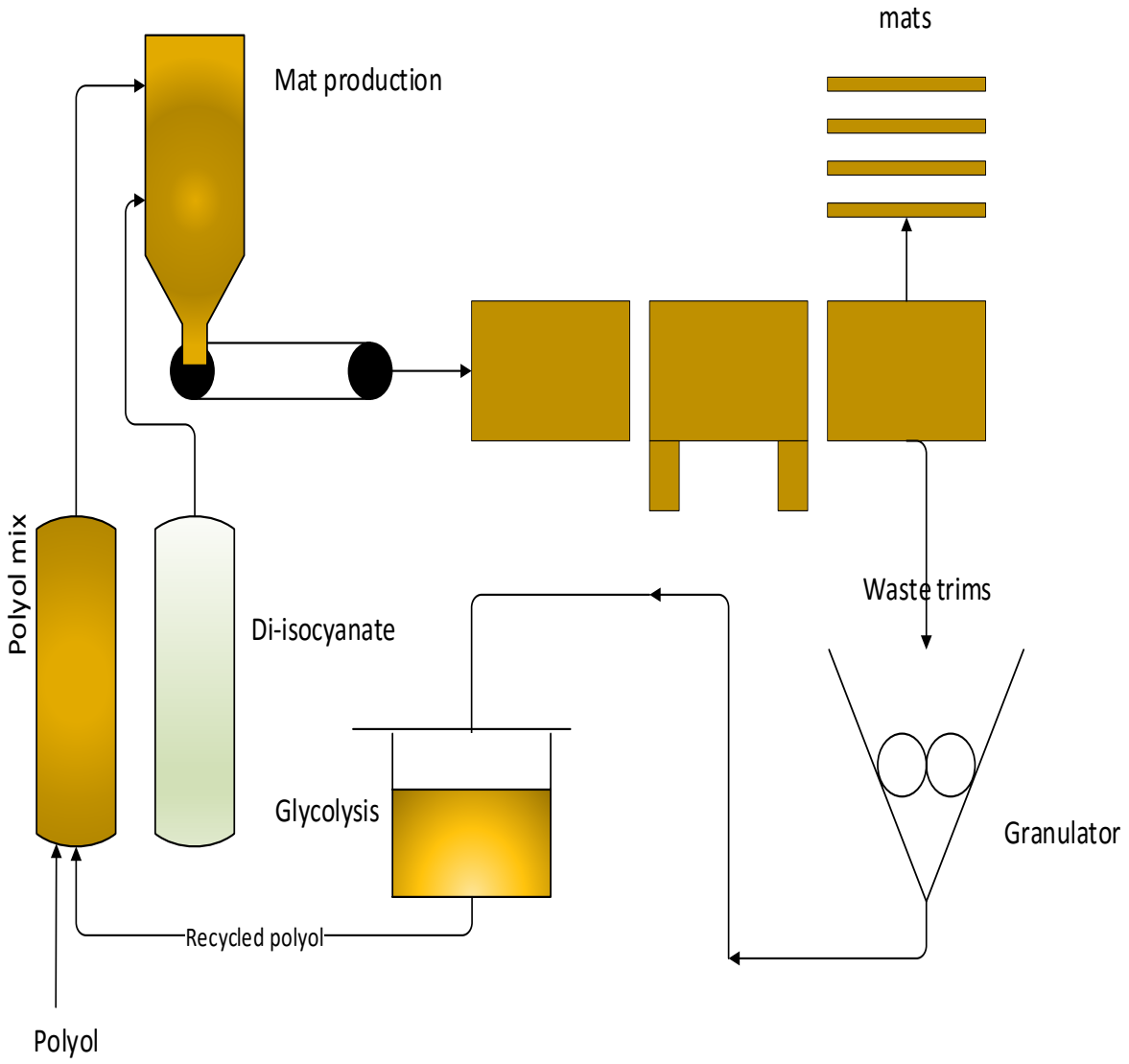


Figure. 2.7: Overall process flow diagram of glycolysis process.

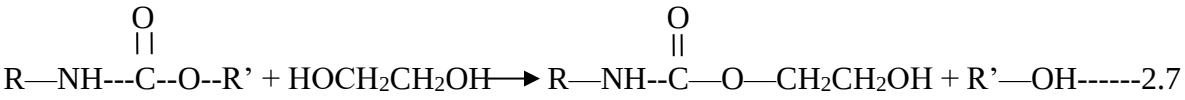
The main aim of this research is recovery of polyol using this chemical recycling approach and to analyze the properties of the recovered product can affected by main glycolysis parameters like, glycolyzing solvent, catalyst type and concentration, reaction time and temperature (Molero, 2006).

2.10.1. Glycolyzing Solvent selection

By the aid of excess amount of glycolysis agent, much more than the stoichiometric quantity the reaction product splits in two phases, where the upper layer is mainly formed by the recovered polyol from the PU (Molero, 2006). Compounds acting as glycolysis agents can be aliphatic compounds or oligomerols contained at least two hydroxyl groups. The compounds can contain in their chains oxygen or nitrogen. The type of glycol used for glycolysis has influence on time and temperature of the reaction. In a two-phase glycolysis of PU, the amount of glycol added is much larger than the stoichiometric quantity required to produce the transesterification.

The most widely used are glycols such as ethylene glycol (EG), propylene glycol (PG), butylene glycol, diethylene glycol (DEG), and dipropylene glycol (DPG) (Lucas & Rodríguez, 2006). The excess is used not only to displace the equilibrium to the glycol substitution, but also to promote the phase splitting which allows the obtaining of a polyol-rich phase. However, a too large excess of glycol would imply huge volume equipment requirements and larger amounts of bottom phase that has to be recycled by distillation. And based on previous researches 60/40 glycol/PU ratio was taken as an optimum value (Garmarudi & Nikje, 2010).

Here in this thesis work ethylene glycol is used among various types of glycol discussed above. The use of ethylene glycol allows the process to be carried out with high, more economical polymer/glycol ratio (up to 1:5) (Borda, 2000). A polyphase product is obtained with a top liquid phase mainly formed by the polyether polyol from the polymer, an intermediate liquid phase formed by the solution of carbametes, ureas and amines in ethylene glycol and a bottom solid phase with aromatic compounds with prevalent urea bonds. When they undergo heating in the presence of glycols the reaction of the urea groups leads to soluble products.



2.10.2. Choice of catalyst

Among other reaction variables, the choice of catalyst is an important factor affecting the properties of the recovered products, as well as the time to reach the complete degradation of the foam. The importance of catalyst lies in the fact that, in contrast to direct esterification, trans-reactions with alcohol groups proceed very slowly in the absence of catalysts under mild conditions (Lucas, 2005.). The most relevance of them is exchange reaction capability of the original ligands with reactants, effects on concomitant reactions and specially solubility in the reaction medium.

On the other hand, the transesterification reaction leads glycol transesterification carbametes for urethane bonds, for urea bonds the resulting product is aromatic diamine. The way to minimize aromatic primary amines quantity is related to the choice of catalyst. Selective catalysts in the glycolysis process against hydrolysis are able to reduce up to the minimum the quantity of these undesirable products (Molero, 2009). Catalysts used in polyurethane glycolysis include bases like amines hydroxides, alkoxides and Lewis acids as well, leading to different extension in secondary reaction. Among organometallic compounds, titanium n-butoxide has been reported as selective catalyst for the urethane group transesterification.

Acetates of Pb, Zn, Mn, Ca, Co and Cd have been described as general catalysts in transesterification reactions (Rodríguez, 2006). Although in the case of transesterification of urethane bonds with glycols, potassium acetate and sodium acetate are mentioned in the literature leading to high amine values in the resulting products. From those listed catalysts a homogeneous organometallic catalyst, zinc acetate was chosen as an alternative of the above and other traditional metal catalysts, to reach total conversion of the polymer based on the decrement of urethane bond band area according to (Santos & Carone, 2013). And also, it is commercially available, eco-friendly and cost effective catalyst.

2.10.3. Temperature Range

The temperature for the degradation of polyurethane foam waste can be affected by factors like isocyanate, polyol and chain extender used to produce the PU, since the different linkages in the polymer chain have different thermal dissociation temperatures, as illustrated in table 2.4 below. Among the groups which form a PU, biuret and allophanate are the less stable, because their complete thermal degradation can be reached at 170- 180. Decomposition of these thermo labile structures yields the precursor groups: urethane, urea, hydroxyl isocyanate and amine. Urethane and urea bonds, followed by isocyanurate structures are the following in the stability range (Ron, 2004). Depending on the PU considered and the analysis method used (typically at atmospheric pressure), thermal degradation of PU has been reported to start in the temperature range 110-270°C.

Table 2.4**:** Thermal dissociation temperature ranges for linkages in PU,

Linkage		**Onset of Dissociation, °C**
Allophanate	aliphatic/aromatic	85-105 / 100-120
Biuret	aliphatic/aromatic	100-110 / 115-125
Urethane	aliphatic/aromatic	165-180 / 180-200
Disubstituted urea		235-250

Typically, glycolysis of flexible polyurethane foams are performed under atmospheric pressure and the optimum range of temperature for polyurethane glycolysis have proved to be 170-220 ^{0}c when catalysts are present. A temperature below 170^{0}c gives too low catalyst activity and temperature above 220 ^{0}c gives unwanted secondary reactions which are competitive with respect to transesterification reactions towards amines (Zia, 2007).

2.10.4. Reaction Time

The reaction time can generally be from less than 1 hour to about 10 hours but preferably the reaction time is from about 1 to 6 hours, most preferably lower than 4 hours, depending on the physical and chemical properties of the polyurethane scrap, the glycolyzing compound and the catalyst employed (Kaminsky & Scheirs , 2006).

3. MATERIALS AND METHODS

3.1. Materials and Equipment used

An industrial sample of flexible PU foam waste scraped from the production process taken from Addis Ababa foam production factory was the main raw material for this study. Ethylene glycol and zinc acetate were used as a solvent and Catalyst respectively for decomposition process. Other chemicals and reagents used during characterization and purification of recovered polyol were; distilled water, Nitrogen gas, Phthalic anhydride, Phenolphthalein powder, Pyridine, Toluene, Isopropyl alcohol, Chloroform, Hydrochloric acid, and Sodium as well as potassium hydroxide.

Equipment and instruments used in the glycolysis process were, grinder, screen sieves, three-necked round bottom flask, oil bath, magnetic stirrer, reflux condenser, separatory funnel, biurets, hotplate, pressure bottles and pressure bottle bags, digital viscometer, thermometer, pipettes and electronic balance.

3.2. Methods

3.2.1. Experimental procedures during glycolysis reaction

Stage One. PU Raw material collection and pretreatment

Industrial samples of flexible PU foam based on polyether polyol and Toluene diisocyanate (TDI) were pretreated by washing to remove any possible dust particles and external solid impurities and it was dried at atmospheric temperature to remove the moisture then, the foam block was grinded in a mesh size ranging from 2 to 3mm diameter.

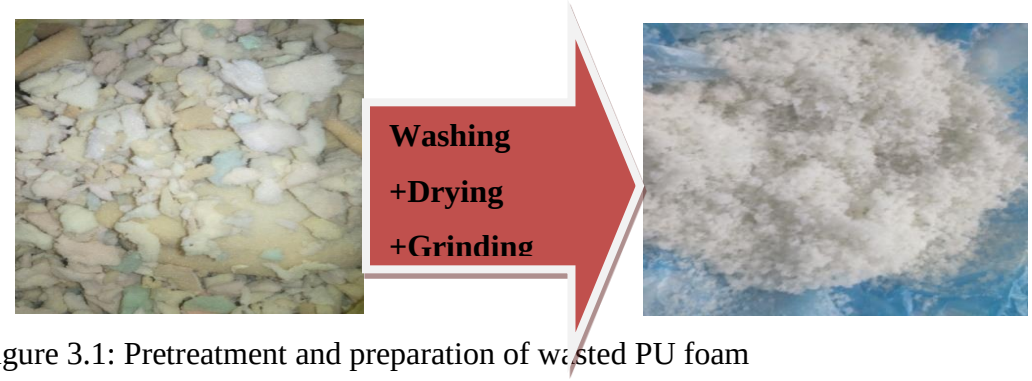


Figure 3.1: Pretreatment and preparation of wasted PU foam

An organic colorless compound, ethylene glycol used as a depolymerization solvent, with the formula $(CH_2OH)_2$, the molecular weight of 62.07g-/mole and with 1.1132g/$_{cm}^3$ density; zinc acetate $(Zn(Ac)_2)$ as a catalyst obtained from Rankem chemical supplier and nitrogen gas also used to create an inert atmosphere with in the reactor. A 1liter three-necked round bottom flask equipped with a stirrer and refluxing condenser to carry out the reaction and an oil bath with a temperature regulation system used as heat supplier were prepared.

Stage Two. Glycolysis reaction and experimental design

When the temperature of oil reaches the desired level of reaction temperature, the reactor was immersed in the bath. Glycolyzing reagents, ethylene glycol and zinc acetate used as a solvent and as a catalyst respectively were placed in the flask after nitrogen gas pumped to flask to create inert atmosphere and when the temperature reaches to the desired level, 20 gram of scrap foam was added to the reactor constantly for each of experiment by hand feeding mechanism. Here, all the reactions were proceeded by the varying value of the controlling reaction parameters stated before, temperature, time and concentration of catalyst with a constant amount of glycolyzing solvent under atmospheric pressure.



Figure 3.2: Glycolysis process and its reaction setup

The zero time for the reaction was taken until all the foam was fed. The starting time for the reaction was taking into account. And the time was recorded after the stirrer started to revolve, which constantly revolved in 250rpm for all experimental runs to prevent the reactor damage due to the higher spped of the stirrer. The temperature was maintained constant during the given reaction period and assured by checking it periodically. When the given depolymerization period completed, a brown mixture containing a polyol was obtained.



Figure 3.3: Crude brown mixture containing recovered polyol

The experiment has three main factors or controlling variables i.e. temperature, glycolysis time, a catalyst to solvent ratio. And the experiment proceeded by taking optimum value for the solvent to polymer ratio based on literature evidence so, (Ethylene glycol/PU ratio of 60/40) selected as an optimum condition.

Factor 1: Reaction temperature: Excessively high reaction temperatures, (above 230°c) cause to appear secondary products that are not of interest for the process and it affects the reaction kinetics of the process and in reverse applying excessively low temperatures (below 170 ^{o}c) can decrease the yield of the reaction. On the other hand, boiling point of glycolyzing agent affected by the applied temperature level taking into account this, temperature of 170, 180 and 190°C were chosen to prevent its evaporation.

Factor 2: Reaction time: Percentage of oligomers remaining in the upper phase after 120 minutes can reach an inappreciable amount. But a preferable degradation time range was lower than 4 hours depending on the glycolyzing compound and for appreciated activity of catalyst employed. For this reason, the reaction time taken was: 60, 120, 180min.

Factor 3: catalyst to the solvent ratio: Uncatalyzed reaction involves the appearance of around 30% of polyol after 150 minutes of reaction; while with the use of a catalyst, the reaction reaches nearly 50% of polyol after 1 hour (Alicia Aguado, Lidia Martínez, Alberto Moral, José Fermoso, Rubén Irusta, 2005). So, the amount of catalyst proves to be a very important process factor. The three mass ratio levels chosen were: 1%, 1.5% and 2%.

Table 3.1: Main operating conditions of the glycolysis process

EG/PU (mass %)	$Zn(Ac)_2$/EG (mass %)	Mass of PU (g)	Reaction time (hr.)	Reaction temperature (^{0}c)
1:1.5	1(0.3 g)	20	1	170
1:1.5	1.5(0.45g)		2	180
1:1.5	2 (0.67g)		3	190

3.3. Characterization of recovered polyol

After the separation and, the upper phase crude product (polyol) was characterized by determining the common properties like hydroxyl number, viscosity, amine value, acid value, and water content. The purified polyol product was also analyzed by measuring each property described before.

3.3.1. Determination of Hydroxyl number

The hydroxyl values were determined by standard titration method (ASTM, D 4274-99). "Pressure bottle phatalation" approach. The apparatus used were; Pressure Bottles; borosilicate glass; Pressure Bottle Bags; Biuret, and Water bath. The determination of OH value was done by preparing reagents like:

- Pyridine Reagent which was prepared from phthalic anhydride and purified pyridine
- Phenolphthalein Indicator Solution was prepared from pyridine and indicator powder
- And finally, the titration solvent, 0.5 N Solution of Sodium Hydroxide

Then the hydroxyl value of recovered polyol was calculated based on the formula below.

$$\text{Hydroxyl value} = \frac{(B-S)*N*56.1}{W} \quad ---------- 3.1$$

Where: N = Exact normality of KOH,
W = Weight of sample in g,
B = Blank reading and S= Sample reading

3.3.2. Determination of acid value

The acid value of the polyol phase was measured by applying standard titration method, (ASTM, D 4662-98). The main reagents prepared were:

- Phenolphthalein Indicator Solution was prepared by phenolphthalein powder mixture of equal volumes of water and ethyl alcohol.
- Standard Alcoholic Solution of Potassium Hydroxide with 0.1N was prepared from potassium hydroxide distilled water and ethyl alcohol.
- And titration Solvent prepared from equal volumes of toluene and ethyl alcohol.

Each sample and blank solution mixed with the reagents were titrated using the titration solvent then the acid value of sample was calculated, using the following formula.

$$\text{Acid value} = \frac{A-B*56.1}{W} \quad ---------- 3.2.$$

Where

A = KOH solution required for titration of the sample, mL
B = KOH solution required for titration of the blank, mL
N = normality of the KOH solution, and
W = sample used

3.3.3. Determination of total amine value

To analyze the total amine value the equipment used were: Erlenmeyer flask; Borosilicate glass, Hot Plate, Magnetic Stirrer and Micro-biuret using reagents like;

- Chloroform ($CHCl_3$).
- Standard Solution of hydrochloric acid with 0.5 N prepared from concentrated hydrochloric acid and isopropyl alcohol.
- Isopropanol solution was prepared from distilled water and isopropyl alcohol

Then total amine value was calculated using:

$$\text{Total amine value} = \frac{V * N * 56.1}{s} \quad ---------- 3.3$$

Where**:**

V = HCl required for titration of the specimen

N = normality of the HCl solution, and

S = specimen weight used,

3.3.4. Determination of Viscosity.

The viscosity of the samples prepared for the verification was measured using digital viscometer at room temperature.

3.4. Experimental Data Analysis using ANOVA

Data analysis was performed by design expert software using general factorial design Method. This program software also used to develop the mathematical model that will describe the effects of the main and interaction factors on the response. Full factorial experiments are the only means to completely and systematically study interactions between factors in addition to identifying significant factors on each of the response. To analyze each main properties of the recovered product polyol there was three factors, namely temperature, time and catalyst to solvent ratio with three levels for each factor.

3.5. Purification of Recovered Polyol

The purification method chosen was a liquid-liquid extraction done by mixing polyol reach phase with the extracting solution which was prepared from demineralized water and hydrochloric acid according to (C. Molero A. d., 2006). The optimal conditions obtained to carry out the extraction process were:

- Water with a pH between 4 and 5 as solvent.
- Solvent to upper phase mass ratio of 1:1
- Extraction temperature of 60 ^{0}c

3.6. Synthesis of Foam block using Recovered Polyol

Once the viability of the glycolysis process of flexible foams has been demonstrated and also the recovered polyol has been properly characterized and purified it should be susceptible of being used as raw material for the PU foams synthesis. The foam block was prepared according to foaming of conventional slab stock foams. Two different flexible foams were prepared by using a crude and purified recovered polyol incorporating the same proportions of recovered polyol to check its foamability. The foam growing process were carried out using recovered polyol at temperature 190^{0}c, 2% catalyst to solvent ratio and decomposition time of 2hour before and after purification. The formulation recipe of sample of flexible foam sample shown in table 3.2.

Table 3.2: Foam synthesis formulation

Components	Amount (gm.)	
Row polyol with Mw 3500 (OH =56)	75	
Recovered polyol (OH=144.53	25	
TDI	35.15	
Water	2.53	
Silicon	0.75	
Tin	0.6	
Amine	0.3	

4. RESULT AND DISCUSSION

The reaction mixture was separated into two phases. The upper phase containing recovered polyol with other byproducts and lower phase contains a variety of by-products obtained from transesterification reaction of urea, urethane and allophanate functional groups as well as decarboxylation by-products. Polyol on the upper phase was characterized by determining the influence of factors that have been controlled in all decomposition process.

4.1. Effect of operating conditions on the resulted polyol properties

4.1.1. Parameters effects on Hydroxyl number

Hydroxyl value can be used as an index of a number of hydroxide groups existing in the reaction system. In the glycolysis process, besides of the transesterification reaction between the PU and the low weight glycol to give a resulted polyol, a low weight carbamate and other secondary reaction byproducts were produced. This happens regardless of glycolysis of the urea groups giving, a low weight carbamate and an aromatic amine (Molero et al., 2008). Due to that hydroxyl values are significantly greater than the ones of the raw polyols in general. This is occurred as a consequence of the glycolysis of such by-products, lower molecular weight and functionality of glycols dissolved in the upper phase at the same time catalyst loading and thermal conditions. Temperature, catalyst to solvent ratio and time of reaction of the study was considered as affecting parameters of the resulted hydroxyl value of the recovered polyol and their effect was tried to analyzed and discussed.

4.1.1.1. Temperature effect on hydroxyl value

After glycolysis carried out at temperature 170, 180 and 190°c, effect of the variations of temperature on the hydroxyl value of the crude polyol was analyzed by taking constant operating conditions of other reaction parameters and the resulted effect was discuss using the following graph. The Figure below showed that variation of hydroxyl value at the definite quantity of catalyst to solvent ratio of 2%, time of reaction (1, 2 and, 3hour) and at a temperature of 170°c, 180°c, and 190°c. It was evident from the figure that there is an increment of hydroxyl values when temperature goes from170 ^{0}c to 190 ^{0}c at each of the reaction time.

Hydroxyl value of 107, 115.22 and 131.25 mg KOH at 170°c, 122.78, 134.91, 145.52 mg KOH at 180°c and 133.88, 144.53 and 153.96 mg KOH at a reaction temperature of 190°c was recorded at each of reaction time respectively.

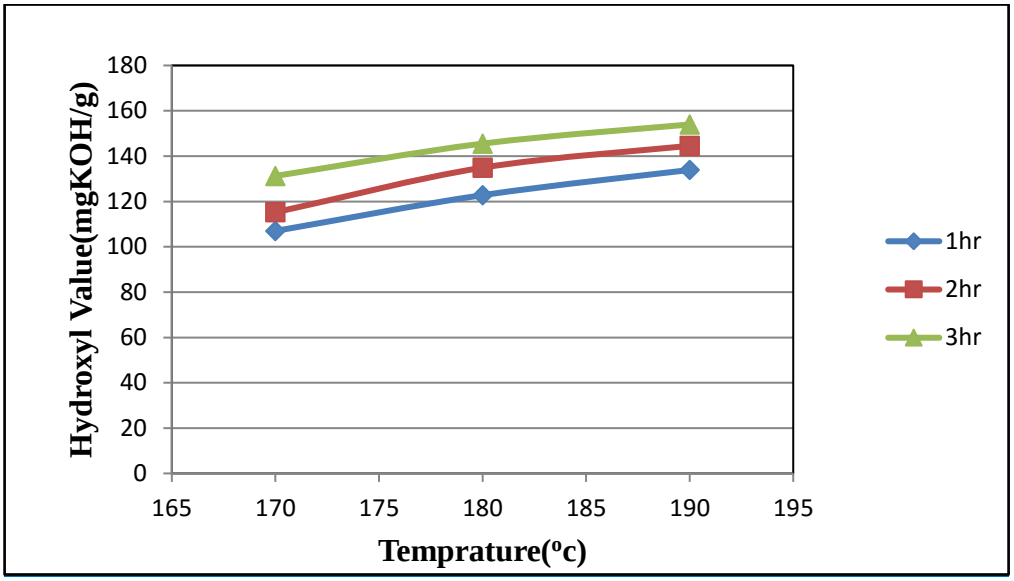


Figure 4.1: Hydroxyl value of recovered polyol at 2% catalyst (Zn (Ac)$_2$) to (EG) ratio.

From this result, it can be concluded that hydroxyl value of a given recycled product can greatly be affected by reaction temperature. The increase in OH values as reaction temperature increases is probably due to, at higher reaction temperature promotes the liberation of secondary reaction byproducts, such as low molecular weight carbamates and an aromatic amine. As these byproducts are basic in nature, they contribute during OH analysis resulting in an increase in hydroxyl number (OH) of the recovered polyalcohol (Ramos, 2010).

4.1.1.2. Catalyst loading effect on hydroxyl value

There are sufficient evidences that an increase in the amount of catalyst reduces the glycolysis time and accelerates the elimination reaction of urethane oligomers. Beside catalyst used for the decomposition reaction, their amount can affect properties of the recyclate polyol by increasing amount of OH group as discussed by (Molero, 2008). In the study, the effect of (ZnAc)$_2$ catalyst on OH value of the product at different reaction temperature and time described before was studied at several catalyst-to-solvent (EG) weight ratio (1%, 1.5%, and 2%) and the results are shown in figure 4.2.

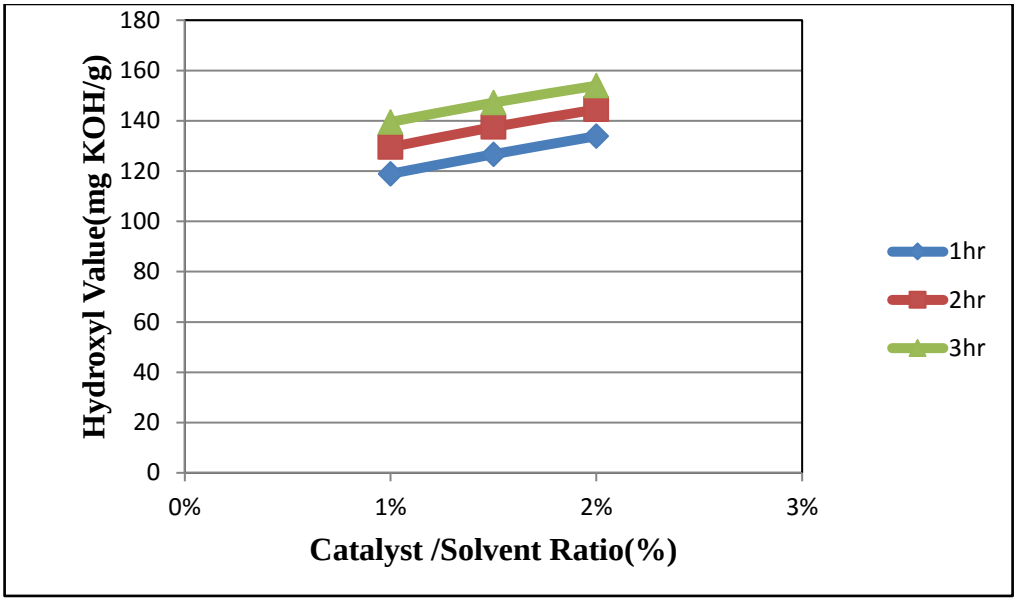


Figure 4.2: Effect of catalyst to solvent ratio on hydroxyl value at temperature 190°c.

From the figure, we can observe that the hydroxyl value increases with the increased amount of catalyst concentration. For example, at 2 hr. of reaction, the hydroxyl value of 129.5, 137.57 and 144.53 mg KOH/g at 1%, 1.5% and 2% w/w ratio respectively were recorded. It indicated that when catalyst concentration increases the hydroxyl value also increases and this is true at the same other parametric conditions (Aguado et al., 2005). When catalyst amount increases, the hydroxyl value becomes increases because of the increment in percent conversion of PU foam block with higher catalyst load, but at higher concentration of catalyst beyond the optimal limit, there is an in increment of amine value due to occurring of reverse reaction which is the cause to raise up the OH value of the recovered product.

4.1.1.2. Decomposition time effect on hydroxyl value

Polyurethane decomposition is highly dependent on dissolution time and the decomposition level can be measured by the hydroxyl value of the resulting product. At a longer reaction time, the amount of hydroxyl value becomes high because of the solvent ethylene glycol can have longer decomposition period which initially has a large number of hydroxyls in its structure (Rodriguez & Borreguero, 2016).

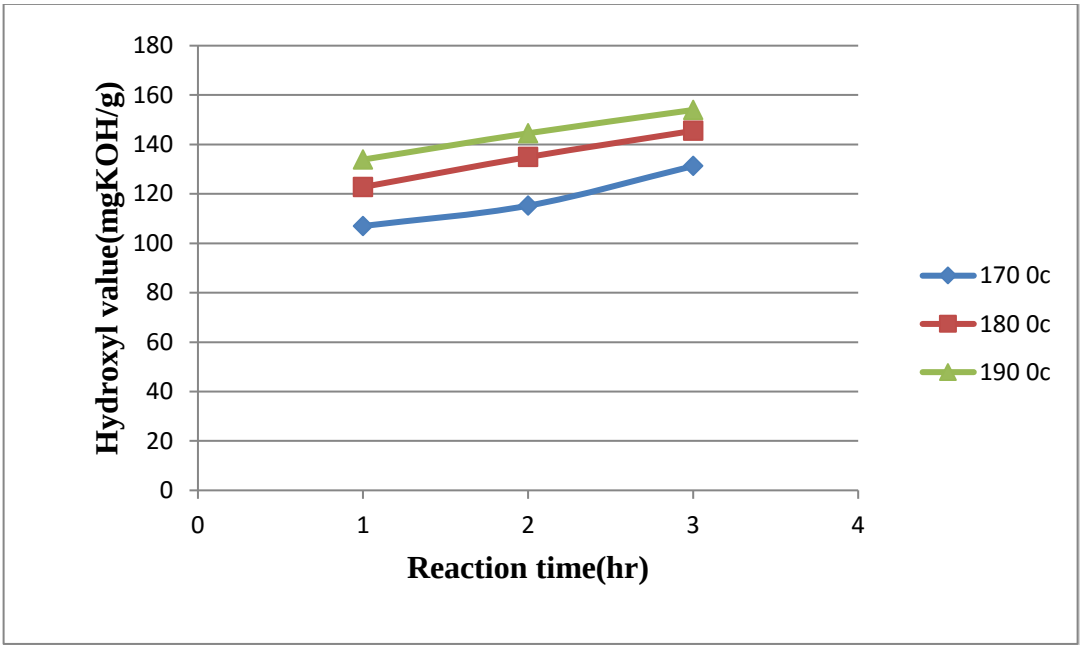


Figure 4.3: Effect of degradation time on hydroxyl value at catalyst to solvent ratio of 2%

The figure revealed the increase of hydroxyl value as time of reaction increases at all tested conditions. For instance, at 170°C, as the time of the reaction increases from 1hr to 3hr, the hydroxyl value also increases from 107 to 131.25mgKOH/g. On the other hand, when the degradation of PU stayed for a longer period the side reaction rather than transesterification was followed to produce unwanted secondary products like aromatic amines those can increase the hydroxyl value.

As general, the increasing of temperature, catalyst concentration and dissolution time affects strongly the hydroxyl value of recovered polyol at any of the conditions. And the OH value of polyol for commercial flexible polyether polyols range is (28 -160 mg KOH/g) according to (Lucas & Rodriguez, 2014). A recovered polyol with OH value out of this grade cannot be used for foaming application, unfortunately the hydroxyl values of recovered polyol of this study at each operating condition were found under the commercial range. In consideration of this fact; the hydroxyl value of the recovered polyol 144.53 mg KOH/g, at temperature 190°c, at 2% catalyst to solvent ratio and two-hour reaction time was selected as abest value by considering other properties of the recovered polyol.

4.1.2. Parameter effect on viscosity of the recovered polyol

Viscosity is one of the most important physical parameter of polyol used intensively during polyurethane foam production. Commonly viscosity value of the recovered polyol greatly affected by the dilution of glycol and reaction by-products derived from the aromatic segments of the isocyanates used during foam production, which obtained in small quantities the polyol phase (Cheng et al., 2003).

4.1.2.1. Effect of temperature on viscosity of recovered polyol

Figure shows the effect of reaction temperature on the viscosity of the recovered polyol.

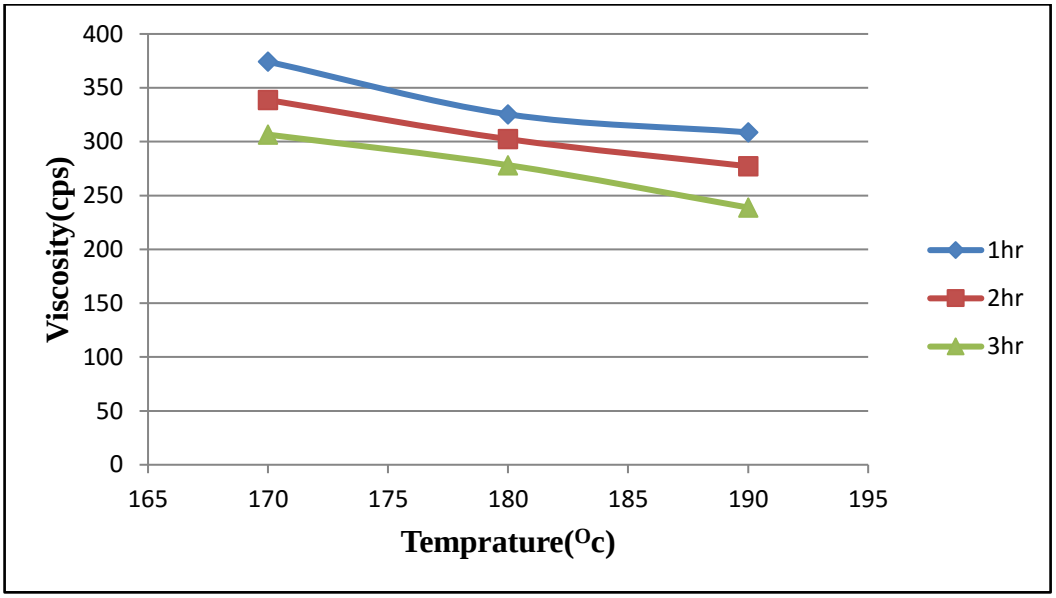


Figure 4.4: Effect of temperature on viscosity of recovered polyol at 2% catalyst loading

The above figure, indicates the relationship between recovered polyol viscosity reaction temperature and reaction time. For instance, at a reaction time of 2hr, viscosity value of recovered polyol decreased from 338.69, 302.35 to 277.16 when the temperature increases from 170, 180 to 190 ^{0}c respectively. It is also important to note that high viscosity of polyol observed at lower temperature is result of an incomplete degradation of PU fragments and as a result, the recyclate has high viscosity in the presence of those un-disappeared polyurethane oligomers. The increment of temperature to a specified value accelerates the glycolysis, oligomer elimination reactions and facilitates phase separation.

And according to (Modesti et al., 2000) raising of temperature during the glycolysis process leads to excessive evaporation of glycol as well as the acceleration of side reactions and a higher probability of initial polyol degradation with dropping of viscosity value occurred.

4.1.2.2. Effect of catalyst loading on viscosity of recycled polyol

The importance of catalyst lies in the fact that in contrast to direct esterification, trans-reactions with alcohol groups proceed very slowly in the absence or small amount of catalysts (Carlos & Santos, 2013). The glycolysis product obtained in this condition still contains PU oligomeric chains, which leads to increasing the recyclate viscosity.

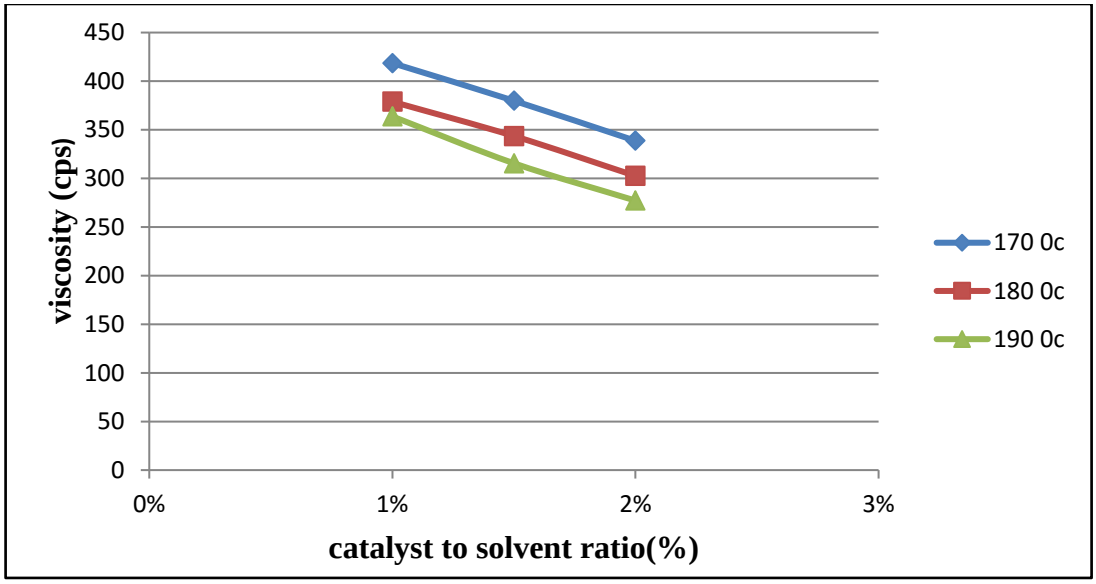


Figure 4.5: Effect of catalyst loading ratio on the viscosity of recovered polyol at time 2hr.

The use of different quantities of Zn $(Ac)_2$ catalyst, changes the final viscosity as shown in figure 4.5. At 190 ^{0}c and time of 2hr the viscosity values had decreasing order of 328 .73, 287.53, 238.79 cps at catalyst to solvent ratio of 1%, 1.5%, and 2% respectively. There was also a reduction at the two-temperature level when catalyst concentration goes to rise, even if the viscosity readings were having higher value related to temperature level. It indicated that higher catalyst load results viscosities with lower values in the same reaction time. Because, low catalyst loading leads to conversion of the polymer and releasing of polyol to the reaction medium after a long period according to (Chao-Yun Yu & Wen-Jau Lee, 2002). Hear PU structure is degraded by glycol and temperature effect only.

4.1.2.3. Effect of reaction time on the viscosity of recovered polyol

Time influences the glycolysis process greatly and viscosity of the obtained polyol. Obviously knowing there is the difference in viscosity when reaction time goes from lower to a higher level. The experimental findings have shown that for reaction times longer than 3 h the glycolysis product is homogeneous. In all reactions the complete disappearance of foam particles was aimed as final dissolution time.

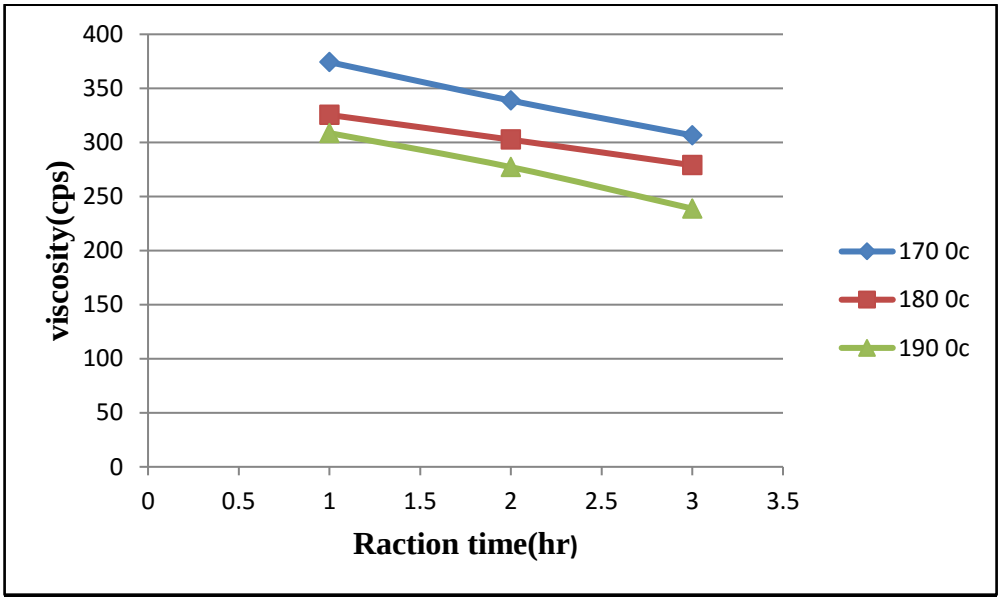


Figure 4.6: Effect of reaction time on viscosity of recovered polyol at 2% catalyst load.

From the Figure 4.6 the viscosity values showed significant variation at the different time interval irrespective of reaction temperature. For instance, at 190 ^{0}c, which was the desired optimum reaction temperature the viscosity readings were 308.63, 277.17, 238.79cps at 1, 2 and, 3 hours. In a study of the influence of the reaction time in the PU depolymerization (Wu CH, 2003) found that two hours is an appropriate time and suggesting that the depolymerization reaction is completed between two and three hours, being in agreement with many literatures.

In all parametrical conditions viscosity value of a given recovered polyol is lower than the original polyol and lower than the viscosity of the virgin polyol and values found in the literatures for glycolysis reaction using different glycol/PU and catalyst/glycol ratio.

The variation can be occurred due to the foam type or internal structure based on its molecular weight (Chen, 2006), catalyst loading and longer reaction period and PU with less crosslinking structure gives a polyol have optimal viscosity at the lower range of reaction controlling factors. Utilized solvent type based on its initial viscosity and evaporation tendency and, catalyst in respect to activation of decomposition also other determinants of viscosity of a recovered polyol (Pérez-Collado, 2007).

And the range of viscosity value for a polyol found from different literature assays which were done at different temperature, time range and catalyst to solvent ratio was (90-3252 cps) (Carlos & Santos, 2013). All the viscosity values of the recovered polyol at different operating conditions were under this range. And viscosity at reaction temperature 190^0c, time 2hour and catalyst to the solvent ratio 2% was chosen as acceptable value in consideration of other properties of the recovered product.

4.1.3. Parameters effect on total amine value of recovered polyol

As a consequence of the degradation process of the polyurethane, the recovered products may contain amine functional group. This amine value is mainly originated from primary amines derived from the starting isocyanates employed in the PU synthesis. On the other hand, the transesterification reaction leads glycol transesterification carbamates for urethane bonds and for urea bonds the resulting product is aromatic diamines (Molero, 2009).

Amines act as a catalyst and enhance the reaction rate between polyol and polyisocyanates by increasing of the electrophilicity of isocyanate functional group and facilitate attaching of polyols and formation of PUs in too short and uncontrollable reaction conditions (Borda, 2000). The combination of both primary and secondary amines value is total amine value. Total amine value of recycled polyol was analyzed by applying standard titration method at different operating conditions and their effect was discussed here.

4.1.3.1. Effect of Temperature on Total Amine Value

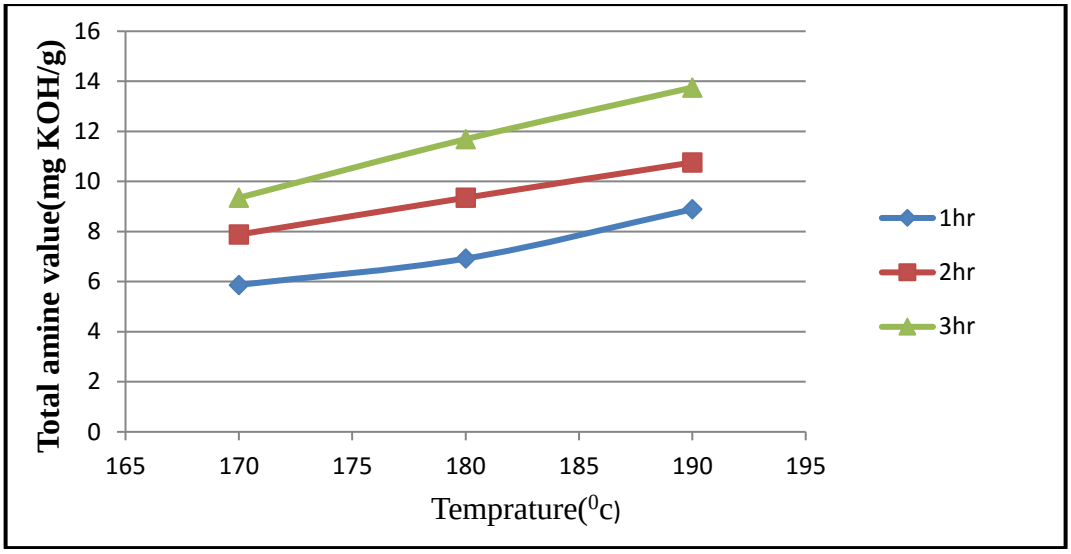


Figure 4.7: Effect of reaction temperature on total amine value

The applied temperature has a significant role for the side production of amines as a result of decarboxylation of trans-esterification carbamates, according to a secondary pathway as proposed by (Borda J, Pa´ sztor G, Zsuga M., 2000). From the graph total amine value showed increment when temperature rise from 170 to 190°c at each reaction time. At 170°c the total amine value of, 5.87, 7.88, 9.35mgKOH/g recorded. Even though there is an increment of total amine number of the recycled polyol by the effect of reaction time still there was no total decarboxylation at this temperature level. And when temperature rises to 190°c, polyol have total amine value of 8.89, 10.76 and 13.75mgKOH/g, it rivaled that at this temperature, and the formed carbamates were highly decarboxile and released a high number of aromatic diamines (Santos & Carone, 2013). So, in conclusion, total amine values of the recovered polyol have an increased amount when the temperature rises up.

4.1.3.2. Effect of Catalyst loading on Total Amine Value

High rate conversion of polyurethane can be achieved by increasing catalyst concentration up to a certain limit. In reverse catalyst used beyond the limit could be a cause for occurring of reverse reaction which can release aromatic amine and the conversion of PU to polyol will be less due to this reverse reaction. And the way to minimize aromatic amines quantity is related to type and amount of catalyst used.

Here Zn $(Ac)_2$ used at 1, 1.5, 2% concentration based the weight of solvent EG, and the effect of these catalyst to solvent ratio on the total amine value of the recovered polyol was analyzed discussed using the graph below.

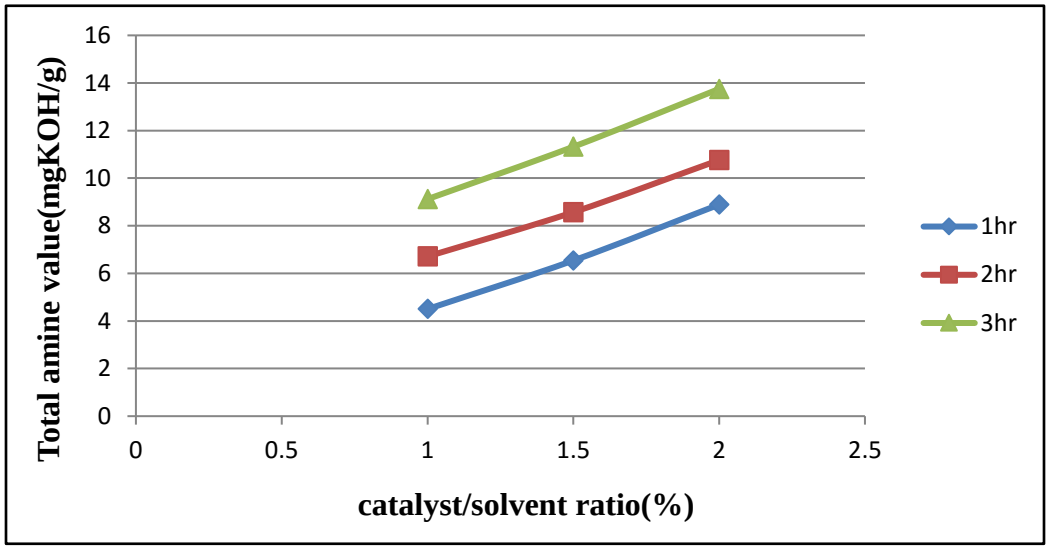


Figure 4.8: Effect of catalyst to solvent ratio on total amine value at temperature 190^0c

According to figure 4.8, an increase in amine value with increase in the concentration of catalyst was found from the analysis. For example, arbitrarily in a 2 hour of reaction time the product has total amine values of 6.71, 8.57, 10.76 mg KOH/g at 1, 1.5, and 2% of catalyst concentration respectively and at each of reaction time, total amine value increment was seen related to the change of catalyst load because of easy and fast liberation of reverse reaction products which release aromatic di-amines at higher loading of catalysts (Lucas, 2005).

4.1.3.3. Effect of decomposition time on total amine value

Decomposition time has a big role in degradation process of polyurethane foam, even if the other operating parameters like temperature and catalyst concentrations not at the desired optimum level to decompose the polymer structure. And even if maximum attainment of polyol can be achieved with in a sufficient decomposition time, there is a great chance of increment of amine value at that longer time of reaction due to the side reactions of trans-esterification carbamates.

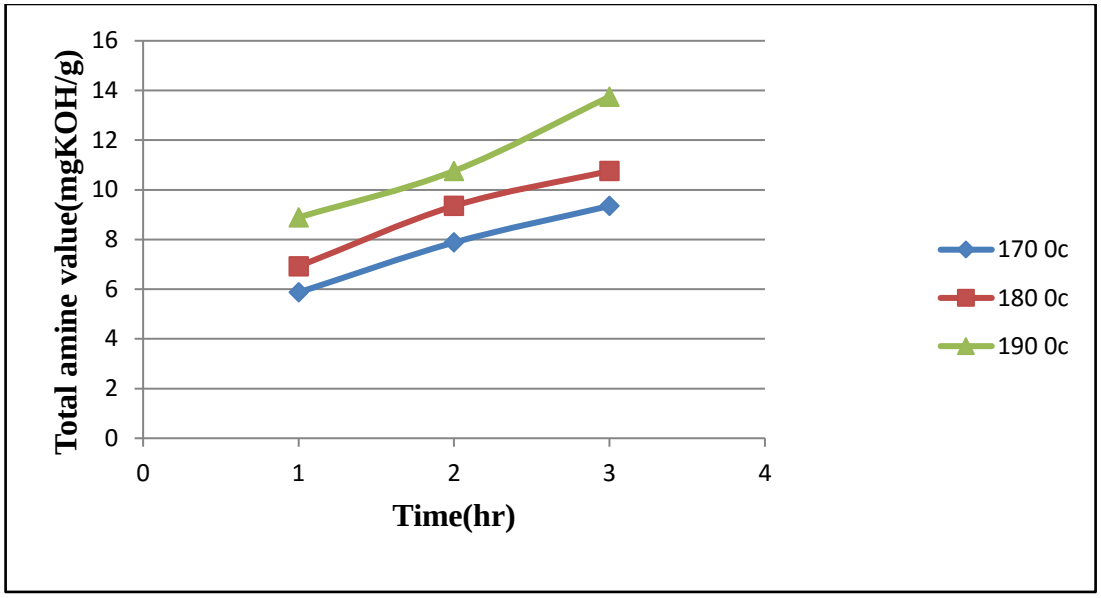


Figure 4.9: Effect of time of reaction on total amine value at 2% catalyst load.

From the figure, results of amine values of the recycled product rise with increasing reaction time from 1 to 3 hours at 0.67g (2%) of catalyst loading and the at three temperature levels. For instance, at temperature 190^0c total amine value were increased from 8.89, 10.76 to13.75 at 1, 2, 3 hours of reaction respectively and also at 170 and 180^oc total amine values showed an increment when the time of reaction goes to high.

4.1.4. Parameters effect on Acid value and Moisture level of recovered polyol

The acidity and water content of recovered polyol were analyzed by standard titration method, (ASTM, D 4662-98) and using moisture content detector instrument respectively. This was done by taking a polyol sample recovered at two hour of residence time and at each temperature level and catalyst loading ratio before purification.

Table 4.1: Acid value (mg KOH/g) of recovered polyol at the three-temperature level, catalyst concentration and 2-hour reaction time.

	1%	1.5%	2%
170^oc	0.016	0.013	0.010
180^oc	0.031	0.027	0.033
190^oc	0.019	0.015	0.012

Table 4.2: Water/moisture content (%) of recovered polyol at each temperature level, catalyst loading and time 2-hour.

	1%(0.3g)	1.5%(0.45g)	2%(0.67g)
170 0c	1.76	2.25	2.54
180 0c	1.41	1.74	2.12
190 0c	1.03	1.39	1.74

From the resulted tabulated data, acid value increased slightly when temperature rise from 170 to 180 ^{0}c because of formation of carbamic acid in this range and decreased when catalyst goes from 1 to 1.5% due to the neutralization reaction between the remaining acid and the catalyst used. But at 190 ^{0}c, acidity decreased by the effect of both temperature and catalyst increment because when the temperature becomes higher the formed carbamic acid can be eliminated, as the same time when catalyst rises acidic part of the resulted polyol became to lower as result of neutralization. And for the majority of polyols, the maximum acidity accepted is around 0.05-0.1 (Ionescu & Mihail, 2005) and from the table 4.1, the acid values were under this range.

The water content of the recovered polyol decreased from 170 to 190 ^{0}c at each of catalyst concentration. As shown from the table these properties have slight difference from commercial requirements for starting polyols (Simon et al., 2014) and water content of the product shows an increment because of occurrence of hydrolysis reaction simultaneously with glycolysis of the given wasted polyurethane foam.

4.2. Investigation of single and Interaction effects using Analysis of variance software

An analysis of variance using the ANOVA commercial software was realized to obtain the contribution of the factors and their interactions over the response variable (hydroxyl value, viscosity and a total amine value of recovered polyol), and to determine the levels that improve these polyol phase properties. The contributions of all no significant factors have been pooled of according to the significance test of general factorial design methodology. The controlling variables were temperature, catalyst to solvent ratio and time of reaction.

4.2.1. Determination of Interaction Effects of Variables on Hydroxyl value

Table 4.3: Analysis of Variance for hydroxyl value.

Source Model	**Sum of Squares**	**DF**	**Mean Square**	**F Value**	**Prob > F**	**significance**
	6326.55	**5**	1265.31	698.55	< 0.0001	significant
A	3116.29	1	3116.29	1720.44	< 0.0001	significant
B	2152.99	1	2152.99	1188.62	< 0.0001	significant
C	991.02	1	991.02	547.12	< 0.0001	significant
A^2	55.57	1	55.57	30.68	< 0.0001	significant
AB	10.68	1	10.68	5.90	0.0243	significant
Residual	38.04	21	1.81			-
Cor Total	6364.58	26				-

According to Analysis of variance (ANOVA) is shown in Table 4.3, the Model F-value of 698.55 implies the model is significant. Prob (P) which was greater than the F value (< 0. 0001), indicating that the model was highly significant. Values of "Prob > F" less than 0.0500 indicate model terms are significant. Where, A stands for temperature, B for time and C, for catalyst to solvent ratio.

The multiple coefficients of determination R^2 was 0.9940, shows that a very good fit of the model and the correlation was good. The adjusted determination coefficient adjusted R^2 was 0.9926, indicate the variability of 99.26% of experimental data can be explained in the regression model. The CV value 1.08 and predicted R^2 of 0.9906, indicated that the reliability and accuracy of the experiment were very good. Based on sequential model sum of squares and model summary statistics data quadratic model was suggested to analyze the experimental response because, p-value was lower than 0.01 for quadratic model only.

Final Equation in Terms of Coded Factors

Hydroxyl number = 126.76 +13.16 *A +10.94*B +7.42*C -3.04*A^2 -0.94*A*B

Where: A = reaction temprature

B = time , and

C = catalyst to solvent concentration

There was a strong alignment of points with the normal plot line and it indicates that the actual value of hydroxyl number of a product does not have a large deviation from predicted value.

Interaction effect of glycolysis process variables on hydroxyl value

From the analysis of variance result, AB (temprature and time) was significant interaction model term and the model graphs of this term were described using countour plot of figure 4.10.

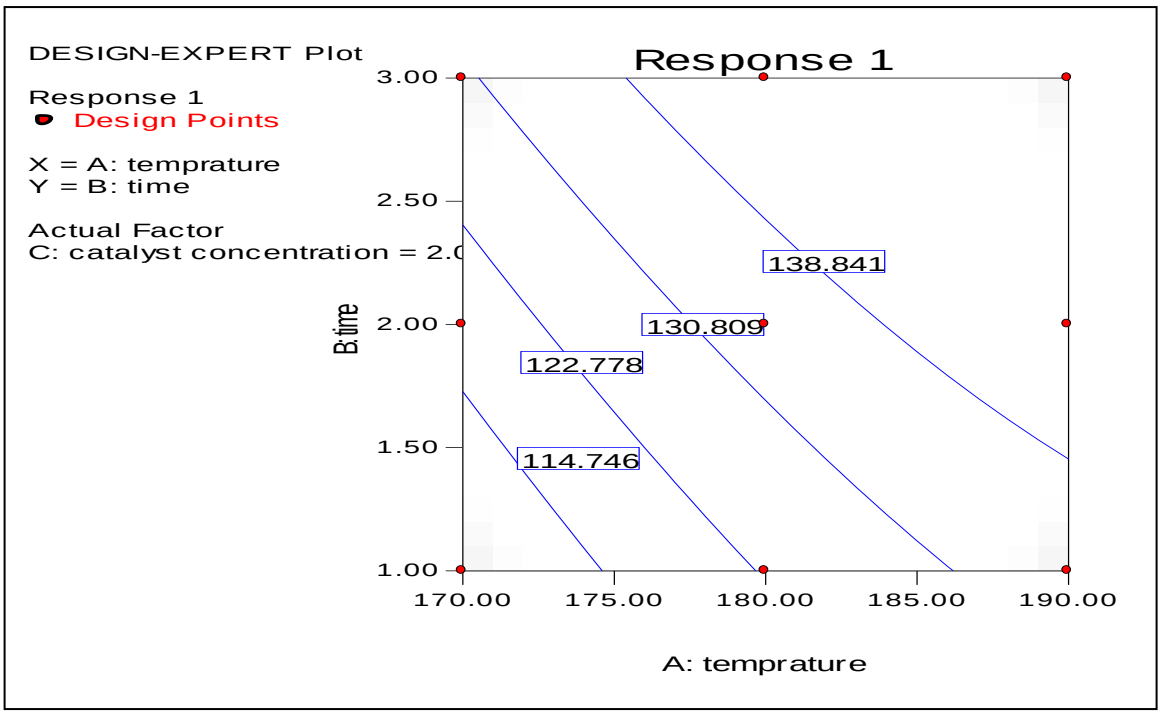


Figure 4.10. Countur plot of hydroxyl value at 2% catalyst to solvent ratio.

The figure shows the interaction effect of temperature and time on hydroxyl value at 2% catalyst to solvent ratio. Each point on the countur plot indicated that at alower level of temperature and decomposition time hydroxyl number of the recovered polyol have lower value and vice-versa at the higher range of both factors. At the lowest temperature level of 170°c and time of 1 hour, result of hydroxyl value was 98.68 mgKOH/g and when temperature rise to 190°c at the same time of reaction the hydroxyl value rose to126.88 mgKOH/g. when reaction time rise up furtherly parallely with temperature there was additional OH increment. This indicates both parameters at their higher level have the tendency to increase the amount of unwanted secondary products which have initial hydroxyl group in their structure.

4.2.2. Determination of Interaction Effects of Variables on viscosity of recovered polyol

Table 4.4: Analysis of variance table for viscosity[Partial sum of squares]

Source Model	SumofSquares	DF	MeanSquare	F-Value	Prob > F	significance
	66892.99	4	16723.25	889.93	< 0.0001	significant
A	17776.18	1	17776.18	945.96	< 0.0001	significant
B	18987.81	1	18987.81	1010.44	< 0.0001	significant
C	29952.10	1	29952.10	1593.91	< 0.0001	significant
A^2	176.91	1	176.91	9.41	0.0056	significant
Residual	413.42	22	18.79			
Cor Total	67306.41	26				

The Model F-value of 889.93 implies the model is significant. Values of "Prob > F" less than 0.0500 indicate model terms are significant. In this case, A, B, C, A^2 are significant model terms. The multiple coefficients of determination R^2 were 0.9939, indicating that a very good fit of the model and the correlation was good.

The adjusted determination coefficient, adjusted R^2 was 0.9927, implied that the variability of 99.27% of experimental data can be explained in the regression model. The CV value 1.25 and predicted R^2 of 0.9901 shows the reliability and accuracy of the experiment were very good. Quadratic model was the highest order polynomial model and found that which have maximum "Adjusted R-Squared" and the "Predicted R-Squared" values. So, it was suggested as a best-fit model.

Final Equation in Terms of Coded Factors:

Viscosity = 343.00 - 31.43 * A - 32.4* B - 40.79* C + 5.43* A^2

Where: A= Temperature

B= Time of reaction

C= Catalyst to solvent concentration

The normality asumption was true, because almost all viscosity value points lied on the normal plot line and few points were very near to the upper and lower region of thenormal line. This indicates the viscosity value difference between the experimental and the predicted results were not significant at each operating parameters.

Interaction effect of parameters on the viscosity of recovered polyol

The operating factors do not have significant interaction effect hear, although each of them has their own strong individual influence on viscosity of recovered polyol, the higher viscosity was recorded at alower range of temperature, time, and catalyst concentration. Because at the higher range of all the factors degradation of the polymer matrix was more accentuated and the recovered polyol also lose its viscosity due to decomposition of its linked structre.

Figure 4.11 shows that, at 1% catalyst concentration, temperature170^{o}c, and 1hour reaction the viscosity reading was 457.55 cps and when temperature increase from180^{o}c, to190^{o}c and time from 2 to 3 hr, viscosity decrease from 378.92 to 328.79 cps.

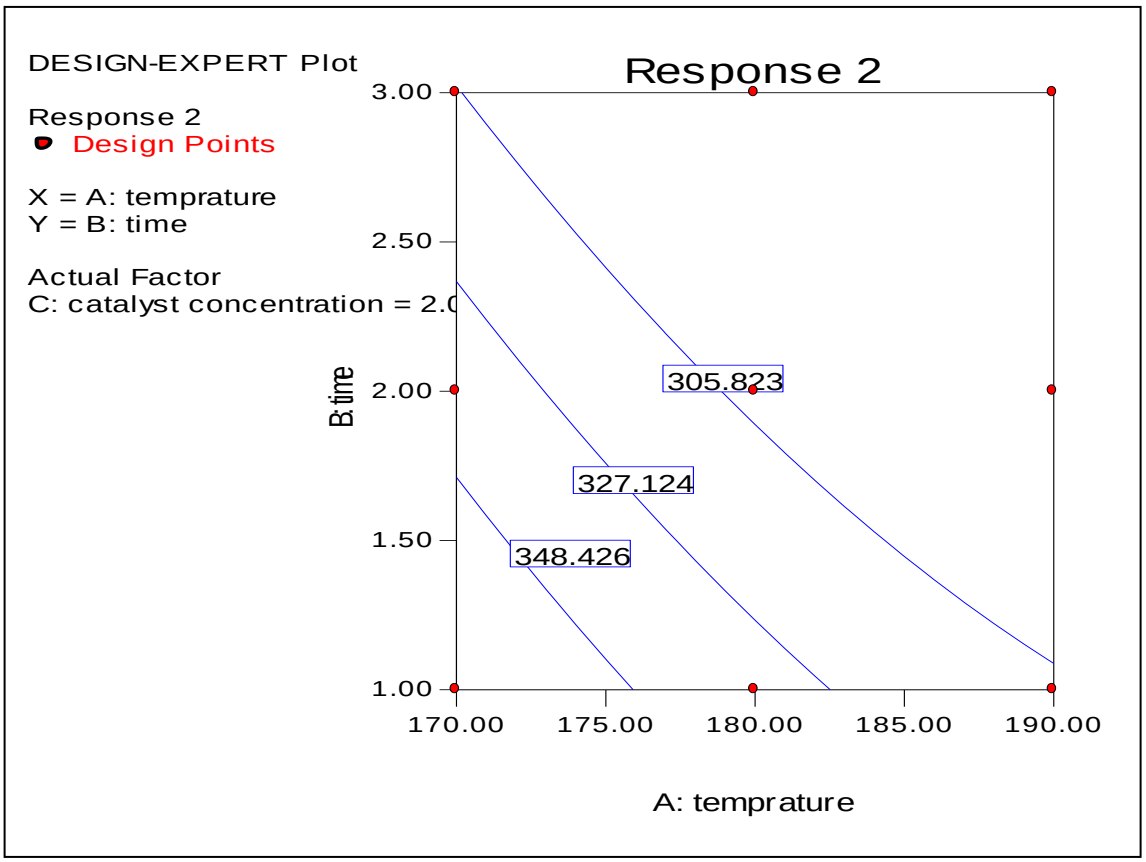


Figure 4.11. Contour plot of the temprature v_s time on viscosity of recovered polyol

Similarly when catalyst concentration increased from 1, 1.5 to 2% viscosity becomes lower and lower to that of 374.24, 302.55 and 238.79 cps respectively at the same reaction time and temperature value. This is because of the improvement of catalyst activity due to their amount, to facilitate progressive disintegration of PU polymer and to turn it into less vicious oligomers.

Higher viscosity for the polyol in the synthesis of new foam block is one of its measurable qualification depending on the type of the foam prepared. Despite to that in glycolysis process a polyol cannot be recovered with the same viscosity to that of the virgin one because of the impact of decomposition factors.

4.2.3. Determination of Interaction Effect of Variables on Total amine value of the Recovered polyol.

Table 4.5: Analysis of variance for total amine value [Partial sum of squares]

Source	Sum of Squares	DF	Mean Square	F Value	Prob > F	significance
Model	186.03	5	37.21	326.99	< 0.0001	significant
A	42.69	1	42.69	375.18	< 0.0001	
B	69.54	1	69.54	611.18	< 0.0001	
C	70.37	1	70.37	618.46	< 0.0001	
AB	2.53	1	2.53	7.88	0.0106	
BC	0.90	1	0.90			
Residual	2.39	21	0.11			
Cor Total	188.42	26				

The Model F-value of 326.99 implies the model is significant.Values of "Prob > F" less than 0.0500 indicate model terms are significant. In this case, A, B, C, AB, BC are significant model terms.

Based on the model adequacy measured data the multiple coefficients of determination R^2 were 0.9873, indicating that a very good fit of the model and the correlation was good. From the adjusted R^2 value 0.9843, the variability of 98.43% of experimental data can be explained in the regression model. The CV value 4.58 and predicted R^2 of 0.9764 showed that the reliability and accuracy of the experiment were very good. The "Pred R-Squared" of 0.9764 was in reasonable agreement with the "Adj R-Squared" of 0.9843. And from the fit summary data of Sequential model sum of squares quadratic model and Model summary statistics, 2FI was selected as an adequate model, because which was the highest order polynomial model and found that have maximum Adjusted R-Squared value.

Final equation interms of coded factor

Total amine value =7.36 +1.54 *A+ 1.97 * B +1.98 *C+ 0.46 *A *B+ 0.27* B* C

.Where: A = tempratue

B = time

C = catalyst to solvent concentration

Normality assumption for this response was true. The resulted total amine value of the recovered polyol and the predicted amine value does not show significant variation. So the closer the estimates fall along the line, the more consistent the data are with an assumption of no true effects and also an evidence for the adequacy of the given model.

Determination of effect of interaction parameters on the resulted total amine value

According to ANNOVA result atotal amine value of the recovered polyol was significantly affected by interacted factors temperature, time and time, catalyst loading.

Reaction temprature versus time

They do have aparallel effect on resulted amine value. And total amine value of the recovered polyol was increased constantly at higher reaction temperature and time with constant amount of catalyst, this was because of the production of secondary products of glycolysis process susceptible to the release of aromatic amines at ahigher level of heat and longer residence time.

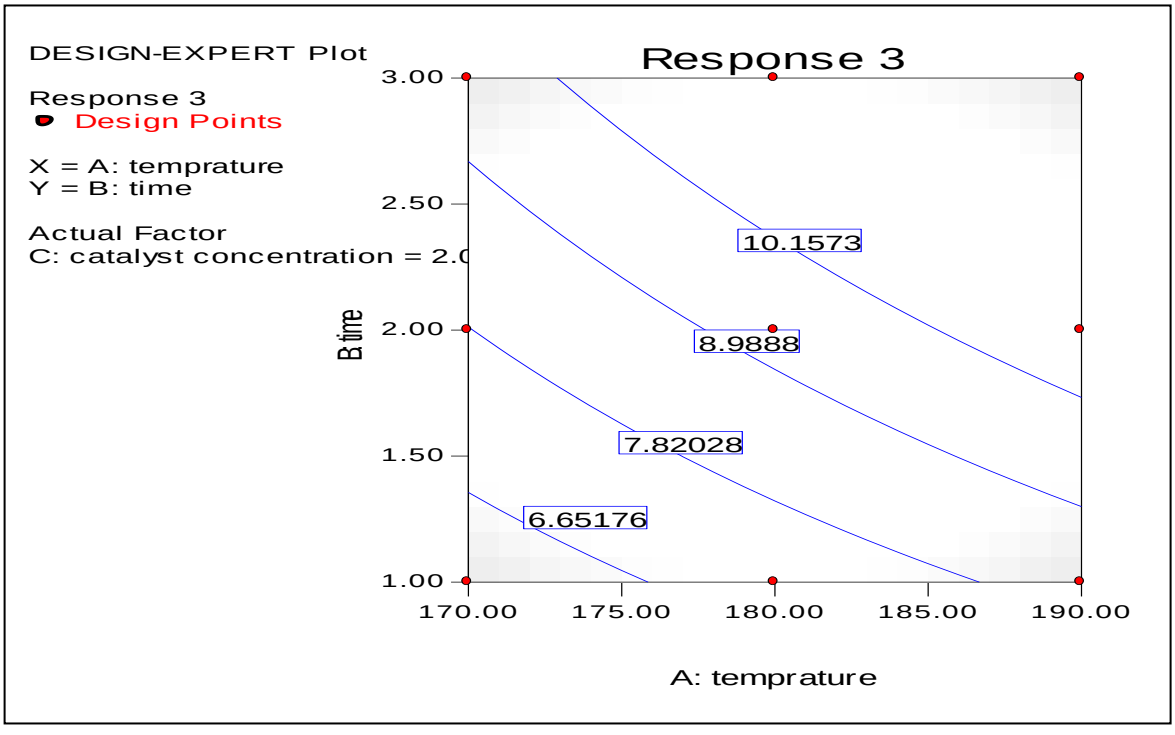


Figure 4.12: Countur plot of temperature versus time at 2% catalyst to solvent ratio.

Catalyst versus decomposition time

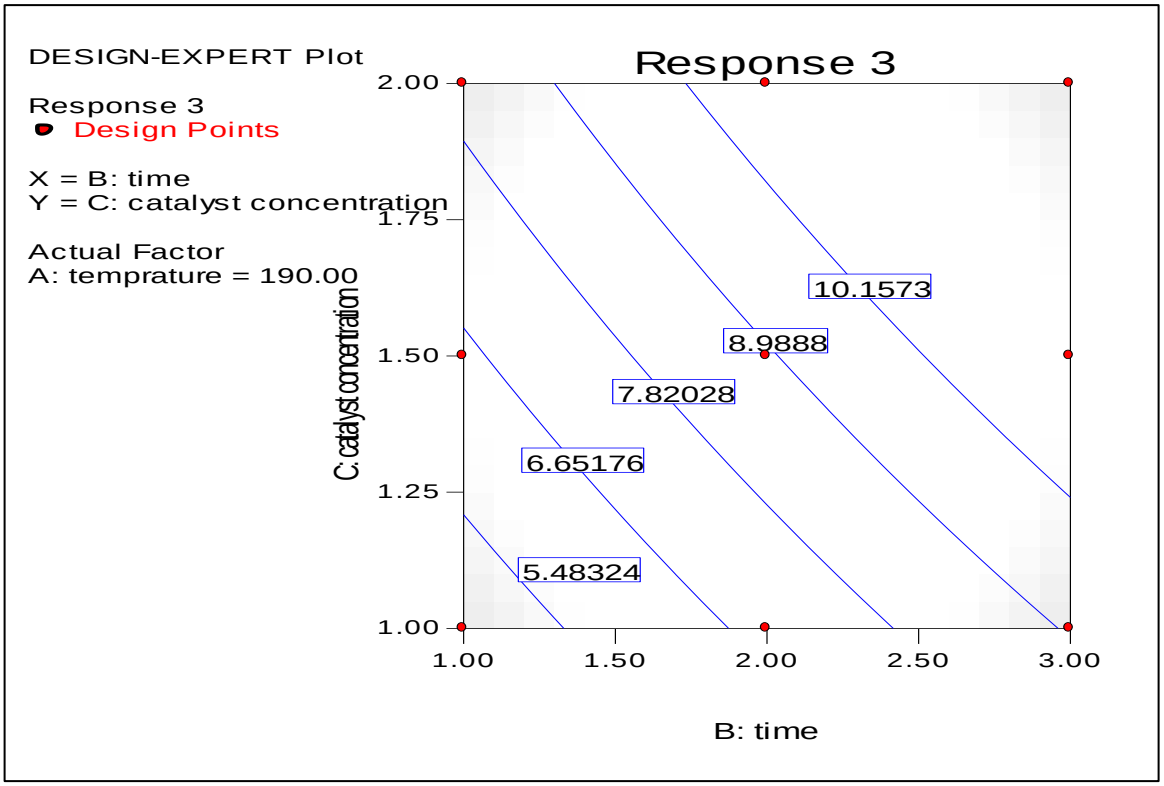


Figure 4.13. Countur plot of catalyst versus time at temperature of 190°c

Catalyst affects the purity of the recovered polyol by facilitating production of secondary or unwanted by products during transesterification process as discussed earlier. As a reuslt of such by products aromatic di-amines were produced and mixed with the recovered polyol of the upper phase in a different proprtion based the amount of catalyst load and time of decomposition, so they have a direct interaction effect for the increment of total amine value a given recovered polyol.

As illustrated on the above countur figures, when the amount of catalyst used increased from lower to ahigher level with that of reaction time, atotal amine value of the product also increased at any of reaction temperature. Foinstance, at 1% of catalyst concentration, time 1hour, and 170 ^{0}c , amine value was 3.05 mg KOH/g and at 1.5% catalyst concentration, time two-hour, polyol have 5.89 mgKOH/g of total amine value at the same temperature. The increment was the same when temperature rises to 180 and 190 ^{0}c.

In conclusion, the total amine value recovered polyol, at higher temperature, time and catalyst concentration have higher magnitude and all the factors were have significant interaction effect on this response. Amines released from PU foam depolymerization simultaneously with transesterification reaction as undesired product due to the effect of operating conditions as discussed before elaborately. And which have great negative impact on the recovered polyol purity by increasing primary amines content of the polyol. This greatly impose polyaddition reaction to make polyurethane foam to complete in faster rate at the early consumption of isocyanate functional group.

4.3. Polyol phase purification

The properties of upper phases, which are mainly constituted by the recovered polyol, were commonly out of Commercial specification due to the presence of by-products and glycol were characterized in order to evaluate the feasibility of their use in substituting commercial polyols (Simon & Modesti, 2014). The chosen purification method was a liquid-liquid extraction mechanism, which works by mixing the recovered polyol with a solution prepared from demineralized water and hydrochloric acid according to previous studies by the research group (Molero, 2006). And it was done by picking up three of recovered polyol which recycled based on specific parametric conditions as described on the table below. After that, hydroxyl value, viscosity and total amine value of the purified polyol were measured then the result was putted by comparing with the crude polyol.

Table 4.6: Properties of crude recovered and purified polyol at reaction time of 2hr, 2% catalyst to solvent ratio and each temperature level.

Properties	Hydroxyl value (mg KOH/g)		Viscosity(cps)		Total amine value (mg KOH/g)	
Temperature	Crude	Purified	Crude	Purified	Crude	Purified
170°c	115.22	95.34	338.69	298.41	7.88	5.75
180°c	134.91	82.76	302.55	275.12	8.89	6.84
190°c	144.53	69. 98	277.16	240.21	10.76	8.45

The decrement of hydroxyl value and total amine values are necessary to use the recovered polyol for foaming application and they should have resemblance with the commercial grade raw polyol have a range of (28-160 mg KOH/g) according to (D. simon, A. de lucas, A.M. Borreguero, J.F. Rodríguez, 2016) as discussed earlier. The recyclate has higher viscosity before purification because of the remaining reaction byproducts in the upper phase, but when purification was applied these bi-products were solubilized within the extract and the viscosity at each point shows reduction as shown from the table and as reported in the previous study by. Therefore, polyol phase purification is an urgent task in order to obtain a recovered polyol susceptible of being used in the foaming process because, purified polyol will have: -

- Low aromatic diamine content which reduce uncontrollable PU formation reaction rate
- Lower bi products activity which interfere polymer formation process
- Reduced OH value proportional with isocyanate functional group, etc.

4.4. Aspect of synthesized foam block

The aspect of the foams synthesized is shown in Fig. 4.15. And during foam synthesis operation tried to see that, the foam which prepared from recovered polyol before purification grew at very fast rate. This is due to the presence of by-products and di amines and these di-amines generated as a result of glycolysis in urea bonds. They act as catalyst enhance the reaction rate between polyol and polyisocyanates by increasing of the electrophilicity of isocyanate functional group and facilitate attaching of polyols and formation of PUs in too short period of time. And this is also due to the faster reaction of isocyanates with amines at room temperature than with alcohol (simon et al., 2016).

In contrast a PU synthesized with purified polyol can grew properly than synthesized with un-purified polyol, even though purification cannot be nullified the amine content of the recovered polyol completely. The foam block which was prepared with crude polyol does not have the desired strength. It may indicate, secondary products within the polyol affect the crosslinking of the recovered polyol and other substances by reducing the capacity of the crosslinking agents.



Figure 4.15: Physical appearance of flexible foams synthesized with a recovered polyol before and after purification.

On the other hand, there was visual difference between the two foam blocks that was the color intensity. Foam synthesized from crude recovered polyol have a dark brown color and from purified one have a light brown color. However, in the PU industry, foams are normally tinted with different colorants so which is not a drawback.

5. CONCLUSION AND RECOMMENDATION

5.1. Conclusion

Glycolysis in two phases for flexible PU foam has been performed using ethylene glycol as a solvent and zinc acetate as a catalyst, to recover a polyol and to characterize its properties by determining the hydroxyl value, viscosity, total amine value, acid value. In this work, the influences of the process parameters, i.e. time at (1, 2 and, 3hr), temperature of (170, 180 and 190 ^{0}c), and Cat/Sol ratios (1, 1.5 and 2%) on the recovered polyol have been investigated individually and simultaneously.

From the result, hydroxyl value shows an increment when each controlling factor increases simultaneously, but decomposition time and temperature have a comparatively stronger impact on the hydroxyl value of recycled polyol. Here decomposition time and temperature have significant interaction effect on the resulted polyol. Viscosity shows a reduction at higher level of each single factors and in reverse for the reaction performed with low catalyst loading, time range and at minimum temperature, highest final viscosity was recorded. Similarly, total amine value raised at higher levels of individual factors. And it also significantly affected by interaction effect of reaction time and catalyst loading.

Acid value increased slightly when temperature rise from 170 to 180 ^{0}c and decreased when catalyst goes from 1 to 1.5% at the same reaction time, but at 190 ^{0}c acidity becomes to decreased due to the higher temperature, catalyst loading and longer time effect. And water content of the recovered polyol decreased from 170 to 190 ^{0}c at each of catalyst loading and reaction time.

In conclusion according to the resulted characterization and analysis, adequate properties of the recovered polyol in the acceptable standard range was achieved at an optimal values of temperature 190^{0}c, time of 2hr and catalyst/solvent ratio of 2%. This result also supported by many researches performed previously.

5.2. Recommendation

From the present study finding, the following recommendations are forwarded.

In the glycolysis operation ethylene glycol was used as solvent because of its availability further studies need to perform using different kinds of solvent like; MEG, DEG, MPG, etc., to check their performance in polyol recovery process with a high quality.

Similar works should be done by using different types of catalyst like; Lewis acid catalyst, amine catalyst, tin catalyst, organometalic catalyst, etc., in different proportion to determine their capability in the evolution of polyol from the glycolyzed PU foam waste.

The determination of concentration of the recovered polyol on the upper phase in comparison with other competitive by products is necessary in the polyol recovery process. Respect to that, additional work is required.

Synthesis of sample foam block using a recovered polyol in different proportion and analysis of its mechanical properties should be done and glycolysis in batch scale also need to try.

Finally, in current situation many foam production factories in Ethiopia have adapted physical recycling mechanisms. So, factory owners and different foam production centers should be aware of this fact through university- industry linkage.

REFERENCES

A. Guo, D. Demydov, W. Zhang and Z. S. Petrovic. (2002). Polyols and polyurethanes from

Alicia Aguado, Lidia Martínez, Alberto Moral, José Fermoso, Rubén Irusta. (2005). Chemical Recycling of Polyurethane Foam Waste Via Glycolysis. Cartif Technology Center.

Amir Bagheri Garmarudi, Mir Mohammad Alavi Nikje. (2010). Regeneration of Polyol by Pentaerythritol-assisted Glycolysis of Flexible Polyurethane Foam Wastes. Iranian Polymer Journal, 287-295.

Andrzej.Zieliński, Wit Witkiewicz,. (2006). PROPERTIES OF THE POLYURETHANE (PU) LIGHT FOAMS. Ship Design and Research Centre.

Antonio de Lucas, Carolina Molero, Juan F. Rodriguez. (2005). Recovery of polyols from flexible polyurethane foam by ''split-phase'' glycolysis with new catalysts. Polyemr Degradation and Stability, 894-901.

Bayer.AG, Yantai Wanhua. (2015). polymer properties.

Borda J, Pasztor G, Zsuga M,. (2000). Glycolysis of polyurethane foams and elastomers. Polymer Degradation and Stability,.

Boustead, I. (2005). Polyurethane Flexible Foam. Hanser Publishers.

Branderup, J., Bittner, M., Menges, G., Micheali, W.,Hanser,. (1998). "Recycling. Germany: Münich.

C. Molero, A. de Lucas & Dr. J. F. Rodríguez. (2006). Purification by Liquid Extraction of Recovered. Solvent Extraction and Ion Exchange.

C. Molero, A. de Lucas, J.F. Rodrı´guez*. (2009). Activities of octoate salts as novel catalysts for the transesterification of flexible polyurethane foams with diethylene glycol. Polymer Degradation and Stability, 533–539.

Carlos L. P.Carone, Leonardo M. dos Santos. (2013). Using Different Catalysts in the Chemical Recycling of polyurethane foam waste. Artigo scintific center.

Carolina Molero, A. d. (2006). Recovery of polyols from flexible polyurethane foam by ''split-phase'' glycolysis with new catalysts. Polymer Degradation and Stability .

Carolina Molero, Antonio de Lucas, Juan F. Rodrı´guez. (2006). Recovery of polyols from flexible polyurethane foam by ''split-phase'' glycolysis: Glycol influence. Polymer Degradation and Stability, 221-228.

Chao-Hsiung Wua, Ching-Yuan Chang, Chien-Min Cheng, Hung-Chang Huang. (2003). Glycolysis of waste flexible polyurethane foam waste. Polymer Degradation and Stability, 103–111.

Chao-Yun Yu, Wen-Jau Lee. (2002). Thermal glycolysis of polyurethane from. Polym Degradation and Stability.

Cheng , Huang, Wu.C.H,Chang, . (2003). Glycolysis of waste flexible polyurethane foam. Polymer Degradation and Stability, 103–111.

D. simon, A. de lucas, A.M. Borreguero, J.F. Rodríguez. (2016). Glycolysis of high resilience flexible polyurethane foams containing polyurethane dispersion polyol. Elesevier, 119-30.

D. Simon, A.M. Borreguero, A. de Lucas, J.F. Rodríguez. (2014). Glycolysis of flexible polyurethane wastes containing polymeric polyol. Elesevier, 115-121.

De Lucas, A., Pérez-Collado,Molero C. (2007). Polyol recovery of flexible polyurethane foams by means of glycoysis. polymer degradation and stability.

De Lucas, A., Rodríguez, J.F.,. (2006). Recovery of polyols from flexible polyurethane foam by "split- phase" glycolysis: Glycol influence. Polymer Degradation and Stability, 221-228.

De Lucas., A., Romero, F., Rodriguez, J.F., Molero, C.,. (2008). Influence of the useof recycled polyols obtained by glycolysis on the preparation and physicalproperties of flexible polyurethane. Journal of Applied Polymer Science, 617-626.

Dimitrios V. Dounis, Garth L. Wilkes. (1997). Structure-property relationships of flexible polyurethane foams. 2819-2828.

E. K. Leitsch, W. H. Heath and J. M. Torkelson. (2016). Polyurethane/ Polyhydroxyurethane Hybrid Polymers and Applications as Adhesive Bonding Agents. Internatioal J. Adhesives, 1-8.

Efstathiou, Kypros. (2014). Synthesis and characterization of a Polyurethane Prepolymer for the development of a novel Acrylate-based polyol.

Fateme Haji Agha Mohammadi, Mir Mohammad Alavi Nikje,. (2009). Sorbitol/Glycerin/Water Ternary System as a Novel Glycolyisi agent for flexible Polyurethane foam in the chemical recycleing using microwave radiation. Ployemry, 7-8.

G. Behrendt, B.W. Naber. (2009). The chemical Recycling Ployurethanes: Review. Journal of University Chemical Technology and Metallurgy, 3-23.

Garforth. (2004). Decomposition of polyurethane foams. Journal of Applied Polymer Science.

Garmarudi, M. m. (2010). Regeneration of Polyol by Pentaerythritol- assisted Glycolysis of Flexible Polyurethane Foam Wastes . Iranian Polyemr Journal , 287-295.

Gist, Double. (2013). production of high quality foam.

Guy Koeckelberghs, Marcel Van Beylen,Celest Samyn. (2001). Synthesis of new polyisocyanates. European Polymer Journal.

Hill, R.M.,. (1999). Silicone Surfactants. Surfactant Science Series.

Ionescu, Mihail. (2005). Chemistry and Technology of polyol for polyurethane. Rapra Technology Limited.

J. Borda, G. Pasztor and M. Zsuga,. (2000). Glycolysis of polyurethane foams and elastomers. Polymer Degradation and Stability, 419-422.

JADHAV, VISHWANATH S. ZOPE and SUMIT V. (2010). COMPARATIVE STUDIES ON CHEMICAL RECYCLING (DEPOLYMERIZATION) OF POLYURETHANE SCRAP MATERIAL. International. J. Chemical science, 1007-1020.

John O. Akindoyo, M. D. H. Beg, Suriati Ghazali, Nitthiyah Jeyaratnama and A. R. Yuvarajc. (2016). Polyurethane types, synthesis and applications. ROYAL SOCITY OF CHEMISTRY, 453-482.

Kaminsky, J. Scheirs . (2006). Feedstock Recycling and Pyrolysis of Waste Plastics. Wiley, Chichester.

Kirk-Othmer. (2001). Encyclopedia of Chemical Technology. Newyork: John Wiley & Sons.

Kopczynska, Janusz Datta & Patrycja. (2016). From polymer waste to potential main industrial products: Actual state of recycling and recovering. ENVIRONMENTAL SCIENCE AND TECHNOLOGY, 905–946.

Krol, Piotr. (2007). chemical structures and phase structures of linear polyurethanes. Materials Science, 915-1015.

Lee, David Randall and Steve. (2003). The Polyurethane Book.

Lee, S.T. (2004). POLYMERIC FOAM Mechanisms and Materials. LONDON: CRC PRESS.

Leonardo M. dos Santos, Carlos L. P. Carone. (2013). Using Different Catalysts in the Chemical Recycling of Waste From Flexible Polyurethane Foams. polymer.

Lucas, A. de, Molero, C., Rodríguez J. F., Málaga, M. (2005.). Process for the Recovery of Reusable Polyols from Polyurethane Foams using a Novel Catalyst. Journal of Applied Polymer Science.

Lucas, A. de, Rodríguez,. (2014). Glycolysis of flexible polyurethane wastes containing polymeric polyol. Polymer Degradation and Stability.

M. F. Sonnenschein. (2014). Polyurethanes. Science, Technology,. The Dow Chemical Company.

M. Haghshenas, M. Nikje and Amir Bagheri Garmarydi. (2006). Polym. Engg. and Sci. 257-265.

M. Ionescu, D. Radojcic, X. Wan, M. L. Shrestha, Z. S. Petrovic and T. A. Upshaw. (2016). Highly functional polyols from castor oil for rigid polyurethanes. Euro,Polymer, 736–749.

M. J. Ramos, A. de Lucas & J. F. Rodríguez. (2010). Chemical recovery of flexible polyurethane foam waste. WIT Transactions on Ecology and the Environment.

M. Nikje, M. Haghshenas and Amir Bagheri Garmarydi. (2011). Polyurethane Waste Reduction and Recycling From Bench to Pilot Scales. Designed Monomer and Polymer, 395-421.

Mahoney, L. R., Weiner, S. A., and Ferris, F. C. (1990). Hydrolysis of Polyurethane Foam Waste. Environ Science and Technology, 135–139.

Mark F. Sonnenschein, Robbyn Prange and Alan K. Schrock. (2007). Mechanism for the compression set of TDI polyurethane foams. Polymer, 616-623.

MC.Robie. (2011). X-Polymers-G-Polyurethane. Union Carbide (N.Z.) Ltd.

Mills, NJ. (2007). Polyurethane foams: Processing and microstructure,. Polymer Foams Hand book, 19-37.

Mir Mohammad Alavi Nikje, Amir Bagheri Garmarudi , and Azni B. Idris . (2011). Polyurethane Waste Reduction and Recycling:From Bench to Pilot Scales. Designed Monomers and Polymers, 395–421.

Modesti M, Simioni F, Munari R, Baldoin N. (2000). Recycling offlexible polyurethane foams with a low aromatic amine content. Reaction Functional Polymer.

Modesti, M. (1998). Recycling of Polyurethane Polymers: Advances in Urethane Science and Technology.

Molero, C., De Lucas, A., Rodríguez, J.F.,. (2006). Recovery of polyols from flexible polyurethane foam by "split- phase" glycolysis with new catalysts. Polymer Degradation and Stability, 894-901.

Molero, C., de Lucas, A., Rodríguez, J.F.,. (2008). Recovery of polyols from flexible polyurethane foam by "split-phase" glycolysis: Study on the influence of reaction parameters,. Polymer Degradation and Stability, 353-361.

Nikje, M. M.A., and Nikrah, M. (2007). Glycerin as a New Glycolysing Agent for Chemical Recycling of Cold Cure Polyurethane Foam Waste in "Split Phase" Condition. Polyemr Pull, 411-423.

Oertel, G. (2000). Polyurethane Handbook. Second edition. Newyork: Carl Hanser Publishers.

Piotr, Krol. (2007). Properties and applications of linear polyurethanes in polyurethane elastomers, copolymers and ionomers. Progress in Materials Science, 915-1015.

Prisacariu, C. (2011). Polyurethane elastomers: from morphology to mechanical aspects. Springer Science and Business Media.

R. Zevenhoven, A. T. (2002). Processing Wastes and Waste-Derived Fuels Containing BrominatedFlame Retardants. . Energy Engineering and Environmental Protection(Espoo).

Ramesh, S.T. Lee N.S. (2004). Polymeric Foams Mechanisms and Materials. London: CRC Press.

Rodríguez, Ana M. Borreguero and Juan F. (2013). GLOBAL PROCESS OF FLEXIBLE POLYURETHANE FOAMS RECYCLING BY SPLIT – PHASE GLYCOLYSIS. Energy and environment.

Rodríguez, J.F.,. (2006). Recovery of polyols from flexible polyurethane foam by "split-phase" glycolysis with new catalysts. Polymer Degradation and Stability,, 894-901.

S. Petrovic, W. Z. (2005). Structure and properties of polyurethanes prepared from triglyceride polyols. Biomacromolecules, 713–719.

Scheirs, J. (1998). Polymer Recycling: Science, Technology and Applications. Wiley, Chichester.

Seymour, Raymond, and Charles Carraher. (1995). Polymer Chemistry. Newyork: Marcel Dekker.

Simon, Modesti M. (2014). Glycolysis of flexible polyurethane wastes containing polymeric polyol. Cellular polymers degradation and stability.

Sperling, L. (2006). Introduction to Physical Polymer Science. New Jersey, Canada: Wiley Interscience.

Szycher, M. (2002). "Szycher's Handbook of Polyurethanes ". London: CRC Press.

Weigand, E., Wagner, J., Waltenberger, G. (1998). . "Energy recovery from polyurethanes in industrial power plants. Abfall Journal, 40-45.

Weight, K. J., & Macgregor, J. G. (2012). Reinforced Concrete Mechanics & Design (6th edition ed.). New Jersey, US: Pearson Education.

Wenqing Yanga, Qingyin Dongb et al. (2012). Recycling and disposal methods for polyurethane foam waste. journal of Procedia Environmental Sciences, 167-175.

Woods.G. (2013). Flexible polyuretane foams, chemistry and technology.

Wu CH, Chang CY, Cheng CM, Huang HC. (2003). Glycolysis of waste flexible polyurethane foam. Polym Degrad Stab.

Zevenhoven, R., Axelsen, E.P., Elomaa, M., Kilpinen, P., Hupa, M. (2003). The behaviour of nitrogen from polymers and plastics in waste-derived fuels during combustion. Finnish National Technology Agency, 104-109.

Zevenhoven, Ron. (2004). TREATMENT AND DISPOSAL OF POLYURETHANE WASTES: OPTIONS FOR RECOVERY AND RECYCLING. Energy Engineering and Environmental Protection.

Zia KM, Bhatti HN, Bhatti IA,. (2007). Methods for polyurethane and polyurethane composites, recycling and recovery. React Functional Polymer, 675-692.

ZOPE, SUMIT V. JADHAV and VISHWANATH S. (2010). COMPARATIVE STUDIES ON CHEMICAL RECYCLING (DEPOLYMERIZATION) OF POLYURETHANE. International journal of Chemical science.

APPENDIXES

Appendix A: Recovered polyol properties data analysis by using design expert software:

Table A.1: Analysis of experimental design (actual) data of recovered polyol properties at various operating conditions.

Run	Temperature (^{o}c)	Time (hr)	$Zn(Ac)_2$/EG (%)	Hydroxyl No (mgKOH/g)	Viscosity (cps)	Total amine value (mgKOH/g)
1	190	1	1.5	126.68	348.06	6.54
2	190	3	1.00	139.52	328.79	9.12
3	190	3	1.5	147.22	287.53	11.32
4	180	2	1.5	127.69	343.56	6.94
5	190	3	2.00	153.96	238.79	13.75
6	180	1	2.00	122.78	325.41	6.92
7	170	1	1.00	92.56	457.55	3.05
8	190	1	1.00	118.9	384.73	4.5
9	180	3	2.00	145.52	278.19	11.69
10	170	3	1.5	124.64	345.77	7.64
11	170	1	1.5	98.98	414.56	4.21
12	170	2	1.5	107.71	379.83	5.89
13	180	1	1.00	110.51	421.67	4.08
14	180	2	2.00	134.91	302.55	8.89
15	170	2	1.00	102.5	418.56	3.78
16	180	3	1.5	137.51	311.63	9.73

17	190	2	1.5	135.72	315.56	8.57
18	180	3	1.00	128.49	347.55	7.45
19	190	1	2.00	133.88	308.63	8.95
20	170	3	1.00	115.21	382.93	4.83
21	190	2	2.00	144.53	277.16	10.76
22	180	2	1.00	118.3	378.92	4.95
23	170	1	2.00	107	374.24	5.87
24	190	2	1.00	129.5	363.75	6.71
25	170	3	2.00	131.25	306.53	9.35
26	170	2	2.00	115.22	338.69	7.88
27	180	1	1.5	116.17	377.48	5.38

Appendix B: Annona model summary statistic tables for each responses

Table B1: Model Summary Statistics for hydroxyl value

Source	**Std.Dev**	**R-Squared**	**Adjusted RSquared**	**Predicted RSquared**	**PRESS**	
Linear	2.13	0.9836	0.9815	0.9782	138.93	
2FI	2.13	0.9858	0.9815	0.9765	149.85	
Quadratic	1.36	0.9950	0.9924	0.9879	77.07	Suggested
Cubic	1.13	0.9980	0.9948	0.9834	105.71	Aliased

Table B2: Model Summary Statistics for viscosity value

Source	**Std. Dev**	**R-Squared**	**Adjusted R-Squared**	**Predicted R-Squared**	**PRESS**	
Linear	5.07	0.9912	0.9901	0.9878	820.81	Suggested
2FI	4.96	0.9927	0.9905	0.9851	1005.70	
Quadratic	4.28	0.9954	0.9929	0.9860	939.45	Suggested

Cubic	4.73	0.9967	0.9914	0.9625	2523.72	Aliased

Table B.3. Model Summary Statistics for total amine value

Source	**Std. Dev**	**R-Squared**	**Adjusted R-Squared**	**Predicted R-Squared**	**PRESS**	
Linear	0.50	0.9691	0.9651	0.9545	8.57	
2FI	0.33	0.9886	0.9852	0.9768	4.37	Suggested
Quadratic	0.30	0.9918	0.9874	0.9751	4.69	
Cubic	0.24	0.9969	0.9919	0.9705	5.56	Aliased

Appendix C: **Normal plot of residual graph for each the responses**

Figure C.1. For hydroxyl value

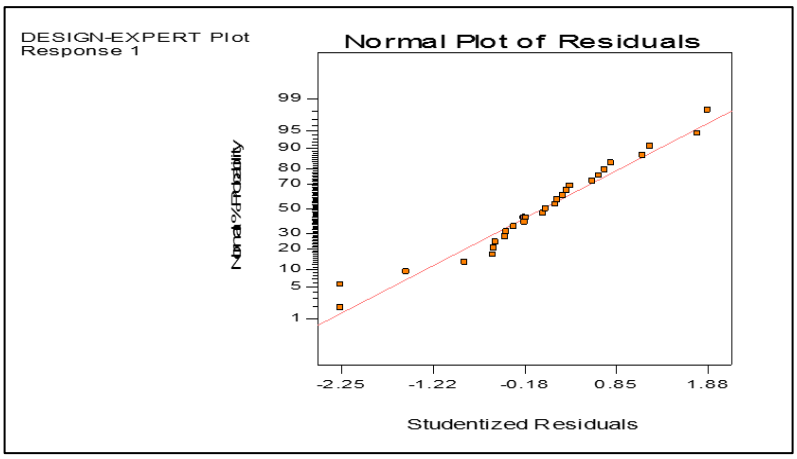


Figure C.2: For viscosity

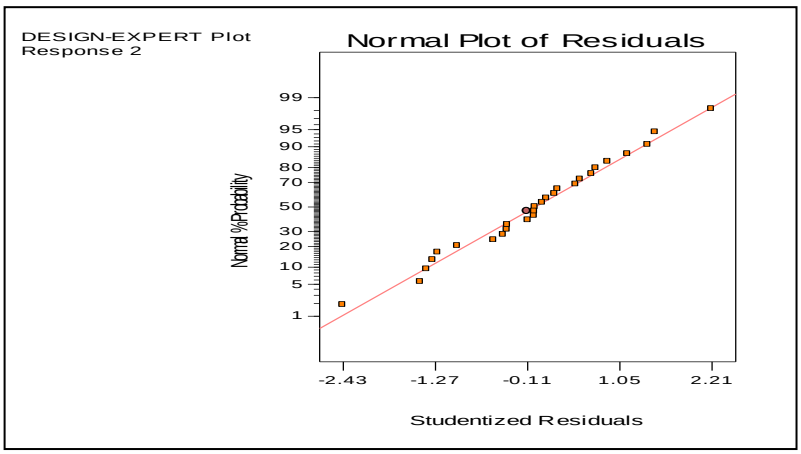
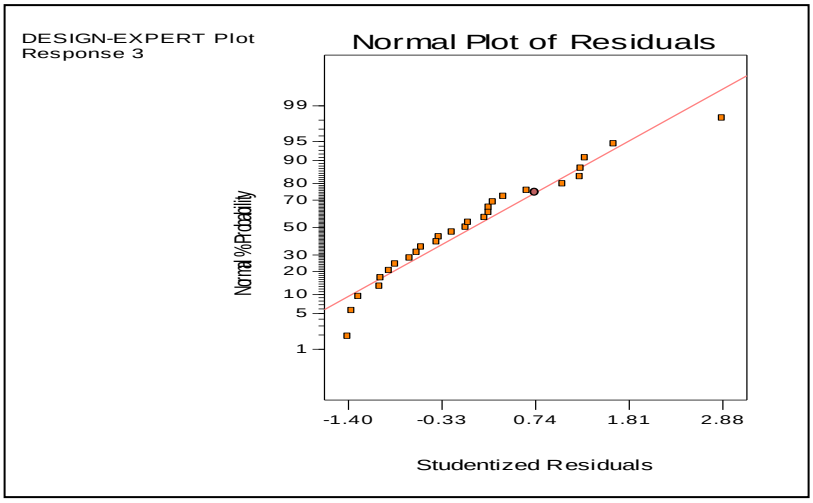


Figure C.3: For total amine value



Appendix D: laboratory work, equipment and sample photos.

Figure C.1: During hydroxyl value determination



Figure C.2: During acid value determination.

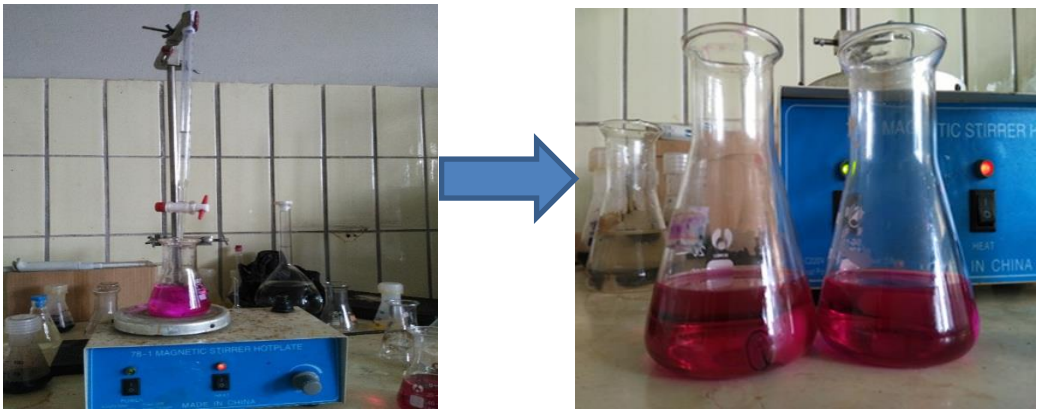


Figure C.3: During foam block synthesis

