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Synthesis of Bipolyol using Intermediate Byproducts from Biotech Industries

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Abstract : Due to higher demand of biodegradable industrial products concept of bioprocess arises. Polyol has been widely used as a raw material for synthesis of polyurethane which has many applications in our daily life such as foam synthesis, thermoset, thermoplastic and mainly coating materials. In general, looking into the environmental aspect associated with the Polyol derived from petroleum base and with the increasing demand of Polyol, effort is needed to find out alternative raw materials in particular potential to feedstock coming from Bio fuel Industrial Waste. Crude glycerin, a useful byproduct of Biodiesel industry is used as a starting material for substitute of petroleum based polyols. The crude glycerol is acting as media for digestion process. The product formed after digestion in acidic condition can be used as raw material for synthesis of polyurethane. Polyurethane is used for making rigid as well as flexible foam which is having wide application in thermal insulation, bedding and mattresses respectively. The effect of key independent variables such as liquefaction temperature, reaction time, concentration of biomass and catalyst on the hydroxyl value of product was quantified. The liquefaction process was performed in a batch reactor equipped with thermometer and reflux condenser using glycerol as a solvent and reactant. A central composite design with four independent variables and one response function was applied to determine the influence of independent variables. The concentration of biomass and acid catalyst has significant effect on the hydroxyl value of bio Polyol product. The hydroxyl value is a linear function of biomass and catalyst concentration. The optimal operating condition was achieved at a temperature of 160°C, reaction time of 300 minutes, using debranned Rice husk as Biomass along with Crude Glycerol along with Acid Catalyst. The viscosity of bio Polyol obtained are in the range of 217.5-727.5 cP.
Keywords : Polyol, crude glycerin, polyurethane, bio Polyol, foam, hydroxyl value.

Introduction

A polyol is an organic compound containing multiple hydroxyl groups also called Polyhydric alcohols. Polyols can used as a major raw material for manufacturing polyurethane foam. Polyols are also used a key additive in Lubricant formulation. In food industry polyols are acting as sweeteners, solublizers, stabilizers in food ingredients.

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Biopolyols can be defined as the Natural Biodegradable polyol free from nonrenewable petroleum sources.Corn and Soybean are primarily used as feedstock to produce bio-based polyols in North America. The demand for Green & Bio Polyols Market is driven from end user industries.

In order to compete the current raw material concept of biomass came in mind to overcome the costing issue.The starting material for synthesis of Biopolyol is Debranned Rice Husk obtained from harvesting of Paddy Crop. It is most abundantly available in the region where Paddy Rice is measure seasonal crop. The Mole ratio of biomass Mass and Crude Glycerin is to be maintained up to 1:5 for digestion process.

The grind rice husk along with crude glycerol taken in digestion reactor and mixed by using overhead stirrer. The acid catalyst Sulfuric acid is added once temperature goes above 60 ºC. The digestion time was around 5-6 hours. The liquid phase was separated by simple filtration when it was 70-80 ºC degrees. The liquid phase is nothing but the biopolyol and can be used as replacement of polyol for polyurethane foam.

Experimental Section

Materials and Methods

1) **Rice Husk**:

It is obtained from Rice mill after debraning process. Generally, it is used for burning in boilers which will create huge air pollution and dust. Rice husk is procured from Vidarbha Rice Mill. Rice husks are the hard protecting coverings of grain of rice. The chemical composition of rice husk is similar to that of many common organic fibers. Rice husk is a potential material, which is amenable for value addition. The usage of rice husk either in its raw form or in ash form is many. Rice production in India is as close as 150 million tons per annum. Therefore, rice husks are abundantly available for producing biomaterials.

The Composition of Rice Husk can be explained below,

Table 1: Composition of Rice Bran Husk

Sl No.	Composition	Percentile
1	SiO2	18.8-22.3
2	Lignin	9-20
3	Cellulose	28-38
4	Protein	1.9-3
5	Fat	0.3-0.8

2) Crude Glycerin:

It is the byproduct of Biodiesel industries. Crude Glycerin is procured from AL Noor Exports which are engaged in Biodiesel production from animal fat.

Following is the certificate of analysis,

Table 2: Quality Parameters of Crude Glycerin

Sl No.	Quality Parameters	Value
1	Glycerol Content	86 %
2	Moisture Content	7 %
3	pH	6-7
4	Density in gm/liters	1.2
4	Chloride Content	4%

3) Concentrated Sulfuric Acid:

The Concentrated sulfuric Acid is taken as the Acid Catalyst for Digestion of Cellulose and Lignin present in De bran Rice Husk.

The liquefaction process was performed in a batch reactor equipped with thermometer and reflux condenser using glycerol as a solvent and reactant. Many protocol used for optimizing the Digestion process. Some of the protocol found with better yield which are included in paper.

Procedure:

A 1000 liter 3 neck flask was taken for reaction along with heating arrangement of 400 watt heating mantel. The central opening was equipped with a mechanical stirrer having glass agitator and a Teflon blade attached to it at the bottom.200 gm of fine powdered Rice husk was added to 3 neck round bottom flask.100 gm crude glycerin (50-75%) was added and heating started gradually. 2% concentrated sulphuric acid was added by weight of Rice husk taken at 40 degree.The reaction time was about 5 to 6 hrs.The total reaction time was calculated from the time of concentrated sulphuric acid addition. Overall reaction temperature was maintained at 160 ºC.After 5-6 hrs the reaction mixture is allow to cool and filtered at 80º C by using filter cloth by vaccum filtration method.

The reaction is repeated with different formulations. Also, the polyol formed is analyzed for Hydroxyl value. The Biopolyol formed is taken for polyurethane foam preparations with multiple formulations.

Table 3: Protocol for Biopolyol Synthesis

Batch No.	Amount of Rice Husk	Amount of Glycerol	Amount of Concentrated H2SO4	Operating Temperature	Yield of Biopolyol after vaccum Filtration
1	200	100	1.5	180 ºC	60%
2	200	150	2	180 ºC	78%
3	200	100	1.5	180 ºC	65%
4	200	150	2	180 ºC	82%

Following parameters were checked after collecting filtrate.

1. Hydroxyl Value
2. Acid Value
3. Viscosity

(Quality Control Lab are traceable to the National Bureau of Standards / NIST)

Analysis of foam

(In accordance with ISO 3386-Part 1 standard)

(1) EDS:

The samples of calcium carbonate were covered with a fine layer of carbon and analyzed under an accelerating voltage of 15 kV and a current of 20 mA.

(2) Mechanical analysis:

The specimens taken, 5.0 cm from the edge, were submit to four compression-decompression cycles at 70% of their original height and a velocity of 100 mm/min. During the fourth cycle the hysteresis are obtained.

(3) Thermogravimetric analysis (TGA):

The TGA/DTG curves were performed in the temperature range of 25-950 °C, with samples of approximately 12 mg packed in alumina crucible, and dynamic air atmosphere (100 mL/min gas flow).

(4) Porosity and Density:

The term "porosimetry" is often used to include the measurements of pore size, volume, distribution, and density.

Formulation of Foam

Raw materials:

1.Polyol

Flexible slabstock foams are made from polyether polyols. These are condensates of propylene oxide and ethylene oxide. They are mainly triols. The hydroxyl values of these polyols are in the range 36-56 mg KOH/g.

2. Isocyanate

Toluene di Isocyanate(TDI) is used as raw material for flexible foams. 2.4 & 2.6 isomers are present in the ration 80:20.

3. Blowing agents

The primary blowing agent which causes the foam to expand is carbon dioxide. Carbon dioxide is produced by the reaction of isocyanate and added water. Soft foams with density less than 21kg/m3 is produced by adding a secondary blowing agent (trichlorofluoromethane or dichloromethane).

4. Catalyst

Amine: This type of catalyst (di-methyl amino ethanol or triethylene diamine) isused to control rate of carbon dioxide formation (water and isocyanate reaction)Stannus octate: this catalyst promotes polyol and isocyanate reaction.

5. Silicone oil surfactant

Foaming process is controlled by the surfactant. The surfactant assists uniform mixing of components and stabilizes the bubbles in the foam to prevent fromcollapsing.

Formulation of foams

Table 4: Formulation of Foam

SL No.	Components	Sample 2	Sample 3	Sample 4	Sample 5	Sample 6
1	Biopolyol	20	5	10	5	10
2	Isocynate	8.07	0.02	4.04	0.02	4.04
3	Amine	0.08	4.04	0.04	0.164	0.04
4	Water	0.654	0.04	0.327	0.012	0.7
5	Stannous Chloride	0.048	0.327	0.024	0.05	0.024
6	Silicon oil	0.2	0.024	0.001	0.17	0.001
7	Sodium bicarbonate	0.8	0.001	-	-	-
8	Acetone	-	-	0.6	-	-
9	HCl	-	0.08	-	-	-
10	Citric Acid	-	-	-	0.130	-
11	Chloroform	0.4	-	-	-	-

Results and Discussion

Characterization of Biopolyol:

Table 5: Physiochemical Properties of General Polyol

Sl No	Properties	Polyethylene Glycol	Polypropylene Glycol
1	Acid value(mg/KOH)	5	0.3
2	Hydroxyl Value	60	130
3	Viscosity	995	1005

Physiochemical Properties of Biopolyol

Table 6: Physiochemical Properties of Biopolyol

Sl No	Properties	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5
1	Acid value 1(mg/KOH)	3	3.5	3	3.8	4.2
2	Hydroxyl Value	100	150	190	197	210
3	Viscosity	600	650	950	960	980

Table 7: Foam Sample

Sample 1: The foam formed is Rigid foam. The foam is quite compact.It does not break on touching it. It took a well-shaped solid form after curing.Improvement in color is required. Sodium bicarbonate was used as blowingagent in its formulation.	
Sample 2: It is a semi rigid foam. It breaks on pressing.The texture is not too compact. It took an irregular shape after curing. It was made using CO2 as blowing agent.	
Sample 3: Acetone was used as blowing agent in its formulation. It did not become Rigid after curing.It was fluid in texture even after curing. It raised to a satisfactory height during making but settled down after curing.	
Sample 4: Sodium bicarbonate along with citric acid was used as blowing agent. Foam rose during the addition of blowing agent but collapse after sometime. Curing had no significant effect on sample.	
Sample 5: In this sample water was used as blowing agent. Foam formed during initial mixing but collapse after few minutes. Color was better than other samples	

Conclusion

Hydroxyl value of synthesized biopolyol were closely similar to commercial polyol. Increase in hydroxyl values of biopolyol was observed when amount of glycerol was increased. The synthesized biopolyol have closely similar physical properties as compared to commercial polyol.As the raw material (Rice Husk) being biodegradable, the polyurethane foam produced was also biodegradable. Thus, Rice husk can be used as lignocellulosic mass for synthesis of Biopolyol which will be further used as raw material for manufacturing Biodegradable Polyurethane Foam. Crude and refined Glycerol can also be used as a liquefaction solvent for digestion of rice husk.

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