

Atmospheric Pressure Liquefaction of Dried Distillers Grains (DDG) and Making Polyurethane Foams from Liquefied DDG

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Abstract In this study, dried distillers grains (DDG) was liquefied in acidic conditions at atmospheric pressure, and polyurethane foams were subsequently prepared from the liquefied DDG. Liquefaction was examined over a range of conditions including liquefaction time of 1–3 h, temperature of 150–170 °C, sulfuric acid (as catalyst) concentration of 1.0–3.0 wt%, and liquefaction solvent (ethylene carbonate) to DDG ratio of 3:1–5:1. The bio-polyols in the liquefied DDG were rich in hydroxyl groups, which can react with methylene diphenyl diisocyanate (MDI) to form cross-linked polyurethane networks. The biodegradability of the prepared polyurethane foams was also evaluated. This study strives to broaden the application of DDG as a feedstock for bio-polyurethane preparation.

Keywords Dried distillers grains · Liquefaction · Bio-polyols · Polyurethane · Biodegradable

Introduction

Dried distillers grains (DDG), a co-product of the distillery industry is abundant in Minnesota. About 98% of the DDG in North America comes from corn plants that produce ethanol for oxygenated fuels. The remaining 1–2% of DDG is produced by the alcohol beverage industry. Approximately 3.2 million metric tons of DDG are produced in North America annually. In recent years, some regions of the USA, especially the Midwest, have required more use of oxygenated fuels (e.g., ethanol–gasoline blends) to reduce air pollution

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and dependency on foreign petroleum. Because of the increased demand on ethanol, the production of DDG is expected to double within the next decade. However, in North America, over 80% of DDG is used as animal feed at a price just a little more than the cost of the corn that goes into it. The economics of ethanol production facilities depends very much on the price of ethanol as well as processing and marketing of byproducts such as DDG and carbon dioxide. Thus, decreasing prices for the dry-grind ethanol process coproducts, especially DDG, suggest that there is significant potential for value-added process by using ethanol coproducts. However, to determine the overall techno-economical feasibility of using DDG as raw material, the general process route, the chemical and physical characteristics of the final products, and the associated capital and operation costs must be determined [1–4]. This research focuses on an innovative method for the preparation of polyurethane from liquefied DDG.

Polyurethane is an important polymer, and its annual market in North America is about 2.8 million tons. Currently, polyurethane is synthesized mainly from isocyanate and hydroxyl groups containing polyols from petroleum resources, such as polyesters and polyethers. The present work was to develop and evaluate a three-step process for making polyurethane foams from renewable biomass, which may be used as packaging material, insulating material in construction, and so on. First, bio-polyols were obtained from liquefaction of DDG in acidic conditions. DDG was pretreated over a range of conditions including liquefaction solvent, residence time, temperature, sulfuric acid concentration, and liquefaction solvent to DDG ratio. Secondly, dilution, pH adjustment, filtration, and evaporation process were developed to separate and purify the bio-polyols in the liquefied DDG. Last, flexible and rigid polyurethane foams were prepared from the liquefied bio-polyols by reacting with diisocyanate.

Materials and Methods

Materials

DDG, provided by Agricultural Utilization Research Institute (Waseca, MN, USA), was milled to 2.0-mm meals before liquefaction [1]. Ethylene carbonate and ethylene glycol (Sigma, Minneapolis, MN, USA) was used as liquefying solvent. Stannous 2-ethyl hexanoate (Sigma), polyether modified polysiloxane (Sigma), and methylene diphenyl diisocyanate (MDI such as Isonate 181 and Papi 27, Dow Chemical, Midland, MI, USA) were used for the preparation of polyurethane foams. All chemicals were reagent grade.

Atmospheric Pressure Liquefaction Procedure

The lab apparatus used for atmospheric pressure liquefaction consisted of a stirring system, a temperature controller, and a 500-ml three-neck flask. One hundred grams liquefying solvent (ethylene carbonate or ethylene glycol) and catalyst (1–5 wt% concentrated sulfuric acid) were first placed in the flask and preheated to 100 °C. Weighed DDG was then added to the flask and well mixed with the liquefying chemicals. The ratio of liquefaction solvent to DDG ranged from 3 to 5. Liquefaction was carried out by continuously stirring at atmospheric pressure. After a preset reaction time, the heater was turned off and the stirrer kept running until the mixture cooled down. The liquefied mixture (bio-polyol) was collected for later use and analysis. All experiments and analysis were performed in three replicates.

When liquefaction reached a predetermined time, the resulting liquefied mixture was washed into a beaker with 200 ml dioxane–water solution (4/1, v/v) and then filtrated

through filter paper under vacuum. The residue was dried to a constant weight at 105 °C. The percent of liquefaction yield was calculated by the following equation:

$$\text{Liquefaction yield (\%)} = (1 - \text{weight of dried residue/dry weight of starting DDG}) \times 100$$

Separation and Purification of Bio-Polyols

A series of chemical unit operations were undertaken to obtain pure bio-polyols. The purified bio-polyols can be used for making higher quality polymers or they can be broken down into hydrocarbon and hydrogen by means of catalytic reforming. Figure 1 shows the procedure used for separating and purifying bio-polyols from liquefied DDG. Raw material (DDG), catalyst (sulfuric acid), and liquefying solvent (ethylene carbonate) were first added to the liquefaction apparatus, holding for 2 h at 160 °C. After that, the liquefied material was diluted tenfold with dioxane–water solution (1/1, v/v). As only liquefied polyols can be dissolved in this solution, it was then separated from the unliquefied residues. To obtain the pH neutralized polyols, the pH of the solvent was adjusted to 6.5–7 with 1 mol/l NaOH followed by filtration to separate the unliquefied residues from the solution. These residues can be recycled to the liquefaction apparatus for secondary liquefaction, resulting in less harm to the environment. This unliquefied mixture included some ash and also some unliquefied substrate. Subsequently, the filtrate was evaporated under reduced pressure to 1% water content. Using evaporation process to get rid of dioxane and water, eventually, pure polyols are obtained. The dioxane–water solution can also be recycled to the dilution process. The purified polyols can be recycled to the liquefaction process, using as a substitute solvent, which will decrease the costs of production [3].

Determination of Hydroxyl Value of Bio-Polyols

One gram liquefied DDG was placed in a 150-ml beaker, and 10 ml of phthalic anhydride solution (dissolving 150 g phthalic anhydride in 900 ml of dioxane and 100 ml pyridine) was added. The beaker was covered with aluminum foil and the beaker put into a boiling

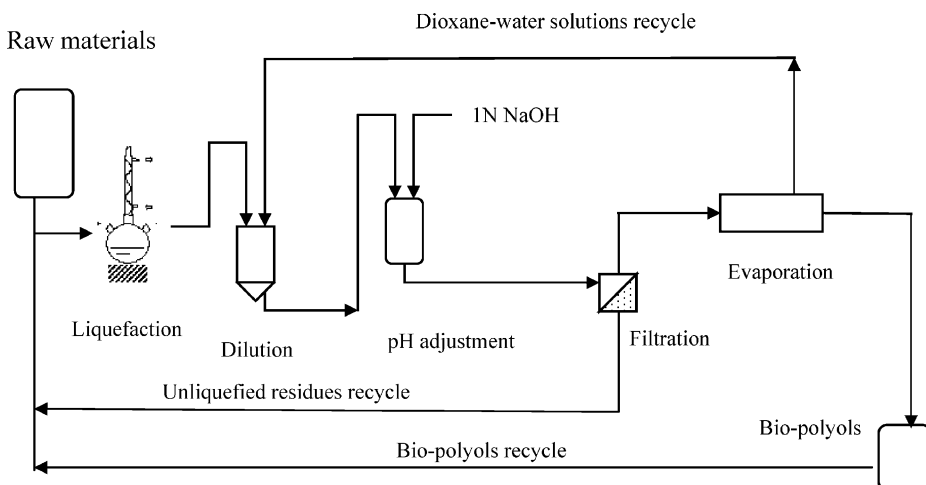


Fig. 1 Procedure used for separating and purifying of bio-polyols

water bath for 20 min. After cooling down, 20 ml of dioxane–water solution (4/1, v/v) and 5 ml of water were added to the beaker and then titrated with 1 mol/l NaOH to pH 8.3 using a pH-meter to indicate the end-point. Blank titration was conducted using the same procedure. Hydroxyl value was calculated by the formula below.

$$\text{Hydroxyl value (mg KOH/g)} = (B - S) \cdot N \times 56.1 / W$$

where

- B* volume of NaOH standard solution consumed in blank titration (ml)
S volume of NaOH standard solution consumed in sample titration (ml)
W sample weight (g)
N equivalent concentration of NaOH standard solution (mol/l)

Preparation of Polyurethane Foams from Bio-Polyols

Weighed amounts of bio-polyols, catalyst (Stannous 2-ethyl hexanoate), surfactant (polyether-modified polysiloxane), and blowing reagent (distilled water) were mixed well in a paper cup. A prescribed amount of MDI was added to the mixture, which was then stirred with a high-speed stirrer (5,000 rpm) for 15 s. After stirring, the mixture was poured immediately into another paper cup, and the foam was allowed to rise and set at ambient conditions (22 °C). Finally, the foam samples were cured at room temperature for 24 h before any analysis can be conducted. The formulations of the prepared foams are shown in Table 2.

Biodegradability of Polyurethane Foams from Bio-Polyols

To evaluate the biodegradability of polyurethane foams, a natural degradation of polymers in soil was simulated in the laboratory [2]. The soil used in this research is merchandised potting soil (Menards, St. Paul, MN, USA). The test samples (about 2×2×2 cm) were buried in flowerpots filled with potting soil. The flowerpots were kept in a cultivating room at 25 °C. The samples were watered once a day to keep the moisture constant. Every month, five samples were taken out, washed with 200 ml water, and dried to a constant weight at 105 °C to determine weight loss of the samples. The rate of biodegradation was indicated by the average weight loss.

Results and Discussion

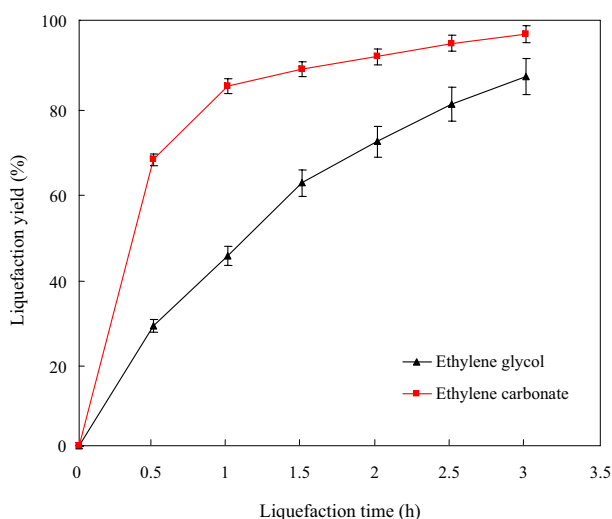
Bio-Polyols from DDG by Atmospheric Pressure Liquefaction

The effect of liquefaction solvent and processing time on the liquefaction of DDG is shown in Fig. 2. It was found that the liquefaction with ethylene carbonate was very rapid and almost completed within 1 h. On the other hand, the liquefaction with ethylene glycol was much slower, and about 18% residue still remained after 3 h of liquefaction [3, 4]. This result agrees with that obtained by Yamada and Ono [4] who found ethylene carbonate promoted the acid-catalyzed solvolysis of cellulose. Ethylene carbonate is an effective liquefaction solvent because of its high permittivity and high boiling point. Atmospheric pressure liquefaction is regarded as a non-aqueous reaction, which can be assisted by sulfuric acid as a catalyst. The acid potential depends on the permittivity of the solvent. The higher the permittivity of the solvent, the larger the acid potential. Therefore, sulfuric acid could

Fig. 2 Effect of solvent and time on the liquefaction of DDG.

[Liquefaction solvent/DDG ratio (g/g): 4; catalyst content: 3%; liquefaction temperature 160 °C].

Error bars represent standard deviations calculated from the data obtained from three replicated experiments



promote rigorous reactions when ethylene carbonate is chosen as liquefying solvent, resulting in a complete liquefaction in a short period of time. In subsequent experiments, ethylene carbonate was used as liquefaction solvent to achieve a reasonable liquefaction yield in an acceptable time range.

DDG contains little starch, but is a good source of fiber and protein. Distillers grains typically contain 42% highly digestible neutral detergent fiber [1], and thus, are alternative biomass feedstock. Figure 3 shows that the reaction mechanism occurs during the DDG liquefaction process. Under the catalysis of sulfuric acid, DDG fibers experience a partial chemical degradation; meanwhile, it reacts with ethylene carbonate to form a series of glucosides. Figure 4 shows that decomposition of ethylene carbonate generates carbon dioxide which caused the bubbles observed during the liquefaction. The reactions illustrated in Figs. 3 and 4 suggest that the liquefied DDG may consist of degraded DDG fragments (oligosaccharides), glucosides, and residual and decomposed liquefying solvent, all of which contain one or more hydroxyl groups. Therefore, it is feasible to cross-link the biopolyol into a network of polyurethane through the esterification reaction between the

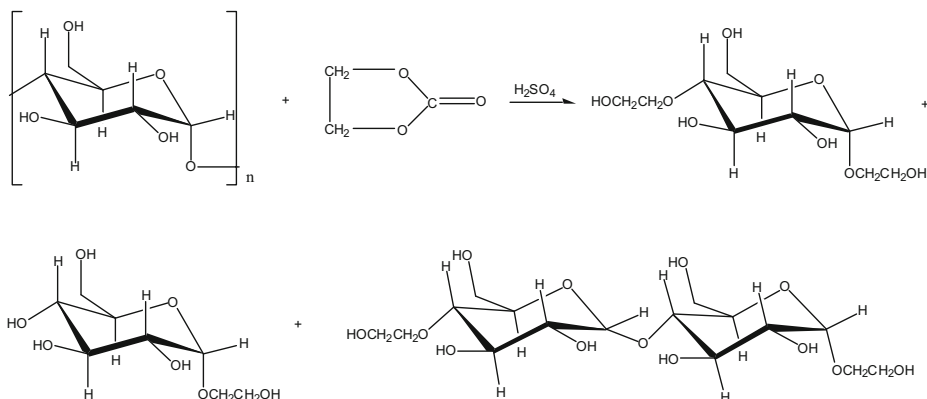
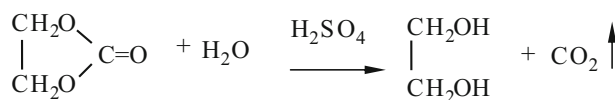
**Fig. 3** Reaction mechanism between DDG fiber and ethylene carbonate

Fig. 4 Decomposition of ethylene carbonate in the atmospheric pressure liquefaction



hydroxyl groups of the bio-polyol and isocyanate in cross-linking chemicals having two or more functionalities, such as diisocyanate [5].

Liquefaction yield achieved by the liquefaction process were 80–98%, indicating that the selected liquefaction conditions, such as temperature, time, sulfuric acid content, and liquefaction solvent to DDG ratio, promoted the atmospheric pressure liquefaction process. These results are summarized in Table 1. Clearly, an increase in liquefaction time and temperature results in increased liquefaction yield. For instance, when the temperature was 160 °C, the liquefaction yield reaches 94.6% at 2 h, whereas further increase in temperature and time resulted in a depressed increase in liquefaction yield. A similar trend has also been observed in the case of liquefaction of corn stover [3]. Typically, the increase of catalyst content should increase in the liquefaction yield. As can be seen in Table 1, 94.6% liquefaction yield was obtained at 3% sulfuric acid in 160 °C 2 h. However, the use of sulfuric acid will cause condensation of degraded residues and increase the viscosity of the liquefied materials. The amount of insoluble residue increased with decreasing liquefaction solvent/DDG ratio. When the liquefaction solvent/DDG ratio reaches 5, the liquefaction yield is 97.8% after 2 h. A higher yield could be expected at even higher liquefaction solvent/DDG ratio, but at the cost of more solvents or lower productivity.

Another key characteristic of bio-polyols from atmospheric pressure liquefaction was their hydroxyl functionality and the structure of the hydroxyl group [6]. The hydroxyl value in liquefied DDG is one of the important factors in the preparation of polyurethane having the desired mechanical properties. The total hydroxyl value was, therefore, evaluated in relation to the liquefaction conditions (Table 1).

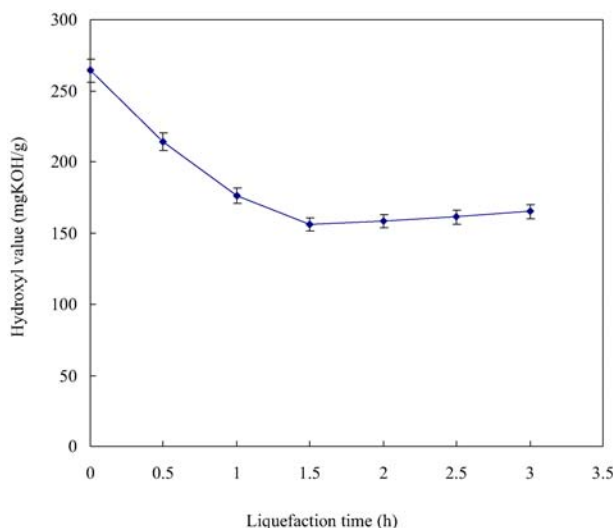
An inverse decreasing relationship was found between the hydroxyl value and the reaction time for the liquefaction system. Figure 5 shows the hydroxyl value decreased steadily from h 0 to h 1.5 and then increased slightly until the end of the liquefaction (h 3). Such decrease in hydroxyl number resulted from dehydration and thermal oxidative degradation of the liquefaction solvent (ethylene carbonate). Yao et al. [7] also reported that alcohol-D-glycosides were produced by the liquefaction between polysaccharides and ethylene glycol under a temperature of 150 °C and catalyst (sulfuric acid) concentration of 3% as used in their

Table 1 Effect of processing conditions on the liquefaction of DDG^a.

Temperature (°C)	Time (h)	Sulfuric acid (%)	Liquefaction solvent/DDG ratio (g/g)	Hydroxyl value (mgKOH/g)	Liquefaction yield (%)
150	2	3	4	226	92.1
160	2	3	4	158	94.6
170	2	3	4	144	94.9
160	1	3	4	176	87.6
160	3	3	4	165	95.1
160	2	1	4	178	80.9
160	2	5	4	151	96.4
160	2	3	3	137	88.3
160	2	3	5	221	97.8

^a Mean values for three replicates are indicated.

Fig. 5 Changes in hydroxyl value in the atmospheric pressure liquefaction of DDG. [Liquefaction solvent (ethylene carbonate)/DDG ratio (g/g): 4; catalyst content: 3%; liquefaction temperature 160 °C]. Error bars represent standard deviations calculated from the data obtained from three replicated experiments



experiment [7]. A reduced hydroxyl value of wood and starch samples with the increase of reaction time was reported.

Preparation of Polyurethane Foams

DDG-based bio-polyols were applied to produce flexible and/or rigid polyurethane foams with a preliminary investigation. Properties of the bio-polyols, diisocyanates, formulate, and other factors showed significant effects on formation, color, and physical properties of bio-polyurethane foams [8]. Table 2 gives example formulas for the preparation of polyurethane foams from the bio-polyols. In general, the formulas consist of two mutually separated phases. One phase includes bio-polyol, blowing agent (to form bubbles), catalyst, and surfactant, and the other is MDI (Isonate 181 or Papi 27). During the polyurethane foaming reaction, carbon dioxide is generated by the reaction between water and isocyanate. Increasing the water content expanded the foam volume, resulting in thinner foam cell walls and larger foam. It was also found that without the catalyst, the bio-polyols phase did not dissolve in the isocyanate phase. Just after addition of the catalyst, the mixture became brown. Up to 2 min after the catalyst addition, the phase separation could be observed in

Table 2 Formulas of polyurethane foams from DDG-based bio-polyols.

Foams	Ingredients	Parts (wt%)
Rigid	DDG-based bio-polyol	100
	Blowing agent (water)	2–5
	Catalyst (stannous 2-ethyl hexanoate)	2–3
	Surfactant (polyether modified polysiloxane)	3–4
	MDI (Isonate 181)	150–200
Flexible	DDG-based bio-polyol	100
	Blowing agent (water)	2–5
	Catalyst (stannous 2-ethyl hexanoate)	2–3
	Surfactant (polyether-modified polysiloxane)	2–3
	MDI (Papi 27)	100–150

portions of mixture, and a considerable increase in viscosity was noted in the mixture. Further continuation of the reaction with vigorous stirring (5,000 rpm) at room temperature resulted in disappearance of the phase separation, enhanced coloration, and the production of an appreciable quantity of water as byproduct. Thus, it was suggested that 2 min was enough for the formation of polyurethane foams.

The foam prepared from the rigid foam formula smelled strongly of MDI even 3 days after preparation, and contracted considerably, which indicates incomplete polyurethane formation. In the preparation of polyurethane using the flexible foam formula, the resulting foam was whitened and never imparted any odor or shrinking behavior. As has been stated above, when DDG-based bio-polyols were used as the starting material for polyurethane synthesis, a strong color change occurred in the ring-opening polymerization at room temperature within a relatively short time.

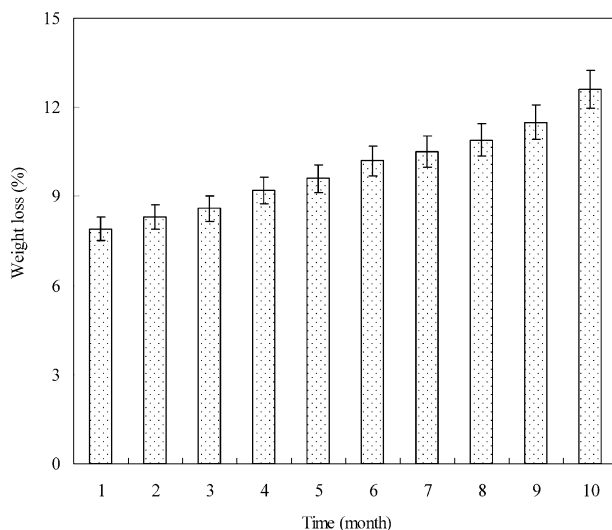
Biodegradability of Polyurethane Foams

Figure 6 shows the biodegradability result of polyurethane foams from DDG-based bio-polyols. The result showed that polyurethane foam lost about 12.6% of its initial weight in 10 months, which may be attributed to the fact that DDG contains many natural extracts, especially proteins and fats. In addition, there is a small amount of uncross-linked or partially cross-linked materials in the polyurethane foams, which might be less resistant to polymer degradation than fully cross-linked materials, and thus, more susceptible to biodegradation. No microorganisms were observed on the surface of the foams or in the surrounding soil, suggesting that less degraded chemicals were carried from the bio-polyurethane foams in 10 months [9]. Further investigation is required to elucidate the pathway and final products of polyurethane foams' degradation.

Conclusions

Bio-polyols were prepared from DDG liquefied using our unique atmospheric pressure liquefaction process. These DDG-based bio-polyols possess suitable characteristics for

Fig. 6 Biodegradability of polyurethane foams from DDG-based bio-polyols. Error bars represent standard deviations calculated from the data obtained from five replicated experiments



making polyurethane foams. The properties of the bio-polyols can be adjusted by changing the liquefaction process conditions. Ethylene carbonate was proven to be an effective liquefying solvent for DDG. The optimum conditions for liquefaction of DDG are liquefaction solvent/DDG ratio of 4, liquefaction temperature 160 °C, liquefaction time 2 h, and catalyst content 3 wt%. Flexible and rigid polyurethane foams can be synthesized from the DDG-based bio-polyols. Polyurethane foams degraded about 12.6% in 10 months.

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