

Preparation of biopolymers from liquefied corn stover

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Abstract: The objective of the present study was to develop processes for liquefaction of solid biomass and explore the potential of making biopolymers from the liquefied biomass. In this study, corn stover was liquefied under acidic conditions, and several polymer materials were subsequently prepared from the liquefied biomass. Liquefaction was conducted using different organic solvents with sulfuric acid as catalyst at different temperatures. The effect of the ratio of solvent to solid biomass on liquefaction rate was also evaluated. Of the two organic solvents used in the liquefaction process, ethylene carbonate was found to be more effective than ethylene glycol in terms of liquefaction rate. The adequate processing conditions for the feedstock used were found to be organic solvent/corn stover ratio of 3, temperature 160 °C, catalyst content 3%, and heating time 2.5 hours. The polyols from the liquefaction were separated and purified through a series of processes, such as dilution, pH value adjustment, filtration, evaporation, and ozonolysis. Processes for making biopolymers, such as polyester films, polyurethane foams and particleboards from the liquefied corn stover containing a high quantity of bio-polyols were evaluated. The film formation was based on the esterification reaction between the hydroxyl groups of the bio-polyols and the carboxyl groups. The foam was prepared through a reaction of the hydroxyl groups with diisocyanate. Polyesters made from the reaction between bio-polyols and anhydrides are shown to be a good adhesive for making particleboard.

Key words: biomass; corn stover; liquefaction; bio-polyols; biopolymer

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0 Introduction

Many polymeric materials are derived from non-renewable petrochemical resources. The U.S. material industry has set a goal of deriving 10 percent of all basic chemical building blocks (polymers, enzymes, etc.) from plant-derived renewable sources in the next two decades. This would be a five-fold increase in market share from today. An economy based on renewable energy and materials provides significant potential for rural economic development, enhances energy security and self-sufficiency, reduces environmental impacts, and increases sustainability. The present study is an attempt to make biopolymers from

corn stover, the number one biomass available in the United States.

There are a number of techniques that can directly use biomass as feedstock to produce energy and chemicals on relatively large scale. These include fermentation of biomass to ethanol and gasification and pyrolysis of biomass to syngas and heavy oil^[1,2,7]. Governmental agencies and private companies have invested heavily in research and development of these techniques. However, these techniques have limited commercial use because of high costs associated with the processes and/or limited knowledge of the processes and their products. The goal of the present study is to develop a systematic approach to the utilization of biomass to produce bioenergy and bioproducts. The first task in the approach is to convert bulky and low density biomass to pumpable and easy-to-transport intermediates or bio-crude in minutes or tens of minutes. This could overcome a major technical barrier, i.e., the need for preprocessing and transportation of bulky and low energy density biomass. The next task is to crack and refine the bio-crude to usable energy and chemicals. The first step involves basically thermochemical liquefaction processes^[8,10]. The objective

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of the present study was to explore the potential of making usable products from liquefied biomass

Corn stover is a domestic feedstock with a great potential for commercial production. A variety of thermomechanical and thermochemical processes have been developed to produce fuel, chemicals, and materials. The goal of this work was to demonstrate three steps for biopolymer production: first, crude biopolyols were produced from corn stover through a novel liquefaction process; second, the crude biopolyols were purified; and third, the purified biopolyols were reacted with diisocyanate to yield polyurethane foam or with dicarboxylic acids and cyclic anhydrides to yield polyester.

1 Materials and methods

1.1 Materials

Dried corn stover, provided by the Minnesota Agricultural Utilization Research Institute, was milled to 0.5 mm meals before liquefaction. Ethylene carbonate and ethylene glycol (Sigma) were used as liquefying reagents. Succinic anhydride, citric acid, hexanediol, and glycerine (Sigma) were used for the preparation of polyester films. Isocyanates were MDI (Papi 27 or Isonate 181) and provided by Dow Company. All chemicals were of reagent grade.

1.2 Methods

1.2.1 Liquefaction procedures

The laboratory apparatus used for liquefaction consisted of a heater, a temperature controller, a flask, and a motor-driven stirrer. Liquefying reagents and a catalyst (sulfuric acid) were first placed in the flask and preheated. Weighed crop residue was then added to the flask and mixed with the liquefying chemicals. Liquefaction was completed 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 (biopolyol) was collected for later use and analysis.

1.2.2 Separation and purification of biopolyols

A series of chemical unit operations were performed to obtain the pure biopolyols. The purified biopolyols can be used for making polymers, or they can be broken down into methane and hydrogen by means of gasification. Figure 1 shows a procedure used for separating and purifying biopolyols from liquefied corn stover. Raw materials, catalyst, and liquefying reagents were first added to the liquefaction apparatus, and then held for 2~3 hours at 160 °C. After that, the liquefied materials were diluted ten-fold with

50% dioxane-water solution since liquefied polyols can be dissolved in this solution, then separated from unliquefied residues. In order to obtain neutral polyols, the pH value of the solvent was adjusted into 6.5~7.0 with 1 N sodium hydroxide, followed by filtration to separate the unliquefied residues from the solution. About 11% was unliquefied mixture. These residues can be recycled to the liquefaction apparatus with 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. The evaporation process was used to get rid of dioxane and water to yield pure polyols. The dioxane-water solution can also be recycled to the dilution process. The last step is the ozonolysis process. The ozonolysis process is designed to increase the hydroxyl groups in the polyols. The purified polyols can be recycled to the liquefaction process and used as a solvent substitute for ethylene glycol and ethylene carbonate, which will decrease the production costs.

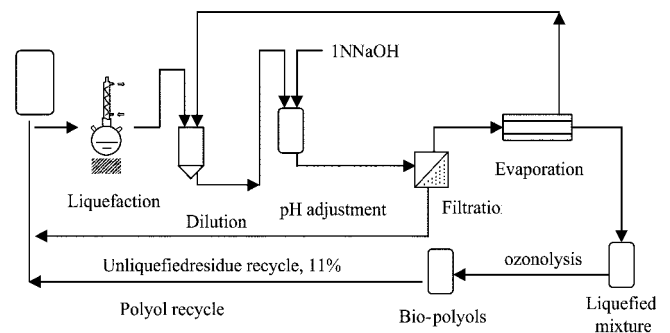


Fig. 1 Procedure used for separating and purifying biopolyols

1.2.3 Determination of liquefaction rate

When liquefaction reached a predetermined time, the resulting liquefied mixture was washed into a beaker with a mixture of dioxane and water (4/1, v/v). The dilute solution was filtered through glass filter under vacuum. The residue was dried to a constant weight in an oven at 105 °C, and the percentage of liquefied biomass was calculated using the following equation:

$$\text{Liquefaction rate (\%)} = (1 - \frac{\text{weight of residue}}{\text{weight of starting biomass}}) \times 100\%$$

1.2.4 Preparation of polyester films from biopolyols

Polyester films were prepared by cross-linking the biopolyols with carboxylic acids or anhydrides to form a network of polyester. First, the weighed biopolyol, cross-linking chemicals, and other additives were

mixed and heated to approximately 150 together while stirring, and then the obtained homogeneous mixture was cast onto a tinned boat to form a thin uniform layer of the mixture (0.15~0.75 mm). The polyester films were obtained after curing at 120~160 for 15~120 minutes, depending on the formulation and thickness of the films

1.2.5 Preparation of polyurethane foams from bio-polyols

The designated amounts of bio-polyols, catalyst, surfactant, blowing reagent, and other additives were premixed in a paper cup, and then the prescribed amount of diisocyanate was added into the cup and mixed with a high-speed stirrer for about 15 seconds. The mixture was allowed to rise at room temperature. The foam was further cured at room temperature for 24 hours before any analysis was conducted.

1.2.6 Preparing particleboard from bio-polyols

Corn stover meal was completely mixed in a given proportion with bio-polyols containing cross-linking chemicals. The mixture was put in a mold and hot-pressed under a selected pressure for a given period.

2 Results and discussion

2.1 Liquefaction of corn stover

The effects of liquefaction solvent and processing time on the liquefaction of corn stover are shown in Fig. 2. It was found that the liquefaction with ethylene carbonate was very rapid, and almost completed within 1 hour. On the other hand, the liquefaction with ethylene glycol was much slower, and about 20% residue still remained after 2.5 hours of liquefaction.

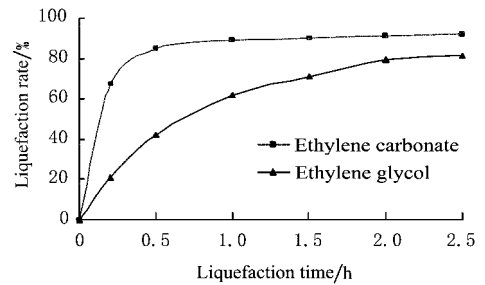


Fig. 2 Effect of solvent and processing time on the liquefaction of corn stover

(Liquefaction reagent/corn stover ratio: 3; catalyst content: 3%; liquefaction temperature 150)

Ethylene carbonate is an effective solvent because of its high permittivity. The liquefaction is regarded as a non-aqueous reaction, which can be aided by sulfuric acid as a catalyst. The acid potential depends on the permittivity of the solvent. Generally, the higher the permittivity of the solvent, the higher the acid potential. Therefore, sulfuric acid could promote rigorous reactions when ethylene carbonate was used as liquefying reagent, resulting in a complete liquefaction in a short period of time.

Figure 3 shows the possible reaction mechanisms involved in liquefaction of lignocellulosic materials. Under the catalysis of sulfuric acid, corn stover experiences a partial chemical degradation and then reacts with ethylene carbonate or ethylene glycol to form a series of glucosides. Carbon dioxide was released as a side reaction of decomposition of ethylene carbonate, as shown in Fig. 4, which was responsible for the bubbles observed during the liquefaction.

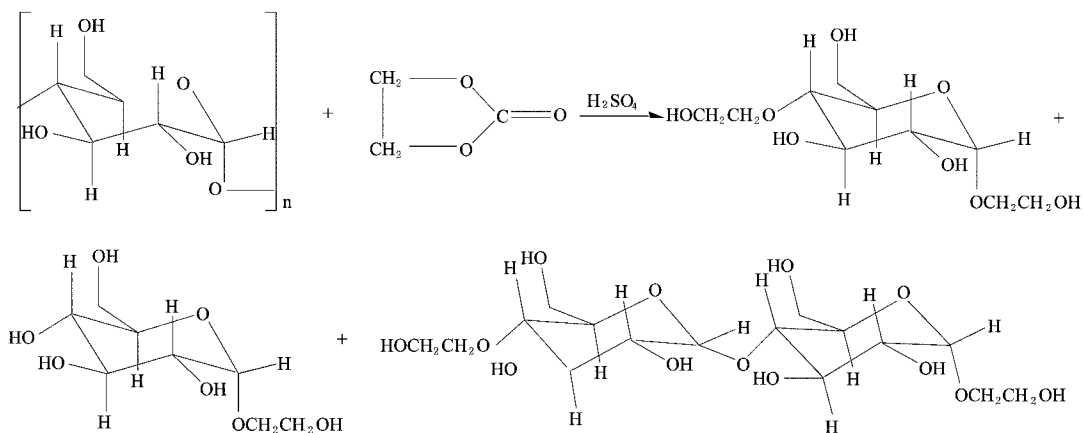


Fig. 3 Reactions between corn stover and ethylene carbonate to produce glucosides

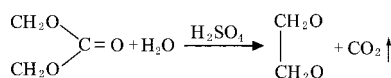


Fig. 4 Decomposition of ethylene carbonate

These results indicate that the liquefied polyol consists of degraded corn stover fragments (oligosaccharides), glucosides, and residual and decomposed liquefying reagents, all of which contain several

hydroxyl groups. Therefore, it is feasible to cross-link the polyol into a network of polyester through the esterification reaction between the hydroxyl groups of the polyol and carboxyl groups in cross-linking chemicals having two or more functional groups, such as dicarboxylic acids or cyclic acid anhydrides. Meanwhile, residual ethylene carbonate undergoes ester interchange reaction with diacids (or anhydrides) to become polymer^[6]. The hydroxyl groups can also react with isocyanate to form polyurethane.

2.2 Preparation of polyester films

The purified polyols react with carboxyl groups to form polyester. Succinic anhydride and citric acid were used to provide carboxyl groups. Table 1 shows example formulas for preparation of polyester films from the corn stover-based bio-polyols. In general, the formulas consist of two parts. One includes the hydroxyl contributor, and the other includes the carboxyl contributor. The carboxyl/hydroxyl ratio was generally (1.1~1.2). Flexible films and rubbery films can be made using different amounts of polyols, acid, and different formulas.

Table 1 A typical formula for polyester films from liquefied corn stover-based bio-polyols

Bio-polyol source	Formula	Curing temperature and time	Film type
Corn stover	Succinic anhydride, 2.7 g Citric acid, 0.4 g Bio-polyol, 10 g PEG 400, 1.2 g Additives, 0.2 g	150 °C, 6 h	Flexible film
	Succinic anhydride, 3.8 g Citric acid, 0.2 g Bio-polyol, 15 g PEG 400, 1.3 g Additives, 0.4 g	160 °C, 5 h	Rubbery film

2.3 Preparation of polyurethane foams

Corn stover-based bio-polyols were also used to produce a series of semi-rigid to rigid polyurethane foams. Properties of the bio-polyols, diisocyanates, formulation, and other factors showed significant effects on formation, color, and physical properties of bio-polyurethane foams. Table 2 shows example formulas for preparation of polyurethane foams from bio-polyols. In general, the formulas consist of two parts. One includes bio-polyol, blowing agent (to form bubbles), catalyst, and surfactant, and the other includes isocyanate. Semi-rigid and rigid foams can be made through varying the formulas.

Table 2 Formulas of polyurethane foams from bio-polyols

Ingredients	Parts
Corn stover bio-polyol	10~15
Blowing agent (water)	0.2~0.5
Catalyst (stannous 2-ethyl hexanoate)	0.2~0.3
Surfactant (polyether modified polysiloxane)	0.3~0.4
MDI (Papi 27)	10~20

2.4 Preparation of particle board

The resultant bio-polyols can be made into not only flexible polyester sheets but also polyester-based wood adhesive. The adhesiveness of the bio-polyols made from the corn stover in this study was very strong.

Corn stover meal was completely mixed in a given proportion (20%) with bio-polyols containing cross-linking chemicals. The mixture was put in a mold and hot-pressed under a selected pressure for a given period. Since bio-polyols can be cross-linked into a three-dimensional network polymer through the reactions of hydroxyl groups, the bio-polyols can be used as adhesives for making particle board or similar products. The particle board obtained appeared very good quality and had strength comparable to regular particle board. The optimum conditions for preparation of particle board are with the polyester/corn stover ratio being 1:4 and curing for 2 hours at 150 °C. The bending strength is around 110 N/cm².

3 Conclusions

Bio-polyols were prepared from corn stover through novel liquefaction process. These corn stover-based polyols possess suitable characteristics for making biopolymers. The properties of the bio-polyols can be adjusted by varying the liquefaction conditions. The optimum conditions for liquefaction of corn stover are as follows: liquefaction reagent/corn stover ratio of 3, liquefaction temperature 160 °C, liquefaction time 2.5 hours, and catalyst content 3%. Polyester films can be synthesized from the corn stover bio-polyols. Decreasing the ratio of carboxyl contributor to hydroxyl contributor can greatly improve the flexibility of the polyester film. In addition, polyurethane foams can be synthesized from the corn stover bio-polyols. Polyester can be used as adhesive for particle board preparation.

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玉米秸秆液化制备生物高聚物材料的研究

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摘 要: 该研究旨在探讨低温生物质液化技术及液化产物应用的可能性。以玉米秸秆为原料在酸性、常压条件下快速液化成多羟基化合物, 再以多羟基化合物为原料合成一系列的聚合材料。采用不同的有机溶剂, 在稀硫酸的催化作用下, 对不同的温度下生物质的液化效果进行研究。同时探讨了液化有机溶剂同生物质物料的混合比率对液化过程的影响。试验表明, 碳酸乙烯酯比乙醇具有较高的液化率。优化试验结果表明, 在较佳的液化效果下, 有机溶剂同玉米秆的混合比率为 3 : 1, 反应温度 160 ℃, 稀硫酸浓度 3%, 反应时间 2.5 h。液化产物经稀释、调节 pH 值、过滤、臭氧氧化一系列过程的处理后得到具有高活性多羟基聚合物。阐述了以多羟基聚合物制备各种生物聚合物材料如聚酯薄膜、聚胺酯泡沫和颗粒板的方法。聚酯薄膜是多羟基化合物上的羟基和多元酸上的羧基通过酯化反应形成的; 聚胺酯泡沫通过多羟基化合物上的羟基和二异氰酸酯反应形成。研究表明以多羟基化合物和多元酸(酐)形成的聚酯型胶粘剂适合于制造颗粒板。

关键词: 生物质; 玉米秸秆; 液化; 生物多羟基化合物; 生物高聚物