

Polyols and Polyurethane Foams from Acid-Catalyzed Biomass Liquefaction by Crude Glycerol: Effects of Crude Glycerol Impurities

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ABSTRACT: The effects of crude glycerol impurities on acid-catalyzed biomass liquefaction by crude glycerol were investigated. Salts (i.e., NaCl and Na₂SO₄) decreased biomass conversion ratios and negatively affected the properties of polyols produced. Regression models were developed and validated as appropriate for describing the relationships between organic impurities and biomass conversion ratios and between organic impurities and the hydroxyl number of polyols. Polyols produced from crude glycerol containing 0–45% organic impurities showed the hydroxyl number varying from 1301 to 700 mg KOH/g, acid number from 19 to 28 mg KOH/g, viscosity from 2.4 to 29.2 Pa s, and molecular weight (M_w) from 244 to 550 g/mol. Crude glycerol containing 40–50 wt % of organic impurities was suitable to produce polyols with suitable properties for rigid and/or semi-rigid polyurethane (PU) foam applications. The produced PU foams showed density and compressive strength comparable to those derived from petrochemical solvent-based liquefaction processes. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 40739.

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INTRODUCTION

Crude glycerol is a major by-product generated from biodiesel production. It is estimated that approximately 1 kg of crude glycerol is generated for every 10 kg of biodiesel produced.^{1,2} With the rapid growth of the world's biodiesel production in recent years, a large surplus of glycerol has been generated,^{1,3} leading to the closure of several traditional glycerol production plants.⁴ At present, biodiesel-derived crude glycerol is of little economic value, i.e., approximately \$0.1/kg.¹ To address this issue, considerable research has been conducted to develop value-added conversion processes for the re-utilization of crude glycerol. One of the major challenges for the development of such processes is the presence of various impurities in crude glycerol. Biodiesel-derived crude glycerol contains not only glycerol but also many other impurities such as soap, free fatty acids (FFAs), methyl esters of fatty acids (FAMEs), glycerides, methanol, water, and ash.⁵ The exact proportions of these impurities in crude glycerol depend on their origins (i.e., feed-stock), operational parameters, post-treatments, and other factors and can vary greatly from source to source.⁵ Crude glycerol impurities have been reported to affect both the biological and thermochemical conversions of crude glycerol.^{6–8}

Soap, methanol, and unsaturated FFAs present in crude glycerol have been reported to inhibit microbial growth during the bio-

logical conversion processes of crude glycerol. Pyle et al.⁹ studied the effects of methanol and soap on the production of docosahexaenoic acid (DHA) from crude glycerol using *Schizochytrium limacinum*. Both methanol and soap inhibited the microbial growth during the DHA production process, leading to decreases in dry cell weight, biomass productivity, and cell yield. In a later report from the same research group, soap and methanol were also found to inhibit the fungal (i.e., *Pythium irregulare*) growth during the production of eicosapentaenoic acid from crude glycerol.¹⁰ Chatzifragkou et al.¹¹ evaluated the effects of inorganic salts (NaCl, Na₂HPO₄, and K₂HPO₄), FFAs (i.e., saturated and unsaturated), and methanol on the fermentation of 1,3-propanediol by *Clostridium butyricum*. While salts, saturated FFAs (i.e., stearic acid), and methanol posed no significant inhibitions, unsaturated FFAs (i.e., oleic acid, 2%, wt/wt in crude glycerol) markedly inhibited the microbial growth during the production of 1,3-propanediol, probably due to the presence of carbon-carbon double bonds in the structure of oleic acid.¹¹ Similar inhibition of unsaturated FFAs on microbial growth was also reported by Anand and Saxena¹² and Venkataramanan et al.¹³

The negative effects of crude glycerol impurities on the thermochemical conversion processes of crude glycerol were also reported.^{7,8,14–17} Ramachandran et al.⁸ studied the production

of syngas by hybrid steam reforming of methane and glycerol. Crude glycerol impurities, including residual alkali catalysts, FAMES, diglycerides, and triglycerides, led to char formation and loss of catalyst activity during the production process. In another example, the effects of methanol, water, and NaCl on the acid-catalyzed reaction of glycerol with acetone were investigated.¹⁵ While methanol had no significant effects on the reaction, water and NaCl drastically decreased the conversion of glycerol. The negative effect of NaCl on the thermochemical conversion of crude glycerol was also observed by Lehnert and Claus,¹⁷ who studied the catalytic conversion of glycerol to hydrogen by aqueous-phase reforming.

Compared to the extensive reports on the negative effects of crude glycerol impurities, there have been few reports on the positive effects of crude glycerol impurities. In one example, Xu et al.¹⁸ studied the effects of methanol, FFAs, soap, FAMES, and glycerides on the microbial conversion of crude glycerol to triacylglycerols. While methanol exhibited inhibitive effects, all other impurities showed positive effects by helping increase biomass concentration and lipid production. In another example, Xiu et al.⁷ studied the mechanism of biofuel production from crude glycerol by hydrothermal pyrolysis and showed that FFAs present in crude glycerol helped increase oil yield.

Previous studies from our research group have shown that crude glycerol impurities can help improve the properties of bio-based polyols and polyurethane (PU) foams derived from crude glycerol-based liquefaction of lignocellulosic biomass.^{19,20} Polyols are major feedstocks used to produce PU foams, which are widely used to produce commercial cushion and insulation materials. Currently, polyols are mainly petroleum-derived and there has been extensive interest in producing bio-based polyols by the liquefaction of lignocellulosic biomass.^{21–23} In our previous study of the base-catalyzed crude glycerol-based liquefaction process, organic impurities, particularly FFAs and FAMES, were essential in producing polyols with appropriate hydroxyl numbers and molecular weights (M_w) for PU foam applications; generally, crude glycerol containing 45–70% of organic impurities was optimal for the production of polyols and PU foams. In this study, we aimed to further study the effects of crude glycerol impurities on the properties of polyols and PU foams derived from an acid-catalyzed biomass liquefaction by crude glycerol process. Compared to base-catalyzed biomass liquefaction processes, acid-catalyzed biomass liquefaction processes are usually conducted at lower liquefaction temperatures and may suffer from detrimental recondensation reactions at low solvent/biomass ratios.²⁴ Because of these differences, results obtained from base-catalyzed liquefaction processes might not be directly applicable to acid-catalyzed liquefaction processes. Therefore, a separate study on effects of crude glycerol impurities in the acid-catalyzed liquefaction process is needed and a comparison between the acid- and base-catalyzed processes is of interest.

EXPERIMENTAL

Materials

Corn stover was harvested from the Ohio Agricultural Research and Development Center (OARDC) farm (Wooster, OH), ground (1 mm mesh screen), and oven-dried at 105°C for 24 h

before being used for liquefaction tests. Chemicals purchased from Fisher Scientific (Pittsburgh, PA) included glycerol, oleic acid, imidazole, NaOH pellets, concentrated HCl (35–38% wt), and standard NaOH solutions (0.1N and 10N). Chemicals purchased from Sigma Aldrich (St. Louis, MO) included technical grade mono-glycerides (i.e., 40% monoglyceride, 15–40% diglycerides, and 15–40% triglycerides) and phthalic anhydride. Chemicals purchased from Pharmco-AAPER (Shelbyville, KY) included pyridine, 1,4-dioxane, HPLC-grade THF (tetrahydrofuran), 98% concentrated sulfuric acid, and ethanol. Unless otherwise stated, all chemicals used were of reagent grade or higher purity.

Crude glycerol and biodiesel samples were obtained from Bio100 Technologies, LLC. (Mansfield, OH). The obtained biodiesel sample, used as a model compound of FAMES, was determined to consist of five major types of FAMES: methyl palmitate (11.7%), methyl stearate (5.1%), methyl oleate (22.6%), methyl linoleate (52.9%), and methyl linolenate (6.4%). Additives used in PU foaming were obtained from Air Products & Chemicals, Inc. (Allentown, PA). Polymeric MDI (methylene-4,4'-diphenyl diisocyanate) was obtained from Bayer Material Science (Pittsburgh, PA).

Experimental Design

The individual effects of NaCl and Na₂SO₄ on the properties of polyols were investigated at 0, 2, and 4% levels (wt % of liquefaction solvent). The effects of organic impurities (i.e., FFAs, FAMES, and glycerides) on the properties of polyols and PU foams were investigated via a three-factor central-composite design (Table I). FFAs, FAMES, and glycerides were independent variables (predictors). The properties of produced polyols and PU foams were dependent variables (responses). The independent variables were coded as follows:

$$x_i = \frac{X_i - X_0}{\Delta X}, \quad i = 1, 2, 3 \quad (1)$$

where x_i represents coded independent variables, X_i represents original un-coded independent variables, X_0 represents the value of X_i at the center point, and ΔX represents the step change value. A detailed illustration of the coded and original levels of the independent variables is shown in Table II. The experimental design and statistical analysis were performed using JMP 9.0.0 and R (3.0.2) (SAS Institute Inc., Cary, NC).

Preparation of Liquefaction Solvent

To study the effects of inorganic impurities, salt (NaCl or Na₂SO₄) was mixed with pure glycerol at three different weight ratios (salt/pure glycerol: 0/100, 2/98, 4/96). The obtained mixtures were then used as the liquefaction solvent. To study the effects of organic impurities, oleic acid, biodiesel, and tech-grade monoglycerides were used as the model compounds of FFAs, FAMES, and glycerides, respectively. Model crude glycerol samples with different compositions were prepared by mixing pure glycerol, oleic acid, biodiesel, and tech-grade monoglycerides according to the recipe shown in Table I (i.e., glycerol content in each treatment was the balance of 100%). The prepared model crude glycerol samples were used as the liquefaction solvent to produce liquefaction-derived polyols.

Table I. Central Composite Design and the Biomass Conversion Ratios and Hydroxyl Number of Polyols Produced from the Acid-Catalyzed Liquefaction by Crude Glycerol Process

Run	FFAs (x_1)	FAMEs (x_2)	Glycerides (x_3)	Biomass conversion (%)		Hydroxyl number (mg KOH/g)	
				Measured	Predicted	Measured	Predicted
1	-1	-1	1	90.5	90.9	1249	1262
2	-1	1	-1	88.2	84.8	1042	1058
3	1	-1	-1	86.7	83.7	1058	1054
4	1	1	1	71.2	71.3	700	703
5	-1	-1	-1	92.6	94.1	1301	1304
6	-1	1	1	80.5	81.6	1014	1023
7	1	-1	1	79.1	80.5	996	985
8	1	1	-1	69.3	74.4	773	765
9	1	0	0	78.8	77.5	903	923
10	-1	0	0	85.1	87.8	1250	1208
11	0	1	0	79.3	78.0	942	922
12	0	-1	0	86.0	87.3	1187	1186
13	0	0	1	82.5	81.1	1059	1045
14	0	0	-1	82.9	84.3	1104	1097
15	0	0	0	82.2	82.7	1062	1085
16	0	0	0	84.4	82.7	1074	1085
17	0	0	0	83.1	82.7	1068	1085
18	0	0	0	85.6	82.7	1095	1085

To validate the regression models built in this study, two crude glycerol samples (CG-A and CG-B) collected from industrial biodiesel plants were used as liquefaction solvents for polyol production. Before being used in the liquefaction process, crude glycerol samples were pretreated to remove inorganic salts, water, and methanol as follows: (1) The sample was acidified by adding a pre-calculated amount of concentrated HCl (35–38 wt %, 11.55N) to completely convert soap to FFAs. (2) Crude glycerol was dried by rotary evaporation at 70°C under vacuum to constant weight to remove water and methanol. (3) Crude glycerol was centrifuged at 10,000 rpm (ca. 11,600 × g) for 10 min to separate crude glycerol into three phases: top (mainly FFAs, FAMEs, and glycerides), middle (mainly glycerol), and bottom (mainly salts). The top and middle phases were collected and used as liquefaction solvents.

Biomass Liquefaction for Polyol Production

Biomass liquefaction for polyol production was carried out in a 500-mL three-neck flask under atmospheric pressure with constant stirring (150 rpm). The reactor was heated by a temperature-controlled heating mantle (Thermo Electron Corp., Madison, WI). Liquefaction solvent (100 g) and catalyst (3 g, concentrated 98% H₂SO₄) were added into the flask and heated to 150°C, followed by the addition of 10 g of corn stover. Liquefaction was then conducted at 150°C for 90 min, after which the flask was cooled to room temperature in a fume hood. Water and other volatiles evaporated during the liquefaction process were recovered by a glass Graham condenser. Poly-

ols were recovered from the flask. All liquefaction treatments were conducted in duplicate.

Characterization of Liquefaction-Derived Polyols

The biomass conversion ratio was determined according to the procedure described in a previous report.¹⁹ Briefly, approximately 2 g of polyol sample was weighed and well dissolved in 30 mL ethanol in a 250-mL Erlenmeyer flask assisted by heating and vibrating. After dissolution, the solution was centrifuged at 10,000 rpm for 10 min. After decanting of the supernatant, the solid residues were recovered via vacuum filtering. De-ionized water was used to rinse the solid residues during filtration until the filtrate became colorless. Then, the dry weight of the residues was recorded after drying at 105°C for 24 h. The biomass conversion was calculated as the percentage of biomass converted (i.e., on the basis of biomass initially added) after

Table II. Coding of the Independent Variables

Independent variables	Levels		
	-1	0	1
FFAs (wt %) ^a	0	10	20
FAMEs (wt %)	0	10	20
Glycerides (wt %)	0	2.5	5

^a wt % represents the weight percentages of experimental variables (i.e., crude glycerol impurities) in model crude glycerol.

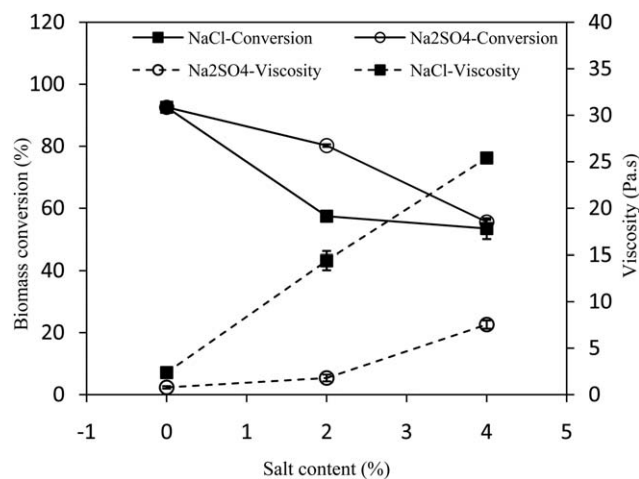


Figure 1. Effects of NaCl and Na₂SO₄ on the biomass conversion ratios and viscosity of polyols.

liquefaction. The acid and hydroxyl number of polyols were determined according to ASTM D4662-08 and D4274-05D, respectively. The molecular weights (M_w) of polyols were determined using a LC-20 AB HPLC system (Shimadzu, Columbia, MD) equipped with a RID-10A refractive index detector and a GPC column (Styragel HR1 THF, 7.8×300 mm, Waters, Milford, MA). The mobile phase used was HPLC grade THF at a flow rate of 1 mL/min. The column and RID temperatures were maintained at 35°C and 40°C, respectively. The injection volume was 10 μ L. An external calibration curve was constructed by analyzing standard polystyrene with M_w ranging from 200 to 2000 g/mol. The data analysis was conducted by using Shimadzu LC solution Version 1.25.

Preparation and Characterization of PU Foams

PU foams were prepared according to the procedure described in a previous report.¹⁹ Briefly, PU foams were prepared in 650 mL plastic cups at an isocyanate index of 100. Polyols, catalysts, and water were stirred vigorously by a stirrer for 10–15 s, after which, a pre-weighted amount of polymeric MDI was added. The mixture was stirred vigorously for another 10–15 s, rapidly poured into the plastic cup, and left to grow at ambient temperature ($23 \pm 2^\circ\text{C}$). All foam samples were allowed to cure overnight before removal from plastic cups. The density and compressive strength of PU foams were measured in accordance with ASTM D1622-08 and ASTM D1621-10, respectively. Compressive strength tests were conducted using an Instron 3300 Universal Testing system (Instron, Norwood, MA) at a cross-head displacement rate of 2.5 mm/min.

RESULTS AND DISCUSSION

Effects of Inorganic Salts on Polyol Properties

As shown in Figure 1, the biomass conversion ratio decreased significantly ($P < 0.05$) with increasing contents of inorganic salts (i.e., NaCl, Na₂SO₄) in crude glycerol, i.e., from 92.6 to around 55% when salt (NaCl or Na₂SO₄) content in the liquefaction solvent increased from 0 to 4 wt %. Figure 1 also shows that the biomass conversion ratio at 2% NaCl (57.4%) was lower than that at 2% Na₂SO₄ (80.2%), due to the lower molar

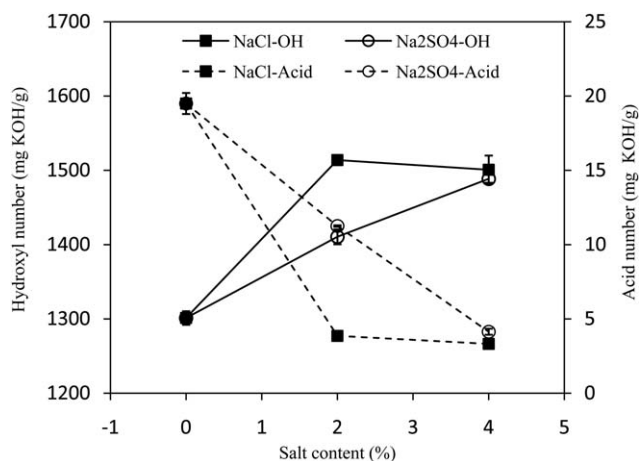


Figure 2. Effects of NaCl and Na₂SO₄ on the hydroxyl and acid numbers of polyols.

mass of NaCl (NaCl: 58 g/mol; Na₂SO₄: 144 g/mol), which led to a higher molarity in the liquefaction solvent at the same weight percentage level. Increasing salt content in crude glycerol significantly increased polyol viscosity, probably due to the decreased biomass conversion ratios.^{22,23} Figure 2 shows that the hydroxyl number of polyols increased significantly ($P < 0.05$) from 1301 to 1500 mg KOH/g and from 1301 to 1489 mg KOH/g when NaCl and Na₂SO₄ contents, respectively, increased from 0 to 4%. The higher hydroxyl number at higher salt levels could be explained by the lower biomass conversion ratio since less glycerol (i.e., thus less hydroxyl groups) was consumed at lower biomass conversion ratios.

The acid number of polyols decreased from around 19.5 to around 3.5 mg KOH/g as salt content (i.e., NaCl or Na₂SO₄) in the liquefaction solvent increased from 0 to 4% (Figure 2), which corresponds to the decreasing biomass conversion ratio shown in Figure 1. Previous reports have shown that high acid potential plays a major role in facilitating rapid and high biomass conversion in acid-catalyzed liquefaction systems.^{23,25} In this study, increasing inorganic salt content in the liquefaction solvent decreased the acid number (i.e., thus the acid potential) of the liquefaction system, which

Table III. ANOVA of the First-Order Model for Biomass Conversion Ratios

Source	Degree of freedom	Mean square	F-value	Probe > F
Model	3	169.63	29.32	<0.0001*
X ₁	1	268.32	46.38	<0.0001*
X ₂	1	215.30	37.21	<0.0001*
X ₃	1	25.28	4.37	0.0553
Residual	14	5.79		
Lack of fit	11	6.76	3.05	0.1946
Pure error	3	2.22		

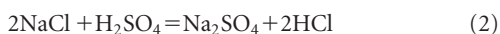
$R^2 = 0.86$; adjusted $R^2 = 0.83$.

*: significant at $\alpha = 0.05$ level.

Table IV. Validation of the Developed Models for Predicting Biomass Conversion Ratios and the Hydroxyl Number of Polyols from Impurities in Crude Glycerol

Samples	Organic impurities (wt %)			Biomass conversion ratio (%)		Polyol hydroxyl number (mg KOH/g)	
	FFAs	FAMEs	Glycerides	Predicted	Measured	Predicted	Measured
CG-A	23.3	23.9	1.3	70.0	77.9	608	629
CG-B	7.6	12.9	6.2	80.2	82.3	1011	966

further led to decreased biomass conversion ratios. Chemical reactions (2) and (3) can be used to explain this phenomenon.^{26,27}



Since the liquefaction process was conducted under atmospheric pressure and under high temperature, HCl produced from the reaction between NaCl and H₂SO₄ was evaporated from the reactor, leading to lower acid potential and lower biomass conversion ratios. The reaction between Na₂SO₄ and H₂SO₄ also decreased biomass conversion ratios because the produced NaHSO₄ is a weak acid that has a lower acid potential and a lower catalytic efficiency than H₂SO₄.

Effects of Organic Impurities on Biomass Conversion Ratios

The liquefaction of lignocellulosic biomass by polyhydric alcohols proceeds mainly via solvolytic reactions, which cleave various chemical bonds (e.g., glycoside bonds) existing in biomass structures and produce smaller biomass-derived molecules or fragments.²⁴ These small biomass derivatives are fairly reactive and can further react with either themselves or liquefaction solvent, forming a large number of biomass and/or liquefaction solvent-derived compounds.²⁴ Thus, biomass liquefaction-derived polyols are usually complex mixtures of liquefaction sol-

vents and derivatives of liquefaction solvents and/or biomass. In this study, the glycerol component in crude glycerol is the main polyhydric alcohol capable of biomass liquefaction. Thus, the increasing contents of other impurities (FFA, FAMEs, and glycerides) in crude glycerol were expected to decrease biomass liquefaction efficiency. Table I shows that biomass conversion ratios decreased with increasing content of organic impurities in crude glycerol. The lower biomass conversion ratio at higher organic impurity levels was due to the decreased glycerol/biomass ratios.¹⁹ Compared to the base-catalyzed crude glycerol-based liquefaction process,²⁰ the acid-catalyzed crude glycerol-based liquefaction process achieved higher biomass conversion ratios at the same organic impurity levels. For example, when crude glycerol with 45% organic impurity was used as the liquefaction solvent, a biomass conversion ratio of 71.2% was obtained in the acid-catalyzed process, compared to a biomass conversion ratio of 54.2% obtained in the base-catalyzed process.²⁰

The relationship between biomass conversion ratios and organic impurity content was fitted into first- and second-order regression models. The fitted second-order model (data not shown) had a higher R^2 (0.90) but a lower R^2 (adjusted R^2 , 0.79) than the fitted first-order model (R^2 : 0.86; R^2 : 0.83), which suggests that the second-order terms in the second-order model provided little explanatory power. Therefore, the fitted first-order model was preferred and is shown below:

$$Y = 94.08 - 0.518X_1 - 0.464X_2 - 0.636X_3 \quad (4)$$

where Y is the biomass conversion ratio, and X_1 , X_2 , and X_3 are the percent of (un-coded) FFAs, FAMEs, and glycerides in crude glycerol, respectively.

As shown in Table I, the biomass conversion ratios predicted by the model are close to their corresponding measured ones, suggesting that the data were well fitted by the model. A summary of the ANOVA of the first-order model indicates that the model could well explain the variations among treatments ($P < 0.0001$, Table III). FFAs (X_1) and FAMEs (X_2) significantly ($P < 0.0001$) affected biomass conversion ratios. Glycerides (X_3) had a higher P -value of 0.055, indicating its moderate or less dramatic effect on biomass conversion ratios. To validate the fitted first-order model, two industrially derived crude glycerol samples (CG-A and CG-B) (compositions shown in Table IV) were used as the liquefaction solvent for polyol production from corn stover. The polyols derived from CG-A showed a measured biomass conversion ratio (77.9%) which was higher than the predicted one (70.0%). The relatively large prediction error (around 10%)

Table V. ANOVA of the Second-Order Model for the Hydroxyl Number of Polyols

Source	Degree of freedom	Mean square	F-value	Probe > F
Model	9	44,402	76.79	<0.0001*
X_1	1	3993	6.91	0.0303*
X_2	1	1925	3.33	0.1055
X_3	1	41	0.07	0.7956
X_1X_2	1	946	1.64	0.2367
X_1X_3	1	378	0.65	0.4421
X_2X_3	1	21	0.04	0.8532
X_1^2	1	1054	1.82	0.2139
X_2^2	1	2727	4.72	0.0616
X_3^2	1	588	1.02	0.3429
Residual	8	578		
Lack of fit	5	801	3.89	0.1466
Pure error	3	206		

$R^2 = 0.99$; adjusted $R^2 = 0.98$; *: significant at $\alpha = 0.05$ level.

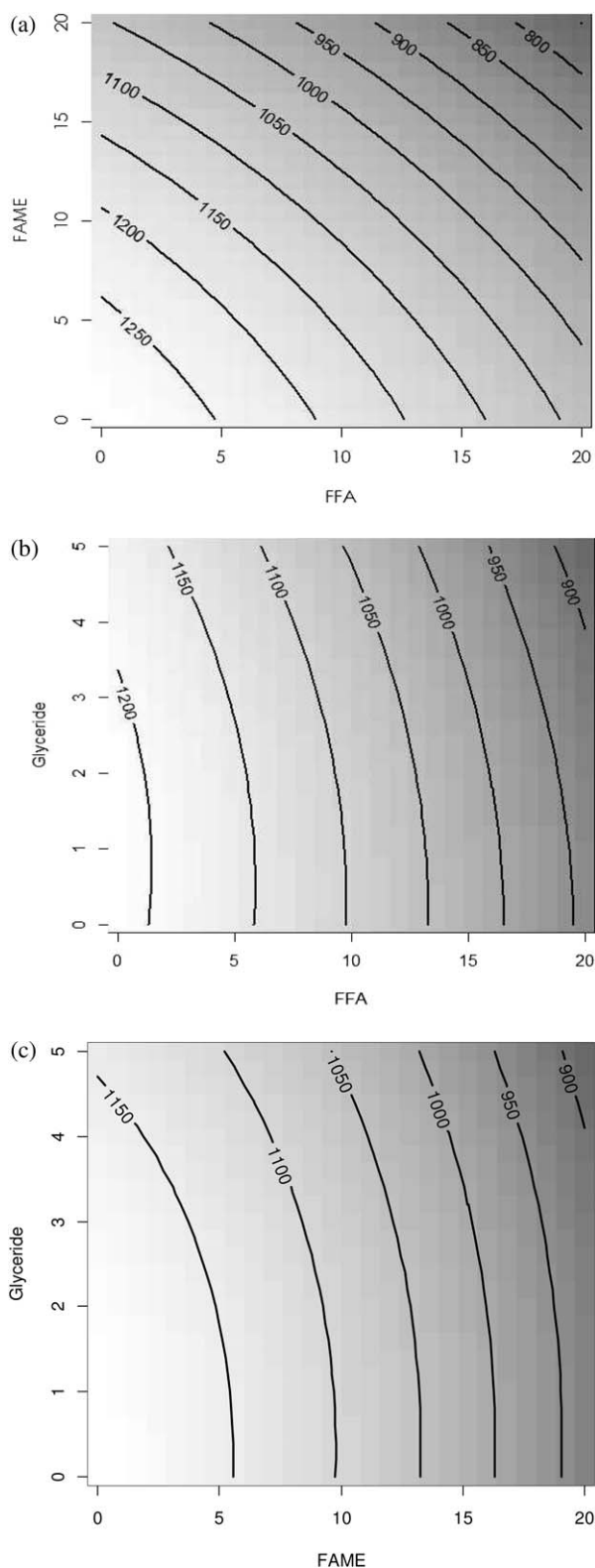


Figure 3. Contour plots of the dependence of the hydroxyl number of polyols on: (a) FFAs and FAMEs (at glycerides: 2.5%); (b) FFAs and glycerides (at FAMEs: 10%); (c) FAMEs and glycerides (at FFAs: 10%).

may be explained by the model's low extrapolation power since the sum of FFA and FAME contents (47.2%) in CG-A exceeded the experimental levels (0–40%) designed in this

study. CG-B had FFA and FAME contents (7.6 and 12.9%, respectively) within the designed experimental levels and the predicted biomass conversion ratio (80.2%) was close to the measured one (82.3%), indicating the model's good predictability.

Effects of Organic Impurities on the Hydroxyl Number of Polyols

To describe the relationship between the hydroxyl number of polyols and the organic impurities in crude glycerol, experimental results were fitted into both first- and second-order models. The fitted second-order model showed higher values in both R^2 (0.99) and R^2 (0.98) than the fitted first-order model (R^2 : 0.95; R^2 : 0.94, data not shown). Therefore, the second-order model was preferred and is shown as follows:

$$Y = 1303.78 - 8.54X_1 - 5.93X_2 + 3.48X_3 - 0.20X_1^2 - 0.32X_2^2 - 2.36X_3^2 - 0.11X_1X_2 - 0.28X_1X_3 + 0.07X_2X_3 \quad (5)$$

where Y is the hydroxyl number of polyols, and X_1 , X_2 , and X_3 are the percent (un-coded) FFAs, FAMEs, and glycerides in crude glycerol, respectively.

The experimental data were well fitted by the model, as evidenced in Table I that the predicted and measured hydroxyl number of polyols were similar. A summary of the ANOVA of the fitted model is shown in Table V. FFAs (X_1 , $P = 0.03 < 0.05$) significantly affected the hydroxyl number of polyols. FAMEs (X_2) and squared FAMEs (X_2^2) showed slightly higher P values of 0.11 and 0.06, respectively, indicating their moderate or less significant effects on the hydroxyl number of polyols. As shown in Table IV, the model was validated with high prediction accuracy (difference between the measured and predicted value less than 5%). Figure 3(a–c) shows the contour plots of the dependence of the hydroxyl number of polyols with FFA, FAME, and glyceride contents in crude glycerol based on the fitted second-order model. As expected, the hydroxyl number of polyols decreased dramatically with increasing contents of FFAs and FAMEs in crude glycerol due to their gradual replacement and consumption of glycerol by esterification and transesterification reactions during the liquefaction process.^{19,28} Compared to FFAs and FAMEs, glycerides showed less dramatic effects on the hydroxyl number of polyols [Figure 3(b,c)].

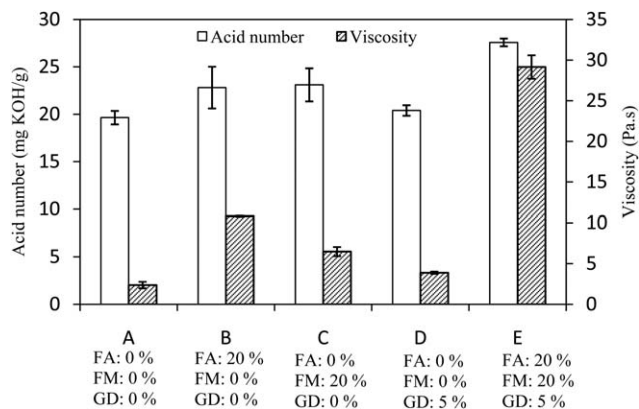


Figure 4. Effects of organic impurities on the acid number and viscosity of polyols (Note: FA: FFAs; FM: FAMEs; GD: glycerides).

Table VI. Effects of Organic Impurities on the Molecular Weights and Functionalities of Polyols

Sample	Organic impurities (wt %) ^a			Molecular weight (g/mol) ^b			f_n^c
	FFAs	FAMEs	Glycerides	M_n	M_w	PDI	
1	0	0	0	214 ± 4 ^d	244 ± 8	1.14 ± 0.02	5.6 ± 0.2
2	0	0	5	217 ± 3	262 ± 13	1.21 ± 0.04	5.8 ± 0.3
3	0	20	0	230 ± 4	309 ± 22	1.34 ± 0.07	5.7 ± 0.4
4	20	0	0	248 ± 1	401 ± 8	1.62 ± 0.03	7.6 ± 0.1
5	20	20	5	306 ± 4	550 ± 5	1.80 ± 0.01	6.8 ± 0.2

^aBalance of 100% being glycerol.

^b M_n : number-average molecular weight; M_w : weight-average molecular weight; PDI: polydispersity.

^cFunctionality.

^dMean ± standard deviation of two replicates.

As organic impurity contents in crude glycerol increased from 0 to 45%, the hydroxyl number of polyols decreased from 1301 to 700 mg KOH/g (Table I). Similar to the base-catalyzed liquefaction process,²⁰ polyols with suitable hydroxyl number (<800 mg KOH/g) and M_w for rigid or semi-rigid PU foam applications were produced when crude glycerol contained 40% (glycerol/biomass weight ratio: 6/1) or more of organic impurities. However, our results (data not shown) also showed the organic impurity content in crude glycerol should be kept at or below 50% (glycerol/biomass weight ratio \geq 5/1) in order to avoid the occurrence of detrimental recondensation reactions during acid-catalyzed liquefaction. Thus, crude glycerol containing 40–50% organic impurities (glycerol/biomass weight ratio: 5/1 to 6/1) is considered to be suitable for the acid-catalyzed liquefaction process to produce polyols with an appropriate hydroxyl number for PU foam applications.

Effects of Organic Impurities on the Acid Number, Viscosity, and M_w of Polyols

The acid number of polyols increased slightly from 20 to 23 mg KOH/g when the FFA content in crude glycerol increased from 0 to 20% (Figure 4), probably due to the presence of residual FFAs in the polyols (e.g., FFA content: 2.1 ± 0.2% at 20% FFA level). When the FAME content in crude glycerol increased from 0 to 20%, the acid number of polyols also slightly increased from 20 to 23 mg KOH/g (Figure 4), probably due to the existence of FFAs in the polyols (e.g., FFA content: 1.8 ± 0.2% at 20% FAME level) produced by the hydrolysis of FAMEs during the liquefaction process. Increasing glyceride content from 0 to 5% caused no significant change in the acid number of polyols (20 mg KOH/g for both 0 and 5% glyceride levels). Although higher than the values obtained in the base-catalyzed liquefaction process (< 5 mg KOH/g),²⁰ the acid number of polyols obtained in this study were similar to those derived from conventional acid-catalyzed biomass liquefaction processes that use petroleum-derived polyhydric alcohols as liquefaction solvent.^{23,29} The viscosity of polyols increased significantly ($P < 0.05$) from 2.4 to 10.9, 6.5, and 3.9 Pa s with the increase of FFAs from 0 to 20%, FAMEs from 0 to 20%, and glycerides 0 to 5%, respectively (Figure 4). The increased polyol viscosity could be explained by the decreased biomass conversion ratios^{22,23} as well as by the intensified condensation

reactions at higher organic impurity levels during the liquefaction process.^{19,28}

Both the M_w and functionality of polyols increased with increasing levels of organic impurities in crude glycerol (Table VI), which agrees with the results from the base-catalyzed liquefaction process.²⁰ Polyols derived from petrochemical solvent-based liquefaction processes have shown M_w varying from 500 to 900 g/mol, depending on liquefaction conditions.^{23,30} In this study, polyols produced from crude glycerol containing \geq 40% organic impurities showed comparable M_w of around 500 g/mol.

Effects of Organic Impurities on the Properties of PU Foams and a Comparison Between Acid- and Base-Catalyzed Liquefaction Processes

The presence of organic impurities in crude glycerol significantly ($P < 0.05$) decreased the density of PU foams (Figure 5), which agrees with the results obtained from the base-catalyzed liquefaction process. The lower density of PU foams at higher organic impurity levels were mainly caused by the lower hydroxyl number of their corresponding polyols. The compressive strength of PU foams decreased significantly ($P < 0.05$) from 174 to 149, 76, and 166 kPa with increases of FFAs from 0 to 20%, FAMEs from 0 to 20%, and glycerides from 0 to 5%, respectively (Figure 5). These results were contrary to the results obtained from the base-catalyzed liquefaction process, during

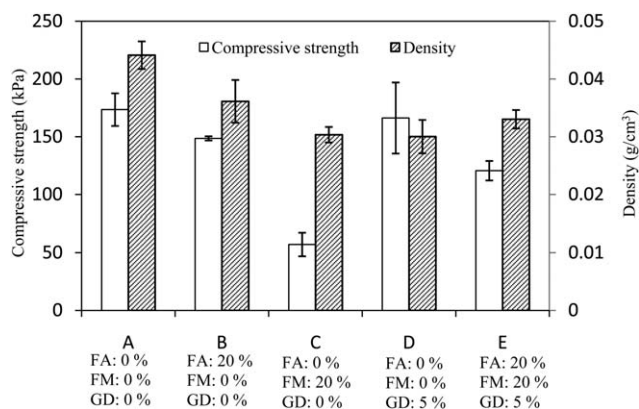


Figure 5. Effects of organic impurities on the compressive strength and density of PU foams (Note: FA: FFAs; FM: FAMEs; GD: glycerides).

Table VII. Comparison Between the Properties of the Polyols and PU Foams Derived from Acid- and Base-Catalyzed Liquefaction Processes

		Acid-catalyzed ^a	Base-catalyzed ^a
Liquefaction conditions	Temperature (°C)	150	240
	Time (min)	90	180
	Solvent/biomass ratio	5/1–6/1	3/1–6/1
	Catalyst (wt %) ^b	3	3
Polyol properties	Biomass conversion ratio (%)	71.2	54.2
	Hydroxyl number (mg KOH/g)	700	761
	Acid number (mg KOH/g)	28	<5
	Viscosity (Pa s)	29.2	>100
	Molecular weight (g/mol)	550	455
PU foam properties	Density (g/cm ³)	0.033	0.043
	Compressive strength (kPa)	121	157

^aCrude glycerol containing 55% glycerol, 20% FFAs, 20% FAMES, and 5% glycerides was used as liquefaction solvent.

^bReagent grade NaOH pellets and 98% concentrated H₂SO₄ were used as catalysts in base- and acid-catalyzed liquefaction processes, respectively.

which the compressive strength of PU foams increased with increasing contents of organic impurities in crude glycerol. This discrepancy could be explained by the different experimental levels and/or different reactions involved in the acid- and base-catalyzed liquefaction processes. In this study, the decreased strength of PU foams at higher levels of impurities can be mainly attributed to the lower hydroxyl number of polyols produced, which led to lower hard segment content and lower intermolecular hydrogen bonding in PU foams.³¹ Among all organic impurities, FAMES (at 20%) caused the most dramatic decrease in PU foam strength (Figure 5), probably due to the high residual FAME content ($5.7 \pm 0.1\%$) in the produced polyols. Since FAMES have little reactivity with isocyanates, their presence in polyols is likely to cause disrupted foam structures and decrease the strength of PU foams. Nevertheless, despite the negative effect of organic impurities on PU foam strength, PU foams produced in this study still exhibited comparable compressive strength to their analogs derived from conventional petrochemical solvent-based liquefaction processes.^{22,23}

Table VII shows a comparison between the acid- and base-catalyzed crude glycerol-based biomass liquefaction processes. Compared to the base-catalyzed process, the acid-catalyzed process resulted in a much higher biomass conversion ratio, indicating its higher liquefaction efficiency. The higher biomass conversion ratio obtained in the acid-catalyzed process also means that more hydroxyl groups were consumed for the solvolytic liquefaction of biomass, producing polyols with lower hydroxyl numbers. In addition, because of its higher liquefaction efficiency, the acid-catalyzed process also produced polyols with lower viscosity and higher M_w than that from the base-catalyzed process. However, compared to the base-catalyzed process, the acid-catalyzed process had the disadvantages of producing polyols with higher acid number and PU foams with lower compressive strength. Polyols with high acid number are unfavorable and need to be treated before being used for PU applications. Moreover, the base-catalyzed process was also more robust for accommodating crude glycerol with a wider range of impurity levels (crude glycerol with 45–70% organic impurities, i.e., glycerol/biomass ratios of 3/1 to 6/1).²⁰ In com-

parison, the acid-catalyzed liquefaction process needed crude glycerol with 40–50% organic impurities (glycerol/biomass ratio: 5/1 to 6/1) to achieve the optimal balance between inhibiting detrimental recondensations during liquefaction and producing polyols with suitable properties for PU foam applications.

CONCLUSIONS

Crude glycerol impurities significantly affected the acid-catalyzed crude glycerol-based biomass liquefaction process and the properties of produced polyols and PU foams. Inorganic salts in crude glycerol negatively affected the efficiency of the liquefaction process and the properties of produced polyols. Despite their negative effects on biomass liquefaction efficiency, organic impurities, with their contents in crude glycerol controlled at appropriate levels (40–50% wt), could help improve the properties of produced polyols and PU foams. Compared to the base-catalyzed liquefaction process, the acid-catalyzed liquefaction process had higher liquefaction efficiency and produced polyols with lower viscosity, but higher acid number. Currently, studies on other aspects (e.g., morphologies and stability) of the properties of liquefaction-derived PU foams are ongoing and will be reported in the near future.

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