Research article

Impact of biomass feedstock variability on acid-catalyzed alcoholysis performance

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A B S T R A C T

Alcoholysis was an efficient way for liquefying lignocellulosic biomass into valuable platform chemicals. In this study, the impact of feedstock types on the acid-catalyzed alcoholysis performance was systematically investigated by comparing the alcoholysis ratio, product distribution and production of main products. Component analysis showed that three major chemical components could be efficiently degraded, further, hemicellulose and lignin were prone to be decomposed than cellulose. The time dependent alcoholysis ratio evolution was highly related to the feedstock types with the variation in lignin content and cellulose crystallinity index (CrI). The alcoholysis product distributions also varied significantly with different feedstocks according to the GC–MS analysis results. Ethyl levulinate (EL), furfural and ethyl *p*-hydroxybenzoate were identified as the major components in the products. The high mass yield 12.4% of EL was obtained from corn stover, and it was highly correlated to the cellulose content and CrI. The maximum mass yield of furfural was produced from wheat straw while a considerable amount of ethyl *p*-hydroxybenzoate was typically produced from poplar wood. With the comprehensive understanding of the impact of feedstock variability on the alcoholysis performance, our study could give an empirical evidence for product-oriented feedstock selection in biofuels and chemicals production.

1. Introduction

Owing to diminishing petroleum reserves and environmental problems, such as global warming and air pollution, it is imperative to utilize biomass resources to produce fuels and chemicals [1–3]. Recently, liquefaction with alcoholic solvent (also called alcoholysis) has attracted considerable attention. As one of the major thermochemical processes, alcoholysis has many advantages, such as the low reaction temperature (< 400 °C) in the comparison with gasification and pyrolysis (400–1000 °C) [4], short reaction time (a few seconds or minutes) when compared with bio-chemical process (several days or weeks) [5]. More importantly, the alcoholysis can simultaneously facilitate the partial decomposition of lignin as well as the cellulose and hemicellulose through the solvolysis rather than remain it in residues [6]. Previous researches have demonstrated that abundant value-added platform chemicals, including glycosides, furan chemicals and levulinate esters, can be produced through the process [4,5,7–10]. However, due to the structural and chemical complexity of raw materials, selection of suitable biomass for biochemicals production is exceedingly necessary to be taken into consideration [5,11,12].

In recent decades, numerous researchers have explored the performance of different biomass, including agricultural residues, woody materials and wastes from pulp industry, etc. [11–18]. Grisel found that a considerable amount of methyl glucosides and furfural could be generated after methanolysis of wheat straw at 175 °C with 40 mM H$_2$SO$_4$, the main by-products were levulinic acid and its alkyl ester [11]. Feng et al. used bamboo as an alcoholysis substrate and subcritical methanol as the solvent, 30.75 wt% of methyl levulinate was obtained with 2.5 wt% H$_2$SO$_4$ at 200 °C, meanwhile, glycosides and phenols (lignin derivatives) were also detected in a large amount [14]. Le Van Mao et al. have compared the alcoholysis products of paper pulp, pine wood and switch grass through two-step process, it was found that the production mixtures including ethyl levulinate, ethyl formate, ethyl acetate, 2-furfural and other compounds, were chemically identical but varied significantly on the yield. Besides, this study demonstrated that ethyl levulinate production depended closely on the cellulose content while 2-furfural derived from hemicellulose properly relied on the hemicellulose content of raw materials [16]. Recently, our group found that 34.9 mol% of methyl levulinate could be obtained as the main product when using corn stover as the substrate, and other major co-products were identified as levoglucosenone (LGO), furfural, and methyl 4-hydroxycinnamate [18]. The alcoholysis product distribution and target chemicals production have been generally explored in above researches. However, these results could not be compared due

to the variation on reaction conditions and the definition of desired product. The study must be carried out at an identical condition to understand the effect of biomass feedstock variability on the alcoholysis performance.

In this study, several common biomass resources, including herbaceous biomass (corn stover, wheat straw, rice straw, rape straw) and woody biomass (poplar wood) were chosen as the experimental substrate. The alcoholysis was conducted with ethanol as the liquefying agent at 180 °C as the reaction time ranging from 0 to 30 min. Microwave heating as a novel technology was applied in this study due to its versatile advantages, such as facilitating heating rates, saving processing times and reducing energy consumption, which cannot be observed in conventional heating methods [18–20]. The alcoholysis ratio, the alcoholysis product distribution, and the production of main products were systematically compared. In addition, the effects of innate variability on alcoholysis performance were discussed here. We hope that this study could profoundly give an empirical support for product-oriented feedstock selection in biochemicals production.

2. Materials and methods

2.1. Materials and reagents

Corn stover was obtained from the Shang Zhuang experiment station of China Agricultural University. Wheat straw and rape straw were collected from Shandong province. Rice straw and poplar wood were acquired from Hunan province and Hebei province respectively. All the lignocellulosic feedstocks were dried at 105 °C, and then milled and screened using a Taiwan RT-34 hammer mill with a 40-mesh screen.

EL (99%), triethyl citrate (99%), LGO (98%), pyrimidine (> 98%), ethyl mercaptan (EtSH, > 98%), and BF_3 (> 98%) were purchased from TCI. Glucose (99.5%), xylose (99%), furfural (98%), and N,O-bis (trimethylsilyl)acetamide (BSO, ≥95%) were supplied by Sigma Aldrich. All other chemicals (analytical reagents) were purchased from Beijing Chemical Plant and used as received.

2.2. Chemical composition and structural property analysis

The chemical composition (cellulose, hemicellulose, lignin, and ash) of each biomass feedstock was determined using NREL/TP-510-42,618 [21]. The lignin monomer composition was analyzed through thioacidolysis according to Hoffmann et al. [22]. The corresponding gas chromatography–mass spectrometry (GC–MS) spectra are shown in Fig. S1 and the thioacidolysis monomer yields are presented in Table 1. X-ray diffraction measurements were performed (2θ = 5°–40° with a step interval of 0.2°) with a Beijing Purkinje General diffractometer using Cu-Kα radiation at 40 kV and 30 mA. The cellulose crystallinity index could be calculated by the following equation according to an empirical method reported by Segal et al. [23]:

$$CrI\ (\%) = \frac{(I002 - Iam)}{I002} \times 100\% \tag{1}$$

where I_{002} is the maximum intensity of 0 0 2 lattice diffraction of cellulose at 2θ = 22.5° and I_{am} is the peak intensities at around 2θ = 18° representing the amorphous part.

2.3. Microwave-assisted alcoholysis of biomass feedstocks

Alcoholysis of each biomass feedstock was carried out in a Milestone microwave apparatus equipped with an internal temperature sensor and a magnetic stirrer. Sulfuric acid was employed as the acid catalyst. A mixture containing 5 g of biomass, 25 g of ethanol, and 0.75 g of sulfuric acid (3 wt%, based on ethanol amount) was introduced into a sealed Teflon reaction vessel (100 mL). The sample was heated to 180 °C for less than 90s under the initial microwave power of 600 W. Then the power was automatically adjusted to keep the temperature constant for a specific time (0–30 min). Subsequently, the vessel was cooled to room temperature using the air-cooling device of the microwave apparatus. All experiments were conducted in quadruplicate. Prior to analysis, 2 g of the resultant mixture was diluted with methanol in a 50-mL volumetric flask and then filtered through a membrane filter (0.22 μm).

2.4. Alcoholysis ratio

The alcoholysis ratio, which indicates the extent of alcoholysis, was determined according to a reported method [24]. The residue was separated from the alcoholysis products using filter paper, washed thoroughly with 80% 1,4-dioxane, and then dried for 24 h at 105 °C. The alcoholysis ratio was calculated as follows:

$$Alcoholysis\ Ratio\,(\%) = \left(1 - \frac{Weight\ of\ residue\ (g)}{Weight\ of\ total\ charged\ biomass\ (g)}\right) \times 100\% \tag{2}$$

2.5. Chemical composition of residues

The chemical composition (cellulose, hemicellulose, and lignin) of each residue was determined according to NREL/TP-510-42,618 (Sluiter A et al., 2008) [21].

2.6. Alcoholysis products analysis of biomass feedstocks

2.6.1. Qualitative analysis

GC–MS (Agilent 7890A/5975C equipped with a DB-5MS capillary column (30 m × 0.25 mm × 0.25 μm)) was used to identify the alcoholysis products. The temperatures of the injection port, ion source, and quadrupole were 280, 230, and 150 °C, respectively. The oven was

Table 1
Chemical compositions and structural properties of various feedstocks.

Lignocellulosic feedstocks	Corn stover	Wheat straw	Rice straw	Rape straw	Poplar wood
Cellulose (%)	32.8 ± 0.8	31.2 ± 0.5	37.1 ± 0.1	26.4 ± 0.1	37.1 ± 0.7
Hemicellulose (%)	18.4 ± 0.3	17.2 ± 0.2	15.6 ± 0.0	9.6 ± 0.1	10.5 ± 0.3
Lignin (%)[a]	14.8 ± 0.5	18.2 ± 0.3	19.9 ± 0.9	20.1 ± 0.7	26.2 ± 0.5
Ash (%)	5.6 ± 0.1	8.5 ± 0.0	10.1 ± 0.1	7.8 ± 0.3	8.6 ± 0.0
CrI (%)	41.2 ± 1.2	43.4 ± 1.1	43.7 ± 1.1	41.7 ± 1.0	52.9 ± 1.4
Thioacidolysis yields of H, G, and S monomers (μmol/g)[b]					
H	29.9 ± 2.0	29.6 ± 1.9	31.5 ± 2.1	27.5 ± 1.7	40.5 ± 2.3
G	38.7 ± 2.5	53.1 ± 1.9	57.5 ± 3.2	83.2 ± 3.8	110.3 ± 3.3
S	47.7 ± 2.2	56.5 ± 2.0	53.9 ± 3.1	101.9 ± 2.5	148.4 ± 3.8
Total content	116.3 ± 6.7	139.2 ± 5.8	142.9 ± 8.4	212.6 ± 8.0	299.2 ± 9.4
Molar ratio	0.77/1/1.23	0.56/1/1.07	0.55/1/0.94	0.33/1/1.23	0.37/1/1.35

[a] The lignin content is the sum of acid-soluble and acid-insoluble lignin.
[b] The yields are relative to the mass of charged dry biomass.