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Sweet sorghum stalk liquefaction in supercritical methanol: Effects of operating conditions on product yields and molecular composition of soluble fraction

Hong-Lei Yan [a], Zhi-Min Zong [a,*], Zhan-Ku Li [a], Jiao Kong [a], Quan-Xi Zheng [a], Yan Li [b], Xian-Yong Wei [a]

[a] Key Laboratory of Coal Processing and Efficient Utilization, Ministry of Education, China University of Mining & Technology, Xuzhou 221116, Jiangsu, China
[b] The Gene and Linda Voiland School of Chemical Engineering and Bioengineering, Washington State University, Pullman, WA 99164, USA

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ABSTRACT

Liquefaction of sweet sorghum stalk (SSS) in supercritical methanol was carried out under different conditions, including temperature, holding time, and SSS-to-methanol ratio. Each reaction mixture was filtrated to afford residue and bio-oil (BO, i.e., methanol-soluble portion). The optimal conditions were determined to be 300 °C and 30 min based on the BO yield and the maximum yield of BO is 40.5 wt% with higher heating value of 25.1 kJ g^{-1}. Low SSS-to-methanol ratio, i.e., either more methanol volume or less SSS dose, benefits the BO yield. According to gas chromatograph/mass spectrometric analysis, the compounds detected in the BOs can be grouped into hydrocarbons, alcohols, phenolic compounds (PCs), methoxybenzenes, ketones, esters, and others. Among them, PCs and esters are the most abundant. Guaiacols and alkylphenols are predominant PCs, which were mainly originated from the decomposition of lignin in SSS. Esters can be further classified into long-chain methyl esters (LCMEs), short-chain methyl esters (SCMEs), dimethyl diesters, and polymethyl benzenepolycarboxylates. The variation of esters mainly relied on LCME and SCME change with varied reaction conditions.

1. Introduction

Biomass, as one of the most abundant carbon-rich and renewable resources, is being considered as a potential alternative for fossil resources [1,2]. Therefore, it is necessary to develop technologies for converting biomass into liquid fuels and valuable chemicals [3,4]. Among various conversion methods, liquefaction in sub-/supercritical solvents was considered as a promising one [5,6]. Previous researches showed that biomass liquefaction depends on biomass composition and operating conditions [7–9]. Brand et al. [10] studied pine wood liquefaction and concluded that reaction temperature and residence time more affect biomass conversion and bio-oil (BO) yield than pressure and biomass-to-solvent ratio. Akhtar et al. [11] found that the biomass with high cellulose and hemicellulose contents is suitable for producing BO. Huang et al. [12] reviewed solvents used in biomass liquefaction and reported that organic solvents could convert biomass into BO with low oxygen content and high caloric value under mild conditions. Among various organic solvents used in biomass liquefaction, methanol has many merits, such as easy availability and high ability to dissolve and degrade biomass under supercritical conditions [13–15]. Additionally, methanol was reported to act as hydrogen donor and esterifying reagent during biomass or coal liquefaction [16–19].

Sweet sorghum is considered to be a new industrial high energy crop due to its high photosynthetic efficiency, high biomass yield per hectare, short growth period (3–5 months), and low fertilizing rate [20,21]. It can be cultivated without region limitation because of its wide adaptability to diverse climate and soil conditions [22,23]. Based on these characteristics, the infertile and saline soils could be utilized to grow sweet sorghum, which might give a potential solution to the completion between food and fuels. The total area of saline and alkaline land in Huanghuaihai region and the northwest of China is estimated to be more than 170,000 km^2, providing space enough for sweet sorghum cultivation. to conventional to agricultural crops, such as corn, wheat, and rice, sweet sorghum has high contents of sugars, cellulose, and hemicellulose, which can be fermented to produce bioethanol [24,25]. However, costly pretreatment with high energy requirement is almost inevitable during enzymatic hydrolysis for obtaining bioethanol. Alternative approach for converting sweet sorghum into BO deserves investigation.

In this work, we investigated sweet sorghum stalk (SSS) liquefaction in supercritical methanol to explore the effects of physical process parameters on the product yields and molecular compositions of the BOs.

2. Experimental

2.1. Materials

SSS was provided by China University of Agricultural, Beijing, China. After air-drying for a week, the feedstock was chopped into pieces and pulverized to pass through an 80-mesh sieve followed by desiccation in a vacuum at 80 °C for 24 h. Table 1 lists proximate, ultimate, and

* Corresponding author.
E-mail address: zong_zhimin@163.com (Z.-M. Zong).

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Table 1
Proximate, ultimate, and group composition analyses (wt%) of SSS.

Proximate analysis			Ultimate analysis (daf)					Group composition (db)		
M_{ad}	A_d	V_{daf}	C	H	N	O [a]	S	Cellulose	Hemicellulose	Lignin
5.98	2.89	89.85	50.74	6.71	0.61	41.85	0.08	41.07	36.57	13.29

daf: dry and ash-free base; db: dry base: M_{ad}: moisture (air dried base); A_d: ash (dry base); V_{daf}: volatile matter (dry and ash-free base); [a] by difference.

group composition analyses of SSS, which were obtained by GB/T 212-2008, Elementar Vario Macro, and Van Soest method, respectively. The commercial analytical methanol used in the experiments was purified by distillation prior to use.

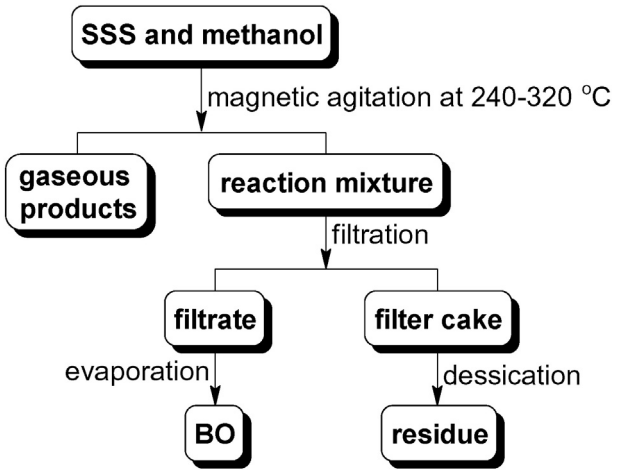

Fig. 1. Procedure for SSS liquefaction.

2.2. Liquefaction procedure and characterization

SSS liquefaction was conducted in a 100 mL stainless-steel, magnetically stirred autoclave. As Fig. 1 shows, SSS and methanol were put into the autoclave. After drawing most of air out from the autoclave with a vacuum pump, the autoclave was heated to a desired temperature (240–320 °C) at 10 °C min^{-1} and maintained at the temperature for a period of time (0–60 min). Then, the autoclave was cooled to ambient temperature. The reaction mixture was taken out with methanol from the autoclave as clean as possible and filtrated to separate the mixture into filtrate and filter cake. The filtrate was distilled with a rotary evaporator to remove methanol to afford BO. The filter cake was dried to a constant weight to afford residue. The yields of the BO (Y_{BO}) and the residue (Y_R) were calculated as the mass ratio of the BO (m_{BO}) and the residue (m_R) to SSS on a dry and ash-free basis, respectively; i.e., $Y_{BO} = m_{BO}/m_{SSS,\,daf}$ and $Y_R = m_R/m_{SSS,\,daf}$. The yield of gaseous products (Y_G) was obtained by difference; i.e., $Y_G = 1 - Y_{BO} - Y_R$. Each experiment was conducted at least 3 times and the standard derivation for the yields of the BOs and the residues is less than 2%.

For comparison, thermogravimetric/differential thermogravimetric (TG/DTG) analysis of SSS, cornstalk, and poplar was performed with a Mettler 2 Toledo TGA/SDTA851^e thermogravimetric analyzer. With argon as carrier gas at the flow rate of 70 mL min^{-1}, ca. 12 mg of a sample was heated from 25 to 900 °C at °C min^{-1} in a ceramic crucible. Functional groups of SSS, the residues, and the BOs were measured with a Nicolet Magna IR-560 Fourier transform infrared (FTIR) spectrometer equipped with an EQUINOX55 spectrophotometer using KBr

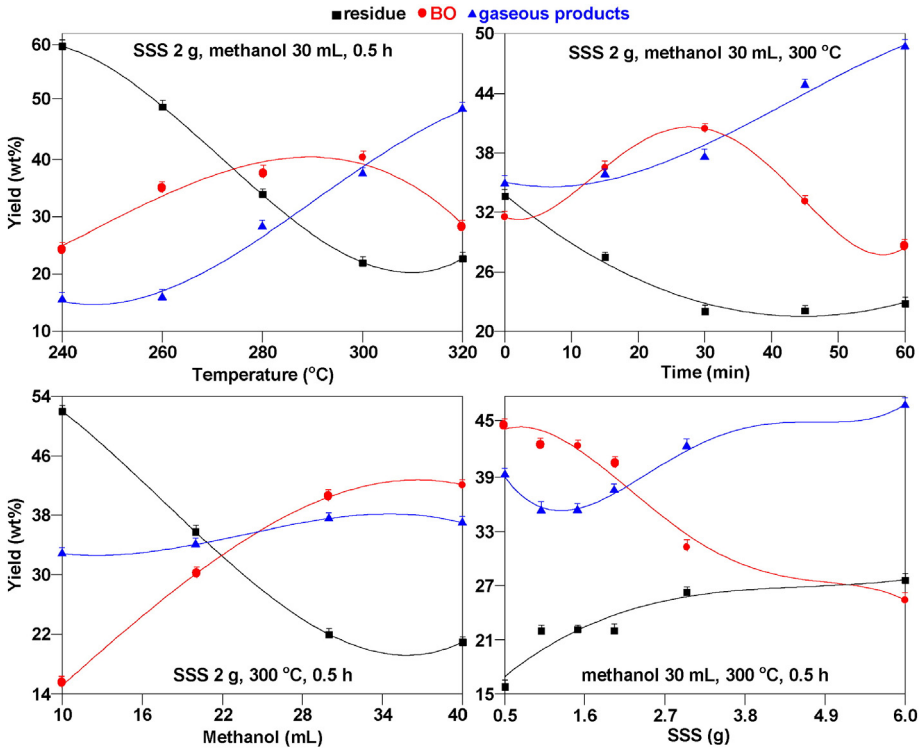

Fig. 2. Effects of reaction conditions on the product yields.

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