



## Cornstalk liquefaction in methanol/water mixed solvents



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### ARTICLE INFO

#### Article history:

Received 31 August 2012

Received in revised form 1 April 2013

Accepted 7 April 2013

Available online 28 April 2013

#### Keywords:

Cornstalk

Liquefaction

Methanol/water mixed solvent

Synergic effect

### ABSTRACT

Cornstalk liquefaction (CSL) in methanol, water or methanol/water mixed solvents was studied at 250–320 °C. Each reaction mixture was separated into extract 1 ( $E_1$ , including the solute in filtrate and methanol-extractable portion), extract 2 ( $E_2$ , methanol-inextractable but isometric carbon disulfide/acetone-extractable portion) and residue (isometric carbon disulfide/acetone-inextractable portion) by filtration and sequential extraction with methanol and isometric carbon disulfide/acetone mixed solvent. The cornstalk,  $E_1$ ,  $E_2$  and the residues were analyzed using a Fourier transformation infrared spectrometer and each  $E_1$  was analyzed using a gas chromatography/mass spectrometer. The microstructures of the cornstalk and its derived residues were observed with a scanning electron microscope. The results show that methanol and water exhibited a synergic effect on the CSL. The isometric methanol and water mixed solvent was found to be most effective for CSL at 300 °C for 30 min. Under such conditions, the total yield of gases,  $E_1$  and  $E_2$  and the yield of  $E_1$  reached 88.1% and 52.4%, respectively. The yields decreased as the temperature or time was further increased, suggesting that some of the extractable species were repolymerized at higher temperatures or for prolonged time.  $E_1$  consisted of hydrocarbons, alkanols, tetrahydrofuranymethanols, arenols, methoxyalkanes, methoxyarenes, ketones, carboxylic acids, esters, chloromethylbenzenes, nitrogen-containing species and several other species.

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### 1. Introduction

With the shortage of fossil energy and the serious pollution associated with the use of fossil fuels, such as acid rain, photochemical smog and haze, many researchers have been paying great attention to renewable energy. As one of the most abundant carbon-rich and clean renewable resources, biomass could alleviate these issues [1–3]. Many efforts, including direct combustion, thermochemical liquefaction, biochemical process and agrochemical process, have been tried to convert biomass to fuels and chemicals. Among these conversion methods for transforming biomass into useful products, thermochemical liquefaction is considered to be a promising one [4].

Hot-compressed water (HCW) has been demonstrated to be an effective solvent for biomass hydrothermal liquefaction [5,6]. The high activity of HCW for liquefying biomass may be ascribed to unique role of HCW in degrading the polymer structures of the lignocellulosic biomass by hydrolysis reactions [5,7,8]. Moreover, HCW has been found very effective for promoting ionic, polar non-ionic and free-radical reactions, which make it a promising reaction medium for direct liquefaction of biomass [9]. However, biomass liquefaction in water is accompanied with many shortcomings, such as corrosive operating conditions and low-heating values of the resulting bio-oil. Several investigations have

been carried out on biomass liquefaction using different solvents [10]. Methanol has been widely used as both solvent and esterifying agent for biodiesel production under supercritical conditions because of its low critical temperature and pressure. Supercritical methanolysis is also considered to be a promising process for converting biomass to clean fuel and chemicals by proper depolymerization of oxygen bridged bonds in the biomass.

Co-solvents have greatest effect on extraction and thermal depolymerization when there are strong, specific interactions with solutes, such as hydrogen bonds and  $\pi$ – $\pi$  interactions. Lignin in woody biomass was effectively extracted using a co-solvent of ethanol/water at 190 °C [11]. Adding water enhanced the decomposition of wood cell wall components, cellulose, hemicelluloses and lignin [12]. Co-solvents, such as ethanol/water, 2-propanol/water and 1,4-dioxane/water mixed solvents, were found to be more effective for lignocellulose liquefaction than a single solvent [13,14]. Isometric methanol/water and ethanol/water mixed solvents were found to show synergic effects on the liquefaction of eastern white pine sawdust [15].

Corn is one of the most widely planted crops over the world [16]. Using cornstalks rather than corn kernels as feedstock for the production of fuels and chemicals not only reduces an increasing pressure on food costs, but also facilitates the reduction of pollution caused by cornstalk discarding and combustion.

In this work, we focused on the comparison of the yields of extractable fractions and compositions from cornstalk liquefaction (CSL) in

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**Table 1**  
Group composition and ultimate analysis of TCSS.

Group composition (wt.%, dry basis)				Ultimate analysis (wt.%, daf)				
Cellulose	Hemicellulose	Lignin	Ash	C	H	N	S	O <sup>a</sup>
24.85	32.20	20.18	12.12	57.26	10.82	1.41	0.18	30.51

<sup>a</sup> By difference.

methanol, water and methanol/water mixed solvents (MWMSs) with different contents of water to understand the effect of co-solvents on CSL. The effects of temperature and time were also examined.

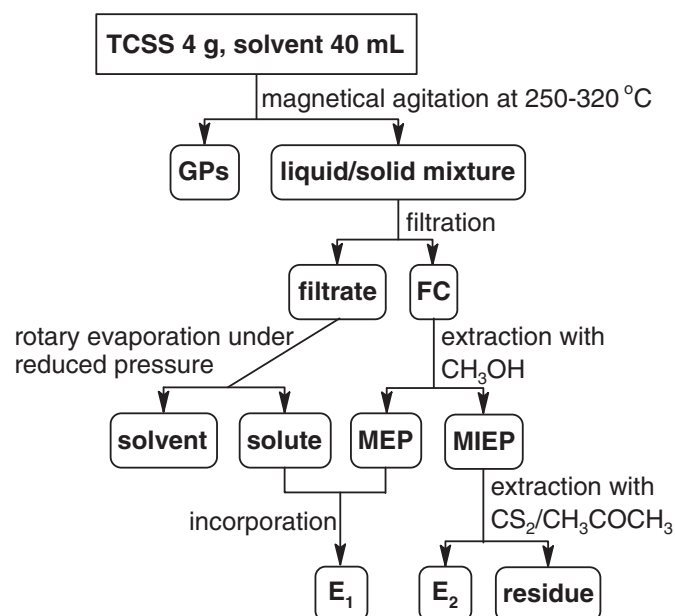
## 2. Experimental

### 2.1. Materials

The cornstalks were collected from Hutubi County, Xinjiang Uygur Autonomous Region, China. They were chopped into small pieces and pulverized to pass through an 80-mesh sieve followed by desiccation in a vacuum at 105 °C for 24 h before use. Table 1 lists the group composition and ultimate analysis of the treated cornstalk sample (TCSS). Surface morphology of TCSS was observed with a Quanta 200 scanning electronic microscope (SEM) and Fourier Transform infrared (FTIR) spectrum of TCSS was recorded on a Nicolet Magna IR-560 FTIR spectrometry. All the organic solvents were commercially purchased analytical reagents and purified by distillation prior to use.

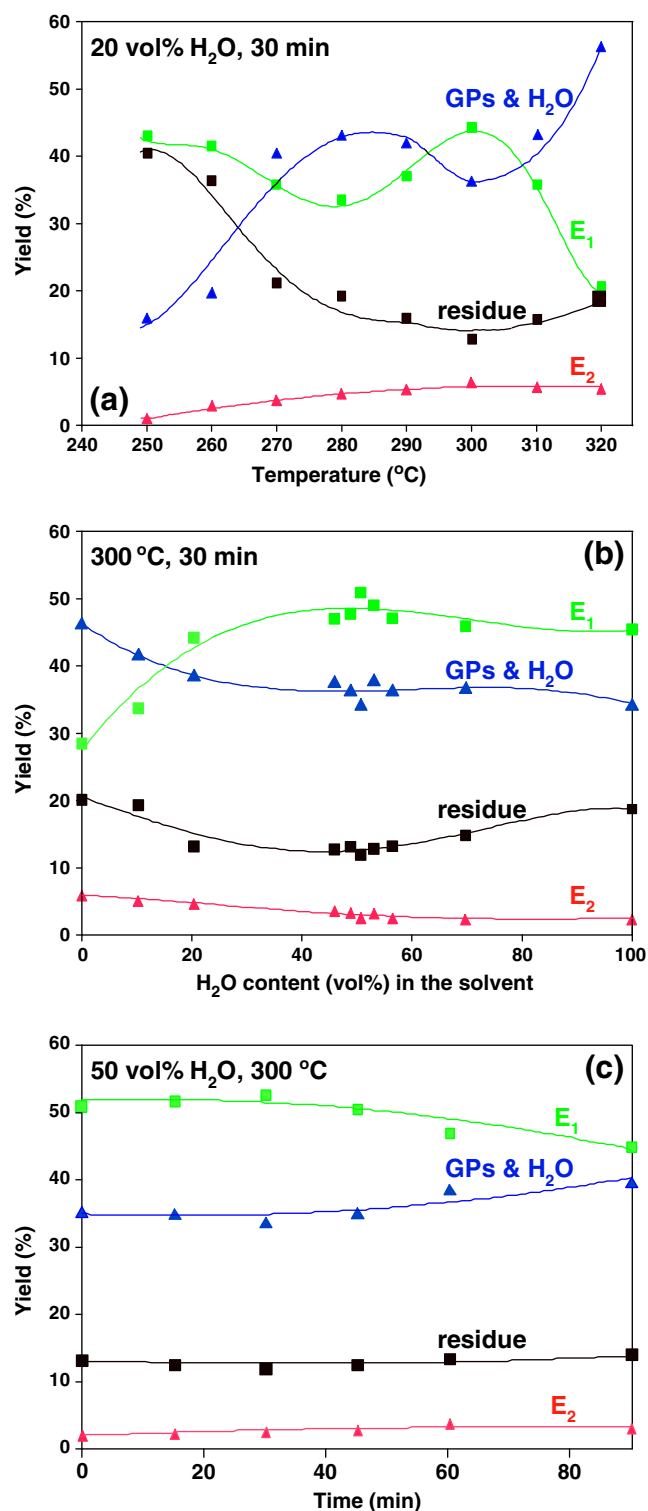
### 2.2. CSL, subsequent separation and characterizations

CSL was performed in a 100 mL stainless steel, magnetically stirred autoclave. As Fig. 1 shows, ca. 4 g TCSS and 40 mL solvent (methanol, water or a MWMS) were put into the autoclave. After replacing air with nitrogen, the autoclave was heated up to a desired temperature at 10 °C/min and kept at the temperature for a described period of time, and cooled down to room temperature in a water bath. After releasing the gaseous products (GPs), the rudimental liquid/solid mixture was filtrated through a 0.45- $\mu$ m membrane filter to afford filtrate and filter cake (FC). The filtrate was separated into solvent (i.e., methanol, water or a MWMS) and solute by rotary evaporation under reduced pressure



**Fig. 1.** Procedure for CSL and subsequent separation.

pressure at 80 °C and the FC was extracted with methanol to afford methanol-extractable portion (MEP) and methanol-inextractable portion (MIEP). The solute and MEP were incorporated and the incorporated portion was denoted as extract 1 ( $E_1$ ). MIEP was extracted with isometric carbon disulfide/acetone mixed solvent to afford extract 2 ( $E_2$ ) and residue. The residue was dried in a vacuum at 80 °C for 24 h before weighing. The yields of  $E_1$ ,  $E_2$  and residue were calculated on



**Fig. 2.** Effects of temperature (a), H<sub>2</sub>O content in the solvent (b) and time on the yields of GPs & H<sub>2</sub>O,  $E_1$ ,  $E_2$  and residues.

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