



Research paper

Alkali catalyzed liquefaction of corncob in supercritical ethanol–water



Kobchok Khampuang, Nuttakorn Boreriboon, Pattarapan Prasassarakich*

Department of Chemical Technology, Faculty of Science, Chulalongkorn University, Bangkok, 10330, Thailand

ARTICLE INFO

Article history:

Received 30 June 2015

Received in revised form

22 October 2015

Accepted 25 October 2015

Available online xxx

Keywords:

Alkali

Corncob

Impregnation

Liquefaction

Ethanol–water

ABSTRACT

Corncob liquefaction in supercritical ethanol–water was performed with and without the addition of an alkali catalyst by direct addition or biomass impregnation in a 250-cm³ batch reactor. The effects of temperature, solvent and alkali addition on the biomass conversion level and oil yield were investigated to find the optimum condition. For non-catalytic liquefaction using a 1:1 (v/v) ethanol: water ratio, a maximum oil yield and conversion level of 49.0% and 93.4%, respectively, were obtained at 340 °C. For alkali catalytic liquefaction, the oil yield with KOH addition (57.5%) was higher than that from KOH-impregnated corncob liquefaction (43.3%). The oil from liquefaction with KOH addition had higher heating value (26.7–35.3 MJ kg⁻¹) than the corncob (19.1 MJ kg⁻¹). The dominant components of the obtained oil were found by GC/MS analysis to be aldehyde, ester, phenol derivatives and aromatic compounds.

© 2015 Elsevier Ltd. All rights reserved.

1. Introduction

Biomass (biological matter) includes wood, wood waste, forestry residues, animal wastes, agricultural crops and also other organic wastes, such as municipal solid waste, sewage and pulp derived black liquor. The use of biomass as an alternative fuel is becoming a more attractive fuel due to the lower contents of sulfur and nitrogen in the biomass. This will lead to a cleaner and safer environment via reduction of greenhouse gases and other toxic gases (NO_x, SO_x) produced by the use of fossil fuels [1]. However, biomass is unsuitable for direct use in energy generation due to its high moisture content and low calorific value [2,3]. Thermochemical liquefaction is one process to convert biomass to a mixture of gas, char and oil. In this process, the solvent acts as a medium for both the decomposition and dissolution of the biomass fragments. Suitable solvents can be non-polar molecules, due to their low dielectric constant and poor hydrogen bonding. The liquefaction/extraction process with the more polar solvents of supercritical water or organic solvents, such as alcohols, has recently become of increasing interest due to the low viscosity and controllable solvent power of the supercritical fluid. Supercritical fluids have previously been reported as being a good media for biomass extraction [3–7].

Several studies have reported on the direct liquefaction of

biomass in a sub/near- or supercritical solvent. For instance, the liquefaction of biomass in supercritical water revealed that the oil yield was dependent on the temperature and reaction time [4,5]. The sub/supercritical liquefaction of oil palm shell using methanol, ethanol, acetone or 1,4-dioxane, reported that the type of solvent used also affected the oil yield [8]. In addition, the use of a co-solvent can also increase the oil yield, where the liquefaction of a woody biomass in a hot-compressed 1:1 (v/v) ratio of alcohol: water co-solvent resulted in the highest oil yield of 65% [9].

Many attempts have been made to improve the biomass direct-liquefaction process, and catalysts have been widely employed to reduce the formation of char and to increase the oil yield. The direct liquefaction of a woody biomass in sub/near-critical water using Ca(OH)₂, Ba(OH)₂ and FeSO₄ as catalysts was found to effectively enhance the heavy oil product yield, and also significantly promoted the formation of gas and water at a higher temperature [10]. From some previous studies on the liquefaction of oil palm shell using an alkali catalyst (NaOH) [11], cotton cocoon shell using NaOH, Na₂CO₃, KOH or K₂CO₃ [12] and cornstalk using catalysts (Na₂CO₃, K₂CO₃ and ZnCl₂) [13], reported the increased solid conversion and liquid product yield significantly, and that increasing the temperature and the addition of catalysts had a synergetic effect on the product yield compared to that obtained without a catalyst. The different catalytic procedures had an important effect on the liquid product yield and composition of the obtained oil.

More extensive research work has reported on the effect of alkali impregnation on the conversion of biomass. By thermogravimetric

* Corresponding author.

E-mail address: ppattara@chula.ac.th (P. Prasassarakich).

analysis (TGA), the impregnation of short rotation willow coppice with potassium was found to promote biomass decomposition and lowered the average apparent first-order activation energy for pyrolysis [14] and enhanced the decomposition and increased the weight loss rates at lower temperatures [15]. In addition, the inorganic matter in the biomass had a catalytic effect on the decomposition behavior and formation of char and pyrolytic compounds during pyrolysis [16].

Residues from food crops in many agricultural countries are abundant and often simply discarded as waste or underutilized. Some of the corncobs are used as boiler fuel in power plants, but the unused corncobs have a high potential to be converted into liquid fuel or chemical feedstock. However, very little research has focused on optimizing the conditions for the corncobs liquefaction [17,18], while their catalytic conversion especially with alkali impregnated corncobs have never been reported [1,5,19]. Given the importance of efficient and economic liquefaction process, the alkali amount should be minimized or partially recovered, the impregnation of the alkali catalyst onto the corncobs would be proposed. This research was to investigate the effect of the direct addition of the alkali catalyst (KOH or NaOH) versus the impregnation of the alkali catalyst onto the corncob liquefaction using ethanol–water in terms of the yield and composition of the oil produced.

2. Experimental

2.1. Materials

The corncobs used in this study are the agricultural waste of field corn (*Zea mays* L.) which is an animal feedstock. The corn was harvested from field at Phetchabun province, central of Thailand (geographical coordinates: 16° 20' North, 101° 06' East). The corncobs were collected, dried in open air and chopped to a piece size of 0.5–1 cm by cutting machine. Then, two kilograms of chopped corncob were ground by pin mill and sieved to a particle size of <0.5 mm. The proximate, ultimate, structural analysis, and the heating value of corncob was indicated in Table 1. The corncob powder was dried in an oven at 110 °C for 24 h and then kept in a desiccator at room temperature before use. Anhydrous ethanol (99.8%), acetone and hydrofluoric acid (HF), all analytical research grade, along with NaOH and KOH were purchased from QReC. Acetone was used to rinse the solid and liquid products after liquefaction. The HF was used for removing inorganic elements before impregnation. Hydrogen gas (H₂; 99.99% pure) was supplied by Thai Industrial Gas Inc.

Table 1
Proximate, ultimate, and structural analysis of corncob.

	Mass fraction (%)
Proximate analysis	
Volatile matter	77.1
Ash	1.7
Moisture	4.8
Fixed carbon	16.4
Ultimate analysis (daf)	
Carbon	46.2
Hydrogen	6.9
Nitrogen	0.8
Oxygen	44.5
Structural analysis	
Cellulose	34.8
Hemicellulose	43.8
Lignin	6.5
Others	14.9
Heating value (MJ·kg⁻¹)	19.1

2.2. Demineralization and impregnation

Before impregnation, the inorganic elements were removed from the corncob powder (50 g) by suspension in 500 cm³ of HF solution with mass fraction of 3% at room temperature for 1 h. The HF-treated corncob was then thoroughly rinsed with deionized water and dried at 110 °C overnight. The demineralized corncob powder was then impregnated with alkali (NaOH or KOH) by immersion in mass fraction of 2, 5 and 10% NaOH or KOH solution (10 cm³ per g of biomass) and stirred at 400 r min⁻¹ at room temperature for 48 h. The sample was then filtered and dried in an oven at 110 °C for 24 h and then kept in a desiccator at room temperature before use.

2.3. Liquefaction

Liquefaction was performed in a 250-cm³ Parr reactor. Typically, 10 g of the dried ground corncob sample was charged into the reactor together with 100 cm³ of ethanol: deionized water mixture (1:0, 9:1, 7:3 and 1:1 (v/v)). For the alkali catalytic liquefaction, the reactor was loaded with 100 cm³ of ethanol: water (1:0 or 1:1 (v/v) ratio), and either 10 g of corncob and the catalyst (NaOH or KOH) at mass fraction of 5 or 10% or the catalyst-impregnated corncob (impregnated at various catalyst concentrations). The reactor was pressurized with H₂ up to 4.0 MPa, then heated to the specified temperature and maintained at that temperature for 60 min with stirring at 100 r min⁻¹. The reactor was then cooled down, the gas inside vented in a hood, and the solid and liquid were rinsed from the reactor with acetone. The resulting suspension was filtered under vacuum through a Whatman No. 4 filter paper to recover the solid residue (SR), which consisted of unreacted sample, coke/char and ash. The SR on the filter paper was dried overnight in an oven at 110 °C and then weighed. The filtrate was evaporated under reduced pressure at 50 °C to remove the solvent (ethanol and acetone) and then at 90 °C to remove the water (formed in the liquefaction process). The % Recovery of the solvent was in the range of 86–95%. The non-volatile liquid-product was then weighed.

The yield of oil, SR and gas plus water, and the biomass conversion level were calculated based on the dry organic matter as shown in Eqs. (1)–(4), respectively:

$$\% \text{Oil yield} = \frac{W_{oil}}{W_{sample,daf}} \times 100, \quad (1)$$

$$\% \text{SR yield} = \frac{W_{SR}}{W_{sample,daf}} \times 100, \quad (2)$$

$$\% (\text{Gas} + \text{Solvent}) \text{ yield} = 100\% - \text{oil yield} - \text{SR yield}, \quad (3)$$

$$\% \text{Biomass conversion} = 100\% - \text{SR yield}, \quad (4)$$

where W_{oil} and W_{SR} are the mass of oil and solid residue, respectively, and $W_{sample,daf}$ are the mass of the starting sample on a dry basis and a dry ash free basis, respectively. The total gas + solvent yield was simply obtained (approximated) by difference. For the catalytic liquefaction, the SR is the residual solid matter less the catalyst weight, and so assumes that the catalysts (KOH and NaOH) are not soluble in supercritical ethanol–water. The reported results were the average values of two liquefaction experiments.

2.4. Characterization

The corncob was subjected to proximate analysis following

Download English Version:

<https://daneshyari.com/en/article/7063720>

Download Persian Version:

<https://daneshyari.com/article/7063720>

[Daneshyari.com](https://daneshyari.com)