

8-Lump reaction pathways of cornstalk liquefaction in sub- and super-critical ethanol

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ABSTRACT

The objective of this work was to develop appropriate reaction pathways to explain the liquefaction behavior of cornstalk in sub- and super-critical ethanol. This reaction system was divided into gas lump, water-soluble oil lump, heavy oil lump, volatile organic compounds lump and residue lump based on the characteristics of cornstalk and liquefaction products, and the residue was further separated into carbon, hydrogen, oxygen and nitrogen. Results showed that the reversible reaction between heavy oil and volatile organic compounds occurred in the liquefaction process, and the decrease in the water-soluble oil yield was mainly attributed to the conversion of water-soluble oil to gas in the sub- and super-critical ethanol. The GC/MS analysis showed that the volatile organic compounds, water-soluble oil and heavy oil comprised a mixture of organic compounds of 6–10, 3–12 and 8–20 carbons, respectively, which mainly included esters, phenols, acids, furans and their derivatives.

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1. Introduction

Biomass can be converted into energy using the thermo-chemical and bio-chemical processes but the thermo-chemical conversion technology is prevailing because of highly efficient conversion to gaseous, liquid and solid products under thermal conditions. During thermal-chemical liquefaction conversion, pyrolysis and solvolysis are two key procedures to convert biomass to more useful chemicals and fuels (Liu and Zhang, 2008). During the pyrolysis processes, the biomass feedstock is heated in the absence of air, forming bio-oils and gaseous products. However, it is critical to design a full-scale system for high heating rates and high temperatures. The solvolysis has many advantages such as preventing the cross linked reactions and reverse reactions because the presence of solvent dilutes the concentration of the products at relative low temperatures (less energy consumption) in comparison with pyrolysis and gasification (Liu and Zhang, 2008). Furthermore, direct liquefaction of biomass in sub-/super-critical solvents (e.g., water, alcohols, and phenol) has been proven to be an efficient approach to convert biomass into low molecular weight chemicals (Wang et al., 2009).

However, the degradation of biomass cannot be described by detailed chemical reaction pathways with well-defined single reaction steps. The reason is that biomass is a combination of cellulose, hemicelluloses, and lignin. These components interact with each other, leading to the formation of chemicals including acids, alcohols, aldehydes, ketones, esters, heterocyclic derivatives, and phenolic compounds (Liu et al., 2010). The knowledge about thermal characteristics and decomposition mechanism of biomass is considerably important for optimization of the conversion process and efficient utilization of the liquid products. Thermo gravimetric analysis (TGA) is one of the most common techniques used to rapidly investigate and compare thermal events and kinetics during the combustion and pyrolysis of solid raw materials (Gil et al., 2010). Recently, many researchers have evaluated these characteristics including kinetic parameters on different biomasses and different dynamic conditions under inert atmospheres by TGA (Simkovic and Csomorova, 2006; Munir et al., 2009; Velden et al., 2010). However, the TGA cannot be used to investigate the thermal characteristics and mechanism of biomass liquefaction in the present of solvents. Some publications have investigated the thermal characteristics and mechanism of biomass liquefaction by the analysis of liquefaction products, development of reaction pathways and dealt with model substances in homogeneous phases (Corma et al., 2007; Liu and Zhang, 2008; Hortal et al., 2010). However, most experimental investigations on liquefaction of biomass often use a single and simplified model substance and the reaction pathways are very complicated.

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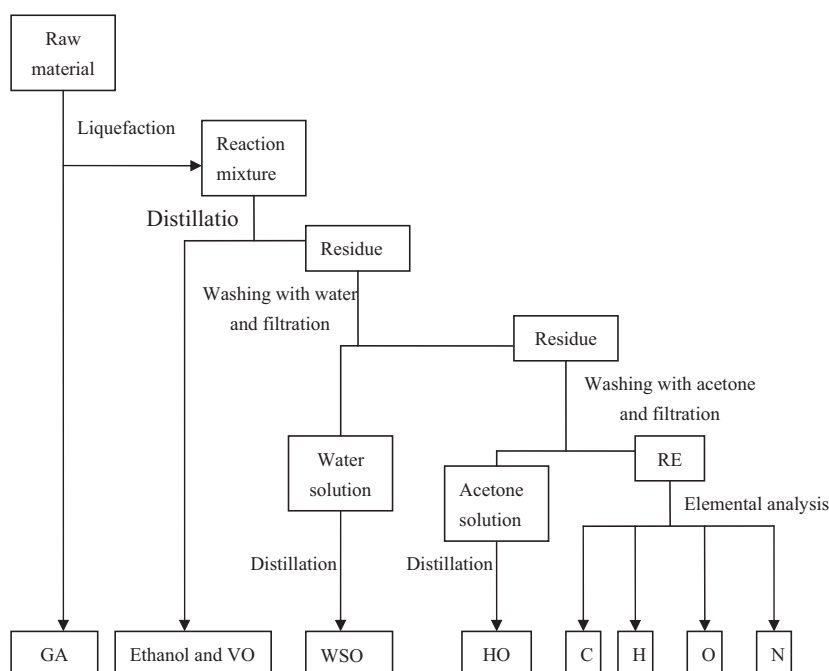


Fig. 1. Procedure for separation of products.

Up to now, the method of lump analysis has been applied to study the complexity of reactive process (fluid catalytic cracking, catalytic pyrolysis processes, et al.) by lumping the large number of chemical compounds into groups of pseudo-components, according to their boiling points and their molecular characteristics (Meng et al., 2006, 2007; Minkina et al., 2010). Just like the fluid catalytic cracking (FCC) and catalytic pyrolysis processes, the liquefaction of biomass is a complex process. Therefore, this is a good way to study the liquefaction mechanism by lumping large numbers of chemical compounds together. The main objective of this study was to develop 8-lump reaction pathways to explain the behavior of cornstalk liquefaction in sub- and super-critical ethanol without catalyst. The lumps of the liquefaction process were defined based on the characteristics of material and products. First, the impact of liquefaction conditions (e.g., temperature, reaction time and ethanol amount) on the lump yields was investigated; and then the lumped components of the complex reaction network were determined. The main compositions of liquefaction products were analyzed by GC/MS.

2. Experimental

2.1. Materials and solvents

The cornstalk sample was collected from the city of Guangzhou, which is located in the south of China. The raw material was first ground using a high-speed rotary cutting mill and sieved through 40 mesh. The cornstalk flour was extracted with distilled water and ethanol to remove water-soluble oil and polar organics, then dried at 105 °C for 24 h and kept in a desiccator at room temperature before being used. Ultimate analysis of the sample was carried out on an Elemental Varian EL Elemental Analyzer. The heating value was obtained from calculation by Dulong's formula. The ash of cornstalk was determined by burning at 650 °C. Analysis showed that the cornstalk used in this study contained about 49.6% carbon, 43.5% oxygen, 5.9% hydrogen, 1% hydrogen, and 5.5% ash (on a dry basis). The sample had a higher heating value (HHV) of 17.4 MJ/kg. The solvents used were analytical reagent grade ethanol and acetone.

2.2. Liquefaction and separation

The liquefaction experiments were carried out using a 1.0 L high-pressure and temperature stainless steel reactor (PARR, America). It is rated up to a working pressure of 2000 psi and a working temperature of 350 °C. In a typical liquefaction experiment, the reactor was loaded with 10 g of cornstalk and 100 mL of ethanol. Then the reactor was purged three times with nitrogen to remove the air/oxygen in the reactor airspace. Agitation was set at 300 rpm and kept constant for all experiments. The reactor was heated up to the setting temperature and the temperature was maintained constant at the setting temperature for the desired holding time. After the reaction completed, the reactor was cooled down to room temperature by cool water, which was installed inside of the reactor. The density of gas was estimated using a gas bag by measuring the bulk and quality of the gaseous component. The bulk of gas was estimated by the way of expelling water from the measuring cylinder. When the autoclave was opened, the reaction mixture was removed for separation. The procedure for the separation is shown in Fig. 1.

In this paper, the material and liquefaction products were defined as eight lumps based on the characteristics of material and products. They were gas (GA), water-soluble oil (WSO), heavy oil (HO), volatile organic compounds (VO) and residue (RE). The RE was further divided into carbon (C), hydrogen (H), oxygen (O) and nitrogen (N). The results obtained in this study were reported using the parameters calculated as following:

$$Y_{GA} = \frac{V_{GA} \times \rho_{GA}}{W_{Dry} \times (1 - Y_A)} \times 100\% \quad (1)$$

$$Y_{WSO} = \frac{W_{WSO}}{W_{Dry} \times (1 - Y_A)} \times 100\% \quad (2)$$

$$Y_{HO} = \frac{W_{HO}}{W_{Dry} \times (1 - Y_A)} \times 100\% \quad (3)$$

$$Y_{RE} = \frac{W_{RE} - W_{RE} \times Y_A}{W_{Dry} \times (1 - Y_A)} \times 100\% \quad (4)$$

$$Y_{VO} = 100\% - Y_{GA} - Y_{WSO} - Y_{HO} - Y_{RE} \quad (5)$$

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