



Investigation of solvent effect on the hydro-liquefaction of sawdust: An innovative reference approach using tetralin as chemical probe



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HIGHLIGHTS

- Tetralin is firstly utilized as chemical probe to investigate the solvent effects on the sawdust liquefaction.
- The higher solvent impact index is consistent with higher sawdust conversion and bio-oil yield.
- The temperature and solvent type have an influence on the solvent effect in the liquefaction process.
- The analysis results showed that product compositions highly depend on the employed solvents.

ARTICLE INFO

Article history:

Received 15 March 2015

Received in revised form 27 September 2015

Accepted 29 September 2015

Available online 9 October 2015

Keywords:

Tetralin
Chemical probe
Hydro-liquefaction
Sawdust
Bio-oil

ABSTRACT

An innovative reference approach was developed to investigate the solvent effects on the liquefaction of sawdust by using tetralin as a chemical probe, and the corresponding solvent impact index was defined in this study. The influence of reaction conditions including reaction temperature and solvent types on solvent impact index were discussed. It was found that larger solvent impact index corresponds to improved sawdust conversion and higher bio-oil yield. The liquid and gaseous products obtained were characterized by ¹H nuclear magnetic resonance (¹H NMR), gas chromatography (GC), and elemental analysis (EA). The component of products highly depended on the employed solvents.

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1. Introduction

With the depletion of fossil resources, biomass, as a carbon-neutral renewable resource, is drawing increasing attentions due to the advantages of its available abundant, cheap and environmentally friendly [1,2]. Several thermo-chemical methods including pyrolysis, gasification, and liquefaction have been utilized to efficiently convert lignocellulosic biomass to gaseous, liquid and solid products [3]. The main drawback of pyrolysis and gasification was the high operation temperature. On the contrary, liquefaction process could be carried out at mild reaction temperature since less energy was needed in the liquefaction reaction [4].

Generally, the product distributions of lignocelluloses liquefaction highly depend on the solvents applied. To date, different

solvents were used for lignocelluloses liquefaction to biofuels. Hydrothermal liquefaction of biomass in water was primarily considered, which could prevent the feedstock dewatering and drying [5]. However, a little amount of water-insoluble liquid products and a large amount of high-oxygen content oil products were obtained in water, resulting in a relatively low heating value [6]. To improve the yield and quality of bio-oil, various organic solvents (tetralin, toluene, methanol, ethanol and ethylene glycol) instead of water were employed in the lignocellulose liquefaction [7–10].

The solvent effect on the lignocelluloses liquefaction was usually estimated by conversion and bio-oil yield. Duan et al. reported that the thermo-chemical liquefaction of *Chlorella pyrenoidosa* was carried out in different solvents, which indicated that the solvent polarity has an influence on the biomass conversion [11]. In addition, the same conclusion was found by Yuan et al. in the liquefaction of microalgae [12]. However, it should be noted that the polarity of solvent under reaction condition was difficult to be detected.

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Tetralin, because of its excellent hydrogen-donating ability, has been employed to explore the hydrogen transfer reaction in the coal and heavy oil treatment [13,14]. To the best of our knowledge, using tetralin as a chemical probe to investigate the solvent effect in lignocelluloses liquefaction was seldom studied. In this complicated reaction system, different intermediates including free radicals and ions would be produced in different solvents system, which may affect the hydrogen-donating ability of tetralin. On the other hand, the solvents themselves with different hydrogen donating ability also have an influence on the performance of tetralin. Actually, both solvent and tetralin acted as hydrogen donor in lignocellulose liquefaction, thus a competitive hydrogen donation reaction would occur between the solvents and tetralin. Therefore, a new index could be provided to evaluate the solvent effect.

In this work, the solvent effect on lignocelluloses liquefaction was comprehensively examined with tetralin as a chemical probe, under different reaction conditions including reaction temperature and solvent type. A new parameter, solvent impact index, was developed and applied to correlate the lignocelluloses liquefaction performance with different solvents. The liquid products were characterized by using EA and ^1H NMR. The gaseous products were analyzed on GC.

2. Experimental sections

2.1. Materials and instruments

The sawdust was collected from hardwood industry, and then the raw material was washed and dried at 105 °C for 24 h. Subsequently, the obtained samples were ground and sieved to the desired particle size (<0.28 mm). The 20 mL capacity micro-reactor was made of stainless steel with dimension of 13 mm i.d., 9 mm o.d. and 300 mm height. The autoclave was designed to be operated at maximum temperature and pressure of 400 °C and 35 MPa. The chemicals (tetralin, methanol, ethanol, propanol, i-propanol and acetone) used are provided by Sinopharm Chemical Reagent Co., Ltd. The used Ni-based catalyst is nickel chloride (NiCl_2).

2.2. Hydro-liquefaction of sawdust and products separation

In a typical run, 1 g sawdust, 10 mL tested solvents, and 300 μg /g Ni-based catalyst were placed into the reactor. Subsequently, the reactor was sealed and purged with pure hydrogen for three times and then increased the pressure to 4.0 MPa. Then the autoclave was heated to a desired reaction temperature and maintained for 30 min. After the reaction, the reactor was cooled down immediately to room temperature in a cool water bath. Additionally, to obtain the corresponding solvent impact index, another series of experiments were conducted under the same conditions in the presence of 1 mL tetralin as chemical probe, to investigate the solvent effect on the sawdust liquefaction.

The illustration of micro-autoclave and separation procedures for liquefaction products are shown in Fig. 1. The gas was collected in a gas-sampling bag, and the solid/liquid products were rinsed with acetone thoroughly. The suspension was filtered through a pre-weighed filter paper to separate the solid and liquid products. The remaining solid in the filter paper was dried at 110 °C overnight and weighed, which is defined as solid residue. Besides, the filtrate was evaporated to remove the solvents and water, and the obtained liquid product was bio-oil.

The yield of solid residue, bio-oil and gas were calculated as follows,

$$\text{Yield of bio-oil} = \frac{\text{Weight of bio-oil}}{\text{Weight of sawdust}} \times 100\% \quad (1)$$

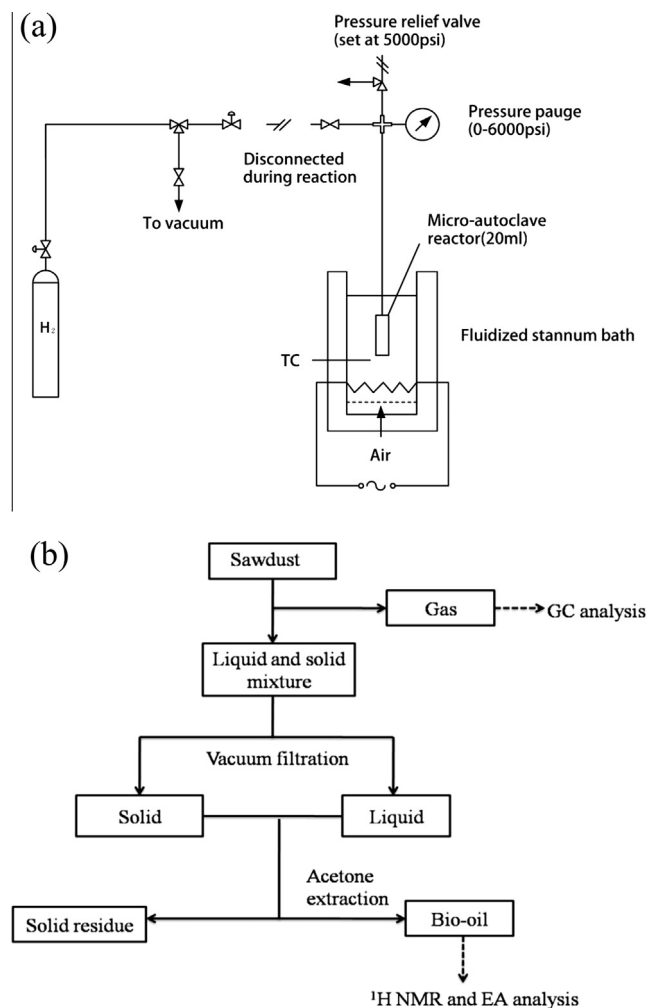


Fig. 1. (a) Schematic diagram of the micro-autoclave; (b) products separation and analysis procedure.

$$\text{Yield of solid residue} = \frac{\text{Weight of solid residue}}{\text{Weight of sawdust}} \times 100\% \quad (2)$$

$$\text{Yield of gas} = 100\% - \text{yield of bio-oil} - \text{yield of residue} \quad (3)$$

The yield of gas included the yield of evaporated hydrocarbons, water and gaseous products.

2.3. Characterization

The elemental compositions (C, H and N) of bio-oil obtained in different solvents system were analyzed by an ElementarVario EL III analyzer. The content of oxygen was estimated by difference. The Higher Heating Value (HHV) was calculated according to Dulong formula [15].

$$\text{HHV (MJ/kg)} = 338.2 \text{ wt.}\%(\text{C}) + 1442.8(\text{wt.}\%(\text{H}) - \text{wt.}\%(\text{O}))/8 \quad (4)$$

The ^1H NMR spectra of bio-oil were obtained on Bruker Avance III 500 MHz NMR spectrometer operating at 500 MHz resonance frequency and CDCl_3 is used as the solvent. Additionally, the liquid products including tetralin were analyzed by gas chromatography (CP-3800) with a 5 m Porapak Q column and a TCD detector. The carrier gas was helium and the temperature program was as follows, started from 110 °C (hold for 2 min) and then ramped to 280 °C (hold for 5 min) with an increasing rate of 8 °C/min.

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