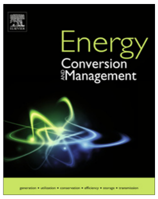
Energy Conversion and Management 89 (2015) 955–962

Contents lists available at ScienceDirect

Energy Conversion and Management

journal homepage: www.elsevier.com/locate/enconman



Feasibility and comparative studies of thermochemical liquefaction of *Camellia oleifera* cake in different supercritical organic solvents for producing bio-oil

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ARTICLE INFO

Article history:
Received 17 August 2014
Accepted 2 November 2014

Keywords:
Thermochemical liquefaction
Camellia oleifera cake
Bio-oil
Energy recovery ratio
Organic solvent
Heavy metal

ABSTRACT

Thermochemical liquefaction of *Camellia oleifera* cake (COC) for producing bio-oil was conducted in supercritical methanol (SCML), ethanol (SCEL) and acetone (SCAL), respectively. GC–MS, elemental analysis and ICP-OES were used to characterize properties of bio-oil. Results showed that thermochemical liquefaction of COC was a prominent process for generating bio-oil. Increase of temperature was beneficial to the increase of bio-oil yield, and yield of bio-oil followed the sequence of SCAL > SCEL > SCML. In spite of the highest bio-oil yield, the lowest calorific value and highest contents of Zn, Pb, Cd, Ni, Fe, Mn, and Cr were found in bio-oil from SCAL. Though SCML has very similar bio-oil composition and calorific value with SCEL, higher bio-oil yield and lower contents of heavy metals could be obtained with SCEL, especially in bio-oil from SCEL at 300 °C. Moreover, the origin of ethanol could make the bio-oil product totally renewable. Therefore, liquefaction of COC in SCEL at 300 °C could have great potential in generating bio-oil.

1. Introduction

Energy demand of the world is known to prospectively increase by almost 50% in 2030, India and China would account for 45% of its usage [1]. Moreover, the burgeoning demand for energy would lead to higher emission of greenhouse gas along with hydrocarbons, particulate matter, oxides of nitrogen, and other carcinogens that pose direct and indirect dangers to mankind and ecosystems [2]. These concerns regarding the dwindling reserves of crude oil and increase in pollutants and greenhouse gas in atmosphere have sparked the development of renewable fuels. Biofuel, which emits lower pollutants on its combustion and has shown a comparable performance as that with mineral diesel and aviation fuel, has aroused global interest [3,4]. Major feedstocks for biofuel production could be divided into categories of edible oils, non-edible oils, and animal fats [1,2]. However, edible oils are known to jeopardize food supplies and biodiversity [5,6]. Herein, many attentions have been focused on the new-generation biofuel resource for use.

Thermochemical liquefaction has been pointed out to be a promising technology for producing bio-oil and a range of chemicals [7,8]. Liquefaction of biomass in supercritical short chain alcohols (e.g., methanol and ethanol) and acetone have gained growing attention in producing bio-oil [9–12]. In addition, bio-oil generated from liquefaction with these solvents has been pointed out to have a high yield and low oxygen content [13,14]. Furthermore, under the supercritical conditions, the reaction is non-catalytic [15] and purification or separation steps are not required [16].

Camellia oleifera is one of the world's and China's four major woody oil plants. *Camellia oleifera* cake (COC) is a by-product from *C. oleifera* oil refining process; it consists of significant concentrations of residual lipids and organic matters that can be used for biofuel production. According to《National Plan for the Development of *Camellia oleifera* oil (2009–2020)》[17], yields of *C. oleifera* oil and COC in China were 0.26 and 0.68 million tons in 2009, respectively. Indicating the output of COC is large. Besides, the total output of *C. oleifera* oil in China could be more than 2.5 million tons by 2020, implying more COC could be generated. Therefore, COC may be a very potential source for bio-oil production owing to its sustainable availability, better supply chain and economic feasibility. Furthermore, the carbon release during combustion of bio-oil that generated from COC could be taken from atmosphere by

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http://dx.doi.org/10.1016/j.enconman.2014.11.003
0196-8904/

photosynthesis during the growth of *C. oleifera* Abel, herein, the usage of COC does not result in a net increase in the CO_2 concentration in the atmosphere [7]. In conclusion, conversion of COC to bio-oil by liquefaction might not only help solve an energy problem but also remove from the environment one of the fastest growing and challenging groups of waste materials.

In this paper, feasibility and comparative studies of thermochemical liquefaction of COC in different supercritical organic solvents for producing bio-oil are studied. As a feasibility study, the primary aim was to evaluate and analysis the yield and composition of bio-oil generated from supercritical liquefaction. Thus, two frequently-used supercritical fluids – supercritical methanol (SCML, $Tc = 239.4$ °C, $Pc = 8.1$ MPa) and supercritical ethanol (SCEL, $Tc = 243$ °C, $Pc = 6.3$ MPa) were applied as the solvent. Besides, aiming at a more comprehensive comparative analysis, acetone was also applied as the solvent for its supercritical point ($Tc = 235.1$ °C, $Pc = 4.7$ MPa) was close to SCML and SCEL. Moreover, energy input/energy output (energy recovery ratio) based on the elemental composition of bio-oil was evaluated. Furthermore, metal contents in bio-oils were quantified in order to evaluate the environmental quality of the bio-oil.

2. Materials and methods

2.1. Materials

COC used as the feedstock was obtained from Yueyang, Hunan province, China. It was dried at 105 °C for 24 h and then ground and passed through a 60 mesh sieve. The primary (TGA, STA 409 model, NETZSCH, Germany) and ultimate characterizations (EuroEA Elemental Analyzer, EA3000) of COC are given in Table 1. The higher heating value of COC was calculated according to Dulong formula: HHV = 0.3383C + 1.442 (H – O/8) [18]. Ash content in COC was obtained by recording the weight of the remaining portion of the predried sample after it had been burned in a muffle furnace at 575 °C for 8 h.

2.2. Supercritical liquefaction

Supercritical liquefaction was performed in a 500 mL autoclave reactor which had been introduced in previous studies [19,20]. A schematic diagram of the reactor is shown in Fig. 1. The reactor, purging lines, and sampling lines are fabricated using 321 stainless steel, main heavy metals (HMs) in this material are Mn ($\leqslant$2%), Cr (17–19%), Ni (9–12%).

According to Brand et al. [21], biomass-to-ethanol ratio from 0.06 to 0.25 g/g was suitable for the reaction. Thus, in this research, COC (8 g) with 152 mL of solvent in each experimental run was loaded into the reactor after homogenous mixing. Excess air in the reactor was completely removed with high purity N_2 from the gas pipeline (Fig. 1) and then the reactor was pressurized to 0.5 MPa using N_2. A 4.0 kW electric furnace was used to heat the reactor to the preset temperature (300 °C or 350 °C) at a proximately heating rate of 3.33 °C/min. A PID temperature controller unit with a K-type thermocouple was used to control the internal temperature of the reactor during the whole reaction process. A magnetic stirrer was used to mix feedstock and solvent during the test. Once the desired temperature was reached, it was maintained for a reaction time of 30 min. During the experimental run, the pressure inside the reactor was read and recorded from the pressure gauge in the reactor. After the heating was stopped, the reactor was cooled to room temperature with the cooling coil. When the temperature of the reactor dropped to the room temperature, the gas products were vented to atmosphere. Then the reactor was opened and all products were removed completely by washing with excessive solvent. Products were separated by filtration using a vacuum filtration apparatus with a 0.45 μm membrane filter. The filtrate obtained was subjected to rotary evaporation at the boiling point of solvent to remove the excessive solvent, and the remaining liquid product was defined as bio-oil. Solid residue, namely biochar, left on the filter was dried at 105 °C for 24 h and then weighted. Detail liquefaction and products separation procedure were shown in Fig. 2. Each experiment was conducted triplicate and average values were reported. Experimental error ratios for M-300, M-350, E-300, E-350, A-300, and A-350 were 8.6%, 13.29%, 4.14%, 4.27%, 2.67%, 2.17%, respectively. The bio-oil obtained was named as $X - Y$, where X was the feedstock added, Y was the reaction temperature.

Table 1
Contents of main elements in COC.

Parameters	COC (%)
Ash (wt%)	1.25
Moisture (wt%)	2.36
C (wt%)	50.15
H (wt%)	7.05
N (wt%)	1.85
S (wt%)	0.25
O[a] (wt%)	37.09
HHV[b] (MJ/kg)	20.02

[a] calculated by mass difference.
[b] Higher heating value.

2.3. Analysis of bio-oil

2.3.1. GC–MS

Oil analysis was carried out with gas chromatograph (GC) equipped with a mass spectrometer (MS) detector (GC–MS, QP2010, SHIMADZU, column: DB – 5ms, 30 m × 0.25 mm × 0.25 μm). Ethanol (GR) was used as the solvent and helium (5 mL/min) was the carrier gas. The injector and ion source were kept at 250 °C and 200 °C, respectively. The oven temperature program was as follows: 40 °C (2 min), increase to 190 °C (8 °C/min, hold for 2 min), up to 280 °C (6 °C/min, hold for 5 min). The MS system was operated in the full scan mode with a mass range from m/z 50 to 700. Chromatograms of the compounds in the oil were compared with the standard compounds in the National Institute of Standards and Technology (NIST) library of mass spectral.

2.3.2. Elemental analysis and calorific value

Elemental composition of bio-oil was determined with an elemental analyzer (EuroEA Elemental Analyzer, EA3000), and content of oxygen (O) was estimated by mass difference. Calorific value of bio-oil was calculated according to the Dulong formula [18]:

$$\mathrm{HHV}\ (\mathrm{MJ/kg}) = 0.3383\mathrm{C} + 1.442(\mathrm{H} - \mathrm{O}/8) \tag{1}$$

where HHV: higher heating value of bio-oil (MJ/kg); C, H and O are the contents of carbon, hydrogen and oxygen in bio-oil, respectively (%).

2.3.3. Energy output and energy input

Since the primary objective of this work is producing bio-oil, especially oil with high calorific value, it is of special interest to evaluate the energy efficiency of the process. Energy output (EO) and energy consumption ration generally used to express the process energy balance [21,22]. EO and EI calculated in this paper were based on the assumption made in the study of Xu and Lancaster [23]. Since the concentration of COC was fixed at 8 g/152 mL, the mean specific heat capacity of COC might be approximated