Fuel Processing Technology 126 (2014) 192–198

Contents lists available at ScienceDirect

Fuel Processing Technology

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

Vacuum pyrolysis of plant oil asphalt for transport fuel production catalyzed by alkali metal compounds

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ARTICLE INFO

Article history:
Received 1 January 2014
Received in revised form 5 May 2014
Accepted 6 May 2014
Available online 22 May 2014

Keywords:
Vacuum pyrolysis
Plant oil asphalt
Alkali metal compounds
Catalysis

ABSTRACT

Plant oil asphalt (POA) is underutilized lipid-based biomass residue generated from the oleochemical industry. In this work, alkali metal compounds were used as catalysts for vacuum pyrolysis of POA. Their effects on the pyrolysis reaction rate, product yields and compositions were studied. The POA feed was characterized by proximate and ultimate analysis and inductively coupled plasma-mass spectrometry (ICP-MS). The pyrolytic oil was analyzed by gas chromatography–mass spectrometry (GC–MS), thermo-gravimetric analysis (TGA) and chromatography-simulated distillation analysis. The results showed that alkali metal compounds accelerated the pyrolysis reaction rate in the order of chlorides ≈ sulphates > hydroxides > carbonates > non-catalyst, and affected the yield of pyrolytic oil in the order of chlorides (80 wt.%) ≈ sulphates (77 wt.%) > non-catalyst (71 wt.%) > carbonates (68 wt.%) > hydroxides (55 wt.%). The quality of the pyrolytic oil was in the order of hydroxides > carbonates > non-catalyst ≈ chlorides ≈ sulphates.

1. Introduction

Fossil fuel resources are showing a progressive declining after reaching a production maximum [1]. The known petroleum reserves are estimated to be depleted in 50 years at the present consumption rate [2]. Biofuels are promising renewable alternatives to fossil fuels, which can reduce the dependence on fossil fuel import [3–5]. Biofuels are environment benign due to their much lower metal, nitrogen and sulphur contents compared with fossil fuel [6–8].

Biomass can be classified into two major categories: lignocellulosic and lipid-based biomass [9]. Pyrolysis and gasification of lignocellulosic biomass are highly energy-consuming processes [10], due to the stable structure of cellulose, hemicelluloses, and lignin [11,12]. In addition, the pyrolytic bio-oil has poor storage stability and low heating value due to its high oxygen content [13–15]. In contrast, conversion of lipid-based biomass into biodiesel via pyrolysis [16] or transesterification [17–19] has low energy consumption. The biodiesel can be directly used as transport fuel. Unfortunately, lipid-based biomass encounters supply crisis in the biodiesel industry due to the limited land and food security policies [20,21]. However, a large amount of lipid-based residue biomass is by-produced in the oleochemical industry [22,23]. It is of great concern to develop new technologies for effective utilization of such lipid-based residue biomass.

The plant oil asphalt (POA), by-produced in the biodiesel and fatty acid industry, is a kind of underutilized lipid-based residue biomass. It is named after its appearance, as a heavy and viscous black liquid. At present, POA is mainly used as heavy fuel in boiler or even abandoned as waste. In 2010, over 600,000 t of POA was produced in China [22,23]. The POA capacity has been increasing rapidly in recent years. This motivated us to develop a new process to convert POA to transport fuel.

A wide range of materials have been studied for vacuum pyrolysis behavior, such as used tires [24–26], plastic waste [27] and lignocellulosic biomass [28–30]. Vacuum pyrolysis can minimize the secondary cracking reactions by rapid removal of pyrolytic vapors from the reaction region, thus enhances the yield of liquid product [24–30]. In addition, vacuum pyrolysis shows a favored effect on the quality of char [26,30]. In 2012, for the first time we reported converting a kind of POA, the biodiesel residue, to transport fuel by vacuum pyrolysis with a yield of pyrolytic oil over 70 wt.% [22]. The pyrolytic oil consists of hydrocarbons, fatty acids and fatty acid methyl esters (FAMEs). The product yields and compositions were affected by vacuum pressure. Vacuum pyrolysis of another kind of POA, the fatty acid residue, also gave 71 wt.% yield of pyrolytic oil with the main contents being hydrocarbons and fatty acids [23]. The pyrolytic oils could be upgraded to pyrolytic biodiesel via esterification. In these previous studies, the pyrolysis of POA was carried out without catalyst. Many works in the literature [31–35] show that most metal oxides and salts, especially those of alkali metals, exhibit catalytic activity for pyrolysis and gasification reactions. Shie et al. [32] studied the catalytic performance of sodium and potassium compounds for the pyrolysis of oil sludge. Dandik and Aksoy [34] reported that sodium carbonates were effective catalysts for the pyrolysis of sunflower oil to produce gas, liquid oil and coke residue. Konwer et al. [35] studied the pyrolysis of *Mesua ferrea* L. seed oil and fatty acids over sodium carbonates, and obtained pyrolytic oil that contained aromatics, olefins and saturated hydrocarbons.

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http://dx.doi.org/10.1016/j.fuproc.2014.05.008
0378-3820/

To the best of our knowledge, the catalytic pyrolysis of POA has not been studied. In the present work, alkali metal compounds, including chlorides (NaCl, KCl), sulphates (Na_2SO_4, K_2SO_4), carbonates (Na_2CO_3, K_2CO_3) and hydroxides (NaOH, KOH), were used as catalysts for vacuum pyrolysis of POA. Their effects on the pyrolysis reaction rate, product yields and compositions were studied. The POA was characterized by proximate and ultimate analysis, and inductively coupled plasma-mass spectrometry (ICP-MS). The composition of pyrolytic oil was analyzed by gas chromatography–mass spectrometry (GC–MS), and the evaporation behavior and boiling point distribution of pyrolytic oil were evaluated by thermo-gravimetric analysis (TGA) and chromatography-simulated distillation analysis, respectively.

2. Materials and methods

2.1. Materials

The POA material was provided by Shandong Bio-Energy Products & Technology Co., Ltd., which produced biodiesel from various waste lipid-based feedstocks, such as waste cooking oil and soap stocks. The POA was the residual liquid at the bottom of the crude biodiesel vacuum rectifying tower.

The sodium and potassium compounds (NaCl, KCl, Na_2SO_4, K_2SO_4, Na_2CO_3, K_2CO_3, NaOH and KOH) are of analytic reagent grade and were purchased from Sinopharm Chemical Reagent Co., Ltd.

2.2. Experimental

A scheme of the experimental setup for vacuum pyrolysis of plant oil asphalt is shown in Fig. 1. The aim of the present work was to study the effect of catalysts on the vacuum pyrolysis of POA. For each experiment, 50 g POA was added to the pyrolysis reactor with a volume of 250 mL. To diminish the effect of mass transfer, the catalyst powders were uniformly mixed within the POA feedstock. For all catalysts, the dosage was fixed to 3 wt.% of the POA feed. The system temperature and pressure were controlled by electric control panel and vacuum pump, respectively. The sample temperature increased from 30 to 350 °C at about 10 °C/min, then ramped to 430 °C at 2 °C/min, and maintained at 430 °C until no more pyrolytic oil was produced. Previous work [22] shows that the vacuum pressure 40 kPa was the optimum condition for a combined consideration of pyrolytic oil yield and energy cost. A further lower pressure led to a higher energy cost, while a higher pressure enhanced the secondary cracking reactions. Therefore, vacuum pressure 40 kPa was used in this work.

The yield of product is defined as the mass fraction of product relative to POA feedstock. During the pyrolysis, the mass of pyrolytic oil was measured using an electronic balance at different reaction times. The volume of non-condensable gas was measured by time integral of the gas flow rate. Then the mass of gas was calculated from the gas volume and the composition measured by GC–MS. The amount of solid char was determined by measuring the ethanol insoluble material in the reaction residue, exclusive of the catalyst. The ethanol soluble material was the unconverted POA feedstock. Using the above quantification methods, the mass balance of the system was acceptable at 100 ± 3 wt.%.

2.3. Characterization

The physical properties, including density (ASTM D86), viscosity (ASTM D445) and acid value (ASTM D974), were measured referring to the ASTM standards. Proximate analysis was performed according to ASTM D121. Ultimate analysis was carried out using a CHNS/O Elemental Analyzer (CE-440). The metal element contents were measured with a ThermoFisher X II ICP-MS.

The compositions of the pyrolytic oil and bio-gas were identified and quantified using an Agilent 6890 Series G1450A GC coupled with an Agilent G2579A MS. The GC was equipped with an Agilent 190915-433 80 m × 0.250 mm column and a flame ionization detector (FID). The TGA experiments were carried out to evaluate the volatility characteristics of the pyrolytic oil using a Perkin Elmer Pyris 1 TGA under nitrogen atmosphere. The chromatography-simulated distillation analysis was carried out to obtain the fraction distribution using an Agilent 7890A GC equipped with a DB-1 30 m × 0.53 mm column and a FID. The detailed operating conditions for the measurements were reported elsewhere [23].

3. Results and discussion

3.1. Properties of POA

The ultimate analysis and selected physical properties of the POA, palm oil and biodiesel are shown in Table 1. The results show that POA, palm oil (triglyceride) and biodiesel (FAME) have very similar element distribution. The contents of carbon, hydrogen and oxygen

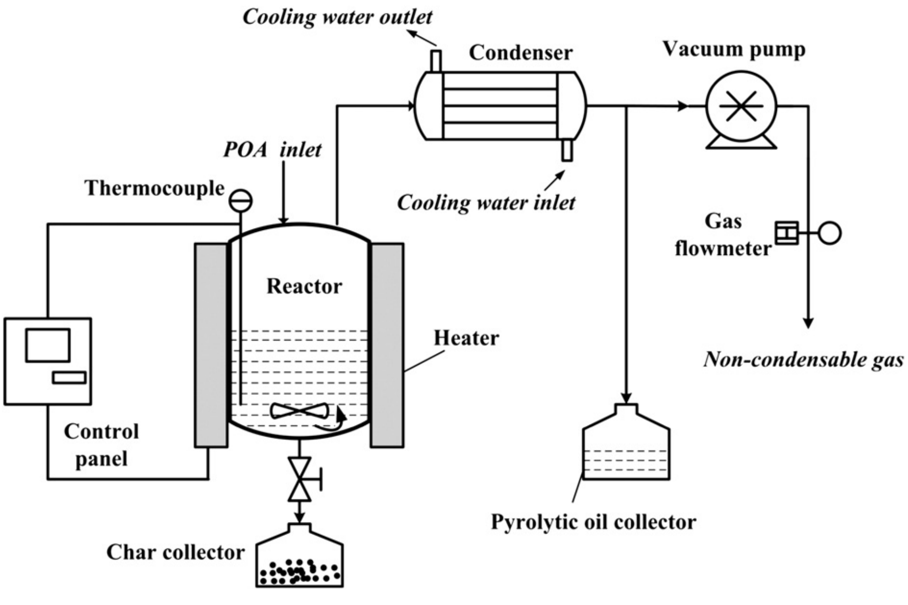

Fig. 1. Scheme of the experimental setup for vacuum pyrolysis of plant oil asphalt.