Applied Energy xxx (2015) xxx–xxx

Contents lists available at ScienceDirect

Applied Energy

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

Investigation on the esterification by using supercritical ethanol for bio-oil upgrading ☆

Qing Zhang [a,b], Ying Xu [a], Yuping Li [a], Tiejun Wang [a,*], Qi Zhang [a], Longlong Ma [a,*], Minghong He [a], Kai Li [a]

[a] Key Laboratory of Renewable Energy, Guangzhou Institute of Energy Conversion, Chinese Academy of Sciences, Guangzhou 510640, China
[b] College of Chemistry and Materials Science, Anhui Normal University, Wuhu 24100, China

HIGHLIGHTS

- A highly efficient removal of carboxylic acids in crude bio-oil by esterification.
- Higher formation of ethyl acetate was found in supercritical ethanol system.
- The restraint of acid esterification by the addition of external acids.

ARTICLE INFO

Article history:
Received 6 August 2014
Received in revised form 24 December 2014
Accepted 28 December 2014
Available online xxxx

Keywords:
Bio-oil
Upgrading
Esterification
Supercritical ethanol

ABSTRACT

Current global resources of fossil fuels are gradually depleting and the energy crisis induces increasing concerns on the research of new effective substitution of these fossil fuels by renewable energy, especially bio-fuels from biomass such as bio-oils. However, bio-oils, generally originated from the pyrolysis of biomass, contain a great deal of carboxylic acids such as acetic acid and these acids can easily decrease the stability and the quality of oil. Meanwhile, these acids are highly corrosive to reaction equipments. Bio-oil could be upgraded before its utilization in the feedstocks of fuels and chemicals. In this work, the removing of these carboxylic acids was investigated by esterification in supercritical ethanol. The effects of reaction temperature, the ratio of ethanol to bio-oil, and reaction time on the conversion of acids were studied as well as the addition of external acid such as H_2SO_4, H_3PO_4 or zeolite. The results showed that carboxylic acids in crude bio-oil easily esterified with ethanol in the supercritical system. More ethyl acetate was formed at higher volume ratio of ethanol to bio-oil and 100% of the selectivity was achieved at the volume ratio of 5:1 after 2 h reaction, whereas more side reactions were present in lower or higher ratio of ethanol to bio-oil. The addition of external acid decreased distinctly the formation of esters, indicating that these carboxylic acids could be effectively removed under the acidic system arising from the internal ionization of ethanol. These would be very useful in the upgrading of bio-oil into high quality fuels in the future biorefinery.

1. Introduction

Bio-oil, mainly generated from the fast pyrolysis of biomass, has been considered as a potential renewable energy source to replace the diminishing fossil fuels because of its cleaning, low cost and abundant raw materials. The crude bio-oil usually shows lower thermal stability, lower heating value and high corrosiveness due to the complicated organic components of bio-oil. Bio-oil is mostly composed of a variety of organic compounds including acids, aldehydes, ketones, and phenols [1–4]. The organic acids (e.g. formic acid, acetic acid, and propionic acid) and aldehydes are inclined to be reactive, and aldehydes can perform homo-polymerization and acetalization with alcohols at low temperature in acidic conditions [5–7], which can cause the instability of bio-oil during the normal storage. Meanwhile, polymerization can also cause the variety in the viscosity of bio-oil which increases greatly with the increasing storage temperature. Then, some solvents such as ethyl acetate, methanol or ethanol were inevitably adopted to decrease the viscosity of bio-oil [8]. Moreover, a large amount of organic acids in bio-oil would lead to high acidity with the pH value less than 3.0 and corrosiveness to the gasoline or diesel engines when it was used as transportation fuels without

☆ This paper is included in the Special Issue of Energy innovations for a sustainable world edited by Prof. S.k Chou, Prof. Umberto Desideri, Prof. Duu-Jong Lee and Prof. Yan.

* Corresponding authors. Tel.: +86 20 8705 7751; fax: +86 20 8705 7789.
E-mail addresses: wangtj@ms.giec.ac.cn (T. Wang), mall@ms.giec.ac.cn (L. Ma).

http://dx.doi.org/10.1016/j.apenergy.2014.12.063
0306-2619/

upgrading. Thus, it is very important that bio-oil should be upgraded to lower acidity and improve the stability of storage and the suitability for fuels. A lot of upgrading techniques such as catalytic cracking, hydrodeoxygenation and steam reforming have been reported for the improvement in the quality of bio-oil [9–16]. Nickel catalysts were usually adopted to upgrade bio-oil for high-quality liquid fuel, whereas these catalysts can be eroded easily with the decrease in the catalytic activity in the presence of acetic acid in crude bio-oil due to its strong acidity [11,17]. Some noble metal catalysts with good acid resistance were screened in the upgrading of bio-oil [13,18].

Another route to solve these issues is to remove these acids before upgrading by esterification with ethanol techniques, which was generally proposed by using a strong acid as a catalyst. The quality of bio-oil can be also enhanced by decreasing acidity, viscosity and other characteristics in the presence of a solid acid catalyst [19–22]. In recent years, esterification under supercritical fluids such as water, methanol or ethanol, especially ethanol, has been attracted on the removing of organic acids in bio-oil to improve the quality of bio-oil with or without catalysts due to the unique properties of the supercritical fluid system with faster rates of mass and heat transfer, liquid-like density and dissolving power, gas-like diffusivity and viscosity [23–27]. Notably, ethanol can not only react with these carboxylic acids in bio-oil to produce the corresponding esters, but also can act as a reaction medium in the supercritical system, meanwhile, ethanol can be mainly obtained from biomass by fermentation [28–30], which makes the lower cost and efficiency of upgrading of bio-oil.

In this work, bio-oil derived from the pyrolysis product of sawdust at 600 °C was selected as the reaction feedstock, which contains about 40% carboxylic acids. To eliminate the adverse effect of acids on the quality of bio-oil, the esterification of these carboxylic acids in sub- or super-critical ethanol was carried out. The effects of reaction parameters such as temperature, the ratio of ethanol to bio-oil, and reaction time on the conversion of acids were studied in detail. In addition, H_2SO_4, H_3PO_4 or zeolite was also selected as external acid to investigate the esterification between these carboxylic acids and ethanol in the supercritical upgrading process.

2. Experimental section

2.1. Materials

The crude bio-oil used in this experiment was provided by Qingdao University of Science and Technology of China and obtained from fast pyrolysis of sawdust at the pyrolysis temperature of 600 °C. Anhydrous ethanol, sulfuric acid and phosphoric acid were purchased from Sinopharm Chemical Reagent Co., Ltd. Zeolite was obtained from Nankai University catalyst Co., Ltd.

2.2. Esterification process

The experiments were carried out in a stainless steel autoclave with a capacity of 100 ml. The autoclave reactor was heated with an electric heating system and the temperature was measured with a thermocouple. Typically, a total amount of 60 ml ethanol and bio-oil with different volume ratios was mixed and fed into the autoclave. The reactor was flushed in advance with N_2 for five times so as to remove air contained in the reactor. Afterwards, the reaction was conducted at the setup reaction temperature (200 or 250 °C) and 7.0 MPa by stirring the mixture at a rate of 500 rpm for 30–180 min and then cooled down with water to room temperature. In addition, to investigate the esterification between ethanol and bio-oil in subcritical or supercritical system, the experiment was performed with the volume ratio of ethanol to bio-oil of 3:1 at 200 or 250 °C, respectively. And subsequently a series of experiments were conducted with other volume ratio of ethanol to bio-oil (10:1, 5:1, 1:1) in the supercritical system at 250 °C and 7.0 MPa. All the liquid products were collected from the reactor per run and filtered before analysis.

2.3. Product analysis

The analysis of bio-oils and all liquid products after esterification were performed on an Agilent GC-7890A gas chromatograph (HP inowax capillary column 19091N-133N, 30 m × 250 μm × 0.25 μm) equipped with a mass spectrometer (5975C) by using 99.995% of He as the carrier gas. The relative content of each constituent was determined by peak area normalization due to the complicated composition of samples. Compounds in the samples were identified by using the Agilent software based on the National Institute of Standards and Technology (NIST) library of mass spectra.

3. Results and discussion

3.1. GC–MS analysis for the components of bio-oil

Table 1 shows the components of crude bio-oil analyzed by GC–MS. Bio-oil is a relatively complicated compounds mainly including acids, aldehydes, ketones alcohols and phenols as well as small amount of other species. Acids were the most in bio-oil with the content of 42.19% and these acids are basically composed of organic monoacid such as acetic acid, propanoic acid and 4-hydroxy-butanoic acid, however, acetic acid was dominated with the content of 35.93%, which arising from the decomposition of hemicelluloses [31]. Aldehydes in bio-oil were in the form of hydroxy-acetaldehyde with the content of 8.41%, accompanying

Table 1
GC–MS analysis results for bio-oil.

Components	Content (%)
Acid	
Acetic acid	35.93
Propanoic acid	3.35
Butanoic acid, 4-hydroxy-	1.19
Acetic acid, hydroxy-	1.72
Aldehyde	
Acetaldehyde, hydroxy-	8.41
Furfural	1.72
5-hydroxymethyl-2-Furancarboxaldehyde	0.98
Ketone	
2-Propanone, 1-hydroxy-	18.15
1-Hydroxy-2-butanone	0.82
2-Cyclopenten-1-one	1.36
5-Hydroxymethyldihydrofuran-2-one	1.32
3-methyl-1,2-Cyclopentanedione	1.59
Alcohol	
1,2-Ethanediol	4.04
Phenol	
Phenol	3.65
Phenol, 2-methyl-	1.60
Phenol, 3-methyl-	1.71
Phenol, 4-methyl-	2.14
Phenol, 2-methoxy-	0.69
Hydroquinone	1.76
Others	
Propylene oxide	1.69
1,2-Epoxy-3-propyl acetate	1.72
1,4:3,6-Dianhydro-alpha-d-glucopyranose	0.83
2-Propanamine	1.02

Please cite this article in press as: Zhang Q et al. Investigation on the esterification by using supercritical ethanol for bio-oil upgrading. Appl Energy (2015), http://dx.doi.org/10.1016/j.apenergy.2014.12.063