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Upgrading fast pyrolysis oil: Solvent–anti-solvent extraction and blending with diesel

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ABSTRACT

In order to upgrade biomass fast pyrolysis oil for excellent applications, solvent–anti-solvent extraction technology (dichloromethane as solvent, water as anti-solvent) was developed to separate organic phase from pyrolysis oil. The optimum extraction efficiency was achieved at pyrolysis oil:dichloromethane:water = 10:10:3 (volume ratio). In comparison to the raw pyrolysis oil, the modified pyrolysis oil (extracted organic phase) had the high concentrations of phenols, while the low sugars and water contents. Then, the pyrolysis oil and modified pyrolysis oil were used to prepare the homogeneous blended fuels with commercial diesel in the presence of 1-butanol by mean of three-phase charts of pyrolysis oil/diesel/1-butanol and modified pyrolysis oil/diesel/1-butanol blends. Three sets of feasible blended fuels (blend-1, blend-2 and blend-3) have been produced. And, the basic physical properties, structural characteristics, thermal degradation properties, combustion characteristics and the combustion kinetic and thermodynamic parameters (E_a, A, $\Delta H^{\ddagger}$, $\Delta G^{\ddagger}$ and $\Delta S^{\ddagger}$) of the prepared blended fuels have been systematically investigated. The physicochemical properties of the blend fuels have been improved compared with the pyrolysis oil. Meanwhile, blend-3 (55% modified pyrolysis oil, 10% diesel, 35% 1-butanol) with the highest combustion efficiency is recommended as burner fuel.

1. Introduction

At present, renewable and clean energy resources have received great attention because of fossil fuel shortage and severe environmental problems. Due to wide distribution, cost-effectiveness, and environment friendly, biomass is widely regarded as a promising energy source which can be converted into several types of fuels (including solid, liquid and gas) to replace fossil energy [1]. The main thermal processes available for converting biomass to a more useful energy include combustion, gasification and pyrolyzation [2,3]. Among these methods, pyrolysis offers a feasible and economical technology to convert solid biomass into a liquid fuel (pyrolysis oil) which has a higher energy density and is easier to handle than bulk biomass [4].

However, the biomass fast pyrolysis oil is the complex unstable colloidal multi-dispersed systems, which contains alcohols, aldehydes, alkenes, ketones, esters, acids, aromatics, furans, phenols, sugars, guaiacols, and water [5,6]. Compared to mineral oil, pyrolysis oil has some undesired properties, including acidity, relatively high viscosity, limited thermal stability and low heating value, which hinder the direct application of bio-oil [7,8]. Therefore, it is very necessary to take actions to improve the physical and chemical property of pyrolysis oil.

Currently, some catalyst techniques have been applied to fully refine pyrolysis oil to obtain transportation fuel, including catalytic pyrolysis, hydrogenation, hydrodeoxygenation, catalytic cracking [9–11]. Although these intensive efforts to upgrade bio-oils by catalytic treatment have resulted in considerable progress, there are still a number of technical barriers to overcome, such as catalyst deactivation, short catalyst lifetime and the additional supply of hydrogen [12]. Therefore, it will take a long time to transfer the above methods from the laboratory to the industrial scale.

In this context, blending process is one of the most convenient and effective technology to utilize the pyrolysis oil [13,14]. Creating blends of pyrolysis oil with diesel could improve some properties of pyrolysis oil, such as the decrease in viscosity and acidity and the increase in heat value and stability, which widen the field of applications as an alternative green fuel. Martínez et al. [15] investigated some key properties of the tire pyrolysis liquid/diesel (containing about 5.8 vol% of biodiesel) blends fuel. And the results indicated that blending the tire pyrolysis liquid with diesel may help to improve fuel quality, including density, cold filter plugging point (CFPP), the calculated cetane index (CCI), water content, the

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total acid number (TAN), sulfur content and shooting tendency. Garcia-Perez et al. [13] prepared the blends of the woody biomasses pyrolysis oil/bio-diesel and investigated its fuel properties, suggesting that although the oxidation stability of the bio-diesel rich phases has been enhanced, the solubility of fast pyrolysis oils in bio-diesel is poor. In fact, the poor solubility of fast pyrolysis oil in biodiesel or commercial fossil fuels (such as 0# diesel) may be ascribed to the great difference in their polarity [16,17]. In order to solve the above-mentioned problem, Majhi et al. [18] first separated polar compounds from the pyrolysis oil by Hempel distillation and then successfully prepared the blending of the modified bio-oil (Initial Boiling Point (IBP) <140 °C) with commercial diesel. Unfortunately, this blended fuel is not attracted by the industrial scale duo to the low utilization of pyrolysis oil and energy-consuming for Hempel distillation [9]. Furthermore, the preparation processes for the homogeneous single blended fuel were not very efficient in the reported literatures, which required a large number of experiments involving in different blending ratio [13]. Meanwhile, so far, the combustion performance of pyrolysis oil/diesel blended fuels has rarely been investigated.

In this work, solvent–anti-solvent extraction technology was used to obtain the modified pyrolysis oil which efficiently isolated water and sugars form the pyrolysis oil. It is mainly because that water and sugars are both low calorific value and polar compounds in pyrolysis oil, which indicates that they are not suitable for the directly utilization as energy. Meanwhile, co-solvent was added in the blended fuel to enhance the solubility of fast pyrolysis oil in commercial fossil fuels (such as 0# diesel). 1-Butanol, 1-pentanol and 1-octanol have been widely regarded as an co-solvent [14,15,19,20]. It's worth noting that the addition of alcohols in blended fuel could improve its combustion performance [21]. Hence, 1-butanol was used as co-solvent in this study and the modified pyrolysis oil was obtained by solvent–anti-solvent extraction technology. In order to easily and efficiently obtain the homogeneous single blended fuel, the ternary phase diagrams for (pyrolysis oil/modified pyrolysis oil + diesel + 1-butanol) mixtures were built. Three sets of feasible blended fuels containing pyrolysis oil/modified pyrolysis oil, diesel and 1-butanol have been prepared. In summary, the multi-step upgrading process, including solvent–anti-solvent extraction technology and blending process, has been designed to refine pyrolysis oil in this paper. Furthermore, this study systematically investigated the combustion performance and the combustion kinetic and thermodynamic parameters of the prepared blended fuels. Comparison of the obtained properties for different blends fuel, the suitable preparation condition for the blended fuel has been recommended.

2. Material and methods

2.1. Rice straw pyrolysis oil

The rice straw pyrolysis oil used in this study was kindly provided by Shaanxi Yingjiliang Bio-energy Corporation, China. The detail of the pyrolysis technology were described in our previous report [22]. 1-Butanol (>0.995) was obtained by Tianjin Guangfu Fine Chemical Research Institute, China. The diesel is the commercial 0# diesel and was provided from Sinopec gas station.

2.2. Modified pyrolysis oil production

Solvent–anti-solvent extraction was used for the production of organic phase (modified pyrolysis oil). Dichloromethane was used as solvent, but it can't cause a phase split. Water, using as anti-solvent, was added to enhance the phase separation. In this work, nine different volume ratios of pyrolysis oil, dichloromethane and water (pyrolysis oil: dichloromethane: water = 10:5:3, 10:5:6, 10:5:10, 10:10:3, 10:10:6, 10:10:10, 10:15:3, 10:15:6 or 10:15:10) have been investigated. In each experiment, dichloromethane was added dropwise into pyrolysis oil under vigorous stirring conditions, while keeping stirring for 10 min. Then, water was also added by drop into the mixture of pyrolysis oil under the same stirring condition. After adding water, the mixture of pyrolysis oil, dichloromethane and water was kept stirring for 30 min. Finally, the ternary mixture was kept in a tightly closed container away from sunlight for 24 h. Then the dichloromethane phase and the water phase were separated. The dichloromethane phase was distillated under 15 kPa and 30 °C to get the modified pyrolysis oil study in this work. Dichloromethane was recycled.

2.3. Pyrolysis oil/modified pyrolysis oil, diesel and 1-butanol blends

The bio-oil (pyrolysis oil or modified pyrolysis oil) was weighted in the container first, followed by the diesel. The 1-butanol was then added and the container was sealed and lightly shaken by hand. The proportions for the three phase diagram of pyrolysis oil/diesel/1-butanol blends and modified pyrolysis oil/diesel/1-butanol blends were listed in Tables S3 and S4, respectively. The detail of the mixing methodology for bio-oil, diesel and 1-butanol have been elaborated on in the open literature [14]. A photograph was taken 48 h later to document its appearance and the quality of the blend.

2.4. Analytical method

2.4.1. Elemental analysis

The elemental analysis of the samples was conducted on elemental analyzer (Vario micro cube, Elementar, Germany). The C, H, N and S contents can be measured directly and the oxygen content was calculated as the difference: O (%) = 1 − C (%) − H (%) − N (%) − S (%).

2.4.2. GC-MS analysis

The analysis was done using Trace 1300 GC-MS (Thermo science, US), with the following parameters: DB-5MS (30 m 0.32 mm 0.5 μm); injection temperature of 300 °C; column oven temperature program: 60 °C (held for 5 min.), then ramped to 200 °C (at 10 °C, held for 0 min), then ramped to 270 °C (at 20 °C/min, held for 5 min); and ion source temperature of 220 °C. The carrier gas was high-purity nitrogen (mass fraction 0.99999) at a constant flow rate of 20 ml min^{-1}. The MS scan was conducted on an electron impact ionization mode (70 eV) with the m/z range from 30 to 450. The samples were diluted by methanol at sample: methanol = 1:10 (mass: mass) and each time 1 μL of the sample was injected.

2.4.3. ^{13}C NMR analysis

The ^{13}C NMR spectra of the samples were obtained on a Varian Inova 500 MHz (Varian, US). The deuterated dimethyl sulfoxide (DMSO-d_6) was used as solvent. Chemical shifts were given in ppm and were referenced to tetramethylsilane (TMS) for ^{13}C NMR spectrum. Quantitative integration of area for each peak associated with each type of carbon was carried out.

2.4.4. Thermal analysis

The simultaneous thermal analyzer TG-DSC (Mettler Toledo, Switzerland) was used to analyze thermal and combustion behavior of different blended fuels [23]. The TG-DSC analysis was performed at the oxygen atmosphere with a flow rate of 50 ml/min. For each test, about 8 mg sample was loaded into the crucible. The maximum temperature was set at 600 °C and the heating rate at 10 °C/min. The TG curves were applied to obtain the key