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Research article

Co-hydrotreating of used engine oil and the low-boiling fraction of bio-oil blends for the production of liquid fuel

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ABSTRACT

The low-boiling fraction (LBF) of bio-oil produced from the hydrothermal liquefaction of peanut straw and used engine oil (UEO) blends were co-hydrotreated. The effects of the catalyst type on the yields of the product fractions resulting from the co-hydrotreating of the LBF with UEO and on the properties of the upgraded oil were first examined. The results revealed that noble metals with one electron in the outermost shell demonstrated high performance in the removal of heteroatoms. Of all of the noble metals tested, Pt/C and Rh/C exhibited the highest performance in the overall removal of heteroatoms from the feedstock mixture. With Rh/C as the catalyst, the effects of the catalyst loading (0–0.3 $kg_{catalyst}/kg_{feed}$), UEO/LBF mass ratio (3:0–0:3), and temperature (350–430 °C) were further examined. A positive synergistic effect occurred during the co-hydrotreating process at a UEO/LBF mass ratio of 2.5:0.5. The UEO/LBF mass ratio significantly affected the product yields and the properties of the upgraded oil. The presence of UEO suppressed char formation. The energy density of the vast majority of the upgraded oils was higher than that of petroleum diesel. This study suggested that UEO is a good solvent for the hydrotreating of bio-oil derived from the hydrothermal liquefaction of peanut straw.

1. Introduction

At present, the cost of raw materials and breakthroughs in core technology (processing technology) are two bottlenecks that constrain the large-scale development of biomass-based fuels. High-quality and low-price non-food biomass feedstocks as well as well-characterized and efficient conversion technologies for these feedstocks are key to addressing these issues and thus are highly sought.

Crop straws show considerable promise for the production of biofuel because of their abundance, low cost and environmentally friendly nature. It is estimated that the total yield of crop straws in China in 2009 was approximately 806.9 million tons [1]. This material can be converted into useful liquid biofuels or valuable chemicals, primarily via biochemical and thermochemical processes [2,3]. Crop straws typically contain a certain amount of moisture after harvesting. Thus, hydrothermal liquefaction (HTL) is a promising method of converting these high-moisture biomass feedstocks because it allows the direct use of high-moisture-content biomass. To date, crop straws for HTL include predominantly rice straw [4], wheat straw [5], barley straw [6], flax straw [7], cotton straw [8], corn straw [9], legume straw [10], and sunflower stalks [11]. The findings of the cited studies suggest that the crude bio-oils resulting from the HTL of crop straws contain twice the energy density of the crop straws themselves. Unfortunately, they also contain significant quantities of O and undesirable amounts of N and S, and they are highly viscous and acidic at ambient temperatures. Thus, they are unstable over long periods of storage, and their combustion would produce NO_x and SO_x, which could lead to air pollution. Therefore, the removal of N, O and S from these crude bio-oils and the reduction of their viscosities are necessary for these products to be used as liquid hydrocarbon fuels for transportation without requiring any engine modifications.

Various technologies have been developed for the upgrading of crude bio-oil [1,12,13]. Of these technologies, hydrotreating is the most common. Hydrotreating involves hydrodesulfurization (HDS), hydrodenitrogenation (HDN), and hydrodeoxygenation (HDO) to remove S, N, and O heteroatoms, respectively, from the crude bio-oil, often accompanied by the hydrogenation (saturation) of olefins and aromatics in the bio-oil feedstocks. To promote the removal of these heteroatoms, catalysts such as conventional Mo-based sulfide catalysts and noble metal catalysts are typically employed [1]. Noble metal catalysts have been the primary focus of recent research because of their excellent catalytic performance and because they do not require the use of environmentally unfriendly sulfur compounds. Furthermore, solvents, particularly hydrogen donor solvents, are typically used during the hydrotreating of crude bio-oil in an attempt to reduce mass-transfer limitations, to effectively retard the formation of coke precursors, and to extract the coke precursors from the catalyst pores in situ [14,15]. However, these solvents tend to react or decompose and need to be isolated from the products after the hydrotreating process, which increases the

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cost of the resulting biofuel. Therefore, suitable solvents for bio-oil upgrading are materials that are highly available, inexpensive, and need not be removed from the product oil.

Various sources of waste lubricating oil, particularly engine oils, have attracted considerable attention as alternative energy sources. Waste oil is renewable and widely available and has proven to be a cleaner and more environmentally friendly fuel source than fossil sources [14]. Lubricating oils can be recycled as lubricating oil, re-used as fuel or converted into diesel-like fuel. Statistically, China produces 25–30 million tons of used engine oil (UEO) annually [16]. If these waste oils were abandoned or handled improperly, they could cause serious pollution of the environment. However, they are a promising solvent for the hydrotreating of crude bio-oil and do not necessarily need to be separated from the product oil.

In this study, a three-stage process was applied to a) liquefy peanut straw to generate crude bio-oil, b) distill the crude bio-oil to obtain the low-boiling fraction (LBF), and c) co-hydrotreating the LBF and UEO to produce upgraded oil. We mainly focused on the third upgrading step, utilizing hydrogen, which produces upgraded oil with lower N and S contents, rendering it a more suitable feedstock for further refinery upgrading. The effects of the catalyst, UEO/LBF mass ratio, catalyst loading, and temperature on the product yields and the properties of the upgraded oil were examined. The thermochemical biomass to liquid (BTL) process is another promising treatment option for the direct conversion of biomass into liquid fuels [17]. However, peanut straw usually contains a certain amount of ash (~15.9 wt.%), which would be deposited on the catalyst surface and deactivate the catalyst. Therefore, in the present study, HTL and upgrading processes were selected. Note that the upgrading process employed in the present study is one of several attractive options for obtaining high-quality biofuels; however, it may not be the optimal option.

2. Materials and methods

2.1. Materials

Peanut straw, which was collected from farmland in Henan Province in Central China, was used. The collected peanut straw was dried and pulverized into particles of 2–3 mm in size. The results of the proximate and ultimate analysis of the peanut straw are listed in Table 1. The inorganic composition of the peanut straw was measured via X-ray fluorescence (XRF) using a Bruker S8 TIGER XRF spectrometer, and these results are also provided in Table 1. The inorganic salts consist primarily of Ca, Cl, Na, and Mg, which may affect the product distribution during the HTL of the peanut straw. Inorganic salts are often noted in the literature as having a positive effect on the HTL of biomass [18,19]. They appear to improve bio-oil yields and decrease the amounts of solid residues. They are also able to catalyze the hydrolysis of biomass macromolecules into smaller fragments, which are subsequently degraded into smaller compounds by dehydration, dehydrogenation, deoxygenation, and decarboxylation. These compounds become further rearranged through condensation, cyclization, and polymerization, leading to the formation of crude bio-oil. The UEO was purchased from a local automobile service station in Jiaozuo, Henan province (Central China). The UEO contained 1.5 wt.% moisture and 0.15 wt.% ash. In the present study, the same UEO was used for all of the experimental runs.

Table 1
Proximate and ultimate analyses (wt.%, dry basis) of peanut straw.

Proximate analysis					Ultimate analysis				
Volatile matter	Lipid	Fixed carbon	Ash	Moisture	C	H	N	S	O
76.2	2.1	7.9	15.9	8.0	40.28	5.35	0.93	0.08	24.66

Inorganic composition (wt.%, dry basis)

Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	Cl
1.59	0.67	0.29	1.94	1.18	2.79
K_2O	CaO	Ni	Fe_2O_3	MnO	MoO_3
0.52	6.29	0.01	0.14	0.11	0.03
SrO	TiO_2	ZnO	As_2O_3	Ti	
0.25	0.01	0.01	0.05	0.01	

All catalysts were obtained from Sigma-Aldrich. The relevant properties of the catalysts were determined experimentally, and the results are reported in Table 2. All catalysts were used as received. Deionized water was used throughout the experiments. Dichloromethane, which was received at a purity of 99.8 wt.%, was used as received as an extraction solvent.

Two custom-made high-pressure and corrosion-resistant batch autoclaves were used to perform the HTL, distillation, and upgrading experiments. The total internal volumes of the reactors used for HTL and upgrading were 1000 and 35 mL, respectively. Prior to their use in the experiments, the two reactors were loaded with water and treated at 400 °C for 4 h to remove any residual organic material and to expose the fresh metal walls to supercritical water. The HTL reactor was heated by an electrical heating jacket. The upgrading reactor was heated by a molten-salt bath that consisted of potassium nitrate and sodium nitrate at a mass ratio of 5:4.

2.2. Procedures

2.2.1. Hydrothermal liquefaction

In each run, 150 g of peanut straw and 400 mL of deionized water were loaded into the 1000 mL reactor. Next, the reactor was tightly sealed. The reaction was initiated by switching on the electrical heater of the autoclave. The speed of the mechanical agitator was set to 600 r/min. The reactor was heated very slowly and reached 310 °C after 80 min. The reactor was isothermally maintained at 310 ± 5 °C by an Omega temperature controller for 60 min. The pressure inside the reactor was maintained at approximately 10 MPa. The main contributor to this pressure was the saturated vapor pressure of water, which is primarily a function of temperature. After 60 min, the reaction was quenched by running cool water through the internal cooling coils.

After the reactor had cooled, we reduced the pressure in the autoclave to the atmospheric level and then opened it. The reaction mixture consisted of a tar-like material floating on the surface of the aqueous phase. Dichloromethane was added to dissolve the crude oil and separate it from the mixture. Next, the dichloromethane extract was filtered, and the solvent was then vaporized using a rotary evaporator at 30 °C under vacuum. The remaining material was the crude bio-oil.

2.2.2. Distillation

The distillation was conducted in the 1000 mL reactor. First, 315 g of crude bio-oil was loaded into the reactor. Next, the reactor was tightly sealed. The distillation was initiated by switching on the electrical heater of the autoclave. The distillation temperature was set to 400 °C. All fractions with a boiling point below 400 °C were collected and used as the feedstock for the subsequent upgrading experiments. The composition of the LBF was similar to that of a mixture of diesel and kerosene.

Table 2
Catalyst compositions.

Catalyst	Composition (from supplier)	BET area (m^2/g)	Metal dispersion (%)
Pd/C	Pd (5 wt.%)	888	39.4
Pt/C	Pt (5 wt.%)	419	5.4
Ru/C	Ru (5 wt.%)	966	23.2
Rh/C	Rh (5 wt.%)	980	21.0
Ir/C	Ir (5 wt.%)	861	11.0
Activated carbon	–	450	–