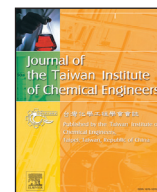




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Low acid value bio-gasoline and bio-diesel made from waste cooking oils using a fast pyrolysis process

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ABSTRACT

Continuous stable and fast pyrolysis of waste cooking oil (WCO) under isothermal conditions was achieved using catalyst pellets with a binder (bentonite) loaded with 25 wt% active materials including: $\text{Al}_2(\text{SO}_4)_3$, Na_2CO_3 , NaOH , and CaO . The experiments were carried out in an instant evaporator pyrolytic system with pyrolysis reactor temperatures ranging from 450 °C to 550 °C. The catalyst pellets were prepared by drying and calculating the extrudates made from the pastes of the active materials and the binder. Low acid value ($\text{AV} < 0.5 \text{ mg KOH/g}$) pyrolytic oils (PO) were obtained using these base catalyst pellets. Long-term tests, performed with these base catalysts, showed that CaO pellets can produce a PO with a near zero AV in a cycle time of 12 h. The physical properties of the bio-gasoline oil (BGO) and the bio-diesel oil (BDO) when separated from the PO almost meets the specifications of commercial petroleum gasoline and diesel, except that the octane number of the BGO (76) was below the target (92). Soap-like matter, in addition to the coke, produced during the pyrolysis of WCO using the catalyst pellets (Na_2CO_3 and NaOH) plugged the pyrolytic reactor, thereby preventing further operation. This soap-like matter was not found using the CaO catalyst pellet, suggesting that CaO was the most suitable base catalyst for WCO pyrolysis. The basic CaO pellets, able to reduce the fatty acids derived from thermal radical cracking reactions of WCO to aldehydes and ketones, produced a minimum aromatic hydrocarbon content in PO (from WCO) with a higher content of saturated fatty acids than from fresh edible soybean oil containing a higher content of unsaturated fatty acids. The resulting environmental friendly PO with a near zero AV, produced from WCO using the CaO pellets, proved the utility of the simple and one-step continuous pyrolytic process presented here.

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1. Introduction

Biomass, being the organic material produced by photosynthesis, is an abundant renewable energy source. In contrast to fossil fuels, biomass offers the benefit of being carbon dioxide neutral; however the use of land for biomass production, which could be used for growing food crops, is often challenged [1]. On the other hand, residues from agriculture and forestry, e.g. wastes from animals, wood, industry and the food industry possess a high content of organic compounds that are environmentally acceptable sources of energy [2]. These residues, or wastes, contain cellulose, hemicelluloses, lignin, triglycerides and fatty acids that can

be used, with appropriate thermo-chemical and biochemical processing, to produce renewable liquid fuels and valuable chemicals [3–6]. Waste cooking oil (WCO), from commercial catering establishments, which contain the triglyceride and fatty acid fractions that currently present a disposal problem are thus a promising feedstock alternative to expensive newly refined edible oils [7]. Without reclamation facilities, waste cooking oils and fats can give rise to significant disposal problems and in doing so create odor and pollution. Addressing this waste disposal problem, while creating a fuel substitute, potentially offers both economic and environmental benefits. Many developed countries have outlawed the disposal of WCO in domestic drainage systems [8]. The utilization of WCO, e.g. as a raw material or fuel, is important, as it not only mitigates risks to diners but also reduces raw material costs. The usual direct utilization of WCO is as a fuel [9–10] by esterification and/or transesterification [11–13] to produce bio-diesel. The major

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Table 1
Properties of feedstock and the catalysts prepared.

Oil	Acid value (mg of KOH/g)	Density (g/cm ³)	Gross heating value (kJ/g)	Kinematic viscosity at 40 °C (mm ² /s)	Water content (wt%)
Soybean oil	0.08	0.92	31.92	32.61	0.04
WCO	9.50	0.92	39.34	37.22	0.32
Catalyst/ Physical properties					
Catalyst pellet*		C1	C2	C3	C4
		Al ₂ (SO ₄)/ Bentonite (75%)	Na ₂ CO ₃ / Bentonite (75%)	NaOH/ Bentonite (75%)	CaO/ Bentonite (75%)
Catalyst composition					
Special surface area (m ² /g)		10.0379	0.7336	0.1368	10.9471
Porous volume (mL/g)		0.0506	0.0120	0.0072	0.0479
Average pore diameter (Å)		201.7702	653.2706	2111.8290	175.0352

* Size of cylindrical pellet: O.D. = 0.5 cm; L/O.D. = 1–1.6

factors inhibiting the utilization of this technology, for bio-diesel production, are the variation of the acid index, the solids content, the need for heavy equipment for large-scale production, and the alcohol required for the recovery and purification [5–7,9] Bio-diesel that leaves the production plant in good condition can become degraded during distribution without proper care and attention, due to e.g. oxidation, contact with water, and/or microbial activity [14]. The thermal or catalytic cracking of the triglycerides contained in WCO is a way of producing renewable bio-based products suitable for use in fuel and chemical applications. This approach has significant advantages over transesterification, including compatibility with engines and fuel standards; and feedstock flexibility: importantly, the final products are similar in composition to diesel fuel. In most triglyceride pyrolysis studies, molecular sieve catalysts, e.g. ZSM-5, MCM-41, and Y zeolite, were used [15–17]. There are also reports of triglyceride thermal cracking without a catalyst [18–19]. In general, partial oxidation or oxidation and cracking reactions of the bio-oil molecules occur with increasing temperatures during the pyrolysis process [20], leading to pyrolytic oils (PO) with high carboxylic acid contents and high acid values (AV) ranging from 17 to 142 [21–22]. These undesirable products have a large effect on the corrosion value, cold filter plugging point and freezing point of the biofuel. Acid values, which are a measure of the free fatty acid content, were determined using the method EN 14,104, GB-T 5530–2005. For the bio-diesel specification, the maximum allowable AV is 0.5 mgKOH/g in Europe and 0.8 mgKOH/g in American using ASTM D664 [23–25]. These undesirable acid products have a large effect on the corrosion value and cold flow properties. To decrease the AV of the pyrolytic oil (PO), by lowering its carboxylic acid content, esterification with methanol or deacidification with alkali solution can be used [26]. The results of Xu et al. [21] have shown that the catalytic cracking of woody oils generates fuels with a chemical composition similar to that of petroleum-based fuels. By using a basic catalyst (1.5–3% of the total amount of soybean oil), it is possible to obtain oils with good cold-flow properties and high heat values. Gas chromatography (GC) and Fourier transform infrared spectroscopic (FTIR) analyses of the products have shown that the distribution of the fractions can be modified by using a basic catalyst. The AV of the gasoline fraction of the pyrolytic oil was ~ 30 while that of diesel fraction was ~ 37. Esterification of either gasoline or diesel, derived from pyrolytic oils, using a solid acid catalyst can reduce the AV to ~ 3.

In this paper we chose to use WCO as a raw material because it is widely available from households and food companies. As WCO has potential in sustainable oil production, we re-

port a catalytic cracking study on WCO using base catalysts in a fixed bed reactor for producing low AV biofuel in a continuous process. It has been reported that low AV (< 5) PO can be produced with base catalysts using a process with a running time of ~ 28 h. In this work, the catalytic cracking reaction was carried out under isothermal conditions using a tubular evaporator and a fixed bed reactor packed with basic pellet catalysts including: Na₂CO₃/bentonite, NaOH/bentonite and CaO/bentonite (all with bentonite in the sodium form). For comparison, Al₂(SO₄)/bentonite (ammonium form) was also used as an acidic catalyst. The resulting POs were characterized by elemental analysis and quantified by product yield. It is hoped to develop a simple, one-step continuous process for producing PO with low AVs to meet the requirements of commercial gasoline bio-diesel standards using basic catalyst pellets in this work. The basic catalysts can be regenerated by introducing air, or ozone [27], to burn off the coke after the AV of pyrolytic oil exceeds 5 mgKOH/g.

2. Experimental section

2.1. Materials and catalyst preparation

WCO was provided from a local food processing company (Chant Oil Corporation, Taiwan). The important properties of WCO as well as the catalyst are listed in Table 1. Soybean oil was purchased locally (Taiwan Sugar Corporation). Typical fatty compositions of soybean oil and WCO are shown in Table 2. The main differences between these two feedstocks (soybean oil/WCO) are the ratios of the unsaturated fatty acids 85:69 and saturated fatty acids 15:31. Other chemicals such as Al₂(SO₄), Na₂CO₃, NaOH, and CaO (all in fine powder form) were obtained from a local chemical

Table 2.
Fatty acid composition of soybean oil and WCO.

Fatty acid composition (wt%)	Soybean	WCO
Unsaturated fatty acids	85	69
Oleic acid (C18:1)	23	36
Linoleic acid (C18:2)	54	29
α-linolenic acid (C18:2)	8	3
Others	0	1
Saturated fatty acids	15	31
Palmitic acid (C16:0)	11	24
Stearic acid (C18:0)	4	5
Others	0	2

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