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Transesterification of non-edible oils over potassium acetate impregnated CaO solid base catalyst

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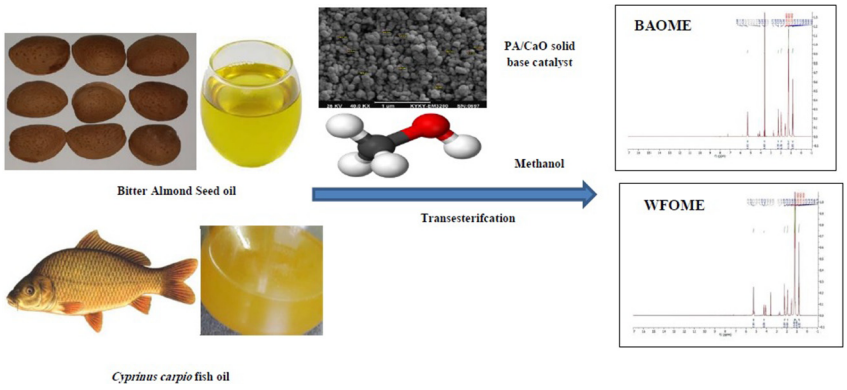
GRAPHICAL ABSTRACT



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ABSTRACT

Biodiesel production through transesterification reaction with methanol using calcium oxide (CaO) as a solid base catalyst is restricted due to the need to the high molar ratio of methanol to oil and long reaction time. Therefore, the CaO catalyst was modified by potassium acetate (PA) to prepare PA/CaO solid base catalyst via wet impregnation method. X-ray Diffraction, Scanning Electron Microscopy, Thermal Gravimetric Analysis, Fourier Transform Infra-Red spectroscopy, Hammett indicator (basic strength), and the Inductive Couple Plasma techniques, were applied to characterize the prepared catalyst. The effect of the PA ratio loaded on CaO and calcination temperature were investigated as well. The catalyst activity was tested through transesterifcation reaction of non-edible oils, namely bitter almond oil BAO and waste fish oil WFO, with methanol. Transesterifcation process was optimized through the parameters involving the solid catalyst amount, methanol to oil molar ratio, reaction temperature, and reaction time. The highest methyl ester yield from both BAO (91.22 wt%) and WFO (93.30 wt%) were achieved by employing 2.0 wt% , and 1.0 wt% of PA/CaO catalyst, respectively, 9:1 methanol to oil molar ratio, 60 °C reaction temperature, and 120 min reaction time. The prepared catalyst was retrievable and thermally stable giving a yield up to 75 wt% after a 4th cycle reuse. The fuel properties of the raw oils were significantly enhanced as a result of transesterification, and were in conformity with the ASTM D 6751 limits. Conversion of the non-edible oils to biodiesel using the catalyst was confirmed by ^{1}H NMR spectroscopy which gives yield percent close to those of the practically obtained. Moreover, the FTIR

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spectroscopy assured the conversion of the non-edible oils into biodiesel. As such, PA/CaO composite may be considered as a promising solid base catalyst for transesterification of non-edible oils with methanol.

1. Introduction

Owing to the expected decline of petroleum reserves and the environmental outrage issues of the exhaust gases produced from petro fueled engines, an alternative fuels for transport sector have received significant attention. In this respect, biodiesel (BD), derived from renewable and locally available resources, is being emerged to replace the petroleum diesel as alternative fuel. BD is produced mainly through transesterification process of triglycerides (vegetable oils, animal fats, waste greases, and algal oil) with short chains alcohols, methanol or ethanol, in the presence of suitable catalyst. BD is known to be a non-toxic, biodegradable, and environmentally clean fuel [1,2].

Transesterification reaction catalyzed by homogenous base catalysts, such as KOH or NaOH dissolved in methanol is the current used process for BD production. Nevertheless, this method is associated with many disadvantages like; separation difficulty of catalyst from the products as well as the incompetence of catalyst reuse. Moreover, it produces massive amount of contaminated water which rise the production costs [3–5]. Consequently, more consideration was paid to replace homogenous base catalysts by solid one, because of the effortless of the catalysts separation from the reaction product, non-corrosive, and low environmental pollution [6–9].

However, different solid alkaline catalysts, like alkali or alkaline earth oxides, supported alkali metals, hydrotalcites, basic zeolites, and activated carbon supported alkali metals have been used as solid base catalysts in the transesterification reaction [10–16]. Calcium oxide (CaO) is one of those heterogeneous base catalysts that arise as a strong candidate in producing BD, due to its practical advantages including the high basicity, non-corrosive, low price, lower solubility, easy to handle, and eco-friendly [17,18]. Various feed- stocks, like $CaPO_4$, $Ca(NO_3)_2$ and $Ca(OH)_2$ were used as precursors for CaO. When CaO is used as a catalyst in the transesterification reaction, it will form methoxide anion, which in turn reacts with triglyceride molecule to yield three moles of methyl esters and one mole of glycerol [19,20]. Nevertheless, it was reported that solid base catalysts tend to lose their activity as a result of adsorption of atmospheric CO_2 and H_2O, which poison the basic sites on a catalyst surface, and change the crystal structure of the solid catalyst [19,21]. Modification of the metal oxide catalysts could increase their basic strength, and thus, increase their catalytic activity as well. Kaur and Ali [22] investigated preparation of Zr/CaO catalyst by impregnation of CaO by different ratios of Zirconium. Li et al. [23] studied functionalization of CaO with strontium to prepare Sr/ZnO catalyst to be used as a solid base catalysts for transesterification of palm oil with methanol.

Doping of CaO catalyst with potassium ion is, known by its high basicity, and expected to produce BD at lower reaction conditions [19]. In this aspect, many studies were reported on modification of CaO catalysts by potassium salts. Impregnation of CaO with potassium hydroxide KOH/CaO was reported by Liao and Chung to prepare a solid base catalyst [24], and implemented for BD production from Jatropha oil. The CaO, also, doped by KCl to obtain KCl/CaO catalyst and utilized for transesterification of refined soybean oil to produce BD [25]. BD was synthesized from canola oil by using functionalized CaO with K_2CO_3 [26]. Finally, the synthesis of a heterogeneous catalyst (KBr/CaO) from commercial calcium oxide and potassium bromide for transesterification of waste cooking oil with methanol was documented by Mahesh et al. [19]. However, functionalization of CaO with an organic salt of potassium, namely potassium acetate, has not been yet published in literature, to the best of the authors knowledge. Furthermore, the used of potassium acetate impregnated CaO as a solid base catalyst in the transesterification of non-edible oils viz. bitter almond oil (BAO) and waste fish oil (WFO) has not been investigated yet as well.

Herein, potassium acetate impregnated CaO as solid base catalyst was synthesized by wet impregnation method followed by calcination, and the activity of the resulting catalyst was investigated in producing of BD from BAO and WFO as non-edible oils. The parameters affecting methyl esters yield, including the quantity of potassium acetate loaded on CaO, the calcination temperature, quantity of the catalyst, methanol to oil molar ratio, reaction temperature, and the reaction period were investigated. The ^{1}H NMR spectroscopy was applied to calculate the conversion of the non-edible oils to BD. In addition, reusability of the used catalyst was evaluated for 5 cycles.

2. Experimental

2.1. Materials and methods

The commercial CaO was used in the preparation of the solid base catalyst. The potassium acetate (PA) was obtained from Fluka with a purity of (≥99.0%). Methanol (HPLC grade, 99.9%) was purchased from Fluka (Germany). Other chemicals, such as n-hexane, diethyl ether, acetone and isopropanol were purchased from BDH (UK). Analytical grade Hammett indicators, such as phenolphthalein, thymolphthalein, 2,4-dinitroaniline, and 4-nitroaniline were obtained from Sigma–Aldrich. The chemicals were used as such without further purification.

The BAO and WFO were extracted from bitter almond seeds and discard part of fish, respectively. Properties and fatty acid compositions of the oils are summarized in Tables 1 and 2.

2.2. Catalyst preparation

The potassium acetate supported CaO catalyst (PA/CaO) was prepared through the wet impregnation method. Typically, 10 g of CaO was immersed in 40 mL of potassium acetate solution with continuous stirring for 5 h to guarantee homogenous contact between the CaO and potassium acetate solution. The resulting slurry was then oven-dried at 110 °C for 24 h. A series of PA/CaO was prepared by varying the PA concentrations within the range of 10–50 wt%. Finally, the samples were calcanied at 600 °C for 4 h, and kept in dark container for use.

2.3. Characterization of catalyst

Many techniques were applied to characterize the CaO and its derived solid base catalyst. Thermo-gravimetric and differential thermal

Table 1
Properties of BAO and WFO compared to other non-edible oils.

CJCO[b]	BT[a]	WFO	BAO	Property
60–55	–	79.0	42.0	Oil content (% w/w)
0.9180	0.9216	0.9111	0.9110	Density @ 15.6 °C
35.40	37.39	23.20	24.12	Kinematic Viscosity @ 40 °C
186.0	165	207	190.0	Flash Point, °C
11.0	4.66	0.94	0.86	Acid Value, mg KOH/g oil
–	172	186.0	175.23	Saponification Value, mg KOH/g oil
101.0	33	86.36	93.22	Iodine Value, 100 mg I_2/g oil
–	1.4780	1.4689	1.4694	Refractive Index @ 20 °C
–	14.0	-3.0	−20.0	Pour point, °C

[a]Beef tallow from Ref. [2]; [b]crude *Jatropha curcas* oil from Ref. [32].