



Deoxygenation of waste cooking to renewable diesel over walnut shell-derived nanorode activated carbon supported CaO-La₂O₃ catalyst



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ABSTRACT

Waste cooking oil (WCO) is a potential non-edible feedstock that is sustainable for production of automotive green diesel. The present study focused on synthesis of WCO-derived green diesel through catalytic deoxygenation (DO) process using bimetallic acid-base CaO-La₂O₃/AC nanosized catalyst under zero hydrogen environment. Results indicated that the prepared nano-catalyst rendered high deoxygenation reactivity with 72% yield of straight chain hydrocarbons (C₈-C₂₀). The CaO-La₂O₃/AC catalysed reaction pathway favour in decarboxylation/decarbonylation route instead of cracking effect, which consistently formed major *n*-C₁₅ fractions at approximately > 80%. In addition, CaO-La₂O₃/AC showed high catalytic stability and reusability up to 6 cycles with > 73% of yield and selectivity to *n*-C₁₅ of > 82%. The catalyst showed an excellent coke inhibitor with less than 2 wt% of coke under TGA analysis.

1. Introduction

Worldwide debate on energy crises and global warming due to the extensive use of fossil fuels as the ultimate energy source prompted researchers to explore alternative energy sources. An interesting idea has been adapted in the form of green diesel (free-oxygenated hydrocarbon compound) which has been identified as clean burning fuel having low quantity of sulphur and aromatics contents, high cetane number, lubricity, renewability and also involve in GHG emission reduction by 70–90% [1,2]. The product not only fungible with petroleum derived fuel but also gave great competitiveness with other well-known alternative biofuel like biodiesel (FAME). Fatty acid methyl ester (FAME) composed of highly oxygenated compound which result in various inevitable disadvantages including high viscosity, poor cloud and pour point properties, low heating value and low oxidation stability [1,3]. In general, the green diesel could be synthesized through catalytic deoxygenation (DO) via decarboxylation/decarbonylation (deCOx) of triglycerides and fatty acid derivatives along with formation of CO₂ and CO + H₂O as by-product [4–6]. Green diesel could also be produced from hydrodeoxygenation (HDO) process where the oxygenated compounds were removed under the presence of H₂ gas and resulting to the formation of water (H₂O) as by-product [7]. However, it requires a large consumption of an expensive H₂ gases under high

reaction pressure [8]. Thus, the DO reaction is more economical, effective and suitable for industrial practices, which results in producing high quality green diesel almost similar to the conventional diesel petroleum derived fuel [9].

The DO reaction have been investigated using various types of catalysts such as Pd-based, Pt-based transition metal oxides such as Ni, Co, Zn, Cu, Ga and Ru [2,10–13]. Undeniably, high efficiency of DO reaction works mainly involve noble-based catalysts on either Pd or Pt, which mainly result in high deCOx activity and formation of high yield hydrocarbons fractions. However, the high cost of such catalysts made it prohibitive for industrial usage. Based on previous literatures, the application of mesoporous acidic metal-catalysts such as zeolite-based, MCM-41-based HZSM-5, ZSM-5, SBA-15 and SBA-16 have been widely used for deoxygenation reaction [11,14–17]. Nevertheless, the application of these catalysts is not only expensive but also tedious to be prepared. Moreover, acid catalysts are also prone to undergo severe deterioration of catalyst active sites due coke formation [18]. Therefore, the awareness of improving the catalyst stability is necessary. Recent studies showed that utilization of basic metal-catalyst in DO reaction results in less coke formation than acidic metal-catalysed DO [1,4]. However, the basic catalysts also results to poor deCOx activity and subsequently leading to occurrence of undesirable cracking activity [19,4]. Thus, results in high formation of light hydrocarbon fractions.

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Therefore, conjugation of basic and acid metal is necessary for providing acid-base properties which could be able to promote deCOx reaction along with low coke formation. Recently, utilization of acid-base catalyst for deCOx was found to be catalytically effective and highly selective toward deCOx reaction along with high formation of diesel-range hydrocarbons (C₁₃–C₂₀). The catalysts have demonstrated high tolerance toward coke-colonization species [5]. It has been proven by recent study, that the incorporation of acid-base catalyst from a mixture of CaO and NiO over SiO₂-Al₂O₃ not only poses high stability as it could be reused till fourth cycles with consistent hydrocarbon product but also resulted in considerable lower coke formation than pure acid catalyst derived from Ni-Cu/Al₂O₃ [20] and Ni-Sn/Al₂O₃ [21]. Thus, indicating that the catalyst deactivation by coke can be diminished by appropriate modification of chemical properties of the catalyst. Previously, it was successfully established that the improvement of acidity-basicity properties by integrating nanosize of CaO-La₂O₃ on carbon support was found effective for biodiesel production process [22]. However, no study reported for the usage of CaO-La₂O₃/AC catalyst on DO reaction.

Even though there is a considerable number of researches in small laboratory scale for green diesel production via DO been reported or set up in recent years, but the usage and the application on the industrial scale is still far from realization. Commercialization of green diesel is the considered as the major obstacle considering the high cost of production which involves raw material cost and the production cost [23]. The analysis of the economic evaluation by U.S. Energy Information Administration (2016) drives to the conclusion that the cost of raw material is a dominant part of the overall cost of green diesel production, covering up to > 57% of the total production cost [24]. Thus, to optimally enhance the economic point of view, utilization of sustainable, non-expensive and non-value added feedstock is extremely important. The WCO is largely abundance as it is produced continuously every day [25]. As been reported by Malaysian government, by the year 2017 Malaysia's palm oil export is expected to increase to 19.4 million from 17.4 million in 2016. About 40% (6.96–7.76 million) of palm oil from 2016 to 2017 is expected to be used for food and oleochemical industry. In food business alone, a single restaurant may produce about 15 L of palm oil-derived WCO per day. Therefore, the use of palm oil-WCO as feedstock for green diesel is not only used for feedstock for green diesel but could also solve waste disposal problem, improving the quality of the environment [9]. In the current research, a selective DO reaction over WCO was evaluated over La₂O₃/AC, CaO/AC and CaO-La₂O₃/AC catalysts. In addition, the effect of reaction conditions towards the product selectivity and yield was studied. The catalyst reusability was further investigated to determine its binary system stability.

2. Experimental

2.1. Materials and methods

Walnut (*Juglans* sp.) shells were collected from Basra market-Iraq. Phosphoric acid (H₃PO₄) with 85.0–87.0% purity was purchased from USA (J.T. Baker). Lanthanum nitrate hexahydrate (La(NO₃)₃·6H₂O) with 99.0% purity was purchased from Merck (USA) while calcium nitrate tetrahydrate (Ca(NO₃)₂·4H₂O) with 99.0% purity was purchased from R & M (Malaysia). The liquid products are both alkane and alkene standard *n*-(C₈–C₂₀) and internal standard 1-bromohexane for gas chromatograph (GC) analysis were purchased from Sigma Aldrich and used without further purification. N-Hexane (GC grade) with purity > 98% from Merck (USA) was used for dilution. The N₂ gas, with 99.9% purity, was supplied by Linde Sdn. Bhd. Malaysia. The feedstock of this work, palm oil-WCO was collected from the restaurant at the Serdang Selongo Malaysia. The oil was used for the reaction without further treatment and purification. The properties of the crude WCO which include FFA content and water content are presented in Table 1. Based

Table 1
Analysis data of properties of the WCO oil.

Properties	Value
Density (g/cm ³)	0.87
Viscosity (mm ² /s)	4.85
Moisture content (wt.%)	1–5
Acid value (mg KOH/g)	36.81
FFA content (%)	18.40
<i>Fatty acid composition</i>	
Myristic acid, C14:0	1.93
Palmitic acid, C16:0	45.68
Stearic acid, C18:0	4.25
Oleic acid, C18:1	40.19
Linolenic acid, C18:2	7.90

on the analysis, the total acid number (TAN) is 36.8 mg KOH/g, which indicated the presence of high free fatty acids (18.4 wt%). The chemical composition of fatty acid of WCO is composed of saturated fatty acids (i.e. palmitic acid (45.68%), stearic acid (4.25%) and myristic acid (1.3%)), unsaturated fatty acid (i.e. oleic acid (40.19%) and linolenic acid (7.90%)).

2.2. Catalyst preparation

The walnut shell was washed thoroughly with hot water in order to remove all the impurity followed by drying in an oven. The shell was grounded into fine powder by a milling machine (Pulverisette 4 vario-Planetary Mill) set at 1200 rpm for 3 h. The powder was sieved through a 200 μm metal sieve (Laboratory test sieve Endecotts Ltd.), then carbonized up to 400 °C for 4 h under N₂ flow. The carbon was then chemically activated using phosphoric acid (H₃PO₄) in a reflux heating at 150 °C for 12 h followed by purification using hot distilled water till the solution adjusted to pH 7. Moreover, the powder was dried at 100 °C for 2 h. The activated carbon was then impregnated with 20% of La(NO₃)₃·6H₂O and 15% Ca(NO₃)₂·4H₂O under continues stirring for 6 h. The metals impregnation on the support were optimized by vacuum impregnating procedure under 6.3 × 10⁻⁶ mbar and followed by drying overnight at 100 °C. Later, the metals doped with activated carbon (AC) were calcined at 700 °C for 4 h under the N₂ flow. The catalyst preparation steps were repeated for using single metal salt. The modified catalyst was known as CaO/AC, La₂O₃/AC and CaO-La₂O₃/AC.

2.3. Catalyst characterization

The X-ray diffraction (XRD) analysis was employed to identify the dispersion state and chemical composition of modified AC catalysts before and after reaction. The XRD analysis was performed using a Shimadzu diffractometer (model XRD-6000). The specific surface area and pore distribution of the catalysts were determined by the Brunauer – Emmett – Teller (BET) method using an N₂ adsorption/desorption analyser (Thermo-Finnigan Sorpmatic 1990 series). The catalysts were degassed overnight at 150 °C to remove moisture and foreign gases on the surface. Adsorption and desorption process of N₂ on the catalyst surfaces were analysed in a vacuum chamber at –196 °C. Furthermore, the basicity and acidity of the catalysts were studied with temperature programmed desorption using CO₂ and NH₃ as the probe molecules (TPD–CO₂ and TPD–NH₃). The analysis was carried out using a Thermo Finnigan TPD/R/O 1100 instrument equipped with a thermal conductivity detector (TCD). The catalyst (~0.05 g) was pre-treated with N₂ gas flow for 30 min at 250 °C. The catalyst was then exposed to CO₂ gas for 60 min at ambient temperature to allow adsorption of CO₂ onto the surface. Excess CO₂ was subsequently flushed by N₂ gas. Desorption of the CO₂ from the basic sites of the catalyst was detected by TCD under helium gas flow (30 ml/min) from 50 °C to 900 °C and

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