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Microwave-assisted transesterification of oils with heterogeneous catalyst prepared by calcination of alkaline-treated eggshells

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Abstract

Active heterogeneous catalysts were prepared by calcination of KOH-treated waste eggshells at 1000°C. The physico-chemical properties of the catalysts were characterized by XRD, FTIR and TGA–DTG, and the catalytic activity was tested in transesterification reactions of soybean oil with methanol under microwave irradiation. The effects of reaction time, methanol-to-oil ratio, amount of KOH used in catalyst preparation and catalyst loading on the fatty acid methyl ester yield were investigated. The experimental results revealed that the catalysts exhibited a high content of CaO (97.4 wt%). The prepared catalyst promoted a significant enhancement in the transesterification reaction rates when using microwave irradiation as opposed to conventional heating. The optimal conditions for attainment of ester concentration of 96.5% (minimum required by international regulations) were reaction time of 1 min, 800 W microwave power, 6:1 methanol-to-oil ratio, and catalyst loading of 5%. The results indicated that the KOH-treated CaO catalysts derived from eggshells presented great potential to be used for microwave-assisted transesterification reactions of oils. However, after being used, the catalyst was demonstrated to have undergone chemical changes, which incurred in a decrease in performance allowing for a maximum ester concentration of 87.2% in 15 min of reaction upon reuse in several cycles.

Keywords: biodiesel; microwave irradiation; heterogeneous catalysis.

1. Introduction

Biodiesel has been largely produced worldwide as a promising alternative to petroleum-derived diesel due to its renewability, near zero emission, biodegradability and capability of direct use in unmodified diesel engines [1]. Conventionally, biodiesel is produced by transesterification of vegetable oils with short chain alcohols (e.g., methanol or ethanol), using homogeneous base catalysts (e.g., sodium methoxide) [2]. Homogeneous base catalysts, although quite effective, present some disadvantages such as non-recyclability and an inevitable generation of large amounts of wastewater [1]. On the other hand, several heterogeneous base catalysts have been recently developed, presenting the advantages of being less corrosive, easier to separate from the products, reusable and economically and environmentally benign [3].

Base catalysts are generally more active than acids in transesterification and hence solid base catalysts, such as alkaline earth oxides, transition metal oxides and alkali-doped materials, constitute the most commonly developed class of heterogeneous catalysts [2]. However, only a handful of these developed catalysts are suitable for use in industrial processes due to their inherently high synthesis costs and to their requirements for extreme reaction conditions (i.e., high temperatures and pressure). To address these issues, researchers have used agri-food wastes, such as mollusk shells, eggshells and lignocellulosic carbon-based materials, as precursors to prepare cost-effective catalysts, and employed either ultrasound or microwave irradiation to efficiently carry out transesterification reactions with these catalysts, with no need for extreme temperature and pressure conditions [4,5]. Although Khemthong et al. [4] were able to maintain low energy input for their transesterification of soybean oil using calcined waste eggshells catalyst, in a short time (4 min) at 900 W, reaction conditions to attain 96.7% fatty acids methyl esters (FAME) in the biodiesel phase were still harsh: 18:1 methanol-to-oil molar ratio and catalyst-to-oil mass ratio of 15%. The same goes for Chen et al. [5], attaining 96.7% FAME in 60 min with 9:1 methanol-to-oil molar ratio and catalyst-to-oil mass ratio of 8% with 120 W ultrasonic power.

Thus, it was the aim of this work to investigate the feasibility of using calcined KOH-doped eggshells as catalyst in a microwave-assisted transesterification reaction of oil to attain standard biodiesel FAME specifications with low input reactant and catalyst requirements in a short reaction time.

2. Methodology

Materials. Refined soybean oil was acquired from local vendors (Belo Horizonte, Brazil). Laboratory grade methanol (100%, Synth, Brazil) and sodium methoxide (30% in

methanol, ISOFAR, Brazil) were used as short-chain alcohol and catalyst, respectively. Waste chicken eggshells were acquired from local food markets.

Catalyst preparation and characterization. Waste chicken eggshells were washed with tap water to remove impurities and ground to a fine powder in a mortar. The ground eggshells were dried overnight at 80°C and were divided into two groups: (1) untreated; and (2) KOH-doped eggshells. The KOH-doped catalysts were prepared using wet impregnation method at concentrations of 10, 30 and 50% weight of KOH by weight of eggshell. Typically, KOH aqueous solutions were prepared, subsequently added to the dried eggshells, and the solution was stirred at 600 rpm for 3 h. The KOH-doped powder was then filtered and dried at 80°C for 3 h. Both untreated and KOH-doped were calcined at 1000°C, in air atmosphere at a heating rate of 5oC/min for 1 h. In all cases, the final product was a fine white powder. The crystalline phases of the calcined sample were analyzed by a PHILIPS X-Ray diffractometer for powder samples (PANALYPTICAL) with the X'Pert-APD system, PW 3710/31 controller, 1830/40 PW generator, and PW 3020/00 goniometer. The chemical compositions were analyzed by energy dispersive X-ray fluorescence spectroscopy (PHILIPS PW-2400).

Microwave-assisted transesterification of oils. The transesterification of the soybean oil was carried out with methanol as a short chain alcohol, and sodium methoxide as homogeneous catalyst and the untreated and KOH-doped calcined eggshells as heterogeneous catalysts. The reaction was carried out in a glass reactor of 500 mL capacity in a microwave-irradiated unit (Model Start Synth, Milestone, Italy), equipped with a reflux condenser, a magnetic stirrer bar and an infrared feedback temperature control system. For the microwave-assisted transesterification, the catalysts concentrations were varied from 1 to 3% (w/w of oil) for the homogeneous catalyst and from 1 to 5% (w/w of oil) for the heterogeneous one; the alcohol-to-oil molar ratio was varied from 3:1 to 12:1, by increments of 3, and the reaction times studied were 1, 7 and 15 minutes. The microwave unit was programmed to reach the maximum reaction temperature (~65°C) with microwave powers varying from 400 of 1000 W (the maximum power output of the microwave unit is 1200 W). The reaction was timed as soon as the system was turned on. Upon reaching the desired time, the reaction was stopped, by immediately immersing the glass reactor in an ice bath, and the mixture was transferred to a separating funnel and left to rest overnight for the gravitational separation of the fatty acid methyl esters (FAME) and glycerol. After separation, the upper layer (FAME) was collected for further purification. The adsorbent Amberlite BD10DRY was added to the FAME fraction (10% weight in relation to the weight of FAME) and shaken in an orbital shaker at 200 rpm for 2 hours to remove the remaining water and free glycerin from that phase. Subsequently, the purified FAME was subjected to rotary evaporation to remove the excess methanol. For the Heterogeneous catalysis, after the transesterification reactions, the untreated and KOH-doped heterogeneous catalysts were filtered and thoroughly washed with ether in a Soxhlet apparatus. Subsequently, the washed catalysts were dried at 80°C overnight. Recovered catalysts were tested for reusability in 5 cycles, following the same recovery procedure. All tests were conducted in duplicates.

Analytical Methods. The purified FAME were analyzed by gas chromatography, performed in accordance with EU norm EN 14103, using a GC–FID HP7820A apparatus (Agilent Technologies, USA) equipped with an auto-sampler (Agilent 7386B series) and data acquisition software EZChrom Elite Compact (Agilent Technologies, USA). Separations were accomplished at a constant hydrogen flow rate of 3 mL min^{-1} in a 15-m long HP-INNOWAX capillary column (0.25 mm I.D. and 0.25 µm film thicknesses). Samples (1 µL) were injected in a split ratio of 1:50. Injector temperature was 250°C and the temperature program of the oven started with an initial temperature of 120°C, followed by an increase in temperature up to 220°C at a rate of 7°C/min for 10 minutes.

3. Results and discussion

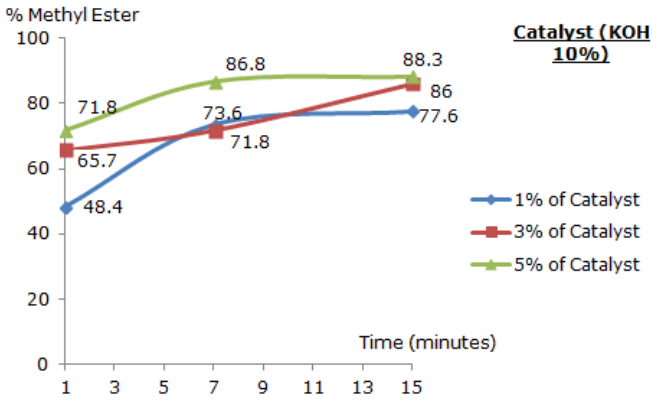
Homogeneous Catalysis. Tests were conducted to verify the effects of reaction conditions (alcohol-to-oil molar ratio, catalyst load and reaction time) for homogeneous catalysis in the microwave-assisted transesterification of soybean oil with methanol and sodium methoxide as catalyst. Considering the lowest values for reaction condition parameters and highest value for ester concentration in the biodiesel phase, the optimum reaction conditions obtained for an ester concentration of 99.5% (m/m) were: alcohol-to-oil molar ratio of 6:1; reaction time of 1 min; and microwave power of 600 W.

Heterogeneous Catalysis. The results for the fatty acid methyl esters concentration with different catalyst-to-oil mass ratio are presented in Figures. 1a, 1b and 1c, for the microwave-assisted heterogeneous catalysis employing different KOH loads in the preparation of the catalyst (10, 30 and 50%, respectively). The alcohol-to-oil molar ratio was 6:1 and the microwave settings were kept constant at 800 W. Reaction temperature was kept at the maximum allowed by the reacting medium (~65°C). Microwave powers lower than 800 W did not allow the reaction temperature to attain its highest value when heterogeneous catalysts were introduced in the reaction medium. From Figure 1a, it is clear that, under the reaction conditions studied, a KOH doping of 10% did not provide basicity to the catalyst high enough to promote an ester yield for the transesterification of oil that would allow the produced biodiesel to comply with international regulations (minimum FAME concentration of 96.5% m/m), even at the highest catalyst load. Specifications for FAME minimum concentration were achieved with a 30% KOH-doped catalyst for a catalyst load of 5% and reaction times longer than 7 minutes, under microwave irradiation (Figure 1b). Increasing

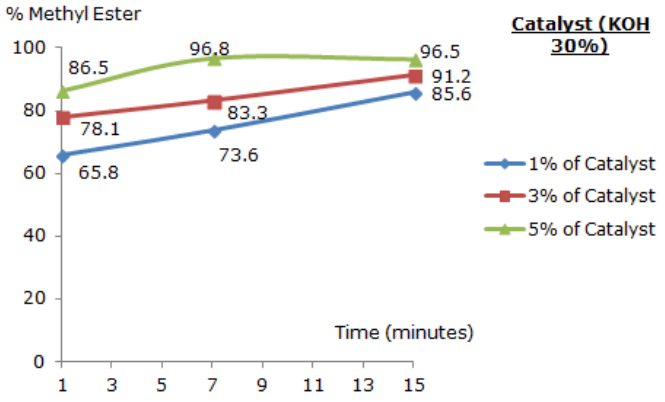
the amount of KOH to 50% did not significantly improve the results for ester concentration, except for the conditions of reaction time of 15 min and catalyst-to-oil ratio of 5%, which produced a biodiesel with ester concentration of approximately 100%. Tests for reusability of the 50% KOH-doped catalyst revealed a decrease in final ester concentration of 14.5 and 12.8 %, respectively for 7 and 15 min of reaction time, under the conditions of alcohol-to-oil molar ratio of 6:1 and catalyst-to-oil ratio of 5% m/m.

For the sake of comparison, employing an alcohol-to-oil molar ratio of 6:1 and a catalyst-to-oil ratio of 5% m/m, the 50% KOH-doped catalyst was used in a conventional transesterification reaction, i.e., in a jacketed reactor with mechanical stirring, and the best results for ester concentration, 76.9%, were attained with a reaction time of 3 h, i.e., an ester concentration way below the minimum specified by international regulations at a much longer time.

Transesterification reactions with the untreated catalyst (i.e., calcined eggshells) have led to very low ester concentrations (~47%) in the biodiesel phase for the conditions of alcohol-to-oil molar ratio of 6:1, reaction time of 15 min and catalyst-to-oil ratio of 5% m/m, under microwave irradiation power of 800 W. Khemthong et al. [4], employing calcined waste eggshells in air (800°C at a heating rate of 10°C/min for 4 h), have attained a biodiesel with a maximum concentration of fatty acid methyl esters of 96.7% for the optimal conditions of reaction time of 4 min, methanol-to-oil ratio of 18:1, and catalyst loading of 15%, under 900 W microwave irradiation power. Thus, it can be concluded that higher methanol-to-oil ratio, catalyst loading and microwave power are necessary to achieve the minimum ester concentration of 96.5% specified by international regulations when using untreated calcined eggshells.



(a)



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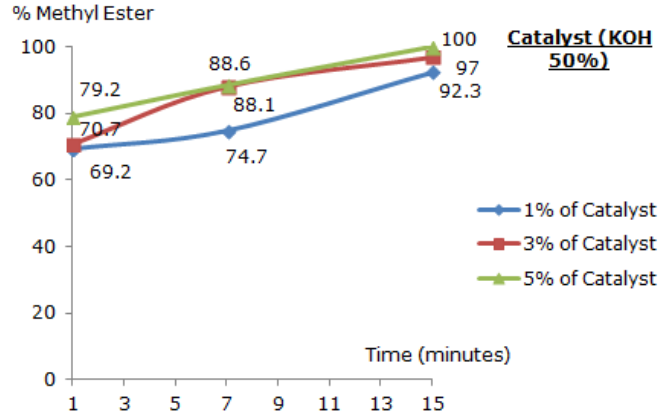

(c)

Fig. 1. FAME concentration for microwave-assisted transesterification with heterogeneous catalyst prepared with (a) 10% KOH, (b) 30% KOH and (c) 50% KOH.

Characterization of the heterogeneous catalysts. The X-ray diffraction analysis revealed that eggshells were predominantly comprised of $CaCO_3$ and that the calcined untreated eggshells were mainly comprised of CaO (98.9%). The composition of the 50% KOH-doped catalyst was determined to be 97.4% CaO, with the presence of potassium ozonide (KO_3) in moderate quantities and of small amounts of mixed calcium and potassium carbonate ($KCaCO_3$). The 50% KOH-doped catalyst was analyzed after use in the transesterification reactions and the X-ray Diffraction analysis revealed its composition to undergo chemical reaction, with a complete disappearance of the potassium ozonide species and an increase in the amount of mixed calcium and potassium carbonates. Tests were conducted to verify the effects of the microwave irradiation on the chemical changes that occurred in the catalyst composition by separately mixing the catalyst with oil and with methanol and subjecting the individual mixture to microwave irradiation. It was demonstrated that the

microwaves alone had no effects on those changes. The chemical changes were then attributed to the high reactivity of potassium ozonides in aqueous and acidic media, considering that during transesterification acidic species are probably formed. Thus, the catalytic activity of the prepared catalysts is attributed to both the CaO and the KO_3 phases, as evidenced by its decrease when the potassium ozonide phase was completely extinguished during the transesterification reactions.

4. Conclusions

Heterogeneous catalysts were successfully prepared by calcination of KOH-doped waste chicken eggshells and used in microwave-assisted transesterification reactions of soybean oil with methanol. With these alkaline-treated catalysts, reaction conditions significantly milder than those employed in the literature allowed for attainment of the minimum FAME concentration specified by international regulations for the biodiesel phase. However, this was attained at the expense of catalyst performance upon its reuse, with the observed decrease in catalytic activity being attributed to changes in the catalyst chemical composition that occurred during transesterification reactions.

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The 1st International Conference on Energy, Environment and Economics (ICEEE 2016) was held at Heriot-Watt University, Edinburgh, EH14 4AS, UK, 16-18 August 2016. ICEEE2016 focused on energy, environment and economics of energy systems and their applications. More than fifty eight delegates from 31 countries with diverse expertise ranging from energy economics, solar thermal, water engineering, automotive, energy, economics and policy, sustainable development, bio fuels, Nano technologies, climate change, life cycle analysis etc. made conference true to its name and completely international. During conference total 51 oral presentations and six posters were shared between delegates. The presentations showed the depth and breadth of research across different research areas ranging from diverse background. ICEEE2016 aimed:

- To identify and share experiences, challenges and technical expertise on how to tackle growing energy use and greenhouse gas emissions and how to promote sustainability and economical, cost effective energy efficiency measures.

In total 11 technical sessions and two invited talks both from academia and industry provided insight into the recent development on the proposed theme of the conference. Preparation, organisation and delivery of the conference started from July 2015 and further co-ordinated by vibrant team of Conference Centre, Heriot Watt University. Conference organisers would like to acknowledge support from the sponsors particularly World Scientific Publication ltd and its team members for the delivery of the conference. Organisers are also thankful to all reviewers who contributed during peer review process and their contributions are well appreciated. At the end and during vote of thanks following awards have been announced and we would like to congratulate all well deserving delegates.

- Best Paper –Academia: Amela Ajanovic, EEG, TU Vienna, Austria
- Best Paper – Student : Christian Jenne,University of Duisburg-Essen, Germany
- Best Poster – Student: Yoann Guinard, University of New South Wales, Sydney, Australia
- Best Poster – Academia: E. Salleh, Universiti Kebangsaan Malaysia, Malaysia
- Active Participation Award - Yoann Guinard, University of New South Wales, Sydney, Australia

At the end we would like to extend our gratitude to all of you for your participation and hopefully welcome you again during ICEEE2017.

Editors:
Dr. Singh is Senior Scientist at Indian Agricultural Research Institute, New Delhi, India. Her area of expertise are bio energy and bio fuels, environmental engineering, carbon accounting and renewable energy integration for rural development.
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