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Esterification of high free fatty acids in supercritical methanol using sulfated angel wing shells as catalyst

O. Nur Syazwani[a,b], M. Lokman Ibrahim[c], Wahyudiono[d], Hideki Kanda[d], Motonobu Goto[d], Y.H. Taufiq-Yap[a,b,*]

[a] Catalysis Science and Technology Research Centre, Faculty of Science, Universiti Putra Malaysia, 43400, UPM Serdang, Selangor, Malaysia
[b] Department of Chemistry, Faculty Science, Universiti Putra Malaysia, 43400, UPM Serdang, Selangor, Malaysia
[c] School of Chemistry and Environment, Faculty of Applied Sciences, Universiti Teknologi MARA, 40450 Shah Alam, Selangor, Malaysia
[d] Department of Chemical Engineering, Nagoya University, Furo-cho, Chikusa-ku, 464-8603, Nagoya, Japan

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ABSTRACT

In this research, shells of *Cyrtopleura costata*, commonly known as angel wing, were used to prepare sulfated calcined angel wing shell (CAWS) catalysts by a simple, low-cost method. The produced CAWS-SO_4 catalyst was characterized by using X-ray diffraction (XRD), Fourier transmission infrared spectroscopy (FTIR), temperature programmed desorption of CO_2 and NH_3 (CO_2-TPD and NH_3-TPD), BET surface area analysis and variable pressure scanning electron microscopy (VP-SEM). The esterification of palm fatty acid distillate (PFAD) by supercritical methanol was successfully performed to obtain the high fatty acid methyl esters (FAME) with yield of 98% at the optimum methanol/PFAD molar ratio of 6/1, 2 wt.% catalyst loading, 290 °C in 15 min. The catalyst could also be reused up to seven cycles with a FAME yield higher than 80% in the last cycle. The characterization of spent catalyst has been performed by using XRD, FTIR, TPD-NH_3 and SEM.

1. Introduction

The environmental issues associated with the burning of fossil fuels and the rapid depletion of crude oil reserves have encouraged many researchers to search for alternative and renewable energy resources. Biodiesel or fatty acid methyl esters (FAME), which can be produced either through transesterification of triglycerides or esterification of fatty acids with short chain alcohols in the presence of a catalyst or enzyme, are considered as the most attractive alternative energy sources since they are renewable, non toxic, biodegradable, and thus sustainable to the environment. In general, homogeneous alkali and/or acid– based catalysts are commonly utilized in biodiesel production. However, heterogeneous catalysts are more beneficial as they can be reused, easily separated and regenerated, while homogeneous catalysts lead to waste management problems during the biodiesel purification process [1]. Although alkali based catalysts can afford high yields of FAME at low temperatures, they happen to be active only for the transesterification of low free fatty acid (FFA) oils, for example palm, sunflower and soybean oil. This causes the biodiesel production to be expensive in the market and increases the food versus fuel concerns. On the other hand, acid based catalysts show activity only with high FFA oils (≥5 wt.%), for instance waste cooking oil (WCO) [2], grease [3] and palm fatty acid distillate (PFAD) [4]. These are known as low-cost feedstock for biodiesel production due to their availability and low value cost. In addition, the utilization of this feedstock also will add value to the waste as well as saving the environment.

More than a decade ago, an effective method for biodiesel production through a non-catalytic transesterification of vegetable oils in supercritical methanol was introduced by Saka and Kusdiana [5]. In their research, the biodiesel production by supercritical methanol was investigated by using rapeseed oil as feedstock and FAME was successfully obtained in a 95% yield with a 42:1 MeOH:oil molar ratio. However, the reaction was performed at very high temperatures between 350 and 400 °C and it consumed an excessive amount of methanol. This is not environmentally friendly and increases the biodiesel production costs. Thus, it was thought that the utilization of a cheap solid acid catalyst in the reaction system could improve and enhance the supercritical methanol reaction. An investigation was carried out by Lokman et al. [6], who reported that the esterification of PFAD by supercritical methanol produced FAME in 97.3 and 95.4% yield at the optimum reaction

* Corresponding author at: Catalysis Science and Technology Research Centre, Faculty of Science, Universiti Putra Malaysia, 43400, UPM Serdang, Selangor, Malaysia.
E-mail address: taufiq@upm.edu.my (Y.H. Taufiq-Yap).

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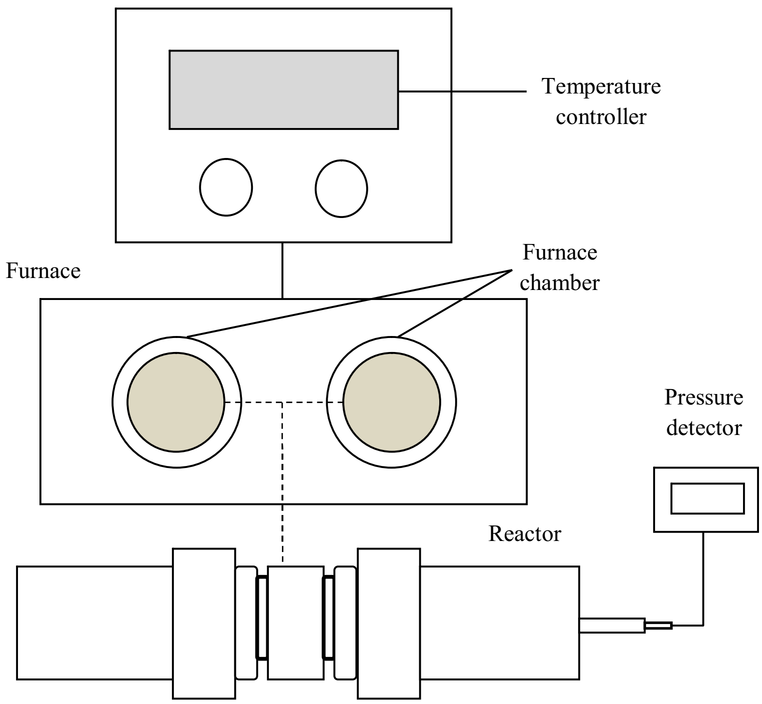

Fig. 1. Schematic diagram of a batch reactor for the esterification reaction in supercritical methanol.

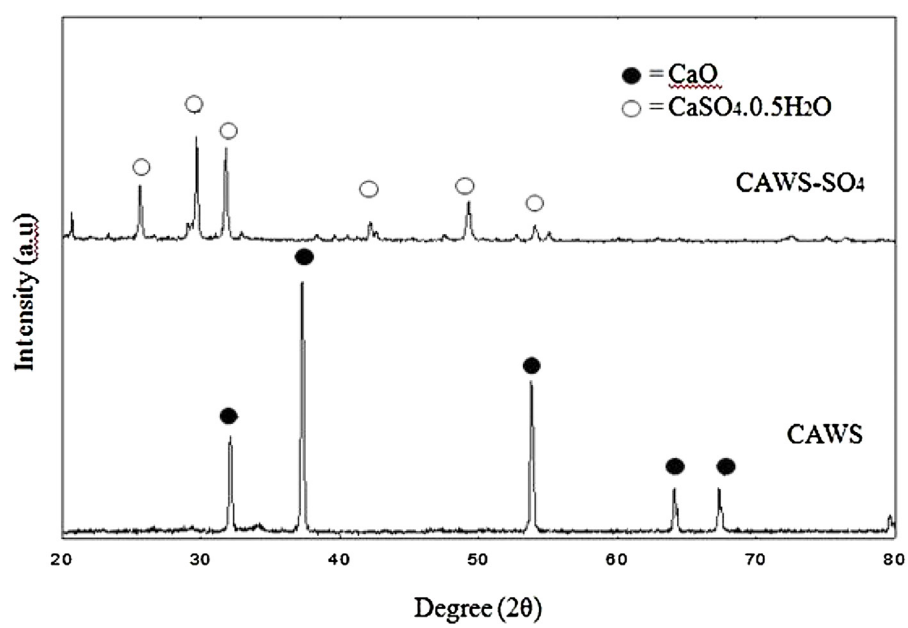

Fig. 2. XRD patterns of CAWS and CAWS-SO_4.

temperature of 290 °C, 6:1 methanol/PFAD molar ratio, 1 wt.% of catalyst amount of and 5 min reaction time, in the presence of sulfonated starch and glucose catalysts, respectively. Another study by Asri et al. [7] also described the transesterification of palm oil with a γ-alumina heterogeneous basic catalyst (CaO/KI/γ-Al_2O_3) in supercritical methanol. In this case almost 95% biodiesel yield was obtained at the optimum temperature of 290 °C, 1:24 ratio of oil to methanol, 3 wt.% catalyst amount over 60 min reaction time.

Recently, many types of heterogeneous acid carbon based catalysts were introduced for methyl ester production from high FFA oils, such as sulfonated carbon [8,9], sulfonated starch [10], biochar [11], and sulfonated carbon nanotube (CNT) [12] for the esterification of PFAD and others high FFA oils. Besides, the usage of sulfated transition metal oxides such as sulfated tin oxide [2], sulfated iron oxide [13–15], and sulfated zirconia [16,17] showed very high performance in the esterification process. However, these sulfated transition metal oxides are expensive. Therefore, the utilization of a low cost catalyst such as waste shell is expected to minimize the biodiesel production costs as well as aiding in waste management. Waste shells such as cockle shell [18], egg shell [19], and mud crab shell [20] gained interest as basic catalyst for biodiesel production since they consist of about 95% $CaCO_3$ that can be thermally converted to produce CaO. However, the consumption of these waste shell derived catalysts can only be used for low acid value feedstock.