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Biodiesel synthesis using heterogeneous catalyst in a packed-microchannel

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ABSTRACT

The goal of this research was to investigate the using of a packed-microchannel reactor to continuously synthesize biodiesel in a heterogeneous catalyst system. Calcium oxide (CaO) was used as a catalyst and was activated with methanol to enhance the catalytic performance for the transesterification reaction of palm oil. The synthesized activated CaO was characterized and confirmed by using X-ray diffraction (XRD), Brunauer-Emmett-Teller (BET), Hammett indicator and field emission scanning electron microscope (FE-SEM) techniques. The results indicated that the catalyst with higher surface area and total basicity was provided after activation and showed the higher catalytic activity compared to that of as-received CaO. The main important factors affecting the biodiesel synthesis were investigated and the optimal reaction conditions based on the purity of biodiesel were also determined. Complete reaction with the purity of biodiesel of 99% was achieved despite the short residence time used in this research. The optimal reaction conditions within the investigated parameter region were 65 °C, methanol-to-oil molar ratio of 24:1, and residence time of 8.9 min. The catalyst sustained high %FAME over 24 h of continuous operation. Furthermore, high fuel quality and superior productivity performance could be achieved via the packed-microchannel reactor.

1. Introduction

In recent years, biodiesel has been one of the most promising options to meet the energy challenges, especially in transportation sectors. Although, the biodiesel cannot fully substitute diesel fuel due to the several drawbacks such as more susceptible to oxidative degradation and higher viscosity than diesel fuel [1]. The biodiesel is still interesting to be the alternative fuel that will partially substitute diesel fuel because biodiesel is sustainable, economical, and environmentally friendly [2]. Furthermore, combustion efficiency of biodiesel is higher than that of petroleum-based diesel fuel [3]. As well, biodiesel is compatible with any conventional diesel engine without the need for modification [4].

Most of the commercial biodiesel is synthesized via transesterification of biological sources such as vegetable oil or animal fat with an alcohol in the presence of a homogeneous catalyst. However, homogeneous catalysts are susceptible to several technical problems that diminish their attractiveness. Homogeneous catalysts are toxic and corrosive agents and their high solubility in reaction substrates results in relatively poor product quality. Also, the product neutralization and washing step simultaneously consume chemical agent and considerable amounts of fresh water, making them economically unviable applications [5]. To overcome the above problems, there have been concerted attempts to replace the conventional homogeneous catalysts by heterogeneous catalysts, which are both non-toxic and non-corrosive. The catalyst can be easily separated and recycled several times. However, compared with homogeneous catalysts, the main problem encountered during the prolonged use of heterogeneous catalyst is partial or total deactivation of a catalyst. But this case, the recovery of catalyst activity is possible and achieved by many researchers [6–8]. In addition, besides chemical reaction limitations (due to the less catalytic sites), the mass transfer limitations are regarded as one of important issues that reflected the slow reaction rate of biodiesel synthesis due to the coexistence of immiscible reactants (oil and alcohol) and solid catalyst. There are many possible solutions for the mass transfer limited process such as microwave assisted technology [9], ultrasound irradiation technology [10] and supercritical fluid technique [11]. However, these technologies are associated with high operating cost and technological complexity compared

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to a stirred batch reactor. Therefore, the researchers are still pursuing a way to overcome the mass transfer problems without those barriers.

For the commercial biodiesel production, mass production with high yield and low operating cost is the key factor driving for the change from batch to continuous process. The packed-bed reactor is one of the most attractive reactor types for the continuous process due to its simple and easy operation, high production efficiency, and good mixing performance [12,13]. Many researchers have been studied and developed the packed-bed reactor for biodiesel synthesis. Table 1 shows some recent research studies on the use of packed-bed reactor for biodiesel synthesis and also presents their optimal operating conditions. Recent research studies in this table can be confirmed that the use of packed-bed reactor for biodiesel synthesis was achieved and interesting reactor performance was presented. Furthermore, the use of novel catalysts in a packed-bed reactor for biodiesel synthesis was the highlight of their works. For example, Melero et al. [14] synthesized the agglomerated Zr-SBA-15/bentonite catalyst for biodiesel synthesis in a packed-bed reactor. They found that this catalyst exhibited high catalytic activity for the transesterification of waste cooking oil. Calcium oxide, a common catalyst used in batch reactor, was firstly applied in a packed-bed tubular reactor for biodiesel synthesis by Miladinovic et al. [15]. They showed that the catalyst had high catalytic activity and stability and also demonstrated that the degree of catalyst leaching during the reaction was less than those found in batch reactor and could be ignored. A review of literature has shown that a packed-bed reactor is considered as one of the promising reactor for continuous biodiesel synthesis.

Many researchers reported that transesterification reaction performance was affected by mass transfer limitations, reaction kinetics, thermodynamic equilibrium in both batch and continuous processes and with both solid and liquid catalysts [17–20]. For continuous packed-bed reactor for biodiesel synthesis particularly at low Reynolds number, the reaction was controlled mainly by external mass transfer (bulk to surface catalyst) [12,20]. Microreactor technology offers the potential for enhancement in mass transfer rate due to the small diffusion distance characteristic leading to the fast and efficient heat dissipation and mass transfer. It can be easily scaled out from lab-scale to the industrial capacity by numbering-up of a single channel and higher production volume per unit of manufacturing area can be achieved. The recently published of successful applications of microreactor for biodiesel synthesis with short residence times are also shown in Table 1. All reports claim that microreactor provided much better quality of biodiesel in a shorter reaction time compared with that of batch reactor [21–23]. A number of literature reviews have been published on the development of biodiesel synthesis via homogeneous catalyst in a microreactor, on the other hand, the study of biodiesel synthesis via heterogeneous catalyst in a microreactor has rarely been published. Thereupon, it is important to thoroughly investigate the possibility of synthesizing biodiesel via heterogeneous catalyst in the packed-microchannel reactor.

Amongst various solid catalysts that have been studied for transesterification, calcium oxide (CaO) has attracted intensive interest as inexpensive catalytic material with relatively high basicity accommodating modest reaction conditions. Several reports have been published using commercial CaO catalyst [24,25] and many works also have been carried out to enhance the activity of this catalyst by doping with alkali metals like Li, Na and K [26,27] or mixed with other oxides such as NiO [7] and ZrO_2 [28]. However, this rather costly pretreatment method requires a series of procedure such as drying and calcination. One of the promising alternative methods is to activate CaO with methanol. A series of articles has been published by the research group of Teo et al. [29,30] and Thram et al. [31]. They successfully applied methanol for the activation of CaO in order to convert into calcium methoxide ($Ca(OCH_3)_2$) with superior catalytic activity. The synthesized catalyst provided much higher transesterification conversion than that of CaO.

The use of CaO catalyst should be thorough and thoughtful even with the received CaO from the commercial manufacturer [25] because the surface sites of calcium oxide can be deactivated easily upon contact with room air. This is due to the adsorption of carbon dioxide and moisture leading to the formation of carbonate and hydroxyl species, which are almost inactive for biodiesel synthesis. This challenge can be overcome by changing some inactive species to the active form by thermal treatment. Li and co-workers [32] employed the thermal treatment to activate the CaO catalyst by using thermogravimetric analysis (TGA). The calcination at 700 °C for 1 h successfully transformed the inactive calcium based compounds into CaO as confirmed by X-ray diffraction analysis (XRD).

This paper represents the first step toward pioneering the use of a packed-microchannel for biodiesel synthesis with CaO catalyst. The effects of operating conditions were necessary to be investigated in order to realize the important factors affecting the biodiesel synthesis. The optimized conditions were also determined based on the FAME content. In addition, as-received CaO was anal-

Table 1
Biodiesel synthesis studies in a various reactor types.

Raw material	Alcohol	Catalyst	Time[c]	Ratio[d]	Temp[e] (°C)	Yield (%)	Ref.
Reactor type: packed-bed reactor							
Waste cooking oil	Methanol	Zr-SBA-15 /bentonite 28 g	0.5 h	50:1	210	95.0	[14]
Sunflower oil	Methanol	CaO 328 g	2 h	6:1	60	98.5	[15]
Palm oil	Methanol	$Ca/Zn/Al_2O_3$[b] 135 ml	6 h	30:1	65	96.8	[16]
Reactor type: microchannel reactor							
Pork lard	Methanol	KOH 1.3 wt.%	5 s	65	6:1	95.4	[21]
Palm oil	Methanol	KOH 1 wt.%	5 s	60	6:1	97.1	[22]
Waste cooking oil[a]	Methanol	KOH 1 wt.%	5 s	65	9:1	91.7	[23]

[a] A two-step esterification-transesterification process.
[b] Premixing of catalyst with commercial methyl ester.
[c] Residence time.
[d] Methanol-to-oil molar ratio.
[e] Reaction temperature.

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