Energy Conversion and Management 115 (2016) 191–199

Contents lists available at ScienceDirect

Energy Conversion and Management

journal homepage: www.elsevier.com/locate/enconman

Biodiesel production using heterogeneous catalysts including wood ash and the importance of enhancing byproduct glycerol purity

Bijaya K. Uprety [a], Wittavat Chaiwong [b], Chinomnso Ewelike [c], Sudip K. Rakshit [d,*]

[a] Department of Biotechnology, Lakehead University, Thunder Bay, Canada
[b] Department of Food Engineering and Bioprocess Technology, Asian Institute of Technology, Thailand
[c] Department of Chemical Engineering, Lakehead University, Thunder Bay, Canada
[d] Biorefining Research Institute (BRI), Lakehead University, Ontario, Canada

ARTICLE INFO

Article history:
Received 7 December 2015
Accepted 10 February 2016

Keywords:
Biodiesel production
Heterogeneous catalyst
Birch wood ash
Flyash
CaO and CaO/γ-Al_2O_3
Palm oil

ABSTRACT

Transesterification of vegetable oils or animal fats with methanol in the presence of catalysts produces fatty acid methyl esters (FAME) and glycerol as a co-product. This study was focused on a comparative study of the transesterification of refined, bleached and deodorized palm oil (RBD palm oil) using a heterogeneous catalysts CaO with and without γ-alumina (γ-Al_2O_3) as a support. The results were also compared to that using sodium hydroxide (NaOH), which is a homogenous catalyst. Parameters like the amount of catalyst, the molar ratio of methanol to oil, reaction time and reaction temperature that affect methyl ester and glycerol formation were analyzed and the optimum conditions were determined. The FAME and glycerol content (96.75% and 92.73% respectively) obtained using CaO were lower in purity compared to that using CaO/Al_2O_3 (97.66% and 96.36% respectively). In the second phase of our work, wood ash from two different sources (birch bark & flyash from a biomass based power plant), which were calcined at 800 °C were studied for their potential use as a cheap renewable alternative heterogeneous catalyst. Both the wood ash samples were found to have good potential for use in such production process, but needs to be optimized further to obtain biodiesel which meets fuel biodiesel specifications. Both CaO and CaO supported on alumina produces FAME to levels that meet the fuel specifications required for blending with diesel. However, the latter produces a purer form of byproduct glycerol that can be easily converted to value added products, without the need for purification. On this basis the supported catalyst is recommended for use in industry as it can add to profits in integrated plants which produces biodiesel and simultaneously uses the byproduct glycerol for value added products.

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1. Introduction

Biofuels and renewable forms of energy are being developed to substitute conventional fossil fuels due to the finite nature, fluctuating costs and climate effects of the latter. Biodiesel has attracted considerable attention as it offers several advantages. It is a mixture of fatty acid alkyl esters derived from renewable feedstock such as vegetable oils or animal fats. Although there are several methods to produce biodiesel, fatty acid methyl esters (FAME) are commonly produced by the transesterification of triglycerides with alcohol. The resultant product has physical and chemical characteristics similar to petroleum based diesel. Therefore, biodiesel can be used in diesel engines without further modification [1]. The advantages of biodiesel over conventional diesel fuel include a high flash point, high cetane number, low viscosity, high lubricity, biodegradability, and environmentally friendly nature as it emits lower levels of carbon monoxide and sulfur dioxide [2].

Transesterification reactions for fatty acid alkyl ester formation can be catalyzed by acids, bases and enzymatic catalysts. Glycerol is produced as a co-product to a level of 10% (w/w) of the biodiesel produced [3]. With the increase in production of biodiesel over the years, there is a simultaneous accumulation of huge amounts of glycerol (also known as crude glycerol) which contains considerable amounts of impurities. Purification of crude glycerol into pharmaceutical and technical grade glycerol is an expensive process and is not commercially feasible for small and medium sized biodiesel industries [3–5]. Additionally, direct conversion of crude glycerol into value added products is hindered by the presence of toxic impurities. An alternative biodiesel production process which produces purer glycerol together with biodiesel which meets fuel

* Corresponding author. Tel.: +1 807 343 8415.
E-mail addresses: buprety@lakeheadu.ca (B.K. Uprety), wittavat@gmail.com (W. Chaiwong), cuewelik@lakeheadu.ca (C. Ewelike), srakshit@lakeheadu.ca, skrait57@gmail.com (S.K. Rakshit).

http://dx.doi.org/10.1016/j.enconman.2016.02.032
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specifications is very important for the biodiesel industry [3,4,6]. This can bring larger profits to the overall biodiesel production process by cutting the cost involved in the downstream processing and make possible the use of glycerol to produce various value added products.

Conventionally, sodium or potassium hydroxide and alkoxides are the common homogenous base catalysts used in this reaction under mild conditions and results in high yields of methyl esters in short reaction times [7]. However, its solubility in the reaction medium leads to formation of soap via saponification which is a serious problem because it reduces biodiesel yield, consumes catalysts and causes significant difficulties in product separation and purification [8]. The use of acids such as sulfonic acid, sulfuric acid and hydrochloric acid as catalysts in biodiesel production can eliminate soap formation from free fatty acid. But the rate of reaction is slower than the use of basic catalysts and also needs high reaction temperatures [9–11]. Enzymatic reaction is highly specific and chemically clean, however the production of a lipase catalysts are considerably costlier compared to a chemical catalyst [10]. Therefore, heterogeneous alkali catalysts are being studied to overcome these problems. The latter can be easily separated, reused and regenerated due to their low solubility and consumption in the reaction. However, heterogeneous catalyst also have some drawbacks such as mass transfer limitation, low active sites availability for catalyst reaction and in some cases they leach into the reaction media. In order to address these issues, various types of catalyst supports (mainly alumina, silica, zinc oxide and zirconium oxide) have been used for biodiesel production [7,11–13]. Alumina, is the most commonly used catalyst support for biodiesel production because of its enhanced thermal and mechanical stability, high specific surface area (as high as 300 m^2/g), large pore size (5–15 nm), large specific pore volume (0.6 cm^3/g) and ability to be shaped into pellets and extruded. In general, attaching catalysts to a supports, like alumina, increases surface area and number of pores for active species. This minimizes the diffusion limitations, a major problem with the use of heterogeneous catalyst, thus improving the rate of reaction [14]. In comparison to the unsupported CaO catalyst, the composite catalyst (CaO/Al_2O_3) has a larger specific surface areas and more active sites and pores. This facilitates the attachment of large triglyceride molecules with the active catalyst species [14].

This study involves biodiesel production starting from refined, bleached and deodorized palm oil (RBD palm oil) by transesterification using heterogeneous catalyst with and without support. The optimum conditions were determined taking into account the conversion to methyl esters, glycerol yield and purity. The quality of biodiesel produced was then evaluated to see if it meets the specifications of commercial biodiesel.

Calcium oxide (a solid heterogeneous catalyst) has a high basicity, low solubility, low price and is easy to handle. However, the transesterification reaction it catalyzes is inadequate for practical applications due to mass transfer limitations as mentioned above [13,15]. Aluminum oxide has been widely used as a support in catalysis processes and many researchers have tried to attach various compounds, including calcium oxide, for the efficient production of biodiesel [16]. However, little work involving a comparative study of calcium oxide and calcium oxide attached to γ-alumina under similar reaction conditions has been reported, in spite of the known advantages of attached catalyst. In our study, the results from these two catalysts have also been compared to sodium hydroxide, a homogeneous catalyst.

Additionally, we also explored the possibility of utilizing wood ash from two different sources (birch bark and flyash from a power station) as a cheaper alternative heterogeneous catalyst to carry out the transesterification reaction. Ash from birch bark is considered an alternative source of calcium oxide and magnesium oxide as they are present in higher levels compared to other woody plants [17,18]. Utilization of ash from birch bark can serve as a reusable catalyst that is widely available in Canada and various other parts of the world. Flyash acquired from Ontario Power Generation Inc. (Canada) was utilized to convert triglyceride into biodiesel in our experiments. This is one of world's first power plants that has been retrofitted from a coal based unit to biomass-fueled power generation plant. Every year it produces large amount of flyash, which can serve as a cheap catalyst. Flyash has limited large scale applications besides being used as a soil stabilizer [19,20]. Hence, utilization of this flyash would be of economic importance for the biodiesel industry. Finally, this paper also tries to make a case, that if a higher purity byproduct glycerol stream can be produced, then it can be used on-site to produce higher value products and increase profits of an integrated plant.

2. Materials and methods

2.1. Materials

The vegetable oil used in this research study was refined, bleached and deodorized (RBD) palm oil which was obtained from Oleen Company Limited, Bangkok, Thailand. The properties and fatty acid composition of the palm oil as provided by the supplier is tabulated in Tables 1 and 2 below. All the chemicals used in this work were of analytical reagent grade and obtained from Sigma Aldrich, Fisher Sci & Merck.

2.2. Preparation of catalyst

Calcium oxide (CaO) supported on alumina (γ-Al_2O_3) was prepared using an impregnation method of an aqueous solution of calcium acetate on alumina support. In this method [1], γ-alumina in powder form was preheated to 600 °C for 1 h to remove absorbed water. It was then added to 100.54% w/v solution of cellulose acetate precursor in distilled water. The mixture was stirred for 4 h at 60 °C. The obtained slurry was heated overnight in an oven. Prior to its use in the transesterification reaction, CaO/Al_2O_3 was calcined in furnace at 718 °C for 5 h. Similarly, pure CaO was prepared by calcination at 600 °C for 4 h.

Birch bark obtained from Trowbridge Falls Park (Canada) was cleaned with water and dried at 80 °C for 24 h in an oven. After 24 h, dried bark was burnt to obtain ash. Similarly, flyash from burnt wood pellets was obtained from Ontario Power Generation Inc., Atikokan, Ontario (Canada). Both these ash powder were calcined at 800 °C for 4 h before they were utilized to catalyze the transesterification of palm oil [21].

Table 1
Properties of refined, bleached and deodorized (RBD) palm oil used in this study.

Properties	Unit	Limits	Method	RBD palm oil
Density at 15 °C[a]	kg/m^3	860 min and 900 max	ASTM D 1298	910
Kinematic viscosity[a]	cSt	3.5 min and 5.0 max	ASTM D 445	44.5155
Free fatty acid (as palmitic acid)[b]	%	0.1% max	A.O.C.S Ca 5a-40	0.06
Peroxide value[b]	meq/kg	2.0 max	A.O.C.S Cd 8-53	0.56
Moisture and impurities[b]	%	0.10% max	A.O.C.S Ca 2c-25	0.03
Iodine value[b]	–	50–55	A.O.C.S Cd 1-25	51.57

[a] European standard specification for biodiesel fuel in EN 14214-2003.
[b] Thai industrial standards for palm oil in TIS 288-2521.

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