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Synthesis of biodiesel from low FFA waste frying oil using calcium oxide derived from *Mereterix mereterix* as a heterogeneous catalyst

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ABSTRACT

Biodiesel was produced from waste frying oil (WFO) using powdered calcined clamshell (*Mereterix mereterix*) as a heterogeneous catalyst. Clamshell calcined at 1173 K for 2.5 and 3.5 h showed different catalytic activities. Calcination for 3.5 h resulted in a catalyst of higher activity and reduced transesterification reaction time. The raw and calcined clamshells were characterized by XRD, FTIR, XRF spectroscopy and BET analysis. The XRD peaks showed the characteristics peaks of CaO at $2\theta = 37.4$, 47.3, and 54.4°. A few high intensity peaks of $Ca(OH)_2$ at $2\theta = 17.9$ and 34.1° in the calcined catalyst were also obtained which might have formed due to exposure of CaO with atmospheric air. The used catalyst showed peaks at 8.2 and 10.1° which were characteristic of calcium glyceroxide which was formed due to reaction of calcium oxide and glycerol. Formation of $Ca(OH)_2$ in the calcined clamshell was also confirmed by FTIR spectra which showed a sharp OH^- stretching band. The catalyst was found to comprise principally of calcium (97%) and a few minor elements (Si, Na, Fe, Al, Sr, S, Mn) as analyzed by XRF. The surface area of the calcined clamshell was found to be 2.6 $m^2\ g^{-1}$. The optimum values for various parameters were found to be 3.0 g of catalyst and 25 ml of methanol per 100 ml of oil (6.03:1, methanol to oil molar ratio) at 333 K in 3 h. A high yield (>89%) and conversion (>97%) were obtained on optimization of variables. With the mandatory compulsion by National Biofuel Policy in India to blend 20% of biofuels i.e. bioethanol and biodiesel in the spark ignition and compression ignition engines respectively from 2017 strengthens the applicability of the present study that utilizes waste resources as feedstock and catalyst in the production of a green fuel i.e. biodiesel.

1. Introduction

One of the prominent alternatives to fossil fuels is biodiesel that is derived from oils containing triglycerides and can be converted to saturated and unsaturated long chain fatty acid alkyl esters (FAAE) by esterification or transesterification (Fazal et al., 2011). Apart from the edible and non-edible oils, it can also be obtained from a variety of other feedstock viz. waste cooking/frying oils, microalgal oil, and can also be obtained from animal fats (Sharma and Singh, 2009; Jorgensen et al., 2012). Biodiesel has shown an improved environmental performance in comparison to conventional mineral diesel on its usage (Tsoutsos et al., 2010). It has been found that by blending biodiesel in mineral diesel, on combustion, reduces the emission of particulate matters, hydrocarbons, and carbon monoxide to a substantial extent with only minor power loss (Xue et al., 2011).

Synthesis of biodiesel requires a catalyst for the fast completion of the esterification and transesterification reactions. Although the reaction can be carried out without a catalyst by supercritical method, the process utilizes a high amount of methanol and its recovery requires additional energy inputs, thus making the overall process cost intensive (Kiwjaroun et al., 2009). The catalyst that is employed for synthesis of biodiesel is either homogeneous or heterogeneous (Stamenkovic et al., 2011). The common homogeneous catalysts are sulfuric acid (an acid catalyst); potassium hydroxide, sodium hydroxide, and sodium methoxide (alkaline catalysts). These catalysts have shown a very good catalytic activity with a high yield and conversion of biodiesel (Sharma et al., 2008). Nevertheless, their separation from biodiesel requires washing with water which results in loss of FAAE, consumes energy, and generates wastewater (Raita et al., 2011).

The problems posed by conventional homogeneous catalysts can be overcome by the use of heterogeneous catalysts (Endalew et al., 2011). Such catalysts can also be reused which makes them

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economically attractive. These catalysts are of two types – solid acid and solid base. Solid acid catalyst is preferred when the feedstock oil is of high acid value where simultaneous esterification and transesterification take place (Serio et al., 2008). Solid base catalysts are suitable for low acid value feedstock oils. Solid base catalyst is also used for transesterification after the acid value of the feedstock is lowered by esterification. A wide range of solid acid and solid base catalysts have been tried by researchers for esterification and transesterification of triglycerides. Solid acid catalysts commonly used are heteropoly acid, resins, sulfated zirconia, and zeolite (López et al., 2005; Morin et al., 2007; Özbay et al., 2008; Giannakopouloua et al., 2010). Solid base catalysts that have been commonly used as heterogeneous catalysts include calcium oxide, hydrotalcite, magnesium oxide, and solid superbase (Dossin et al., 2006; Liu et al., 2008; Sun et al., 2008; Zeng et al., 2008). Another group of heterogeneous catalyst is enzymes which can act on the soil water interface phase. They can also be immobilized on a material such as resin or other matrix as support (Liu et al., 2011a, 2011b). Recent researches put forward that an enzyme, combined lipase as catalyst can greatly reduce the cost for synthesis of biodiesel. The cost of the combined lipase process comes to only 0.15 Yuan Renmingbin per liter biodiesel (Liu et al., 2010). The production of biodiesel using enzymes as catalyst has already started at industrial scale at Yueyang City, Hunan province, P.R. China with the capacity of 20,000 ton per year of biodiesel.

The key issue for a large scale application of biodiesel is its high cost as compared to that of conventional petroleum based diesel (Silalertruksa et al., 2011). The high cost of biodiesel is due to the scarcity of the feedstock oil as both the edible and the non-edible oils are limited. Though, the non-edible oils may be diverted as feedstock for biodiesel production, they have other applications viz. manufacture of soap. Also, the arable land is a scarce resource that has to be utilized meticulously and should not be utilized for cultivation of biofuel crops (Ponton, 2009). The cost of biodiesel can be reduced if a waste feedstock and/or a waste catalyst is used in the synthesis process. The used cooking oil is often discarded in sewers and in soil which degrades the environment (Giracol et al., 2011). Hence, any attempt to utilize the used cooking oil for biodiesel feedstock will serve the dual purpose of prevention of environmental degradation and energy generation. Waste oil has been tried as feedstock for synthesis of biodiesel by several researchers (Leung and Guo, 2006; Lou et al., 2008; Lapuerta et al., 2008; Özbay et al., 2008; White et al., 2011). The major constraint, however, is an irregular supply of oil and lack of awareness (Lin and Li, 2009). Along with the feedstock, waste materials can be used as catalyst to further reduce the biodiesel cost. Recent studied have explored the potential of various waste materials as heterogeneous catalyst for synthesis of biodiesel.

Table 1 depicts various waste as raw materials material used as heterogeneous catalyst (Boey et al., 2009; Nakatani et al., 2009; Wei et al., 2009; Sharma et al., 2010; Viriya-empikul et al., 2010). Among these, calcium oxide has been the commonly used solid base catalyst for the transesterification of triglycerides. The mechanism that is involved in the transesterification reaction is the formation of methoxide anion from the reaction occurring from methanol–oxygen ion and methanol–hydroxide ion. The methoxide ion attacks the carbonyl carbon of the triglyceride molecule to form a tetrahedral intermediate which upon rearrangement forms methyl ester and a diglyceride molecule. The same reaction proceeds with diglyceride where monoglyceride and ester are formed. In the last step a methyl ester and glycerol are formed. This thus results in the formation of three molecules of methyl ester from a triglyceride molecule (Boey et al., 2009).

The productivity of CaO in terms of yield of FAAE is similar to that obtained with NaOH and is preferred over the latter as it can be recovered for reuse and is thus environment friendly (Zhang et al., 2010). Calcium oxide is in general characterized by high strength of basic sites of $15.0 < H\_ < 18.4$ and surface area of 13 $m^2\ g^{-1}$ (Kouzu et al., 2008). Unlike NaOH, CaO is less sensitive to the presence of small amounts of water in the reaction medium. Hydration of calcium oxide prior to calcination has shown enhancement in its catalytic activity (Yoosuk et al., 2010). Zhang et al. (2010) reported that the presence of water (0.41%) in CaO enhanced the reaction rate for biodiesel synthesis. It has also been reported that the CaO surface easily gets covered with moisture when exposed to ambient air and the exposed surface is converted to $Ca(OH)_2$. The $Ca(OH)_2$ on dissociation (being soluble to some extent in methanol, i.e. 0.035 wt %) forms OH^- ion which on interaction with methanol gives CH_3O^-. This enhances the overall catalytic activity of CaO (Granados et al., 2007; Veljkovic et al., 2009). Eggshell and clamshell are a good source of calcium carbonate (Chen et al., 2010). The clamshells are abundant in the source river, the Ganges as well as the Indian coasts including the estuaries and backwaters along the east and west coast of India. The world production of clams in 1966 was 5,00,000 m tons. In Indian scenario, the total production of all mollusks (unclassified) during 1961–1966 was 100, 100, 300, 500, 300, and 1000 m tons respectively as per the data provided in Food and Agriculture

Table 1
Selected list of reported work on biodiesel production using CaO derived from biological calcareous deposits.

Source	Oil	Calcination temperature, time (h)	Reaction details	Reference
Oyster shell	Soybean	700 °C, –	Catalyst amount = 25 wt% Reaction time = 5 h Yield > 73.8% Conversion = 98.4% wt	Nakatani et al., 2009
Scylla serrata	Refined palm olein	700 °C, 2	M:O mass ratio = 0.5:1 Catalyst amount = 5 wt% Reaction temperature = 65 °C Stirring rate = 500 rpm	Boey et al., 2009
Eggshell	Soybean	1000 °C, 2	M:O molar ratio = 9:1 Catalyst amount = 3 wt% Yield > 95% after 3 h	Wei et al., 2009
Eggshell	*Pongamia pinnata*	900 °C, 2	M:O molar ratio = 8:1 Catalyst amount = 2.5 wt% Yield = 95% Conversion = 97.4% in 2.5 h at 65 ± 0.5 °C	Sharma et al., 2010
Mollusk & eggshell	Palm olein oil	800 °C, 2–4	Yield > 95% M:O molar ratio = 12:1 Reaction temperature = 60 °C Catalyst amount = 10 wt%	Viriya-empikul et al., 2010

M:O Methanol to oil.
– Not Stated.