COMBUSTED MOLLUSCS SHELL AS SOLID BASE CATALYST FOR TRANSESTERIFICATION TO PRODUCE BIODIESEL IN AN ULTRASONIC FIELD

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FEBRUARY 2016

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5. Report

5.1 Proposed Executive Summary

The production of biodiesel can significantly reduce harmful emissions and contributing to domestic energy security(Eevera et al., 2009). For the production of biodiesel, triglycerides, the major component of vegetable oils undergoes transesterification with alcohol to form esters in basic conditions(Van Gerpen et al., 2004).However, (Kouzu et al., 2008) suggest that the common base used for such reaction such as potassium hydroxide (KOH) and sodium hydroxide (NaOH) can lead to massive wastewater discharge to wash the dissolved alkali-hydroxide. They suggest the use of calcium oxide (CaO) which is milder. Although the transesterification reaction rate of CaO is lower than KOH and NaOH, the catalytic activity can be improved by calcination process(Granados et al., 2007). Ultrasonic energy can also improve transesterification reaction using CaO as catalyst (Stavarache et al., 2005). It was also reported that ultrasonic field can accelerate transesterification reaction due to effective emulsification compared to the conventional mechanical stirring condition(Hanh et al., 2009). This is because ultrasonic irradiation can produce emulsions of immiscible liquids thus increasing the reaction area(Mason & Phillip, 2002).

In Malaysia, the shellfish industry flourish with the support of the government and it was estimated that the industry to produce 130 000 tons per year mainly in the form of cockles (Sulaiman K., 2007). With that estimation, the problem for shell disposal can be predicted. The need to dispose of mollucs shells from the food industry namely oyster shell lead to researchers to investigate its usage as transesterification catalyst for biodiesel production(Nakatani et al., 2009).Molluscs shell such as oyster and cockles also have high content of calcite(Yoon et al., 2003). Thus, calcium oxides can be produced from combusted molluscs shell(Nakatani et al., 2009).Commercially available calcium oxides are usually produced from combusted calcium carbonate stones.

5.3 Introduction

Among the most critical problems that threat humanity towards a sustainable future are the depletion of fossil resources and environmental pollution. The attention is currently turned towards the use of biomass or biomass-derived materials as substitute to petroleum fuel (Badday et al., 2012). Biodiesel is considered an alternative energy to the widely used petroleum-derived diesel fuel since it can be generated by domestic natural sources such as soybeans, rapeseeds, coconuts and even recycled cooking oil and hence reduces the dependence on the depleting petroleum fuel (Balat & Balat, 2010).

Biodiesel is a mixture of mono alkyl esters with long chain fatty acids that is derived from vegetable oils or animal fats (Van Manh et al., 2011).Some of the advantages of using biodiesel over petroleum based diesel is that it is biodegradable, can be used without modifying existing engines and produces less harmful gas emissions such as sulfur oxide (Helwani et al., 2009). In addition, biodiesel reduces net carbon dioxide emission by 78% on a life-cycle basis when compared to conventional diesel fuel (Tyson, 2001).

There are four methods to produce biodiesel from biological resources namely direct use and blending, micro-emulsion, thermal cracking and transesterification. Transesterification can be defined as chemical reaction of vegetable oil or animal fat with alcohol in presence of a catalyst to form glycerol and ester(Boro et al., 2012). It is the most commercially favourable method since the other methods are not economical in terms of production cost (Atabani et al., 2012)

Transesterification is mainly affected by the methanol and oil molar ratio, catalyst, reaction temperature and reaction time. Generally, biodiesel production via transesterification can be catalyzed in four basic routes viz. base-catalyzed, acid catalyzed, enzyme catalyzed and non catalytic transesterification (Demirbas, 2009).Among the different routes mentioned, the preferred method is the base-catalyzed transesterification of vegetable oils with simple alcohol producing high purity and yield of biodiesel product at lower process temperatures (Freedman et al., 1986).

Although transesterificationis usually carried out with homogeneous base catalystssuch as sodium hydroxide and sodium methoxide, heterogeneousbase catalysts have their own advantages: reusability, simpler operational procedures, easier catalyst, and product separation, reduction in the amount of wastewater produced, and they are not very sensitive to water (Ebiura et al., 2005; Xie & Li, 2006).Among the heterogeneous base catalysts that are being used in transesterificationreaction, CaO has a promising place and many reportshave been published on CaO-catalyzed transesterification(Granados et al., 2007; Kouzu et al., 2008; Liu et al., 2008).

5.4 Brief Literature Review

Biodiesel production employing homogeneous base-catalyzed process is still favourable due to the fact that it is kinetically much faster than heterogeneously catalyzed transesterification and is economically viable (Wang & Yang, 2007). The high consumption of energy and costly separation of the homogeneous catalyst from the reaction mixture, however, have called for development of heterogeneous catalyst(Helwani et al., 2009). Most of these catalysts are alkali or alkaline oxides. Calcium oxide, CaO used as a solid basic catalyst possesses many advantages such as long catalyst lifetimes, higher activity and requirement of only mild reaction conditions. The reaction rate, however, was slow in producing biodiesel because the reaction mixture is a three-phase system (oil-methanol-catalyst) in which mass transfer diffusion usually limits the overall reaction rate(Leung et al., 2010; Liu et al., 2008).

The use of heterogeneous catalysts significantly simplifies the process of separation and purification of the products, reduces environmental problems, allows reuse of the catalysts and contributes to positive economic effect. Among the heterogeneous catalysts that are being used in transesterification reaction, CaO has a promising place and many reports has been published on CaO-catalysed transesterification using laboratory grade CaO(Gryglewicz, 1999; Kawashima et al., 2009; Liu et al., 2008).However, the utilization of waste materials as heterogeneous catalysts has been of recent interest for sustainable process. CaO has attracted much attention due to the fact that there are several natural calcium sources from wastes such as egg shells or mollusc shells. These shells are composed of calcium oxide that can be used as a catalyst for the production of biodiesel(Cho & Seo, 2010; Viriya-Empikul et al., 2010).

Pioneering work in the transesterification of vegetable oil with egg shell as heterogeneous catalyst has suggested an easy way of 'green' catalyst synthesis (Wei et al., 2009). Based on this study different researchers have also proposed the utility of industrial waste shell as catalyst not only for biodiesel production but also in other fields of catalysis. Shrimp shells(Yang et al., 2009), shells of golden apple snail and meretrixvenus(Viriya-Empikul et al., 2010), oyster shell (Nakatani et al., 2009), mud crab shell (Boey et al., 2009)are some of the examples which have been successfully used by the researchers as heterogeneous catalysts for biodiesel production. It is reported that these catalysts can be reused, are environmental friendly and at the same time add value to the recycled waste (Boro et al., 2012).

Characterization results on the use of waste shells as a source of calcium oxide to transesterify palm olein into biodiesel revealed that the main component of shell was calcium carbonate which is transformed into calcium oxide when activated above 700^{o}C for 2 hours. Parametric studies were conducted and optimal conditions found to be methanol/oil mass ratio, 0.5:1; catalyst amount, 5 wt.%; reaction temperature, 65^{o}C; and a stirring rate of 500