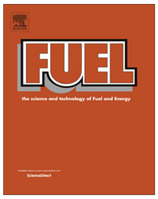
Fuel xxx (2015) xxx–xxx

Contents lists available at ScienceDirect

Fuel

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



The application of calcined marlstones as a catalyst in biodiesel production from high free fatty acid coconut oil

Phaedra Jaggernauth-Ali, Ejae John *, Puran Bridgemohan

Waterloo Research Centre, University of Trinidad and Tobago, Trinidad and Tobago

HIGHLIGHTS

- Calcined marlstones were used as catalysts in the transesterification reaction.
- Calcined marlstones and sodium hydroxide comparably catalyze transesterification.
- A higher biodiesel yield was produced with calcined white marlstones as the catalyst.
- Gas chromatography spectra confirmed the presence of methyl esters.

ARTICLE INFO

Article history:
Received 9 July 2014
Received in revised form 6 May 2015
Accepted 12 May 2015
Available online xxxx

Keywords:
Marlstone
Transesterification
Biodiesel
Heterogeneous catalyst
Catalyst characterization

ABSTRACT

The price of biodiesel compared with petrodiesel is sufficiently high to be a deterrent to consumers. By utilising calcium oxide catalysts, the cost of one of the operational inputs, the catalyst amount, can be decreased. These catalysts are derived via calcination from calcium carbonate containing materials such as marlstones. This research investigated the catalytic potential of two types of marlstones in the transesterification of high free fatty acid (FFA) non-edible coconut oil. The marlstones were calcined at 700, 900 and 1000 °C for 1.5, 2 and 3 h. For the transesterification reaction, 5 and 15 wt% catalyst were used at 2 h reaction time, 60 °C and a 6:1 methanol to oil molar ratio in the presence of vigorous stirring. 15 wt% catalyst for both red and white marlstones produced yields $\geqslant$90%. The highest yield of 97% was produced by 15 wt% white marlstones calcined at 1000 °C and 1.5 h, with an additional 6 calcined marlstones producing yields $\geqslant$90%. All marlstones where yield was $\geqslant$90% were fully characterized for surface morphology, elemental analysis, functional group analysis and basicity.

1. Introduction

Biodiesel is a renewable, readily available, and environmentally attractive alternative to petroleum-based diesel. Comprised of monoalkyl esters of long chain fatty acids produced by transesterification of methanol and vegetable oil or animal fats, it has characteristics so similar to conventional diesel it can be used in a compression ignition engine with little or no modifications [1].

One of the major challenges to biodiesel mass production is its higher consumer price relative to petroleum-based diesel [2]. This non-competitive position on the supply market is due to its production cost. Although the feedstock, 60–75% of production cost, has been determined as the most expensive operational input [3], another important cost is that of the catalyst.

Feedstock costs can be decreased using unrefined non-edible oils, animal fats and waste oils instead of refined oils [4,5]. However, one drawback to using these lower cost feedstocks is that they contain higher free fatty acid (FFA) values than recommended for base transesterification. When the FFA content is >0.5% [6], the free fatty acids react with the alkaline catalysts to form soap. This inhibits the separation of the methyl esters from glycerol, as well as augments the formation of emulsions whilst washing. As such, an acid catalyzed esterification step to decrease FFA content before base catalyzed transesterification is recommended [1,7]. In this study, a non-edible, lower cost, high FFA coconut oil was chosen as the triglyceride source.

Currently, homogeneous alkaline or acid catalysts are used commercially [3]. Of these, the alkaline homogeneous catalysts such as sodium hydroxide are more frequently used due to their high rate of catalysis [8]. There are several drawbacks to the use of homogeneous alkaline or acid catalysts: difficulty in separating the catalyst from the product mixture, lack of catalyst reusability, environmental disposal considerations, operational problems

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* Corresponding author. Tel.: +1 (868) 223 8888x32236.
E-mail addresses: phaedra.jaggernauth@utt.edu.tt (P. Jaggernauth-Ali), ejae.john@utt.edu.tt (E. John), puran.bridgemohan@utt.edu.tt (P. Bridgemohan).

http://dx.doi.org/10.1016/j.fuel.2015.05.022
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Please cite this article in press as: Jaggernauth-Ali P et al. The application of calcined marlstones as a catalyst in biodiesel production from high free fatty acid coconut oil. Fuel (2015), http://dx.doi.org/10.1016/j.fuel.2015.05.022

linked to the hazardous, caustic and hygroscopic nature of the catalyst and reaction being highly energy intensive [3,7]. In addition to the direct cost of the catalyst itself, these factors add indirect costs to the process [8].

The challenges of using these caustic homogeneous catalysts can be addressed by using low cost, environmentally friendly heterogeneous catalysts. Calcium carbonate ($CaCO_3$) rich raw materials such as eggshells [9,10], crab shells [11], oyster shells [12], clam shells [13], mussel shells [14], animal bone waste [15,16] and dolomites [17–19] can be converted via calcination to calcium oxide (CaO), a recognized catalyst for transesterification [3,8,20,21]. Calcination is the process of drying solids at high temperatures, typically 300–800 °C [22]. During calcination of the organic shells, bone waste and dolomitic rock, carbon dioxide is removed from the carbonate structure such that the $CaCO_3$ content is converted to the more catalytically active, porous CaO.

Marlstones, the raw material of interest in this research, are similar to dolomites as they are calcium carbonate rich but non-waste rock sources, and are therefore a potential catalyst for transesterification. Marl generally refers to white, yellowish brown or dark yellowish brown deposits of calcium carbonate and clays, silts or sands, and can contain between 35% and 65% calcium carbonate with some reports listing the content at 98% [23]. Red marlstones are present in excess of 100 million tonnes in the city of Mayo in Trinidad [24]. Beyond Trinidad and Tobago, marlstones can also be found in the Venetian Region in northern Italy [25] and the Valley and Ridge Province of Virginia, USA. As such, marlstones are a sustainable source of potential catalysts.

The objectives of this study were to (a) investigate the potential of the low cost, environmentally friendly calcined marlstones (both red and white) to be a viable catalyst in the transesterification of high FFA non-edible coconut oil, and (b) to investigate the required time and temperature to calcine the marlstones. Catalyst concentrations of 5 and 15 wt% were selected for the transesterification reaction. Although NaOH concentrations have been reported with high yields from as low as 0.5 to 2 wt% of oil [1,26], heterogeneous catalysts require higher concentrations due to their larger particle sizes and because the process is highly mass transfer limited due to its immiscible liquid/liquid/solid 3-phase system [3]. Highest methyl ester yields were obtained with calcined $CaCO_3$ catalyst concentrations ranging from 3 wt% – 25 wt% [9–16,19]. Our 5–15 wt% therefore encompassed a low to medium range of catalyst concentrations. The higher range values of 20–25 wt% were not considered as previous research indicated that large catalyst quantities encourage the formation of slurries with subsequent mixing challenges and increased power consumption [9,27].

The temperatures and times at which calcination occurs influence the quantity of conversion of the carbonate to the oxide. The calcination times previously investigated were constant in the experimental designs and ranged from 2 h to 6 h [9–14,16,17]. Apart from clam shells being calcined at 900 °C [13], ostrich egg shells at 800 °C [10] and dolomite rocks at 900 °C [17], calcination temperature was varied and its effect on catalyst properties were examined in the literature. Bovine bone waste was calcined between 350 and 1100 °C [16] and animal bone waste between 200 and 1000 °C [15]. Powder X Ray Diffraction (XRD) data for calcined bovine bones indicated that CaO conversion was complete at >950 °C [16] and Fourier Transform Infra Red (FTIR) spectral peaks of calcined animal bones indicated that carbonate was present at 200–600 °C but disappeared through 800 °C until absent at 1000 °C [15]. Calcined marine shells included those of oyster, crab and mussels. Oyster shells were calcined from 100 to 1000 °C [12], crab shells from 700 to 900 °C [11] and mussel shells from 550 to 1050 °C [14]. First appearance of CaO with the $CaCO_3$ in XRD results occurred at 700 °C for both oyster shells [12] and crab shells [11] and at 750 °C for mussel shells [14]. XRD patterns were those of only CaO at 800 °C for calcined oyster shells [12], 750 °C for calcined crab shells [11] and 950 °C for calcined mussel shells [14]. Eggshells [9] were calcined from 200 to 1000 °C with the XRD results indicating that, like oyster and crab shells, first appearance of CaO peaks occurred at >700 °C but complete conversion to CaO occurred at 800 °C [9]. Niu, Huo, Lu, Liu, & Li (2014) conducted calcinations on dolomites from 700 °C to 950 °C, and from thermogravimetric analysis, observed that the carbonates in the dolomites were completely converted to CaO at over 750 °C [19]. Thus, the time and temperature of marlstone calcination was varied at 1.5, 2 and 3 h and 700, 900 and 1000 °C. The shortest time and lowest temperature of 1.5 h and 700 °C, respectively, were included to determine if economic viability in the transesterification reaction can still be achieved whilst decreasing fuel consumption required for catalyst preparation. From previous research, CaO is produced under the other conditions of 2 h [9,11,14] and 3 h [12,17], as well as 900 °C [11–13,17] and 1000 °C [9,12,14,15]. Thus, these were also included to ensure the reaction occurred. Characterization properties were examined in order to determine any correlations between the physical properties of the catalysts and its performance in the transesterification reaction.

2. Methods

2.1. Materials

Marlstones were obtained from the Central Range in the Republic of Trinidad and Tobago: the white marlstones (MW) from Coryal and the red marlstones (MR) from Mayo. Non-edible coconut oil sold under the brand name Roland Gopaul (RG) was purchased in Trinidad, Trinidad and Tobago. Analytical grade sodium hydroxide, calcium oxide, methanol and sulphuric acid were used in the transesterification reactions.

2.2. Catalyst preparation

The MR and MW marlstones were received as ground particles and sieved such that the effective particle size was in the range 38–425 μm. They were dried at 100 °C for 2 h in a Gallenkamp Hotbox Oven and stored in a dessicator. A Nabertherm Furnace, range 30–3000 °C, was used to calcine the marlstones. In this study, three calcination temperatures of 700, 900 and 1000 °C [9,11–15,17] and calcination times of 1.5, 2.0 and 3.0 h [9,11,12,14,17] were selected based on previous literature for the conversion of the marlstones to the catalyst.

2.3. Catalyst characterization

A Phillips SEM 515 scanning electron microscope (SEM) equipped with EDAX (Energy Dispersive X-ray Analysis) was used to examine the surface structure and elemental composition. A qualitative assessment of the elemental composition was also completed using a Thermo Scientific Nicolet 380 Fourier Transform Infrared (FTIR) spectrometer with horizontal attenuated total reflectance (HATR) and multi-bounce crystal.

The basic strength of the materials was tested using Hammett indicators. The following indicators were used: neutral red ($pK_{BH+} = 6.8$), bromothymol blue ($pK_{BH+} = 7.2$), phenolphthalein ($pK_{BH+} = 9.3$), nile blue ($pK_{BH+} = 10.1$), 2,4-dinitroaniline ($pK_{BH+} = 15.0$) and 4-chloro-2-nitroaniline ($pK_{BH+} = 17.2$). 25 mg of the sample was weighed and 1 ml of indicator in methanol added to it. This mixture was left for 2 h to equilibrate and the colour noted. The base strength was quoted as being stronger than the weakest base that exhibited a colour change but weaker than the strongest indicator that produced no colour change [17,28].

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