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Cavitation assisted synthesis of fatty acid methyl esters from sustainable feedstock in presence of heterogeneous catalyst using two step process

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ABSTRACT

The present work reports the intensification aspects for the synthesis of fatty acid methyl esters (FAME) from a non-edible high acid value Nagchampa oil (31 mg of KOH/g of oil) using two stage acid esterification (catalyzed by H_2SO_4) followed by transesterification in the presence of heterogeneous catalyst (CaO). Intensification aspects of both stages have been investigated using sonochemical reactors and the obtained degree of intensification has been established by comparison with the conventional approach based on mechanical agitation. It has been observed that reaction temperature for esterification reduced from 65 to 40 °C for the ultrasonic approach whereas there was a significant reduction in the optimum reaction time for transesterification from 4 h for the conventional approach to 2.5 h for the ultrasound assisted approach. Also the reaction temperature reduced marginally from 65 to 60 °C and yield increased from 76% to 79% for the ultrasound assisted approach. Energy requirement and activation energy for both esterification and transesterification was lower for the ultrasound based approach as compared to the conventional approach. The present work has clearly established the intensification obtained due to the use of ultrasound and also illustrated the two step approach for the synthesis of FAME from high acid value feedstock based on the use of heterogeneous catalyst for the transesterification step.

1. Introduction

In recent years, synthesis of fatty acid methyl esters (FAME) based on esterification or transesterification reactions has gained worldwide attention due to number of applications in perfume and flavor industry and also due to the use of biodiesel as a source of alternative fuel [1–4]. For the specific use of FAME as biodiesel, it is important to note that the biodiesel demand in India is increasing with rapid industrialization, globalization and rapid changing lifestyle and considering the fact that India is planning to use biodiesel blend B20 by 2017, the expected increase is at a rate of 6.2% per annum. Biodiesel is a mixture of alkyl esters, which can be used in conventional compression ignition engines, without any significant modifications. Transesterification has been generally used for the synthesis of fatty acid esters from vegetable oils and animal fats using homogeneous catalyst (mainly sodium or potassium hydroxide dissolved in methanol). Traditional homogeneous catalysts (basic or acid) possess advantages including high activity and requirement of mild reaction conditions (from 40 to 65 °C and atmospheric pressure). However, the use of homogeneous catalysts can lead to soap formation especially in the case of feedstock with high free fatty acid content. The total cost of the production using homogeneous catalysis, is not yet sufficiently competitive as compared to the cost of diesel production from petroleum.

An alternative approach for synthesis of fatty acid methyl esters can be based on the use of heterogeneous catalysts. Use of heterogeneous catalyst can be helpful in avoiding the soap formation (produced in presence of the homogenous alkali catalyst) and also reduce the load on the downstream processing of separations possibly leading to considerable saving in terms of energy requirements and avoiding wastewater generation. There have been many studies reported in the literature relating to the synthesis of biodiesel using heterogeneous catalyst [5–8]. Georgogianni et al. [5] studied the transesterification of rapeseed oil in the presence of heterogeneous catalysts (Mg MCM-41, Mg–Al Hydrotalcite, and K+ impregnated zirconia), using low frequency ultrasound reactor (24 kHz). It has been reported that Mg–Al hydrotalcite gives the highest activity with 97% conversion in a reaction time of 5 h. Biodiesel synthesis from *Jatropha curcas* oil using solid catalyst Na/SiO_2 in the presence of ultrasound gave yield of 98.53% at optimal molar ratio of oil to methanol as 1:9, catalyst concentration of 3 wt% of oil and 15 min of reaction time [6]. The ultrasound assisted biodiesel synthesis from palm oil [7] gave yield of 77.3%

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(CaO), 94.2% (SrO) and 95.2% (BaO) for a reaction time of 60 min. The optimum parameters for the ultrasound assisted biodiesel synthesis from soybean oil were catalyst (CaO) loading of 6 wt%, temperature of 62 °C, and molar ratio of oil to methanol as 1:10. The approach of ultrasound assisted biodiesel synthesis from palm oil using calcium oxide was reported to give a yield of nearly 100% in 2 h of the operation [7]. The reported work in the literature on heterogeneous catalyzed biodiesel synthesis in the presence of ultrasound has concentrated mainly on the feed stock (virgin oil) with lower acid value requiring only one step processing. The current work presents a novel approach of intensification of two step processing for the sustainable feed stock containing higher acid value (which is expected to create problems of soap formation if used with alkaline catalyst) based on the use of heterogeneous catalyst. The feedstock used in the present work is Nagchampa oil containing higher amount of the oil (65–70%) which is almost twice as compared to the other non-edible feedstock like Karanja (25–30%), Jatropha (30–35%) [9]. Nagchampa is abundantly found in the costal part of the India. The major problem associated with Nagchampa as a feedstock is initial higher amount of free fatty acid (31 mg of KOH/g of oil), which requires more processing like two stage approach of esterification (to reduce the free fatty acid content) followed by transesterification [9]. It is important to note here that the two step synthesis is highly energy intensive operation and hence investigating the process intensification aspects with an objective of decreasing the material/temperature requirement is significant. In the past, the various approaches used for intensification of biodiesel synthesis include ultrasound, microwave, use of supercritical conditions, hydrodynamic cavitation, etc. [1–5]. Process intensification using cavitational reactors can be a promising approach due to the fact that operation is at ambient conditions and the physical effects of cavitation such as liquid circulation associated with turbulence can eliminate the mass transfer resistances and mixing issues associated with esterification/transesterification [9,10]. The work also presents comparison of the FAME synthesis from Nagchampa oil using conventional reflux method with ultrasound assisted approach to establish the degree of intensification. The effect of molar ratio, catalyst concentration and temperature has been investigated for both the steps of esterification and transesterification.

2. Materials and methods

2.1. Materials

The raw Nagchampa oil was procured from M/s Amit Oil Mill, Vengurla, Dist: Sindhudurgah, Maharashtra, India. The chemical composition of Nagchampa oil is Palmitic acid as 12%, Stearic acid as 13%, Oleic acid as 34.1%, Linoleic acid as 38.3% and Linolenic acid as 0.3%.

Methanol (HPLC grade), sulfuric acid (98%) (A.R.) and hexane (HPLC grade) were obtained from M/s Thomas Baker Chem. Pvt. Ltd., Mumbai, India. Calcium oxide (A.R.) was obtained from S.D. Fine-Chem. Ltd., Mumbai, India.

2.2. Reactor configuration

The reactions were performed in a 5.0 cm (ID), 150 cm^3 capacity glass reactor equipped with reflux condenser. Reactor was kept in a water bath to maintain constant temperature. Water bath was procured from M/s Ganesh Scientific Industries, Mumbai, India and has provision for maintaining the temperature within ±1 °C. A pitched blade glass stirrer having 1 inch diameter was used to achieve uniform mixing of the reactants in the conventional approach. The schematic representation of experimental setup is shown in Fig. 1a.

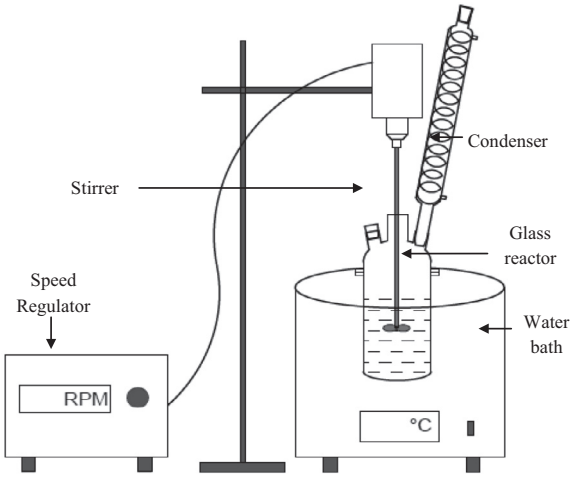

Fig. 1a. Experimental setup for conventional approach.

The equipment used to study the effect of cavitation on synthesis was an ultrasonic horn, procured from M/s Dakshin Pvt. Ltd. Mumbai, India. Ultrasonic horn operates at a frequency of 20 kHz with a power rating of 120 W. The ultrasonic horn was fitted with a piezoelectric transducer with a tip diameter of 1 cm and immersed to a depth of 1 cm below the liquid level in a 150 ml capacity glass reactor. Reactor was kept in a water bath to maintain desired temperature within ±1 °C. The typical arrangement of the experimental setup used for the ultrasound assisted approach is shown in Fig. 1b.

2.3. Experimental methodology

100 ml of Nagchampa oil was taken in a glass reactor and preheated to the desired value. After 10 min, when the temperature of oil uniformly remained constant, mixture of methanol (at the desired molar ratio) and sulfuric acid was added in appropriate proportions for the first stage of esterification. The acid value was checked after every 1 h of reaction time. After reaching the constant acid value, esterified oil was kept for phase separation for 4 h in a separating funnel. The lower layer was separated and upper acid layer was used for second stage. The upper layer from first stage esterification was now taken in the reactor and kept for 10 min so as to reach constant temperature. Calculated amount of catalyst (H_2SO_4) and methanol was added. The acid value was checked after every 1 h of time. After reaching the desired acid value, esterified oil was kept for phase separation for 4 h in separating funnel. For preparing the catalyst to be used in the actual reaction, CaO was heated to remove moisture and volatile matter

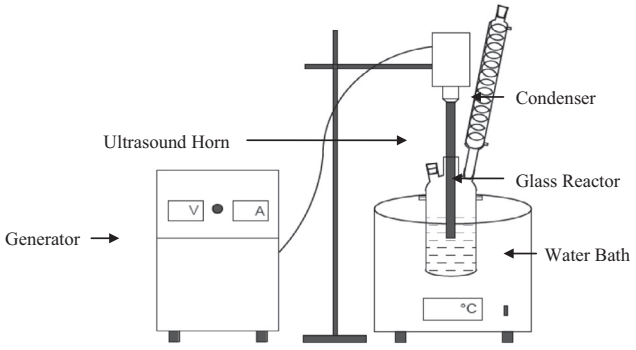

Fig. 1b. Experimental setup for ultrasound assisted approach.

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