Chemical Engineering and Processing 71 (2013) 70–76

Contents lists available at ScienceDirect

Chemical Engineering and Processing: Process Intensification

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

Hydrodynamic cavitation as an efficient approach for intensification of synthesis of methyl esters from sustainable feedstock

Vitthal L. Gole, K.R. Naveen, Parag R. Gogate*

Chemical Engineering Department, Institute of Chemical Technology, Matunga, Mumbai 40019, India

ARTICLE INFO

Article history:
Received 14 September 2012
Received in revised form 9 October 2012
Accepted 15 October 2012
Available online 23 October 2012

Keywords:
Methyl esters
Process intensification
Hydrodynamic cavitation
Non-edible oil
Two step approach

ABSTRACT

Investigations related to process intensification of synthesis of methyl esters from sustainable feedstock is gaining importance because of considerable energy requirements and higher reaction time in the conventional approach. The present work illustrates the use of hydrodynamic cavitation for intensification of methyl ester synthesis from the high acid value non-edible oil. Two-step synthesis of acid esterification followed by alkaline transesterification has been employed for obtaining the methyl esters. In first step, acid esterification is used to reduce the acid value of oil from 18.7 to less than 1.5 mg of oil/g of oil beyond which alkaline transesterification can be used without any problems of soap formation. The molar ratio and catalyst concentration have been optimized for the esterification and transesterification stages. The optimized molar ratios were 1:3 and 1:6 for esterification and transesterification respectively. Under optimized conditions, 92% conversion has been obtained in the transesterification stage. It has been established that due to the use of hydrodynamic cavitation, the energy requirement for the synthesis is significantly reduced as compared to the conventional approach. The novel route discussed in the present work provides a viable option and can be explored easily for the industrial scale of operations.

1. Introduction

Nagchampa is known for higher amount of the oil content and is found in the coastal parts of India, and some other Asian and African countries. The fresh Nagchampa flower is also a rich source of fragrance, which is mainly attributed to the presence of multi-component mixture of natural and synthetic aromatic materials. Due to these facts, the esters prepared from the oil extracted from this natural source have an excellent prospect in the cosmetic industries and also these materials can be effectively used for the medicinal applications. The synthesis of methyl esters from this feedstock is highly energy intensive and slow operation as it requires considerable processing due to higher initial acid values [1,2]. Generally, the two-step processing of acid esterification followed by alkaline transesterification is used, which requires more amount of energy and time for processing. Thus there is need to develop sustainable process intensification technology for methyl ester synthesis from non-edible oil sources with an objective of reducing the overall production cost. There are various process intensification technologies based on the use of alternate energy sources such as ultrasound and microwave, which can be effectively applied to meet the demand of cutting edge technologies [3]. The reported literature illustrates that these technologies can significantly intensify the process by multifold [3–8] but scale up of these reactors has been a great challenge.

The rate of synthesis of methyl esters is controlled by the mass transfer effect. The physical effect of cavitation such as the micro-emulsification and streaming eliminates mass transfer resistances in the process. Acoustic and hydrodynamic cavitation can produce these effects. Acoustic cavitation is produced by passing ultrasound (frequency of sound > 16 kHz) through the liquid medium and it has limitation of non-uniform cavitational density. These limitations can be overcome by hydrodynamic cavitation, which can simply be generated by the passage of the liquid through a constriction such as throttling valve, orifice plate, and venturi [9]. At the constriction, due to a sudden increase in the velocity of liquid, the local pressure falls down and with adequate adjustments of the geometry and operating flow rate, the local pressure can be lowered enough below the vapor pressure of the medium at the operating temperature. This results into generation of cavities, which travel downstream and are subjected to pressure fluctuations giving rise to different stages of the cavitation phenomena. Very high intensities of turbulence are created downstream of the constriction which helps in reducing in the mass transfer limitation of the process [4]. Hydrodynamic cavitation has been widely used for the wastewater treatment, but very few works can be observed in literature for esterification/transesterification processes resulting in synthesis of methyl esters.

* Corresponding author. Tel.: +91 22 33612024; fax: +91 22 33611020.
E-mail addresses: pr.gogate@ictmumbai.edu.in, paraggogate@yahoo.co.in (P.R. Gogate).

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http://dx.doi.org/10.1016/j.cep.2012.10.006

The earlier reports dealing with the use of hydrodynamic cavitation reactors for synthesis of methyl esters are based on the single stage processing. Kelkar et al. [5] investigated the esterification of fatty acid cuts using concentrated H_2SO_4 as a catalyst in the orifice plate hydrodynamic cavitation reactor [5] and observed that the cavitational yield for hydrodynamic cavitation was more than the acoustic cavitational approach under the conditions of optimized molar ratio of reactants as 1:10 and 1% catalyst concentration with reaction time as 180 min. Another investigation dealing with alkali catalyzed transesterification of soybean oil reported that the acoustic and hydrodynamic cavitation processing operations are more efficient than the conventional mechanical stirring approach [6]. Another work on alkali catalyzed transesterification of rapeseed oil reported that the hydrodynamic cavitation reduced the processing time requirement and enhanced the conversion from 96 to 99% compared to the conventional operation [7]. All the studies have indicated that the hydrodynamic cavitation reactors can be effectively used for the one step synthesis at ambient conditions of operating pressure and temperature and with energy requirements lower than the conventional reflux based high temperature processing. A drawback of the earlier works is that the starting material is based on the use of edible oil which cannot be considered as a sustainable feedstock due to the issues related to the food security. Also these studies have been for the feed stock with lower initial free fatty acid content resulting into comparatively easier one step synthesis approach. The present work is based on using hydrodynamic cavitation reactors for the intensification of methyl ester synthesis using Nagchampa oil as a sustainable raw material, which is a very good prospect due to significantly higher oil content (~65%–75%) [10]. However, the synthesis of fatty acid methyl esters from this feedstock has certain limitations in terms of the high initial free acid content (18–20 mg of KOH/g of oil). Due to the high initial acid content, transesterification is not recommended due to the operational problems pertaining to the soap formation during the processing and acid based esterification can result in much slower synthesis rates. The novelty of the present work is that intensification of synthesis of methyl esters based on non-edible oils with high-acid-value content has been investigated using a two-stage process of acid esterification followed by alkaline transesterification in the presence of cavitating conditions generated by hydrodynamic means. Similar studies have not been reported in any of the earlier works to the best of our knowledge. Also, a comparison has been made with conventional approach for synthesis and approach based on the use of sonochemical reactors. The obtained results are likely to be applicable to any other non-edible oils such as Karanja, Jatropha, Neem, Cotton, and also other waste sources such as waste vegetable oil and waste cooking oil, which are considered to a good feedstock for the synthesis of biodiesel. Over the years, biodiesel from the non-edible sources has been considered as one of the promising options with an objective of reducing the production costs which has hampered effective utilization of biodiesel as an alternative to the conventional fossil based fuels. Thus, the overall importance of the current work is clearly established.

2. Materials and methods

2.1. Materials

The raw Nagchampa oil was procured from M/s Sanjay Shirsat Oil Mill (Vengurla, Dist: Sindhudurg, Maharashtra, India). The initial acid value for the oil was observed to be 18.7 mg of KOH/g of oil. Sulfuric acid (98% concentrated), methanol, ethanol, and potassium hydroxide (GR grade), as well as methanol and hexane (HPLC grade), were procured from M/s Omkar Traders, Mumbai.

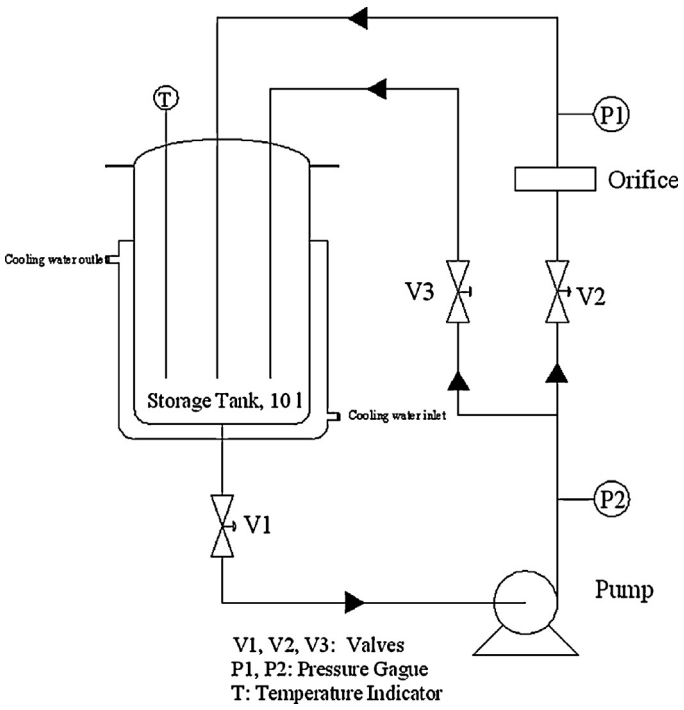

Fig. 1. Schematic representation of hydrodynamic cavitation reactor.

HPLC standards of methyl oleate and methyl linoate were procured from M/s Sigma–Aldrich. All the chemicals were used as received from the supplier.

2.2. Reactor configurations

The hydrodynamic cavitation reactor used in the present work consists of a reservoir with 10 l capacity that is connected to a multistage centrifugal pump with power rating of 1.5 kW. The centrifugal pump is the main device for energy dissipation in hydrodynamic cavitation reactor. The schematic representation of hydrodynamic cavitation reactor has been shown in Fig. 1. The suction side of the pump is connected to the bottom of tank. The discharge from the pump is divided into two branches which helps in control of the inlet pressure and the inlet flow rate into the main line housing the orifice (flange is used to accommodate the orifice plate) with the help of valves V_2 and V_3. The pressure gauges P_2 and P_1 are used to measure the inlet and fully recovered downstream pressure respectively. The operating temperature of the reactor was maintained below the boiling point of methanol by circulating water in the surrounding jacket. The circulation of water is required to counter the heat energy dissipation due to the cavitating events.

2.3. Experimental procedure

The oil procured from supplier was used without any pretreatment. The two-step processing of esterification followed by transesterification was used for the synthesis of methyl esters. In esterification, oil, methanol and sulfuric acid in appropriate proportions were initially mixed together. The reaction volume was kept constant for all runs. The withdrawn samples of the reaction mixture at regular interval were taken in a flask, cooled to room temperature and kept for separation. The acid value of the lower layer was measured to monitor the progress of the reaction. In second stage, alkaline transesterification was carried out using the esterified oil as the starting raw material in the presence of potassium hydroxide as a catalyst. The heavier glycerin layer was separated from the transesterified product using