

Process Intensification for Biodiesel Production via Transesterification Reaction, Using a Hydrodynamic Cavitational Reactor System

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Abstract: Productions of biodiesel from fish oil and methanol via transesterification were carried out in a reactor system consisting of a hand-made hydrodynamic cavitational mixer, as well as in a conventional stirred reactor system, for comparison purpose. With a starting mixture of methanol/fish oil (molar ratio = 6/1), reaction temperature of 60°C, and homogeneous catalyst (NaOH in methanol, 1wt% of fish oil), 92% conversion of fish oil was obtained in the cavitational mixer connected reactor system after only 1 minute of reaction, while the reaction time needed to reach the same conversion in conventional reactor is 90 minutes. It is postulated that this is caused by the improved mass transfer, induced by an increase in interfacial area of the mixture after being subjected to the hydrodynamic cavitational mixer. Therefore, the hydrodynamic cavitational mixer is believed to intensify the transesterification process, and allows (i) the use of a smaller amount of NaOH catalyst; (ii) the use of heterogeneous solid metal oxide catalysts for the reaction; and (iii) continuous biodiesel production to become achievable.

Keywords: Biodiesel, Alternative Green Fuels, Process Intensification, Transesterification, Hydrodynamic Cavitation

Introduction:

Biodiesel is a type of biofuels that could effectively replace traditional diesel. It has various advantages including high biodegradability; decreased emission of exhaust gases; more complete combustion [1 - 4]. Being monoesters of fatty acids originated from vegetable oils or animal fats, biodiesel can be synthesized via transesterification reactions between oils/fats and alcohols – most commonly methanol – in a presence of an acidic or basic catalyst. Basically, methanol is used in excessive, with the typical methanol/oil molar ratio of 6/1. The transesterification is a heterogeneous reaction, occurring only on the interfacial surfaces of the two immiscible liquid phases (oil and alcohol); and proceeds relatively slowly [5]. Therefore, current biodiesel production technology is based on batch process with moderate efficiency.

Intensifying biodiesel production efficiency is basically to increase the reaction speed. This can be done when the mass transfer effectiveness is enhanced. In another words, the reaction speed increases when the interfacial surface's area increases. Fine dispersion of methanol droplets in oil phase becomes the key for this purpose. Several methods for increasing surface areas have been investigated to achieve this goal. One of those is the preparation of micro-emulsion reaction mixture via use of microwave energy [5]. With this technique, interfacial surface areas increase significantly. However, this method has been proved to be costly and could still only be realized in a batch process. Another method involves the use of a co-solvent, in which solvents like tetrahydrofuran, dimethyl ether, acetone, isopropyl alcohol are used in order to enhance solubility of methanol in oils [6]. The drawback of this method lies in the difficulty of co-solvent removal from the product.

Very fine dispersion of methanol in oil, in fact, could be considered as the formation of an emulsion system, and could be achieved as a result of cavitation process. Cavitation phenomenon occurs when the pressure of the fluid suddenly drops below the saturated vapor pressure of that fluid, creating many vapor bubbles, which will consequently collapse as the pressure increases again. The bubbles generations/collapses take place continuously with high frequency, leading to the formation of an emulsion of two immiscible fluids [7]. Some authors [8,9] reported the use of cavitation effect in biodiesel production, however, details on apparatus and equipment design and the capability of improved reaction process effectiveness, in comparison with traditional technology, were not well documented.

In this paper, we report experimental results and comparisons when the transesterification reactions are carried out in a traditional stirred tank reactor and a home-made cavitational mixer connected reactor. Along with these results, the process intensification ability of the newly designed reactor system is evaluated in terms of reduced reaction time and catalyst amounts used to complete the reactions.

Materials and Methods:

Materials

Basa-fish fat (with an average molecular weight of 845g/mol) was purchased from Delta AGF, An Giang Province, Vietnam, having acidic index of 4.27 mg KOH/g. Methanol (purity of 98%); NaOH (as catalyst), and all other chemicals were of industrial grades and purchased from local chemical providers.

Equipment setups

The cavitation mixer (Cavitator) connected reactor system was designed and fabricated by our group.

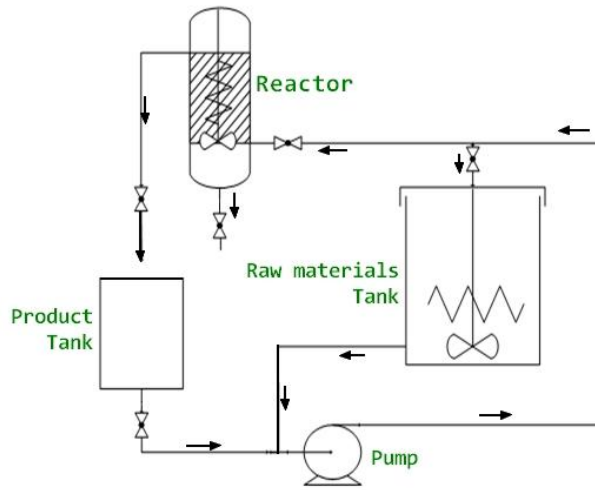


Fig. 1. Scheme of the reactor system.

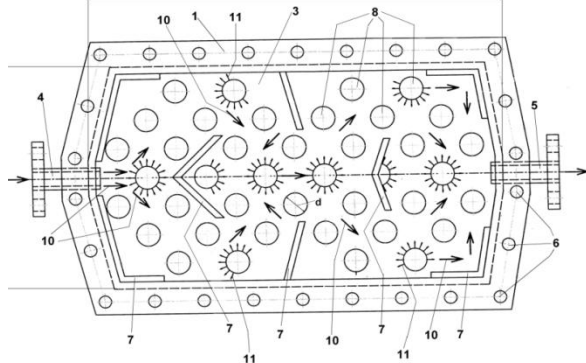


Fig. 2. Design of Cavitator includes (1) Cavitator's housing; (3) flow orientation frame; (4) inlet; (5) outlet; (7) flow orientation elements; and (8) collision elements.

Reaction procedures:

In traditional stirred tank reactor

Fish fat was fed to a 3 necked reactor equipped with a mechanical stirrer and heated to 60oC. Methanol, with a proper amount of NaOH catalyst pre-added, was then added to the reactor, and the stirrer was turned on and set to 500 rpm to start the reaction. Samples were taken from the reaction mixture every 5, 10, 30, 50, 70, 90 and 120 minutes to determine the correspondent conversions of fish fat.

In the newly developed reactor connected with Cavitator

Fish fat and methanol (with proper amount of NaOH catalyst pre-added) were added to the raw materials

Scheme of the reactor system is given in Fig. 1; while principal design for Cavitator is described in Fig. 2.

tank, gently mixed and heated to 40oC. The reactants mixture was then pumped through Cavitator and then to the reactor, where the temperature was set to 60oC. From the reactor samples were taken every 1, 2, 3.5, 5 and 10 minutes in order to determine the correspondent conversions.

Analysis methods

Determination of conversion of fish fat

The conversion of fish fat was read, as an interpolated value, from a viscosity vs. methyl ester content calibration curve. At the beginning of the reaction, the viscosity was high, and then decreased during the reaction as the result of the formation of methyl esters. At 100% of conversion, the viscosity reaches its theoretical minimum. A calibration curve describes the variation of viscosities with different methyl ester contents was built by preparing different methyl ester/fish fat mixtures and measuring these mixtures' viscosity at 40oC in accordance with ASTM D445.

The methyl ester content in final biodiesel product was double checked by taking measurements with a GC-MS device.

Determination of average size and density of dispersed methanol in fish fat

Average methanol droplet size and density were determined by cell counting method, employing an electronic microscope to observe the emulsion sample. The photos are captured with a digital Canon EOS D2 camera. Four samples were prepared and coded M1, M2, M3 and M4. M1 was prepared by mixing methanol and fish fat in a conventional mechanical mixer in 1 hr; while M2, M3 and M4 were prepared in the Cavitator in 1, 5 and 10 mins, respectively.

The formula used to calculate the number of droplets in 1 mm³ of reaction mixture is as follows:

$$A = \frac{B}{5 \times 16 \times 0.05^2 \times 0.1} = B \times 50$$

In which: A – droplet density;
B – numbers of droplets in one big square, which includes 16 smaller squares sized 0.05 × 0.05 mm.

Average droplet size, d_{TB}, was estimated as:

$$d_{TB} = \frac{2,5 \times x_1 + 7,5 \times x_2 + 12,5 \times x_3 + 17,5 \times x_4 + 22,5 \times x_5}{x_1 + x_2 + x_3 + x_4 + x_5} \text{ (um)}$$

In which, x₁, x₂, x₃, x₄, x₅ are the numbers of methanol droplets of different size ranges of 0~5; 5~10; 10~15; 15~20; and 20~25 um, respectively.

Results and Discussion:

Fish fat conversion in the reactor systems at the same reaction conditions

GC-MS spectrum of biodiesel product is given in Fig. 3. It can be observed that biodiesel consists of methyl esters of mainly C₁₆ and C₁₈ fatty acids that exist in the fish fat. The appearances of these esters' peaks in the spectrum show that the

transesterification reactions have occurred. As the reaction proceeds, the viscosity of the reaction mixture decreases gradually, therefore, the conversion of fat could be tracked by measuring the viscosity. Fig. 4 shows the viscosity vs. methyl ester content calibration curve used in this study.

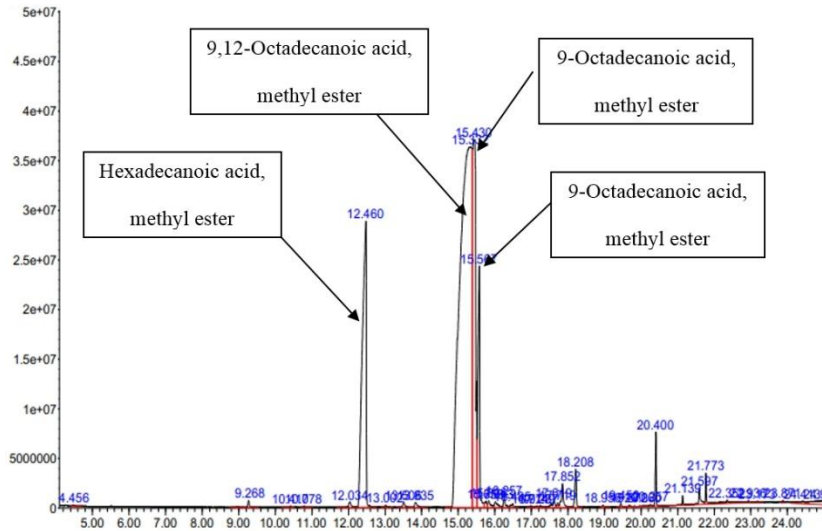


Fig. 3. GC-MS of biodiesel product

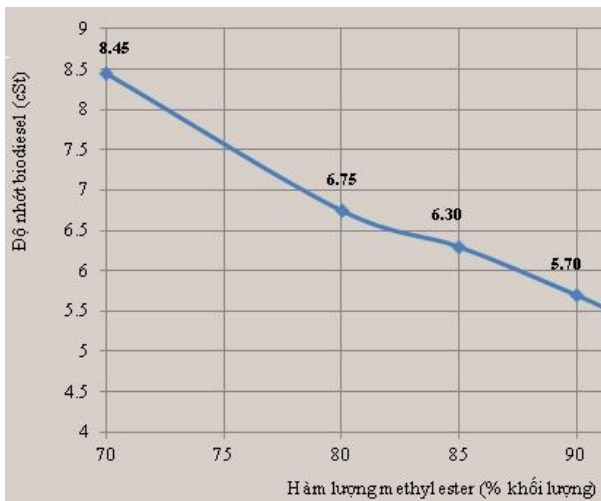


Fig. 4. Viscosity vs. methyl ester content calibration curve (methyl ester content ≥ 70 wt%)

In the first series of experiments, the reaction times required for $\geq 90\%$ fish fat conversion were compared when carrying out the transesterification in conventional stirred tank reactor and in cavitational reactor system, respectively, at the same reaction conditions of molar ratio of methanol/fat = 6/1, and catalyst amount of 1wt%. Results are given in Fig. 5. Reaction time is significantly reduced when using the cavitational reactor system. Compared to the case of conventional reactor, where 92% fat conversion was obtained after 90 mins, it took only 1 min to reach the same conversion in the cavitational reactor system.

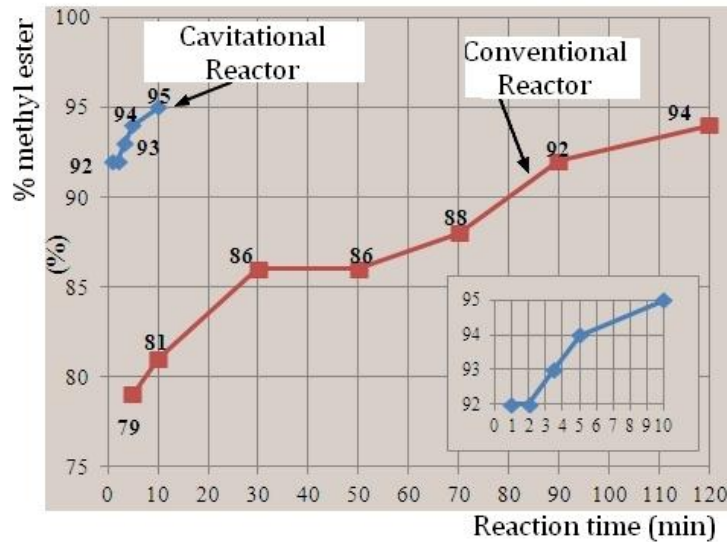


Fig. 5. Fat conversion vs. reaction time in different reactors

Dispersed methanol droplet's average size and density

The reduced reaction time could be attributed to an increase in interfacial surface area between methanol (dispersed phase) and fat (dispersing medium), which, in turn, is a result of the cavitation phenomenon taking place in the Cavitator. Dispersed methanol droplets are considered as small spheres under observations with electronic microscope (Fig. 6). The average size (diameter of spheres - d_{TB}) and density of these droplets for the four samples M_1, M_2, M_3, M_4 are given in Table 1.

It has been found that d_{TB} of M_1 , prepared in conventional mechanical mixer, is 13.0 μm ; while that of M_2 , prepared with Cavitator in 1 min, is only 7.8 μm . Consequently, the interfacial surface area of M_2 is more than 150% larger than that of M_1 sample. The current conformation of Cavitator does not ensure further increase of surface area with increasing mixing time. However, the geometric

properties and aspects of Cavitator, such as number and shapes and surface of colliding elements, volume ratio of colliding element, etc... could be modified in order to maximize the dispersion effect and reduce the mixing time.

Other process intensifications for transesterification with Cavitator

Decreasing NaOH catalyst amount

The homogeneous NaOH catalyst is always contaminated in the final product. It poses some problems in the purification of the product, and negatively affects the quality of the biodiesel, as well. Therefore, it is desirable to decrease the catalyst amount as much as possible. Less amount of catalyst used means more efficient biodiesel production. Generally, the amount of catalyst must be $\geq 1\text{wt}\%$ (as of fat amount) in a conventional reactor, as lower loading would lead to too prolonged reaction time to reach the required conversion.

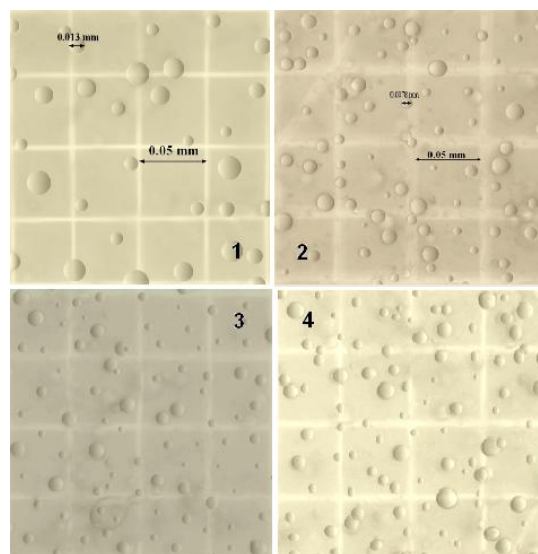


Fig. 6. Observations of methanol droplets in M_1, M_2, M_3, M_4 samples.

Table 1. Calculation results for interfacial surface areas

Properties	Samples			
	M_1	M_2	M_3	M_4
Density (numbers of droplets / 1mm^3 mixture)	6.450	25.900	33.500	34.500
d_{TB} (um)	13,0	7,8	6,9	6,8
Interfacial surface area (m^2/m^3)	0,840	1,240	1,263	1,268

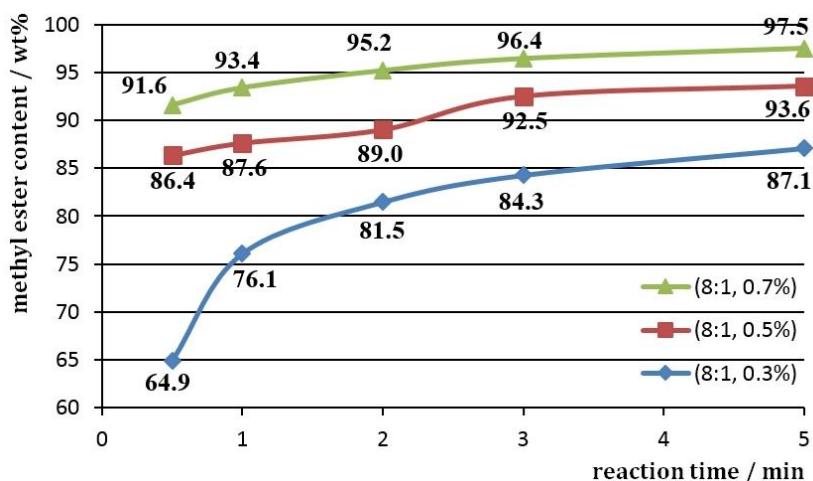


Fig. 7. Fat conversions vs. time at different catalyst loadings in the cavitational reactor system

Fig. 7 describes fat conversions vs. reaction time in our cavitational reactor system, at 60°C; molar ratio for methanol/fat = 8/1; and NaOH catalyst contents of 0.7; 0.5 and 0.3 wt%, respectively. It is obvious that the conversion reaches desirable values after quite a short reaction time at the catalyst loading of 0.7wt%, and acceptable conversions are obtained at 0.5wt% catalyst loading, as well. Reaction times in the range of only 1 ~ 5 mins show remarkable improvement in effectiveness of this cavitational reactor, compared to the conventional setup. It is also worth noticing that, with lower catalyst content used for the reaction, the side reaction of saponification is limited, resulting in an increased yield of the final product.

The possibility of using solid CaO catalyst for the transesterification

Many solid catalysts, based on metal oxides, have been investigated to use in the transesterification reaction. These solid catalysts have some

advantageous aspects, including the easier post-reaction purification and reusability of the catalyst, and therefore could improve the economics of the biodiesel production. The downside is that, the amount of solid catalysts must make a huge 3 ~ 20 wt% (of the fat/oil amount), with relatively high molar ratio for methanol/oil (~ 20/1), and long reaction time (~120 mins), in order to acquire the desirable conversion. [10]

With CaO solid catalyst, the reaction occurs on the catalyst's surface, hence, it becomes a heterogeneous 3 phased reaction. The dispersion of fine catalyst particles is a key factor for the reaction's kinetics, as finer dispersion would induce more reaction sites and would increase the reaction speed. In the experiment series with CaO catalyst, reaction temperature was kept at 60°C; molar ratio of methanol/fat at 8/1; and the CaO contents were 3, 7, and 10wt% of fat weight. Comparative results for both conventional and cavitational reactors are given in Table 2 and Fig. 8.

Table 2. Conversion with CaO catalyst (7wt%) in different reactors

Reaction type	Reaction time (min)	Fat conversion (%)
Conventional reactor	90	93
Cavitational reactor	20	93

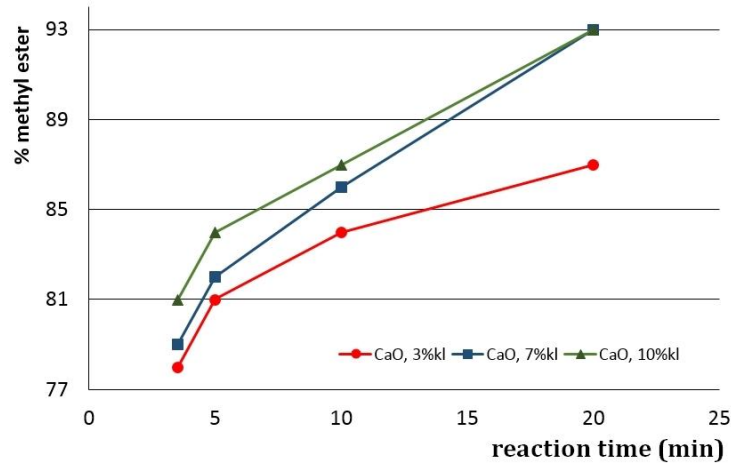


Fig. 8. Conversion in cavitational reactor with different CaO catalyst contents.

Experimental results show that the transesterification occurs faster in the cavitational reactor, where the conversion increases with increasing catalyst content. At even as low catalyst content as 3wt%, the conversion reaches a promising level of > 85% after 20 mins of reaction time. When the catalyst particles go through the Cavicator, they are further broken down to finer particles with smaller size. Consequently, more catalyst surfaces are generated

with more active sites to initiate the transesterification. The particle size distribution measurement with X-Ray diffraction device (Fig. 9) confirm this argument. The cavitational effect has broken starting CaO agglomerates to very fine particles of mean size of only 7.4 μ m, much more smaller than those obtained in a conventional mechanical mixer (23.6 μ m).

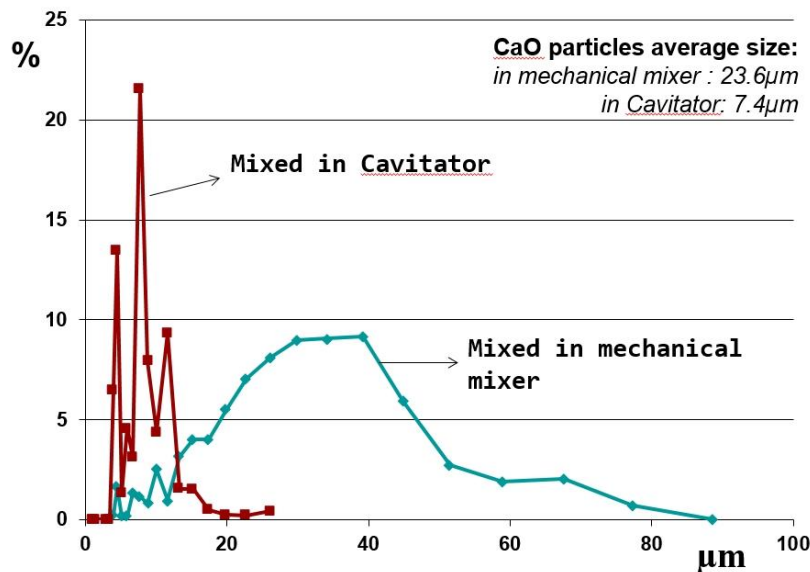


Fig. 9. CaO particle size distribution after mixed in different mixers

Conclusion:

A novel cavitational mixer (Cavicator) was designed and fabricated successfully, and then used in a reactor system to produce biodiesel via transesterification. With this device, smaller and denser methanol droplets were generated in fish fat medium, which increases significantly the interfacial surface area of the two fluids. As a consequence, the mass transfer process was improved leading to a remarkable increase in reaction kinetics. Compared to the conventional reactor setup, reaction time in our newly developed reactor system was hugely

shortened (1 ~ 2 mins vs. 90 mins). Short reaction time is one of key factors to make the continuous production of biodiesel possible. Employing this cavitational reactor system could reduce the catalyst needed for the reaction, with which the side saponification reaction could be minimized and the quality of final product could be improved. Experimental results showed that the catalyst amount could be reduced by 50% without any negative effect to the reaction time nor conversion. In addition, the Cavicator could also disperse finely CaO solid catalysts, therefore could

improve significantly the effectiveness of the biodiesel production process with solid catalyst. With simple design and conformation, high flexibility, easy modification, the cavitational reactor system could be a good choice for continuous production of biodiesel via transesterification.

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