

Micro-Reactor Device For Dbsa-catalyzed Biodiesel Synthesis from Microalgae *Chlorella Sp.*

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Abstract. The micro-reactor device was fabricated from Teflon and tested as a tool for biodiesel synthesis process from micro algae using Dodecylbenzenesulfonic acid catalyst. The variables influencing on the biodiesel yield were optimized. The maximum yield of biodiesel of 99% was obtained at the reaction conditions of (temperature: 373.15 K, residence time: 20 min, methanol/oil ratio: 20, co-solvent amount: 30 wt% and catalyst amount: 11wt%). The influence of water content also investigated and recommended to be less than 0.5 wt %. The acid value also reduced to a value of less than 0.5 % at the optimum reaction condition. DBSA was found highly active catalyst for the esterification and transesterification reaction in the micro – reactor device. Biodiesel was produced in micro- reactor device at a small residence time (20 min) compared to the very long time consumed by the conventional batch process. Isopropanol was used as a co-solvent in the process and showed highly active in the biodiesel production.

1 Introduction

Currently, the biodiesel production needs to be enhanced to overcome the technical and ecological problems of long time consumption, low productivity, high energy consumption and mass transfer limitation associated with the conventional processes. Many research concentrated on the improvement the process towards a sustainable process for biodiesel synthesis [1-3]. Micro-reactors, are considered efficient technology for biodiesel synthesis and need to be intensified due to the lower residence time consumed by the process. Physically, the dispersion of the oil and alcohol in the micro-reactor would be increased and solve the problem of transport phenomena (mass and heat transfer) limitation in the conventional route [4-5]. Micro-reactor devices can be used industrially simply by stacking a number of micro-reactors for the commercial production [6-7]. The intensification of the micro-reactors has two main research divisions. The chemical intensification which concentrated on the investigation of the unusual reaction parameters [8-9] and process design intensification that search for a new and simple design [10-11]. Microtube reactor had been tested for the transesterification of palm oil and the influence of catalyst concentration and residence time were investigated for two different tube internal diameters [12]. The flow characteristics had been investigated in a milli-channel reactor used of the transesterification of a mixture of castor and sunflower oil [13]. In an experimental and simulation study, the

biodiesel synthesis from sunflower oil in a microreactor was investigated for the operating conditions and compared the performance of microdevice with the batch reactor [14]. Recently, biodiesel had been produced in a CaO packed-microchannel and enhanced by using Isopropanol co-solvent. The reactor conditions were optimized using the BBD (Box- Behnken design) with the RSM (response surface methodology) approach [15]. The objective of the present work is to design a micro-reactor fabricated from teflon for the biodiesel synthesis from microalgae *Chlorella sp.* oil. Dodecylbenzenesulfonic acid had been used as a catalyst for both the transesterification and esterification reactions and isopropanol was used as a co-solvent in the process. The variables affecting the biodiesel yield methanol/oil ratio, catalyst concentration, co-solvent concentration, reaction temperature, residence time, and water content were investigated and optimized.

2 Experimental

2.1. Materials and measuring

Dodecylbenzenesulfonic acid (>0.99) was procured from Shanghai Hanhong Scientific Co., Ltd. Anhydrous MgSO₄ (99.8 wt. %), chloroform (99.8%), methanol (99.9%), isopropanol (96%), hexane (98.8%) and gas chromatography (GC) standard methyl heptadecanoate for the quantitative analysis of FAME were provided

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from Sigma-Aldrech. All the chemical materials used were analytical reagents. *Chlorella* sp. extract was supplied from Shaanxi Jintai Biological Engineering Co., Ltd. The microalgae are dried at 343.15 K. The independent examination of fatty acids shows that the lipid consists primarily from C16:0, C18:3, C18:2, C16:3, C16:2, and C18:0. The analysis of biodiesel produced at the optimum conditions for the free fatty acid profile and quantification are done using GC-2010-flame ionization detector (Shimadzu, Japan) armed with a split-splitless injector (oven temperature of 483.15 K, injection volume=2 μ L, split injection temperature of 513.15 K, split ratio=1:50, flow rate=1ml/min, column specification of 30 m length, 0.25 mm inside diameter.-0.25 thickness of film, analysis time of 30 min and detector temperature of 523.15 K. Water content in microalgae sample was tested with the Karl Fischer tester (KF-1A). The acid value (mg KOH/g) of the oil extracted from microalgae was measured using the standard titration method according with the approved method of American Oil Chemists Society (AOCS). Each test was conducted in triplicate.

2.2 Extraction of oil

Extraction of oil was done in a Soxhlet extraction by adding 50 g of dry *Chlorella* sp. into the upper part of the system with 150 ml of (chloroform / methanol) as a solvent mixture and conducted at 338 K under magnetic stirring of 600 RPM in a 250-mL round-bottom flask for a period of 3.5 hr. The resulted mixture then was filtered, evaporated and finally dried at 338 K. the detailed extraction process was according to Yuvarani et al., 2017 [16].

2.3 Transesterification and esterification in a Micro-reactor

Continuous transesterification and esterification of micro algae was conducted in a micro-reactor (internal tube diameter= 0.5 mm, tube length= 500 mm, number of tube=100 tubes). The reactor temperature was kept under constant temperature using a water bath at normal pressure. The schematic diagram and photograph of the micro-reactor device are shown in figure 1. Methanol was mixed with a suitable amount of DBSA as a catalyst. Catalyst- methanol mixture and *Chlorella* sp. oil was charged into the system using a glass syringe pumps. The parameters had been studied in the micro-reactor were as follows: reaction temperature (303.15 to 413.15 K), methanol/oil ratio (5 to 50), residence time (5 to 30 min), catalyst amount (1-15 wt%), co-solvent amount (0-35 wt%), and water content (0.5-6 wt%). The different parameter was investigated and the experiments were repeated in triplicate (standard deviation was less than 5% for any point). Afterwards, for purifying the biodiesel product, excess alcohol was evaporated using rotary evaporator and hexane was added. Finally, The mixture was vacuum filtrated and the filtrate was dried over anhydrous $MgSO_4$. GC-FID was used for the characterization of the product obtained from the packed

bed reactor system. The tests were conducted in triplicate. The yield of microalgae biodiesel was calculated according to the following equation:

$$\text{Biodiesel Yield (wt. \%)} = \frac{W_b}{W_t} \times 100 = \frac{CF_b A_b W_s}{CF_s A_s W_t} \dots (1)$$

Where W_b , W_t , W_s , are the mass of biodiesel, total sample, and internal standard added to the sample, respectively, A_b , A_s is the peak area of biodiesel, and internal standard, respectively, CF_b , CF_s is the correction factor of biodiesel, and internal standards.

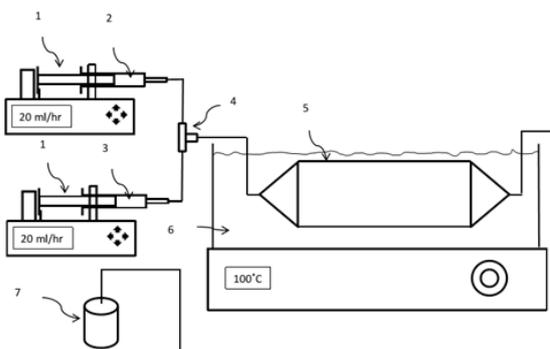


Fig. 1. Schematic diagram of the micro-reactor device set-up: 1- Syringe pump; 2- Methanol and catalyst mixture; 3- Microalgae oil; 4- T- shaped mixer; 5- Micro-reactor device; 6- Water bath with thermostat; 7- Biodiesel product.

3 Results and discussion

3.1. Influence of methanol/oil

Figure 2a shows the effect of methanol/oil molar ratio at the reaction conditions of (reaction temperature: 373.15 K, residence time: 20 min, co-solvent: 30 wt%, and catalyst amount: 5wt% and 9wt%). Biodiesel yield in figure 2a shows an a rise as the methanol/oil molar ratio increased from 5 to 20 molar ratio. The reason beyond that increase can be as a result of the favor the forward direction in the transesterification reaction. The same result was observed by other researchers [17]. Then, a slight decrease was observed in the biodiesel yield, which may be due to the remaining portion of the biodiesel in the glycerol phase and can not be separated. Mansourpoor and Shariat also observed the same behavior [18]. Figure 2a shows that the biodiesel yield at a catalyst amount of 9 wt% (biodiesel yield=99%) was higher than that one at a 5wt% (only 60%). Effect of methanol/oil molar ratio on the acid value was shown in figure 2b. The acid value was reduced due to the increasing the methanol/oil ratio and showed an acid value of less than 0.5% at a methanol/oil ratio of 20. Catalyst ratio of 9 wt% was found to be the optimum ratio for decreasing the acid value due to the changing the FFA (free fatty acids) in the microalgae oil. Afterward, It was observed that there is a slight increase in the acid value due to the dilution of DBSA catalyst and this is agree with a previous study [19].

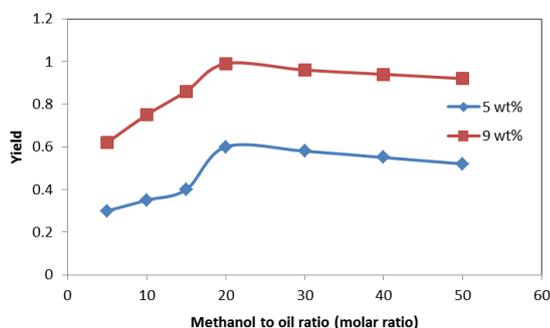


Fig. 2.a Influence of methanol/oil ratio on biodiesel yield: reaction temperature 373.15 K; residence time 20 min; co-solvent 30 wt; catalyst to oil 5 and 9 wt%.

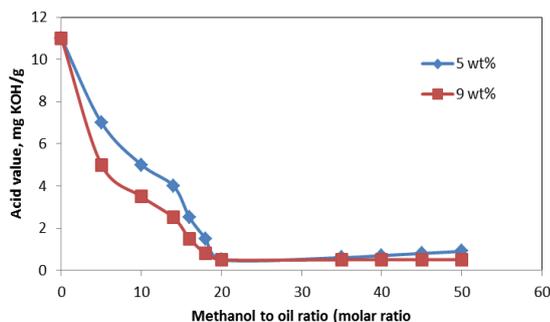


Fig. 2.b Influence of methanol/oil ratio on acid value: reaction temperature 373.15 K; residence time 20 min; co-solvent: 30 wt%; catalyst to oil 5 and 9 wt%.

3.2. Influence of catalyst amount

The influence of catalyst concentration on the biodiesel yield was investigated as shown in the figure 3a. The reaction conditions were (reaction temperature: 338.15; 358.15; and 373.15 K, methanol/oil ratio: 20, residence time: 20 min, and co-solvent: 30 wt%). Catalyst concentration was varied in the range of 1-15 wt%. Figure 3a shows a rise in the biodiesel yield with changing temperature from 338.15 to 373.15 K. Moreover, biodiesel yield improved with increasing the catalyst amount until reaching the maximum value of 99% at the catalyst amount of 9 wt% and a temperature of 373.15 K. A slight decrease in biodiesel yield was observed when increasing the catalyst amount beyond the value of 9 wt% due to the carbonization in the presence of DBSA as stated by other researchers also using an acid catalyst [20-21].

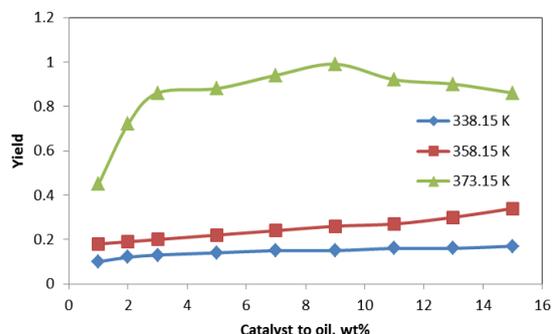


Fig. 3.a Influence of catalyst to oil ratio on biodiesel yield: residence time 20 min; methanol/oil ratio 20; co-solvent 30 wt%, reaction temperature 338.15, 358.15, and 373.15 K.

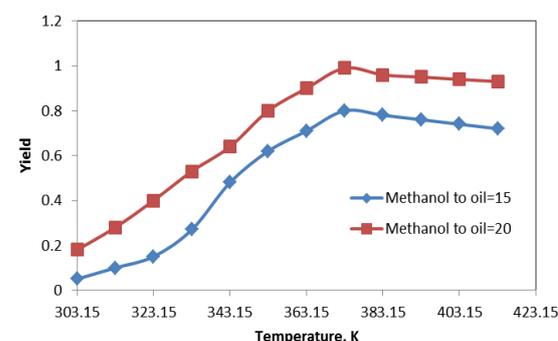


Fig. 3.b Influence of reaction temperature on biodiesel yield: residence time 20 min; catalyst to oil 9 wt%; co-solvent 30 wt%; methanol/oil ratio 15 and 20.

3.3. Influence of reaction temperature

Figure 5 shows the effect of reaction temperature on the biodiesel yield at variables (catalyst amount: 9 wt%, methanol/oil ratio: 15 and 20, residence time of 20 min, and range of temperature: 303.15-413.15 K). The increase of temperature would increase the kinetic energy of the reacted molecules and led to that increase in the biodiesel yield until reaching the temperature of 373.15 K. Afterward, further increase of temperature showed a slight decrease in biodiesel yield due to the miscibility of biodiesel product in the glycerol by-product.

3.4. Influence of residence time

The influence of the reaction time on the biodiesel yield was shown in the figure 4a. The reaction conditions for the experiments were (catalyst amount: 9 wt%, methanol/oil ratio: 15 and 20, co-solvent: 30 wt%, reaction temperature: 373.15 K, and range of residence time of 5-50 min). As stated by other researchers [22-23] and agree with the present study, the biodiesel yield

increase with increasing the residence time. The maximum biodiesel yield of 80%, 99% were obtained at a residence time of 20 min in the micro-reactor using a methanol/oil molar ratio of 15, and 20 respectively. Beyond the residence time of 20 min, a slight decrease in the biodiesel yield was observed and can be deduced to the increase of di and mono glyceride molecules by the reversible transesterification reaction which agree with the results of Encinar et al., (2016) [24]. A shorter residence time was consumed by the micro-reactor in the present study compared to the conventional batch process make a sense to use it industrially.

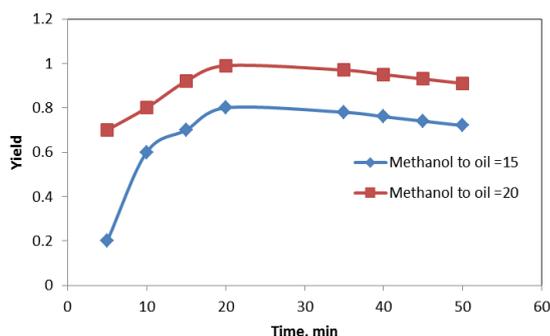


Fig. 4.a Influence of residence time on biodiesel yield: reaction temperature 373.15 K; catalyst to oil 9 wt%; co-solvent 30 wt%; methanol/oil ratio 15 and 20.

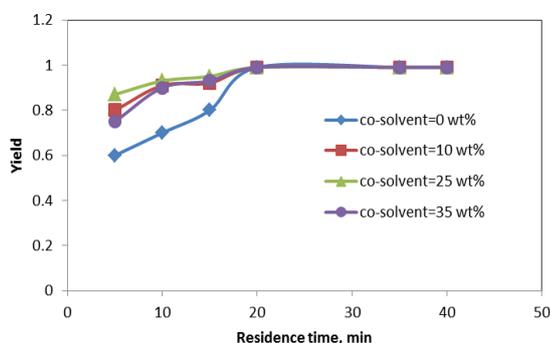


Fig. 4.b Influence of co-solvent on biodiesel yield: reaction temperature 373.15 K; catalyst to oil 9 wt%; methanol/oil ratio 20; residence time 20 min.

3.5. Influence of co-solvent

Figure 4b shows the influence of co-solvent on the yield of biodiesel. Isopropanol was selected as a co-solvent due to the very low reactivity of it towards the transesterification reaction based on the literature reports [25]. A primary experiment was conducted at the reaction conditions of (methanol/oil ratio: 20, catalyst amount: 9 wt%, residence time: 20 min, and a reaction temperature: 373.15 K) for the clarification regarding the reactivity of isopropanol in the transesterification reaction. Then, at the same conditions mentioned above, the biodiesel yield was studied in the range of co-solvent amount influence between 10 – 35 weight%. Figure 4b shows an enhance in the biodiesel yield with increasing the co-solvent ratio

at an appropriate residence time and this phenomena attributed to the increase the dispersion of oil-methanol system and interface mass transfer rate [26]. Isopropanol was found an influenceive co-solvent in the transesterification reaction of microalgae.

3.6. Influence of water content

The water content had a negative influence on the biodiesel yield as shown in the figure 5. The experiments were conducted at the reaction conditions of (methanol/oil ratio: 20, catalyst amount: 9 wt%, residence time: 20 min, co-solvent: 30 wt% and a reaction temperature: 373.15 K). By adding 1-8% of a distilled water to the microalgae oil and conducting the reaction, was found that the maximum value of accepted water content in the microalgae oil must be less than 0.5 %. The present results agree with the literature [27].

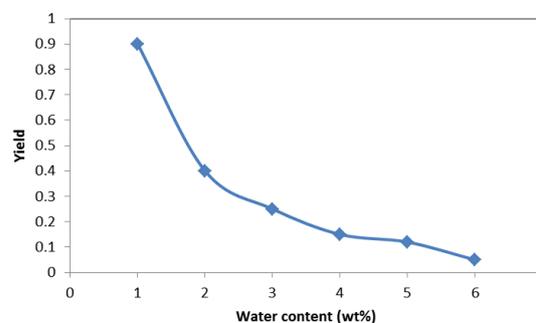


Fig. 5 Influence of water content on biodiesel yield: reaction temperature 373.15 K; catalyst to oil 9 wt%; co-solvent 30%; methanol/oil ratio 20; residence time 20 min.

4 Conclusion

The esterification and transesterification reactions of microalgae oil using DBSA catalyst were investigated in the micro-reactor device. The device showed high activity for the production of biodiesel in a short residence time. Also, the catalyst DBSA was a found to be a suitable catalyst for the reactions due to the hydrophobicity which can reduce the high content of FFA (free fatty acids) in the microalga oil. The optimum reaction conditions were found as follows: reaction temperature 373.15 K, residence time 20 min, methanol/oil ratio 20, co-solvent 30 wt %, and catalyst amount 9 wt %. The water content value of less than 0.5 % was proved of negligible influence on the biodiesel yield. The present study, recommend the use of a stacked micro-reactor industrially for the production of biodiesel from microalgae using DBSA which would be an efficient economic process compared to the batch process.

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