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The rotor-stator type hydrodynamic cavitation reactor approach for enhanced biodiesel fuel production

Bahram Hosseinzdeh Samani[a], Mehrsa Behruzian[a,b], Gholamhassan Najafi[b,*], Ebrahim Fayyazi[b,*], Barat Ghobadian[b], Ava Behruzian[a], M. Mofijur[c,f], Mohamed Mazlan[d], Jun Yue[e]

[a] Department of Mechanical Engineering of Biosystems, Shahrekord University, Iran
[b] Biosystem Engineering Department, Tarbiat Modares University, Iran
[c] School of Information, Systems and Modelling, University of Technology Sydney, NSW 2007, Australia
[d] Advanced Material Cluster, Faculty of Bio Engineering and Technology, Universiti Malaysia Kelantan, Jeli, Kelantan, Malaysia
[e] Department of Chemical Engineering, Engineering and Technology Institute Groningen, University of Groningen, 9747 AG Groningen, The Netherlands
[f] Mechanical Engineering Department, Prince Mohammad Bin Fahd University, Al Khobar 31952, Saudi Arabia

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ABSTRACT

Today renewable energies such as biodiesel have considerable role in the bio-based economy. Long production time and low efficiency are a number of problems in biodiesel production that is essential to be considered when designing and operating the biodiesel production systems. In this study, using safflower oil in a hydrodynamic cavity reactor, biodiesel fuel was produced in the possible shortest time and maximum efficiency. The effect of reaction time (30, 60 and 90 s), concentration of potassium hydroxide catalyst (0.75%, 1% and 1.25%), alcohol to oil ratio (6, 8 and 10) and rotor-stator distance (1 cm, 2 cm and 3 cm) on the reaction yield were analyzed. The results were analyzed by response surface methodology. Among the independent variables, reaction time was the most important factor on the reaction yield, which had a positive impact on the quality of methyl ester. The optimum values obtained were: 63.88 s reaction time, 0.94% catalyst concentration, 1: 8.36 alcohol to oil molar ratio, 1.53 cm rotor-stator distance, and 89.11% yield. Several properties and compounds of biodiesel obtained were measured and compared with ASTM D6751 (American Society for Testing and Materials) and EN 14214 standard (European Standards). The results showed that most of the features conform to the afore-mentioned standard. Therefore, transesterification of safflower oil with a hydrodynamic cavitation reactor can function as a good alternative to the diesel.

1. Introduction

The pollution caused by fossil fuels and their endlessness are factors that have led humans to seek alternative fuels for these resources. In addition, in today's society, given the fluctuation in the price of fossil fuels, alternative fuels are in demand more than ever. Although fuels such as coal, natural gas, and other fossil fuels are in use today, their dependence is steadily increasing [1–3]. Biofuels are one of the major sources of renewable or alternative fossil fuels. In recent years, considerable efforts have been made in the development of biofuels to solve problems associated with fossil fuels. The most important characteristic of biofuels is their renewability and bio-friendliness, with no concern for their completion [4]. Biodiesel is one of the most suitable biofuels, which due to the high molecular similarities between the biodiesel and petroleum diesel can be a good alternative to meet the needs of common liquid fuels such as the diesel [5–8].

Biodiesel is a fuel consisting of long-chain monoalkyl esters of vegetable oils or animal fats [9–11]. Chemically, biodiesel is a combination of long-chain fatty acid methyl esters (FAME) and is typically produced from waste or biological sources such as the vegetable oils, animal fats and even used frying oils (UFOs) [12–16]. The advantages of biodiesel fuel can be mentioned as cleanliness and renewability, and it can be used instead of the diesel fuels in compressor combustion engines with little or no change [17].

Other advantages of biodiesel over diesel include combustion efficiency and high cetane number, low sulfur content and aromatics, and consequently lower toxic exhaust gases [18]. So far, several methods for producing biodiesel have been developed worldwide. The type of feed used and the tonnage of process production are the most important factors influencing the type of process selected. Biodiesel is produced

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[*] Corresponding authors.
E-mail addresses: g.najafi@modares.ac.ir (G. Najafi), e.fayyazi@modares.ac.ir (E. Fayyazi).

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through different processes including direct mixing (dilution), microemulsion, pyrolysis, and transesterification [19–22]. Among the methods mentioned, transesterification is the most common method for biodiesel production [23–25]. Most of today's commercial biodiesel produced worldwide is achieved by the transesterification reaction of triglycerides with alcohol in a reactor in the presence of catalysts [26,27]. Transesterification of triglycerides produces fatty acid alkyl esters and glycerin where diglyceride and monoglyceride are intermediate products [28,29]. The problems and challenges of performing a transesterification process using stirred tank reactors (STRs) can be the limited reaction rate because of lower mass transfer rate between oil and alcohol, longer reaction time, higher molar ratio, and higher catalyst absorption. The transesterification reaction is often slow and for the acceleration purpose, it is necessary to extend the contact surface between the two immiscible phases through the use of methods such as intensified mixing [6,30,31].

Some technologies have been developed for improving the mixing process as well as the mass and heat transfer between the two fluid phases to reduce the reaction retention time [6,17,32,33]. In recent years, hydrodynamic cavitation reactors have emerged as a promising approach for the highly efficient and continuous production of biodiesel [6]. Hydrodynamic cavitation reactors use fluid flow energy to create a cavitation phenomenon. During the cavitation process, a severe collapse of the cavities formed by the pressure changes caused by the sound energy, results in the release of a large amount of energy in a very small space, yielding a very high increase in pressure and temperature [34]. These reactors intensify the mass transfer rate and heat transfer of chemical processes by causing local perturbations and micro-circulation within the reactor [35]. Hydrodynamic cavitation reactors provide narrower and more stable thin emulsions compared to the conventional reactors, which in turn increase the reaction rate [36].

Biodiesel can be made from a variety of sources including the edible oil, non-edible oil, animal fats etc. In general, the common biodiesel sources are soybean oil, rapeseed oil, mustard oil, palm oil, sunflower oil, mahua oil, pongamia oil, jatropha oil, castor oil, algae extracted oil, waste vegetable oils, chicken fat and fish oil [37–42]. To reduce the cost of biodiesel production, it is important to choose the most cost-effective raw materials.

Safflower (*Carthamus Tinctorius L.*) is a multifunctional agricultural crop generally cultivated for oil production. An important chemical property of safflower is the presence of polyunsaturated fatty acids in its triglyceride structure [43]. Safflower oil has saturated (palmitic and stearic) and unsaturated (oleic-linoleic) fatty acids [44]. In general, safflower seeds contain 25% to 45% oil, depending on their genotype, with over 90% of fatty acids being unsaturated fatty acids, linoleic acid, and oleic acid [43]. The wild types of this plant, which are scattered throughout Iran, indicate it well adapts to Iran's climatic conditions. Relative tolerance to soil salinity and air dryness as well as having high-quality oil are the prominent characteristics of this plant [45–47].

Due to the adaptation of safflower to Iranian climate, high potential of this plant for the cultivated area, and other mentioned advantages, safflower seed was selected as a suitable raw material for biodiesel production in Iran. Hydrodynamic cavitation reactor, compared to the conventional reactors used in transesterification to convert oils and fats to biodiesel, requires a lower alcohol to oil ratio and lower catalyst concentration, lower temperature, and shorter residence time [36]. Therefore, using a such reactor can reduce the cost and energy required to produce high-quality biodiesel.

In summary, although there have been several studies on biodiesel production using different intensification reactors and different raw materials, almost no study has concentrated on the use of a hydrodynamic cavity reactor for biodiesel production from safflower oil. In this study, using safflower oil in the hydrodynamic cavity reactor, the biodiesel fuel was continuously produced in the shortest possible time and with the highest production efficiency, and biodiesel production characteristics were examined accordingly. Also, the built-in hydrodynamic cavitation reactor settings were evaluated to improve the quality of the produced biodiesel fuel and to improve the device performance by finding the optimum conditions. The effect of independent variables such as the reaction time, catalyst percentage, alcohol to oil molar ratio, and rotor–stator distance was evaluated to examine the biodiesel yield. The results were analyzed using the RSM and Box-Behnken design in Design-Expert software.

2. Materials and methods

2.1. Materials and reagents

Safflower seeds were collected from the lands of Rey city in Tehran. Alcohol methanol (CH_3OH) with the purity of 99.9%, propanol (C_3H_8OH) with the purity of 99.9%, potassium hydroxide (KOH) as a catalyst with the purity of 99.8%, n-hexane with the purity of 96% as solvent aid provided from Merk Company of Germany. Also, phenolphthalein with a purity of 98% used as a detector and provided from Biochem Company of France, were used in the current experimental work.

2.2. Preparation of feedstock

Safflower seeds were first dried and then milled. To achieve the desired powder size, the milled grains were passed through the relevant mesh following Iranian National Standard (ISIRI 2010). 500 g of the powder was subjected to the Soxhlet oil extraction process during 5 steps (100 g was used at each step). Extraction was performed with 500 mL normal hexane solvent and Soxhlet device for 4 h, and then the mixture of oil and normal hexane was separated based on the boiling point difference with a rotary evaporator at 80 °C and 150 rpm. The oil obtained from this method contained impurities and suspended particles which were refined through passing the filter. Finally, 140 g of oil was obtained, representing 28% oil yield [48,49].

2.3. Determination of SFO (safflower oil) acidity

The acidic number is expressed as mg of potassium hydroxide needed to neutralize the free fatty acids in a gram of oil or fat. Also, acidity is defined as the percentage of free fatty acids. The acidity of the oil was determined by the Phenolphthalein Detector method according to Iranian National Standard (ISIRI No. 199 (Third Revision)). Thus, safflower oil was mixed with propanol at a ratio of 1:10. Three drops of phenolphthalein indicator followed by the 0.1 mol/l KOH solution were further added into the oil and alcohol solution. This was followed by stirring the mixture until it is neutralized (constant pink colour). By replicating the experiment three times, the average volume of the consumed potassium solution was obtained. The acidic number and oil acidity were calculated using the Eqs. (1) and (2) [50].

$$AV = \frac{56{\bullet}1 \times V \times C}{m} \tag{1}$$

$$A = \frac{282 \times AV}{56.\ 1} \tag{2}$$

where AV = acidic number of oil (mgKOH/g oil); A = acidity of oil (percent), V = average volume of consumed KOH (mL), C = concentration of KOH solution (mol/L), and m = weight of the oil sample. To perform the transesterification reaction, the oil acidity should be < 3% [51]. In this study, the oil acidity index was obtained as 0.67.

2.4. Characterization of SFO fatty acid structures and its blends

Oleic acid plays an important role in the fatty acid structure of vegetable oils since it optimizes the balance between the thermal stability and oxidative stability, and improves the oil viscosity, all of which

Table 1
SFO characterization [54,55].

Properties	Linear formula	Percentages
D (g/cm^3)	–	0.91
KV (cSt)	–	28.16
SN (mg K/g oil)	–	211.60
IN (g I_2/100 g oil)	–	96.11
Myristic (wt. %)	$CH_3(CH_2)_{11}COOH$	0.24
Palmitic (wt. %)	$CH_3(CH_2)_{14}COOH$	7.07
Stearic (wt. %)	$CH_3(CH_2)_{16}COOH$	2.76
Oleic (wt. %)	$CH_3(CH_2)_7CHCH(CH_2)_7COOH$	15.22
Linoleic (wt. %)	$CH_3(CH_2)_4CH]CHCH_2CHCH(CH_2)_7COOH$	74.54
Linolenic (wt. %)	$CH_3(CH_2CHCH)_3(CH_2)_7COOH$	6.26
Other fatty acids (wt. %)	–	0.27

D = Density; KV = Kinematic Viscosity; SN = Saponification Number; IN = Iodine Number.

can affect the physical properties of biodiesel produced [52,53]. Therefore, to select oil as the primary feed of biodiesel, it is necessary to extract its fatty acid profile. Accordingly, the fatty acid profile of the sample was determined by employing a GC (gas chromatography). Table 1 shows the results of these measurements. As seen in Table 1, linoleic and oleic fatty acids had the highest share of fatty acid profile as 74.54% and 15.22%, respectively. Therefore, safflower oil is a suitable source for biodiesel production due to its high oleic acid content.

2.5. Hydrodynamic cavitation setup

For the production of biodiesel, the hydrodynamic cavitation method was utilized by a laboratory system consisting of three main sections, namely, reactor, feed injection section, and magnetic stirrer. The reactor of this laboratory system consists of three parts, including the polycarbonate transparent stator to observe the process, a stainless steel rotor with holes around to produce bubbles, and an electric motor to provide rotor drive power. The characteristics of the reactor components (stator, rotor, rotor holes, and electromotor) are given in Table 2. In this laboratory system, the Heidolph model 5206 peristaltic pump was used for oil injection with a precision of 1.1% and a discharge rate of 0.85–861 mL/min. The magnetic stirrer of MR 3001 model made by German Heidolph Company with high efficiency was used for mixing the reaction material.

2.6. Transesterification of mixed SFO with methoxide

To increase the solubility and reactivity of the homogeneous catalyst, the methoxide solution (a mixture of potassium hydroxide and methanol) was dissolved in a separate vessel using a magnetic stirrer and then transferred to the primary methanol tank. In this case, there are more homogeneous catalyst molecules available for the methanol and oil molecules, and the reaction will be performed more quickly. This solution is then pumped into the chamber with the desired oil through the use of the peristaltic pump, while according to the rotor test treatments, the rotor rotates at 1000 to 3000 rpm, and the fluid rotates between the rotor and stator by the centrifugal force. The holes in the rotor environment reduce the pressure suddenly resulting in cavitation in the solution, thereby increasing the mass transfer between the oil and alcohol (without the need for high temperatures). The result of such an intensified mixing is the formation of glycerin, methyl ester, and some extra alcohol.

Table 2
Characteristics of the cavitation instrument.

Parameter	Value
Rotor diameter (m)	0.09
Rotor length (m)	0.08
Rotor density (g/L)	905
Stator diameter (m)	0.097
Stator length (m)	0.09
Hole diameter (m)	0.004
Number of holes	40
Electric-motor power (w)	75
Electric-motor rotational speed (rpm)	3200

Separator hopper was used for the separation of biodiesel and glycerin. Glycerin was positioned on the lower part of the biodiesel due to its higher density than biodiesel [32]. After glycerin separation for biodiesel purification, the excess alcohol was first recovered by rotary evaporator at 80 °C and 150 rpm, and then crude biodiesel was washed 3 to 4 times by the water including 1% volumetric phosphoric acid. Finally, the purified biofuel was dried by vacuum distillation [6]. The schematic diagram of the hydrodynamic system used to produce biodiesel is shown in Fig. 1.

2.7. Calculating methyl esters conversion and biodiesel yield

After separation and washing, the samples were first weighed to determine the reaction conversion percentage (methyl ester content) and the yield, then the combination of the methyl ester percentage was measured by gas chromatograph (PerkinElmer-Clarus 580) with a Flame Ionization Detector according to ASTM D6751standard [56]. Reaction yield is a criterion that determines the amount of oil converted to biodiesel and the amount of oil present in the sample as unreacted. The FAME yield was calculated according to Eq. (3) [57–59].

$$\text{FAME \%} = \frac{\sum A - A_{IS}}{A_{IS}} \times \frac{M_{IS}}{M} \times 100 \quad (3)$$

where ΣA = total sub-peak area corresponding to fatty acids C_6 to C_{24}; (μV × sec), A_{IS} = sub-peak corresponding to internal standard (Methyl nonadecanoate); (μV × sec), M_{IS} = internal standard mass (mg); and M = produced biodiesel sample mass (mg).

2.8. Design of experiment

To optimize the reaction parameters of biodiesel production using RSM and Box-Behnken design in Design Expert 7.0.0 software with four independent variables, including the reaction time, catalyst percentage, molar ratio, and distance between rotor and stator, were analyzed for attaining the maximum performance (yield of reaction). The model used in the RSM method is the quadratic equation. In the RSM method, for each dependent variable, a model is defined that demonstrates the main effects of the factors on each variable [60,61]. Each of the independent variables and their levels are shown in Table 3 [6,17].

3. Results and discussion

3.1. Tests design

Box-Behnken design predicted 29 tests with 5 replications at the central point to obtain the experimental error for four independent variables. Software-specified test treatments and the related results for all 29 tests are listed in Table 4.

3.2. RSM analytical and statistical analysis

Analysis of variance (ANOVA) for stepwise regression is reported in Table 5. In Table 5 which presents criteria for determining the model accuracy and meaningful evaluation of independent parameters on the maximum reaction yield. In this model, the effect of all variables except time × molar ratio (ac), time × rotor and stator distance (ad), catalyst concentration × rotor and stator distance (bd), molar ratio × rotor and stator distance (cd), and the square of rotor and stator distance (d^2) are

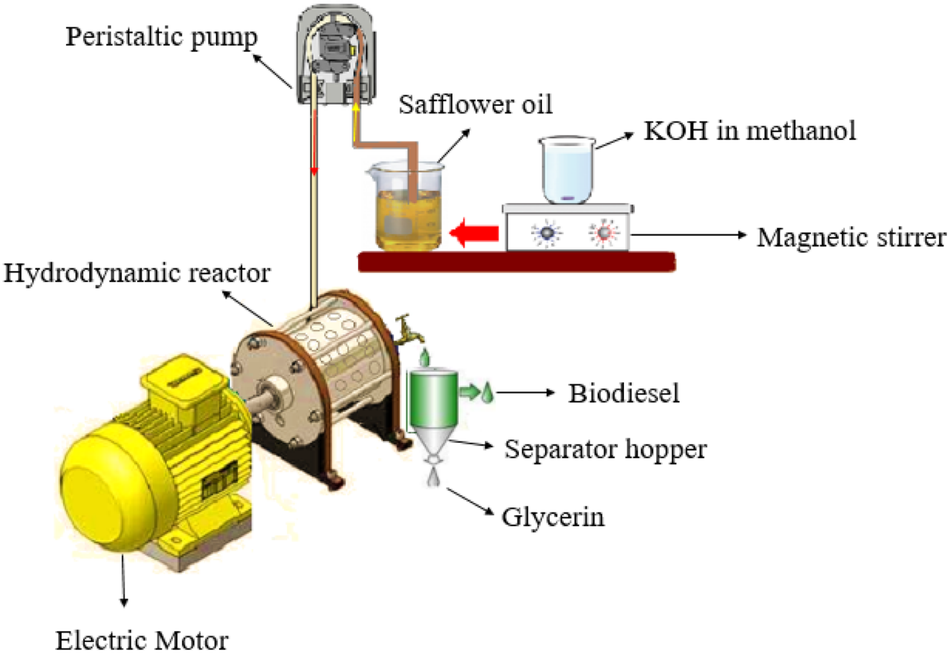


Fig. 1. The hydrodynamic system used in this study.

Table 3
List of independent variables on the RSM.

Independent variable	Symbol	Unit	Range of level		
			−1	0	1
Reaction time[a]	a	s	30	60	90
Catalyst concentration	b	w/w%	0.75	1	1.25
Alcohol to oil ratio	c	–	6:1	8:1	10:1
Distance between rotor and stator	d	cm	1	2	3

[a] Defined as the residence time of mixture of oil and methoxide inside the reactor.

significant at 10% level. F-value of 0.87 for lack of fit indicates that it is not significant due to the net error [62,63]. The F-Value of the model is 522.06, which indicates that the used model is significant, emphasizing the appropriate choice and importance of the selected model. The influence of independent variables on the dependent variable can also be predicted using the quadratic polynomial equation.

Table 6 shows the statistical parameters calculated in the stepwise regression based on the predicted model. The coefficient of determination (R^2) calculated as 0.9960 indicates that the model fits the data well and 99.60% of the dependent variables are determined by the independent variables. The coefficient of variance (C.V) (0.42) indicates the high correspondence between the data obtained from the experiment and the data simulated by the software.

Based on Box-Behnken design and the experimental data (Table 4), stepwise quadratic regression model (based on coded factors) was obtained as Eq. (4). This equation (based on the coded factors) can be predicted and distinguished by the FAME yield under different operating conditions.

$$\text{FAME}\ \% = +88.41 + 2.22 * a - 1.31 * b + 1.42 * c - 0.74 * d - 0.60 * a * b + 0.69 * b * c - 4.02 * a^2 - 7.62 * b^2 - 2.80 * c^2 \quad (4)$$

Also, the actual equation for the FAME yield was obtained as follows:

$$\text{FAME}\ \% = -91.78342 + 0.69050 * a + 232.58225 * b + 10.55528 * c - 0.73500 * d - 0.080667 * a * b + 1.37500 * b * c - 4.46524E-003 * a^2 - 121.99946 * b^2 - 0.70124 * c^2 \quad (5)$$

Table 4
Tests design based on the Box-Behnken.

Run	Reaction time (a)	Catalyst concentration (b)	Alcohol to oil molar ratio (c)	Rotor-stator distance (d)	Biodiesel Yield (%)
1	30	1.25	8	2	74.39
2	60	1.25	8	1	79.87
3	90	0.75	8	2	80.82
4	30	1	10	2	80.73
5	60	1	6	1	84.82
6	90	1	8	3	85.84
7	60	0.75	8	3	80.94
8	30	1	8	1	82.41
9	60	1.25	8	3	78.66
10	60	1.25	6	2	74.64
11	60	1.25	10	2	78.45
12	60	1	8	2	88.14
13	30	1	6	2	77.85
14	60	1	8	2	89.01
15	30	1	8	3	81.13
16	90	1	8	1	87.2
17	60	1	10	3	86.6
18	60	1	8	2	88.62
19	60	1	8	2	88.58
20	90	1.25	8	2	77.15
21	60	1	6	3	83.51
22	30	0.75	8	2	75.64
23	60	0.75	10	2	79.68
24	90	1	6	2	82.36
25	60	1	10	1	87.97
26	60	0.75	8	1	83.23
27	90	1	10	2	85.42
28	60	0.75	6	2	78.62
29	60	1	8	2	88.14

According to the correlation coefficients of Eq. (4), it can be claimed that the reaction time (a) and molar ratio (c) have the highest influence on the biodiesel yield produced, followed by the catalyst concentration (b) and the rotor and stator distance (d).

Diagram of interaction between model inputs (reaction time (a), catalyst concentration (b), the molar ratio (c), and rotor and stator distance (d)) concerning the model output (reaction yield) is given in Fig. 2. In this diagram, the model output is plotted by changing one

Table 5

The results of ANOVA using RSM.

Parameter	SS	df	MS	F-value	p-value prob > F
Model	569.63	9	63.29	522.06	< 0.0001
a-Time	59.14	1	59.14	487.82	< 0.0001
b- Catalyst concentration	20.72	1	20.72	170.94	< 0.0001
c- Alcohol to oil molar ratio	24.23	1	24.23	199.82	< 0.0001
d- Distance between rotor and stator	6.48	1	6.48	53.47	< 0.0001
ab	1.46	1	1.46	12.08	0.0052
bc	1.89	1	1.89	15.59	0.0021
a^2	108.65	1	108.65	896.16	< 0.0001
b^2	391.12	1	391.12	3226.15	< 0.0001
c^2	52.93	1	52.93	436.58	< 0.0001
Residual	2.30	19	0.12		
Lack of Fit	1.76	15	0.12	0.87	0.6281
Pure Error	0.54	4	0.14		
Cor Total	571.93	28			

SS: Sum of Squares, df: Degree of Freedom; MS: Mean Square.

Table 6

The coefficients performance model of hydrodynamic reactor in RSM.

Parameters	value	parameters	value
Standard deviation (Std. Dev)	0.35	R^2	0.9960
Mean	82.43	Adjust R^2	0.9941
C.V%	0.42	Pred R-Squared	0.9884
PRESS	6.65	Adeq Precision	71.274

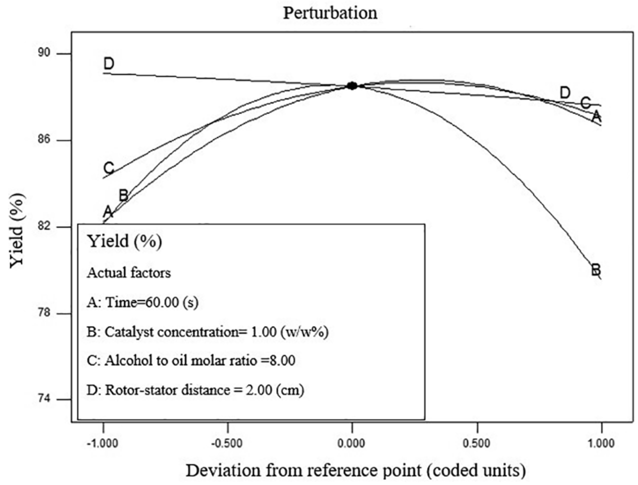


Fig. 2. Interaction of model inputs relative to each other.

input while the other inputs are considered constant [62]. This diagram presents a comparison of the impact of each parameter on the percentage of biodiesel fuel yield at a reference point. Accordingly, the yield is more sensitive to changes in parameter (a).

Fig. 3 shows the conformance of the test data to the software predicted data for the biodiesel yield. Such conformity tests the assumption of constant variance and is suitable for finding inaccurate values assumed by the predicted model [62]. As Fig. 3 shows, the values predicted by the model are very close to the values obtained from the experiment and thus the model presented for the yield has good validity in terms of the process variables.

3.3. Analysis of the main effect of parameters on reaction yield

The diagram of the effect of single input variables on the test output is shown in Fig. 4. The result of the analysis of the contribution of one input to the output shows the linear effect concerning the level change of each parameter studied.

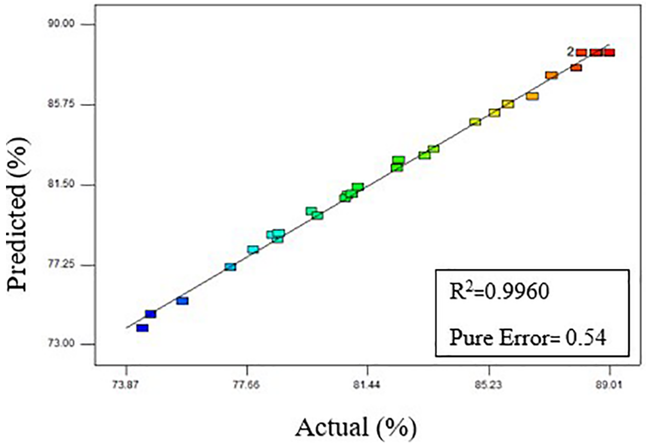
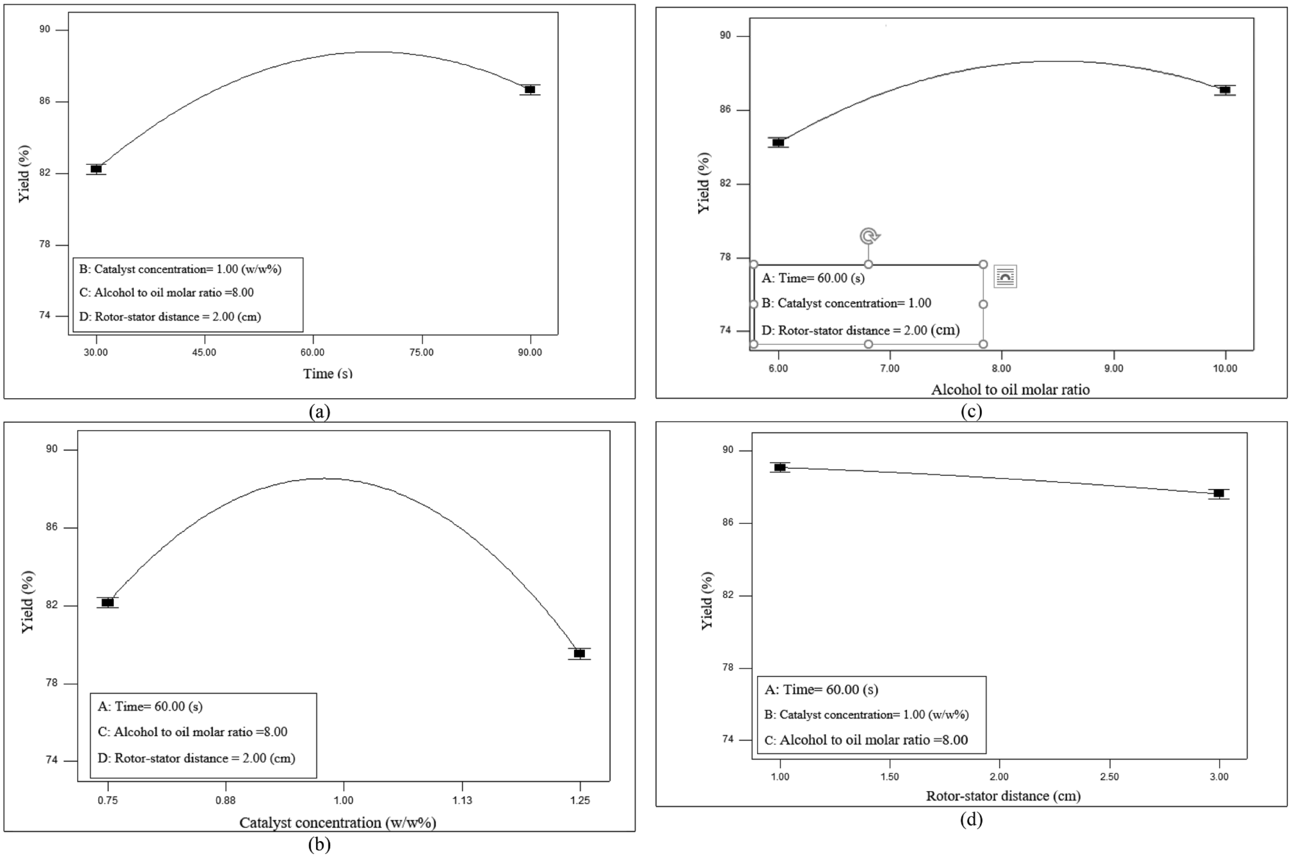


Fig. 3. Measured FAME yield in the experiments versus the model prediction.

Reaction time is one of the significant factors affecting the reaction yield. Due to having a higher coefficient in Eq. (4), the reaction time can have a more pronounced linear effect on the yield. Fig. 4a shows the effect of this factor on the yield of reaction. Among the independent variables, the reaction time is the most important factor in the reaction yield, which has a positive effect on the methyl ester content [17]. Initially, with increasing reaction time, the yield of biodiesel fuel produced increased, but as time passed, it was reduced. Due to the reversibility of the afore-mentioned reaction and its tendency to produce methanol, higher reaction time resulted in reduced yield [4]. By increasing the reaction time from 30 s to 60 s, the production of fuel increased from 82.23% to 86.78%, indicating a 5.5 percent increase in the percentage of converted fuel. This result can be interpreted as the fact that increasing the reaction time to a certain extent results in the more mass transfer of methanol and oil, resulting in increased solubility and performance miscibility [54]. As the reaction yield has declined over a long period, some studies have explained the fact that glycerin and methanol are both polar and jointly dissoluble. Thus, more methanol is dissolved on its surface by increasing the reaction time to produce more glycerin. Therefore, the reaction is converted to methanol production and the efficiency of the main reaction is reduced [6,64].

Fig. 4b shows the reaction yield as a function of the catalyst concentration. To perform the transesterification reaction, the catalyst is also added to the reaction in addition to the oil and alcohol at a rate of approximately a few percent by weight of the oil, thus lower levels of catalyst result in failure to obtain the desired yield [65]. In the present experiment, due to the negative coefficient of the catalyst concentration in Eq. (4), it can be concluded that the catalyst concentration has a reverse relation with the yield of reaction. As the catalyst concentration increased from 0.75% to 1.25%, the yield decreased from 82.10% to 79.95%, indicating a 2.68% decrease in the yield. This is because the increased use of the catalyst decreases the biodiesel yield and saponification of the transesterification reaction [6,17,65].

Another factor affecting the yield of biodiesel fuel is the molar ratio of alcohol to triglycerides. In order to complete the transesterification reaction, the minimum methanol required for complete conversion of triglycerides to the corresponding fatty acid methyl ester is equal to the stoichiometric ratio (1:3) [66]. The reaction between one mol of triglyceride and three mol of alcohol produced three fatty acid esters and 1 mol of glycerol based on its stoichiometric coefficients [57]. The use of more alcohols causes the reactive molecules to interact with each other more efficiently, resulting in an increased yield in a short period [32,67]. Fig. 4c shows the effect of the molar ratio of alcohol to oil on the yield. According to this figure, the highest yield (87.08%) was



(a) (c)

(b) (d)

Fig. 4. The effects of parameters on reaction yield: a) reaction time b) catalyst concentration c) molar ratio d) Rotor- stator distance.

obtained at a molar ratio of 10 and the lowest (84.10%) at a molar ratio of 6, indicating that the yield increased by 3.54% with rising molar ratio from 6 to 10. Also, because the molar ratio coefficient is positive in Eq. (4), it can be concluded that the molar ratio has a direct relationship with the yield. Given that the reactor used in this study utilizes hydrodynamic stirring, it can be argued that due to the lower residence time in this type of reactor compared to the Stirred Tank Reactor (STR) to conduct a transesterification equilibrium reaction toward the methyl ester production, more alcohol is needed in the hydrodynamic reactor compared to the STR reactor.

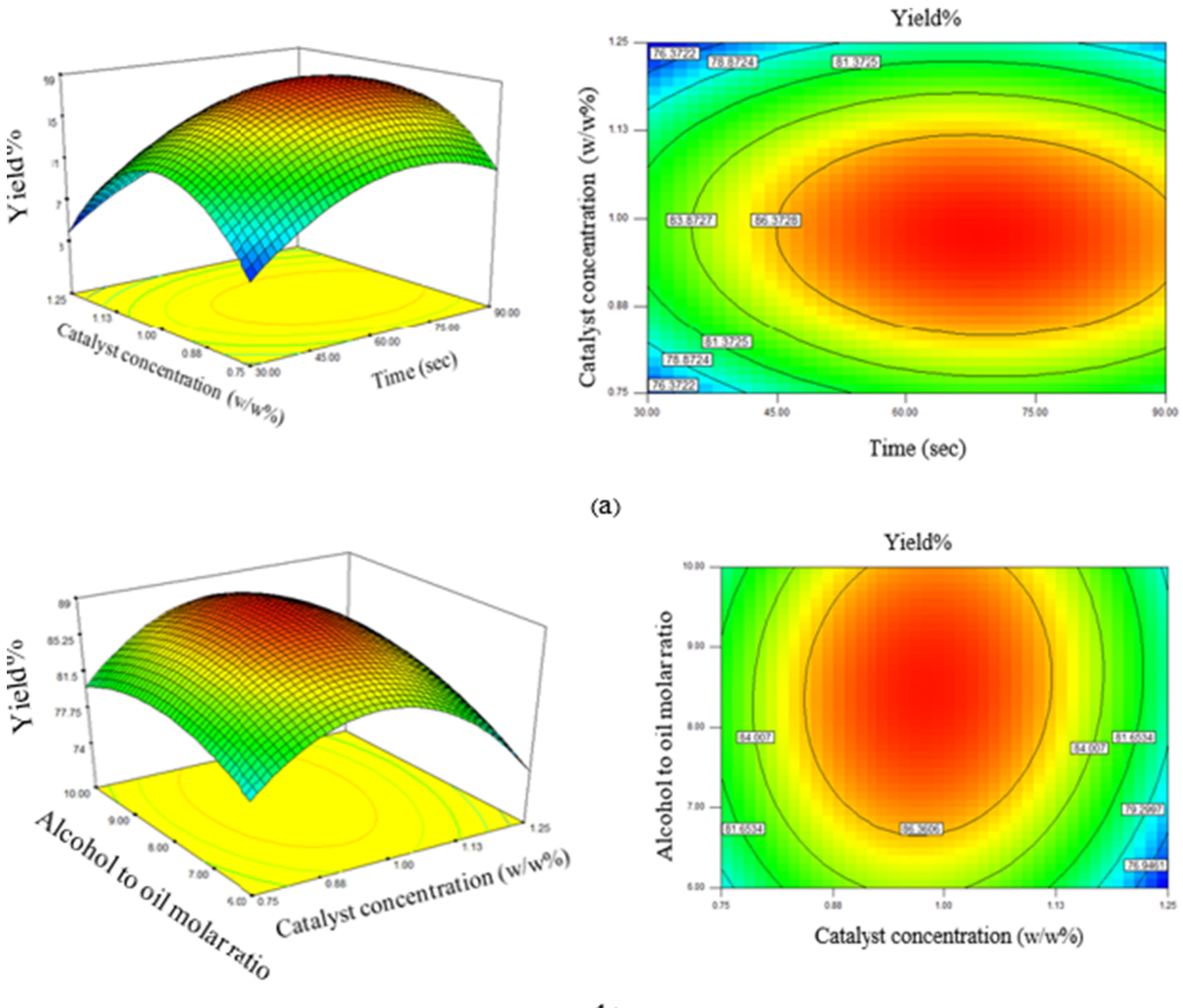
Fig. 4d shows the effect of rotor and stator distance on the yield of biodiesel produced. According to the figure, in1cm rotor and stator distance, the yield is 89.09%, but widening the distance up to 3 cm results in a reduction of yield by 87.62, emphasizing 1.67% reduction in yield of the produced fuel. It is also inferred from Eq. (4) that because of the negative coefficient of rotor and stator distance, this parameter has an adverse effect on the yield of biodiesel produced. Hydrodynamic cavitation reactors, due to the presence of holes on the rotor as well as the fluid rotation between the rotor and the stator with high speed, cause shear force in the liquid and create bubbles and then collapse of the bubbles. The longer the distance between the rotor and the stator, the less effect of shearing force and the miscibility of mixture, resulting in a reduced yield. Also, the thin film formed between the rotor and the stator, which increases the mass transfer between the reactants, decreases when distance increases (extends) [65].

3.4. Analysis of the interactive effect of parameters on reaction yield

The results of the single independent variable analysis show that the effect of each independent variable depends on the settings of the other variables. Contour plots and three-dimensional reactor yield percentages using the RSM versus four input reaction times, catalyst concentration, molar ratio, and the distance between the rotor and the stator are shown in Fig. 5.

According to Fig. 5a, the yield followed an increasing trend per an increase in reaction time and decrease in catalyst concentration, with the highest value being 88.62% at 60 s reaction time and 1% catalyst concentration. In a similar study, Farvardin et al. (2019) studied the biodiesel production from waste oil by hydrodynamic and ultrasonic cavitation. The results showed that increasing the reaction time led to an increase in the reaction yield, but an increase of 1.25% in the catalyst concentration reduced the yield by 7%, indicating a reverse relationship between the catalyst concentration and the yield [6]. In another study, Hosseinzadeh et al. [68] investigated the production of biodiesel from Pistacia Atlantica oil using the ultrasound. The results showed that when the reaction time was increased in the range of 5–7 min, the methyl ester content increased accordingly. However, when this parameter is out of range, the reaction yield percentage is reduced.

Increasing the molar ratio and decreasing the catalyst concentration simultaneously increases reaction yield (Fig. 5b). The use of a higher molar ratio results in a higher percentage of yield due to more efficient contact of the reactive molecules with one another [69]. The optimization of the hydrodynamic cavitation process in biodiesel production was investigated through the use of RSM by Chitsaz et al. (2018). The results showed that to achieve 95% reaction yield, the molar ratio of alcohol to oil should be 6:1. With 5:1 molar ratio of alcohol to oil and 1 wt% catalyst value, the efficiency was 92.5%, indicating a high yield of this method (hydrodynamic cavitation process). It was also found that increasing the catalyst content by > 1.5 wt% reduced the yield e of the reaction [65]. Hosseinzadeh et al. [17] produced biodiesel from safflower oil using ultrasonic technology. The results of their investigation indicated that with changing molar ratio from 1: 4 to 1: 6, the reaction yield initially increased 11.42% and then remained



(a)

(b)

Fig. 5. Interaction of Independent Variables on the reaction yield.

unchanged from 1: 6 to 1: 8 point. Due to non- significance status concerning the interactive effect of time × molar ratio (ac), time× rotor and stator distance (ad), catalyst concentration × rotor and stator distance (bd), molar ratio × rotor and stator distance (cd), the reaction yield does not have a significant change in line with the interactive effect of these parameters.

3.5. Characteristics of produced biodiesel

For a methyl ester to be capable of being introduced as the biodiesel fuel, some of its physical and chemical properties must meet the existing standards. Some physical and chemical properties of biodiesel obtained from the safflower oil in a hydrodynamic cavitation reactor, including the density at 15° C, viscosity at 40° C, iodine content, acid content, flash point, free glycerine and cetane number were measured according to ASTM D6751standard test and results were compared with the EN 14214 standard (Table 7). The results showed that most of the properties conform to this standard.

3.6. Process optimization

In the optimization of the RSM, conditions corresponding to Fig. 6 were used to find the proper settings with the highest yield. In this figure, four input parameters of the model, namely, the reaction time, catalyst concentration, molar ratio, and rotor–stator distance, can be changed in the range of experimental treatments. The goal of this optimization is to achieve the conditions for the input parameters which have the highest yield, and the results are plotted on the diagrams. The highest yield was achieved at 63.88 s, 0.94 wt% catalyst concentration, 8.36:1 alcohol to oil molar ratio, and 1.53 cm rotor and stator distance

Table 7
Some key characteristics of safflower oil-derived biodiesel.

Properties	Unit	EN 14214	ASTM D6751	SFO methyl ester
EC	% (m/m)	< 96.5	–	95.9
D at 15 ˚C	g/ cm^3	0.86–0.9	–	0.87
KV at 40 ˚C	mm/s	3.5–5.0	1.9–6.0	4.52
AN	mgKOH/g	< 0.5	< 0.5	0.37
IN	g Iodine/100 g oil	< 120	–	117.47
FP	˚C	> 101	> 130	157
CN	–	> 51	> 47	48
FG	%mass	0.02	–	0.017
TG	%mass	0. 24	–	0.25

EC: Ester Content; D: Density; KV: Kinematic Viscosity; AN: Acid Number; IN: Iodine Number; FP: Flash Point; CN: Cetane Number; FG: Free Glycerine; TG: Total Glycerine.

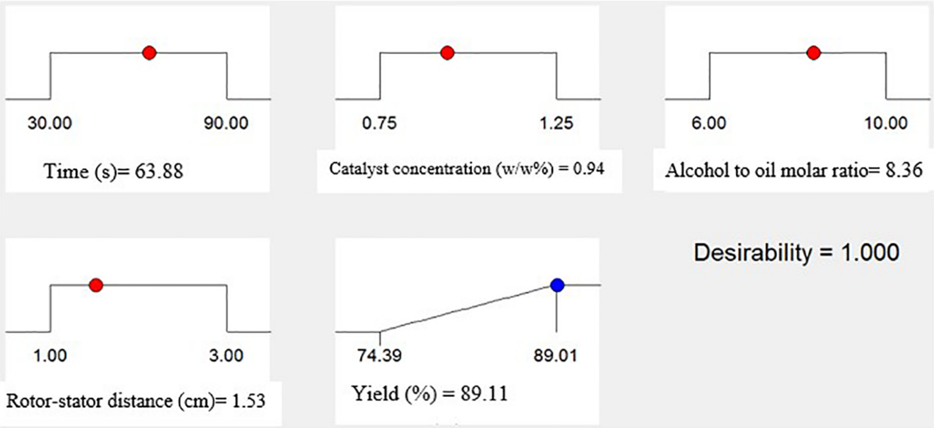


Fig. 6. Optimization of the biodiesel production process in hydrodynamic cavitation reactor based on the RSM model.

(equal to 89.11). To evaluate the optimization results under laboratory conditions, the proposed software settings were implemented as far as possible and a reaction yield of 88.18 was obtained, which is acceptable because of the closeness to the results obtained from the software.

4. Conclusions

Although there have been several studies on biodiesel production using different intensified reactors and different raw materials, no study has concentrated on the use of a hydrodynamic cavity reactor for biodiesel production from safflower oil. According to the studies conducted, the efficiency of biodiesel production in hydrodynamic cavitation reactors is higher than that of the ultrasonic reactors, and in turn, is more common and easier to implement in industry. Therefore, in this research, the hydrodynamic cavitation reactor was utilized to obtain the optimum settings for biodiesel fuel production. Safflower oil was used as the feed. Increasing the reaction time from 30 s to 60 s resulted in a 5.5% increase in the yield of reaction. Also, the yield decreased by 2.68% as the concentration of catalyst increased from 0.75% to 1.25%. Over the long (extended) distance of the rotor and stator, the effect of shear force and blending of the mixture decreased, resulting in a reduced yield. According to this study, with the alcohol to oil molar ratios 10 and 6, the yield was obtained as 87.08% and 84.10%, respectively. The highest yield in this study was 88.62% and the lowest yield was 74.39%. Analysis of the biodiesel produced by the hydrodynamic cavitation reactor showed that some of its fuel properties met the characteristics listed in EN 14214 standard. Therefore, transesterification of safflower oil with a hydrodynamic cavitation reactor can be a suitable alternative to the conventional diesel.

CRediT authorship contribution statement

Bahram Hosseinzdeh Samani: Conceptualization, Writing - original draft, Software. **Mehrsa Behruzian:** Writing - original draft, Formal analysis, Investigation. **Gholamhassan Najafi:** Investigation, Validation, Supervision. **Ebrahim Fayyazi:** Writing - original draft, Investigation, Methodology, Supervision. **Barat Ghobadian:** Investigation, Visualization, Data curation. **Ava Behruzian:** Visualization, Data curation. **M. Mofijur:** Writing - review & editing. **Mohamad Mazlan:** Conceptualization, Writing - review & editing. **Jun Yue:** Investigation, Methodology, Writing - review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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