RESEARCH ARTICLE

Biodiesel from fish waste oil: synthesis via supercritical methanol and thermodynamic optimization

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Abstract

This study evaluates the potential of local fish waste oil as a feedstock for biodiesel via supercritical methanol transesterification (SCMT). Hexane was used as a cosolvent and the transesterification reaction was carried out in a continuous reactor under supercritical conditions. The response surface methodology (RSM) method was applied to analyse the effect of four independent variables, including the weight ratio of methanol to fish-waste oil (W), the reaction temperature (T), the pressure (P) and the feed flow rate (F), on the yield of the biodiesel production in supercritical methanol. According to the calculated optimal operating condition for the RSM, the values of W (22.3 weight ratio of methanol to fish waste oil), T (270°C), P (112.7 bar) and F (2.0 mL min−1) were achieved. Under the optimum conditions, the highest yield was estimated to be 94.6% (g/g). The obtained yield was found to be close to the theoretical yield (95.2%). This value suggests that the proposed strategy has a promising potential in the production of biodiesel fuel.

Graphic Abstract

Keywords: bioenergy; supercritical methanol; fish waste oil; biodiesel; transesterification; response surface methodology
Introduction

Recently, among renewable sources, biodiesel has drawn the attention of researchers and engineers as one of the practical and promising solutions for energy issues and as a replacement choice for traditional fossil-based fuels. The biodiesel is normally synthesized through the transesterification reaction of vegetable oils, animal fats or waste oils with short-chain alcohols [1]. In a typical method, due to the slow formation of the two phases of oil and alcohol, the presence of a catalyst (an alkaline substance such as sodium hydroxide or potassium hydroxide) in biodiesel production is essential. Applying the catalyst presents a series of restrictions and disadvantages, including the requirement for excessive energy consumption for complex purification operations and the production of undesirable side reactions that are not able to provide an acceptable conversion rate [2]. To provide a practical solution, Saka and Dadan [3] proposed a new breakthrough in catalyst-free production for biodiesel under supercritical conditions. This innovation promises a lot of advantages including no need for a catalyst, separation with less complexity and higher reaction rates without producing wastewater [4]. Basically, methanol under supercritical conditions turns into a wonderful solvent that dissolves the feedstock. Therefore, these molecules of the reactant react simply without any particular catalyst [5]. The fact that the alcohol is present under pressurized conditions in the reaction medium leads to higher solubility of the substrate, increasing the reaction rates and ester yields [6]. The use of supercritical methanol has potential in the economical conversion of low-quality feedstock and oils with a high free-fatty-acid (FFA) content, such as waste oils [7]. Biodiesel holds many advantages over conventional petroleum diesel, such as high biodegradability, high cetane index, and significant reductions of engine exhaust emissions of carbon monoxide and hydrocarbons as compared to petroleum diesel [8]. The only limitation of using this fuel may be its high cost in comparison with that of conventional diesel fuel. This high cost of biodiesel production is because of the high price of the feedstock in this process [9]. To reduce these costs, waste animal fats can be used as a potential feedstock. Some oils of low quality, including of trap grease, cooking oils (contains 2–7% FFAs) and animal oils (contains 5–30% FFAs), are used as feedstocks in biodiesel production [10]. The fish industry poses a high potential threat to the environment if their waste is not disposed of properly, which provides an opportunity to use waste fish oil as a source of renewable fuel for cleaner power generation [11]. A pretreatment step is needed to reduce the FFA level. Consequently, a low amount of the FFA in pretreated oil can be transesterified, converting the triglycerides into biodiesel, using an alkali catalyst [12]. In a recent study focusing on biodiesel from vegetable oils, the effects of various types of vegetables on the characteristics of biodiesel fuel were investigated [13]. In another study, the authors synthesized fatty-acid methyl ester using oil from viscera fish through an enzymatic catalysis and analyzed the biodiesel in terms of physico-chemical characteristics [14].

The addition of a cosolvent improves the mass transfer between oil and alcohol by increasing the solubility and the creation of a single phase [15]. In this study, the utilized alcohol for biodiesel production has a high degree while triglyceride has a low degree of polarity. As a result, the cosolvent should have a medium level of polarity [16]. The yield in biodiesel obtained in the present study utilized hexane as a cosolvent, as it has a medium level of polarity [17], with 20% hexane (v/v) [18].

The primary motivation and novelty of this study is the “efficient production of the biodiesel from fish waste oil and methanol under supercritical conditions” to reduce significant costs of producing biodiesel in comparison with conventional approaches, which typically need pretreatment of the raw materials at very high costs (please see the graphical abstract). The novelty relies on the application of supercritical methanol transesterification (SCMT) and the use of fish waste. However, supercritical conditions have been applied to other types of oil such as fish waste, but fish waste as a source of oil was not considered in other studies. This paper also relies on a feasibility study of using local fish waste in Iran as a source of biodiesel. There exists a remarkable potential for the utilization of fish oil as biodiesel in Iran, as its potential is great among other renewables in Iran. Fish waste amounted to 300 000 tons in the Persian Gulf and ~33 000 tons in the Caspian Sea, with an overall rate of ~442 000 tons throughout the year 2003 [10]. Another objective of this paper is to investigate the use of local fish waste oil in Iran as a raw material in the economical and easy production of biodiesel fuel.

The transesterification reaction was carried out in a continuous reactor under supercritical conditions and the transesterification of fish waste oil was performed via supercritical methanol. The response surface methodology (RSM) method was applied to analyse the effect of four parameters, including temperature (T), pressure (P), the molar ratio of alcohol to oil (W) and the feed flow rate (F) on the yield of the biodiesel production in supercritical methanol.

1 Materials and methods

1.1 Materials

The fish waste oil was purchased from Arman Jonoub Co. Normal hexane and methanol (purity >99%) were ordered from Iran Chemicals Co. and Shiraz Petrochemical Co., respectively. The fatty-acid compositions of the fish waste oils are listed in Table 1.

1.2 Apparatus and experimental design

Schematics of the experimental set-up to perform the reaction are depicted in Fig. 1. Because of the supercritical treatment conditions and in order to sustain high levels of pressure and temperature, a tubular reactor was placed in an oven. It comprised 316 tubes made from stainless steel with internal diameter of 0.74 cm and length of 0.55 m. After temperature stabilization, the feed consisting of fish waste
1.3 Experimental design

An experimental procedure was designed for the process to study the effective variables in the esterification reaction. This method was performed using the central composite design (CCD), which takes into account four independent thermo-physical variables including the methanol-to-fish-waste-oil-weight ratio (W), feed flow rate (F), reaction temperature (T) and reaction pressure (P) at five coded levels (−2, −1, 0, 1, 2). These ranges were selected based on several prior experiments and, consequently, the rest of the experiments, as depicted in Table 2, were carried out according to the analysis of the design matrix. In the next step, after completing all the experiments, the obtained results as the biodiesel yield were modelled by the RSM via a quadratic polynomial interpolation as:

\[ Y = b_0 + \sum_{i=1}^{n} b_iX_i + \sum_{i=1}^{n} \sum_{j=1, j>i}^{n} b_{ij}X_iX_j \]  

(1)

In Equation (1), Y is the outcome, n shows the number of investigated parameters and optimal variables in the experimental runs, \(X_i\) and \(X_j\) are the coded independent variables and \(b_0, b_i, b_{ij}\) and \(b_{ij}\) are the intercept, linear, quadratic and interaction coefficients, respectively. The coded values, as well as the real values corresponding to each code, are given in Table 3. The sequence of the experiments was random and a central point was performed in seven replicates to evaluate the repeatability. Minitab 17 was used for the statistical analysis of the experimental runs in which the significance evaluation for the developed polynomial function was carried out using analysis of variance (ANOVA) and determination of the correlation coefficient.

2 Results and discussion

The general quadratic function represented by Equation (2a) is the expanded version of Equation (1), which was employed to derive a model for regression based on a polynomial after fitting the output from the series of experiments:

\[ Y = \beta_0 + \beta_1X_1 + \beta_2X_2 + \beta_3X_3 + \beta_4X_4 + \beta_{12}X_1X_2 + \beta_{13}X_1X_3 + \beta_{14}X_1X_4 + \beta_{23}X_2X_3 + \beta_{24}X_2X_4 + \beta_{34}X_3X_4 + \beta_{11}X_1^2 + \beta_{22}X_2^2 + \beta_{33}X_3^2 + \beta_{44}X_4^2 \]  

(2a)

and interaction coefficients, respectively. The coded values, as well as the real values corresponding to each code, are given in Table 3. The sequence of the experiments was random and a central point was performed in seven replicates to evaluate the repeatability. Minitab 17 was used for the statistical analysis of the experimental runs in which the significance evaluation for the developed polynomial function was carried out using analysis of variance (ANOVA) and determination of the correlation coefficient.
T-time \((P < 0.05)\) were coded as effective parameters in the proposed model based on the coded variables. The determination coefficient \((R^2)\) and the corrected determination coefficient \((\text{Adj-}R^2)\) were estimated to be 98.99% and 97.35%, respectively. These results indicate that the appropriate precision of the proposed model for correlating the experimental data was successfully achieved. Each of the coefficients in the equation has been determined where the significant coefficients of the developed quadratic models were calculated using analysis of the standard deviation (Table 6). The value of \(P\) shows the probability for the situation in which a coefficient becomes 0. This value is <5% if the confidence level is assumed to be 0.95. Moreover, another indicator, \(R^2\) or the coefficient of determination, is considered for the analysis. Coefficient \(R^2\) represents the level of quality for fitting where a polynomial model function is used. For this study, the coefficient was obtained to be 98.5%, which reveals a great correlation among \(T, F, P\) and \(W\) with the response (Fig. 2).

### 2.2 GC analysis

The recorded chromatogram for the GC analyser system equipped with an FID detector was applied for quantitative measurement. The detector response of the FID with regard to different compounds is not the same in the recorded chromatogram. This can be attributed to several reasons, such as the number of unequal injections and the speed of the unequal injections, which have an effect on the peak integral area. To solve this problem and to reduce the uncertainty in the chromatography methods, the internal standard (IS) and the peak area normalization were used. To calculate the percentage value of each compound from the peak area of the chromatogram, the peak area of one of the compounds that was not participating in the reaction was used as the IS. Equation (3) was applied to increase the accuracy of the method. The RRF is the relative responses factor:

\[
A\% = \frac{\text{RRF} \times \text{Area}_A}{\sum \text{RRF} \times \text{Area}_A} \times 100
\]  

The recorded chromatogram of the biodiesel under supercritical conditions is depicted in Fig. 3. After analysing the fatty-acid methyl ester (FAME) content using the GC technique, the following results were obtained for the fish-oil biodiesel for the ratio and retention time (RT):

- oleic acid methyl ester (C-18:1) where RT = 13.88;
- palmitic acid methyl ester (C-16:0) where RT = 12.38;
- eicosapentaenoic acid methyl ester (C-20:0) where RT = 14.55;
- stearic acid methyl ester (C-18:0) where RT = 14.10;
- docosahexaenoic acid (C-22:6) where RT = 16.35.

The related peaks confirm that the biodiesel was successfully synthesized [19]. Furthermore, Equation (4) was used for calculation of the yield value:

\[
\text{Yield \%} = \frac{\text{Weight of Methyl Ester}}{\text{Weight of total oil in sample}} \times 100
\]
A generic chromatogram of the methyl esters for the selected sample with optimal values is shown in Fig. 3.

### Investigation of the effects of the process parameters

To investigate the different operating parameters such as P, F, W and T on the biodiesel-production efficiency, RSM diagrams were plotted. These diagrams were used to describe the effects of two variables on response values while the other two variables were constant. The biodiesel response graph (Yield%) as a function of the two parameter values of the reaction in a 3D graph is depicted in Fig. 4.

#### 3.1 Effect of the temperature (T) and pressure (P)

To investigate the effect of the pressure, the yield as a function of the T and P values of the reaction was researched. In this study, F and W were selected to have constant values

| Run no. | T (˚C) | P (bar) | F (mL min⁻¹) | ^w | Yield% |
|---------|--------|---------|-------------|----|--------|
| 1       | 270    | 120     | 2           | 15 | 93.7   |
| 2       | 170    | 80      | 2           | 25 | 90.6   |
| 3       | 270    | 80      | 1           | 15 | 77.2   |
| 4       | 170    | 80      | 2           | 25 | 87.8   |
| 5       | 170    | 80      | 1           | 25 | 72.4   |
| 6       | 170    | 120     | 2           | 25 | 92.1   |
| 7       | 270    | 80      | 2           | 25 | 93.0   |
| 8       | 270    | 80      | 2           | 15 | 92.8   |
| 9       | 220    | 100     | 1.5         | 20 | 87.7   |
| 10      | 170    | 120     | 2           | 15 | 89.8   |
| 11      | 220    | 100     | 1.5         | 30 | 88.3   |
| 12      | 220    | 100     | 1.5         | 20 | 89.8   |
| 13      | 220    | 100     | 1.5         | 20 | 90.3   |
| 14      | 220    | 100     | 1.5         | 20 | 90.6   |
| 15      | 270    | 120     | 2           | 25 | 96.3   |
| 16      | 220    | 100     | 1.5         | 20 | 89.1   |
| 17      | 220    | 60      | 1.5         | 20 | 85.1   |
| 18      | 220    | 100     | 1.5         | 10 | 83.3   |
| 19      | 270    | 120     | 2           | 15 | 78.7   |
| 20      | 220    | 140     | 1.5         | 20 | 86.1   |
| 21      | 220    | 100     | 1.5         | 20 | 88.4   |
| 22      | 220    | 100     | 2.5         | 20 | 91.6   |
| 23      | 320    | 100     | 1.5         | 20 | 90.0   |
| 24      | 270    | 120     | 1           | 25 | 76.4   |
| 25      | 220    | 100     | 0.5         | 20 | 63.1   |
| 26      | 220    | 100     | 1           | 1.5 | 87.5 |
| 27      | 120    | 100     | 1.5         | 20 | 82.4   |
| 28      | 270    | 120     | 1           | 25 | 83.7   |
| 29      | 270    | 80      | 1           | 25 | 80.9   |
| 30      | 170    | 120     | 1           | 15 | 68.8   |
| 31      | 170    | 80      | 1           | 15 | 68.5   |

^wThe weight ratio of methanol to oil.

| Term | Coefficient | T-value | P-value |
|------|-------------|---------|---------|
| Constant | 89.063 | 1760.3 | 0 |
| T | 2.734 | 10.01 | 0 |
| P | 0.759 | 2.78 | 0.013 |
| F | 7.786 | 28.49 | 0 |
| W | 1.557 | 5.7 | 0 |
| T² | -0.658 | -2.63 | 0.018 |
| P² | -0.843 | -3.37 | 0.004 |
| F² | -2.888 | -11.54 | 0 |
| W² | -0.787 | -3.14 | 0.006 |
| TW | -0.335 | -1 | 0.033 |
| TF | -1.172 | -3.5 | 0.003 |
| TP | 0.11 | 0.33 | 0.747 |
| WF | -0.815 | -2.44 | 0.027 |
| WP | 0.485 | 1.45 | 0.167 |
| FP | -0.008 | -0.02 | 0.982 |

3. Investigation of the effects of the process parameters

To investigate the different operating parameters such as P, F, W and T on the biodiesel-production efficiency, RSM diagrams were plotted. These diagrams were used to describe the effects of two variables on response values while the other two variables were constant. The biodiesel response graph (Yield%) as a function of the two parameter values of the reaction in a 3D graph is depicted in Fig. 4.
of 1.5 mL min\(^{-1}\) and 20:1, respectively. The reaction pressure in the interval 60–140 bar varies directly and proportionally with the amount of biodiesel produced. According to Fig. 4a, increasing the pressure up to an optimal amount (~112.7 bar) enhanced the solubility of the oil in alcohol to form a more homogeneous mixture [20]. Moreover, an increase in collisions between molecules of the alcohol and oil leads to an increase in the amount of methyl ester production, while a further increase in the pressure leads to enhancement of the dilution of the reactants and prevents the reaction between them. Therefore, the efficiency rate decreases at higher pressures [20]. According to Fig. 4a, increasing the pressure over an optimal level at low temperatures results in a further decrease in the amount of methyl ester produced and the yield of the production of biodiesel.

Pressure affects the thermo-physical properties as well as the hydrogen bonding, especially around the fluid’s critical point. Hence, the higher the pressure, the higher the fluid density, which results, at a specific reaction temperature, in stronger interaction among the particles [21].

### 3.2 Effect of the feed flow rate (F) and methanol-to-fish-waste-oil-weight ratio (W)

To investigate the effects of the F value on the biodiesel yield with T and P constant at values of 220°C and 100 bar, this parameter was studied within the range of 0.5–2.0 mL min\(^{-1}\). At high W values, increasing the F value leads to a reduced amount of produced biodiesel due to the lack of sufficient time for a reaction between the alcohol and the feed [22]. Due to the F value increasing, the likelihood of degradation of the methyl esters increases, so the biodiesel yield is reduced. Therefore, there is a slight reduction in the amount of biodiesel produced at high values of F and W (Fig. 4b).

Several experiments under different conditions have been conducted with the methanol-to-fish-waste-oil-weight ratio in the range of 10:1 to 30:1 in order to investigate the impact of its variation on the amount of produced biodiesel. Table 3 shows the results obtained from ANOVA in which the process response is significantly affected by the methanol-to-fish-waste-oil-weight ratio. Higher levels of excessive methanol reduce the temperatures of the critical products in the reaction products. The reason for this is that the critical state of the methanol is smaller in comparison with the conditions of the constituents of the mixture. If the critical temperatures of the components in the product are reduced, the FAME decompositions will improve and, as a result, the amount of produced biodiesel will decrease [23].

### 3.3 Effect of the methanol-to-fish-waste-oil-weight ratio (W) and temperature (T)

In Fig. 4c, the yield value has been shown as a function of the W and T values of the reaction. The P and F values have constant values of 100 bar and 1.5 mL min\(^{-1}\), respectively. Increasing the W value leads to an increase in the alcohol and oil contact levels, resulting in more products.
Furthermore, increasing the $W$ value reduces the critical temperature of the reaction mixture. At higher $T$ and $W$ values, by lowering the critical temperature of the reaction mixture, the biodiesel-production efficiency is decreased due to the decomposition of the produced methyl esters. Therefore, at high values of $T$ and $W$, the biodiesel yield goes down slightly [23].

The temperature of the reaction plays an important role in biodiesel-production efficiency under supercritical conditions, as it instantly impacts the stabilization of
the FAME production [20]. It is known that, by increasing the temperature of the reaction significantly up to 270°C, FAME achieves stability; however, beyond this level, decomposition begins as a result of isomerization between cis- and trans-forms [20]. So, with higher T and W values, the biodiesel-production efficiency is decreased due to the decomposition of the produced methyl esters. Therefore, the yield of the produced biodiesel reduces slightly at high values of T and W [22]. If the volumetric ratio of methanol to oil increases to a certain value, the biodiesel impurity will decrease, as was reported by similar observations in the literature [24].

3.4 Effect of the feed flow rate (F) and reaction temperature (T)

The effect of the T and F values of the reaction on the yield with W and P constant at values of 20:1 and 100 bar was studied. As can be seen in Fig. 4d, a high reaction temperature leads to increasing the chance of collision between the materials and, consequently, the speed of the reaction is increased. So, an increase in the yield value is achieved by the temperature increasing up to an optimum value of 270°C. At higher temperatures, the decomposition of unsaturated methyl ester of the fatty acid leads to a slight decrease in the yield value. Similar results have been observed by researchers in Ref. [25], in which it is reported that, if the reaction temperature increases to >271°C, the efficiency of the biodiesel production will start to reduce. Furthermore, the F value is effective on the biodiesel-production efficiency. At low F values, due to the prolongation of the reaction time, the possibility of producing side reactions of the decomposition of the produced methyl esters is increased. Consequently, biodiesel-production efficiency is decreased [20]. The related contour plots for this study are shown in Fig. 4e–h. Similar observations have been reported by recent studies when transesterification has been carried out at higher levels of reaction temperature [26].

3.5 Optimal level of variables

Using Minitab and its response optimizer package, the optimal levels of the selected reaction variables were achieved. The optimum operating conditions were determined and summarized by the RSM method (Table 7). Under optimum conditions, the predicted maximum yield was estimated to be 95.2%. To verify the predicted yield by the model developed, the optimal levels for the response variables were analysed for the predicted optimal conditions. Finally, the yield of biodiesel production was calculated to be 94.6%, which is close to the predicted yield (95.2%).

Table 7: Optimum operating conditions determined by the RSM

| Variables                  | Optimum value |
|----------------------------|---------------|
| M = methanol-to-oil-weight ratio | 22.3          |
| T = temperature            | 270°C         |
| P = pressure               | 112.7 bar     |
| F = flow rate              | 2.0 mL min⁻¹  |

Table 8: Optimum operating conditions determined by the RSM

| Alcohol                  | Experimental conditions                                                                 | FAME (wt%) | Reference                        |
|--------------------------|-----------------------------------------------------------------------------------------|------------|----------------------------------|
| Methanol                 | 22.3:1 methanol-to-oil-weight ratio; 270°C; 112.7 bar; 2.0 mL min⁻¹ | 94.6%      | This work                       |
| Methanol                 | 37:1 methanol-to-oil-weight ratio; 253.5°C; 198.5 bar                                  | 91%        | Aboelazayem et al. [27]         |
| Methanol                 | 43:1 methanol-to-tobacco-oil molar ratio; 300°C; 90 min                               | 92.8%      | García-Martínez et al. [28]     |
| Methanol                 | 40:1 methanol to Krating oil molar ratio; 260°C; 10 min; 160 bar                      | 90.4%      | Samniang et al. [29]            |

4 Conclusions

To sum up, the production of biodiesel fuel from fish waste oil was investigated using a transesterification reaction under supercritical conditions of methanol in a continuous system. The conventional catalytic methods caused some problems due to the sensitivity of the FFAs and the water present in the primary oil. Unlike these methods, the supercritical-alcohol method performs the transesterification reaction without the need for a catalyst, which eliminates catalyst-consumption problems and the need for separation and purification of the products from the catalyst. The operating conditions were optimized by designing the experiments using the CCD method. According to the optimal operating conditions calculated by the RSM, the values of W (22.3), T (270°C), P (112.7 bar) and F (2.0 mL min⁻¹) were achieved. The maximum efficiency predicted by the RSM was estimated to be 95.2%. The experimental yield of the biodiesel production under the optimum conditions was calculated to be 94.6%, which is close to the predicted yield (95.2%).
Conflict of Interest
None declared.

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