Biofuels

Evaluation of an enhanced ultrasonic-assisted biodiesel synthesized using Safflower oil in a diesel power generator

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Abstract

Given the energy crisis, fossil fuel reserves crisis, climate mitigation, and energy efficiency increase, scientists have embarked on producing alternative fuels such as the biodiesel. This study was conducted to investigate the feasibility of biodiesel production from safflower oil using the ultrasonic system, and to evaluate the produced fuel using a diesel power generator. In this study, the effects of alcohol-to-oil molar ratio, ultrasound power (W), catalyst concentration (w/w %), and the reaction time (min) on methyl ester yield were investigated. By increasing the molar ratio to a point between the ratios 4:1 and 6:1, the conversion rate first increases 11.42%, and then it remains unchanged from the point 6 to 8. As the ultrasonic power increases, the rate of conversion increases incrementally. The optimization was obtained at 7.02 molar ratio, 160 W ultrasound power, 0.95 (w/w%) catalyst concentration, and 8.47 min reaction time. The results showed that the brake torque and broke power increased when the amount of biodiesel in fuel increased from B0 to B50. The results showed that CO emissions decreased and NOx increased when there was an increase of amount of biodiesel.

Keywords: Renewable Energy, Optimization, Biodiesel, Safflower Oil, Response surface methodology.

1. Introduction

Alternative fuels refer to substances that share similar characteristics with fossil fuels which also can function effectively as alternative. Biodiesel is ethyl or methyl ester that is produced from vegetable oils or animal fats and used as the fuel in diesel engines or thermal systems [1]. Although the pure biodiesel (B100) can be used directly in standard diesel engines, the problem with using the pure biodiesel is its high viscosity, which weakens the engine's performance. To solve this problem, biodiesel is generally combined with standard diesel fuel [2]. Most of the biodiesel produced in the world is produced by the transesterification of triglycerides (vegetable oils and animal fats) with alcohol (methanol and ethanol) in the stirred-tank reactors (STRs) in the presence of acidic or alkaline homogeneous catalysts [3,4]. The transesterification is performed in a liquid-liquid, two-phase system, the rate of which is limited by the low-mass transfer due to the incompatibility of triglycerides and alcohol. One of the main challenges concerning the conduction of the transesterification using STRs is the limited speed of reaction due to the low mass transfer rates between oil and alcohol (incompatible mixture), the limitation of the upper limit of production efficiency due to lack of separation mechanism of the product during the reversible transesterification, and the discontinuous production of biodiesel. One of the intensification methods which could improve the quality of biodiesel production process is the use of ultrasound [5]. For more agitation and effective surface contact between alcohol and oil molecules, ultrasonic waves can be used. Ultrasound has proven to be a very useful tool in enhancing the reaction rates in a variety of reacting systems. It has successfully increased the conversion, improved the yield, changed the reaction pathway, and/or initiated the reaction in biological, chemical, and electrochemical systems [6]. When the mixture is subjected to ultrasound, ultrasonic waves create cavitation at exposure point [7]. As a result, an emulsion of oil and alcohol is formed that provides a large surface for the reaction, and the response time is significantly reduced [8]. Sonochemistry is generally performed in a liquid medium. During each 'stretching' phase (rarefaction), provided that the negative pressure is strong enough to overcome intermolecular binding forces, a fluid medium can be torn apart, producing tiny cavities (micro bubbles) [6,9]. In succeeding cycles, these cavities can grow and then collapse violently with the release of large amounts of energy. Experimental results have shown that approaching 5000 ^{o}K temperatures and 2000atmpressures are produced during this collapse [10].

Fayyazi et al., (2014) produced biodiesel fuel using an ultrasound system (24 kHz and 400 watts) from the waste oil. Also, other studies reported similar results regarding the increase in biodiesel conversion using ultrasound [11,12].

Hosseinzadeh et al. (2015) sought to reduce the production time of biodiesel from *Pistacia atlantica* oil with the lowest possible energy consumption (process optimization) using ultrasound. They investigated the effects of variables, including molar ratio of alcohol to oil, ultrasound amplitude, ratio of the duration of ultrasound on to that of ultrasound off (pulse), and reaction time on the rate of methyl ester conversion [5].

Moreover, many researchers have investigated the effects of biodiesel fuel blends on engine indicators such as the brake power, brake torque, brake thermal efficiency (BTE), exhaust gas temperature (EGT), Brake-specific fuel consumption (BSFC), NOx, Exhaust particulate matter (PM), CO, CO_2, hydrocarbon emission (HC), and smoke density in comparison to those of diesel.

The results of these studies showed that different sources of biodiesel feedstocks led to different engine indicators.

The researchers have also addressed the engine performance and emissions when using biodiesel, and most of them have reported that when using biodiesel, engine power and torque decreases due to the loss of biodiesel heating value [13,14]. Some studies have shown there is no significant difference between B100 and diesel with respect to the engine power [15,16]. However, some researchers have reported that there may be unanticipated increase in power or torque of diesel engines [2,17]. On the other hand, evidence has shown similar trends of engine power performance with load or speed of engines fueled with B100 and B0 [18].

Carthamus tinctorius L., commonly known as safflower, is one of the world's oldest crops belonging to the Asteraceae family and is native to the Middle East. Safflower is a tap-rooted annual crop that can withstand environmental unpleasant conditions (drought, salinity), the production of which reaches to above 420000 ton annually, distinguishing it as a potential bioenergy crop. Safflower is a highly branched, thistle-like, herbaceous plant. It is commercially cultivated for the oil of its seeds. The seeds contain 27–32% oil, 32–40% crude fiber, 5–8% moisture, 14–15% protein, and 2–7% ash. Safflower is a valuable plant due to the variety of its fatty acid content. The composition of standard safflower oil is 2–3% stearic acid, 16–20% oleic acid, 6–8% palmitic acid, and 71–75% linoleic acid [19]. This study was conducted to investigate the feasibility of biodiesel production from safflower oil using the ultrasonic system, and to evaluate the produced fuel on a diesel power generator to investigate the including engine performance and emission parameters when using different levels of diesel -Safflower biodiesel blends.

2. Material and Methods

2.1. Oil extraction

Soxhlet extraction, which is a conventional method and used for the extraction, was carried out in a classic Soxhlet extractor in the presence of n-hexane as a solvent (Figure 1). 10 g of safflower seeds were milled using a laboratory mill. Subsequently, powdered seed was placed in an extraction thimble and then Soxhlet was extracted for 8 h using 200 ml of n-hexane. After extraction, the solvent was evaporated by rotary evaporator and weighed. This procedure was repeated until a constant value for the extracted weight was obtained [20]. Oil yield was further calculated and presented as a weight of extracted oil per weight of sample. Some of physical and chemical properties of safflower oil are shown in Table 1.

Figure 1. A schematic representation of a Soxhlet extractor

Table1. Fatty acid profile and properties of used Safflower oil

2.2. Transesterification reaction

In this section of the experiment, the oil reacts in the presence of methoxide and results in the production of biodiesel and glycerol. Then, oil to methyl ester conversion (yield of the reaction) was investigated in different levels of desired independent variables. . Methoxide is the mixture of a catalyst and methanol. To prepare the methoxide according to Table 2, at each step, the desired amount of alcohol was poured into a beaker, and after adding the catalyst, the stirring method was used to reduce the dissolution time and evaporation rate of alcohol. The alcohol used in this study was methanol (Merck Co., Germany) with a purity of 99.9%. Potassium hydroxide tablets (Merck Co., Germany) with purity of 99.8% were also used as catalyst.

The pre-heated oil was then mixed with the previously prepared methoxide. Afterward, the mixture (*Safflower* oil and methoxide) was transferred to the reaction chamber to be subjected to ultrasound waves. An ultrasonic processor (Topsonic Model, UP400, Iran) was used to perform the transesterification reaction. The equipment consisted of the processor, sonotrode, and PC controller. The processor operated at 400 W and 20 kHz frequency (Figure 2).

The PerkinElmer-Clarus 580 gas chromatograph (made in the USA) was used in this study which was set up based on the BS EN 14103 standard [21]. The Fatty acid methyl ester (FAME) yields of each transesterification step were calculated from the weight of FAME in the FAME phase and the theoretical material balance of the transesterification reaction (BS-EN 14103 standard), as shown in Equation (1):

$$FAME(\%) = \frac{W_{FAME}/M_{FAME}}{3W_{SO}/M_{SO}} \qquad (1)$$

Where W_{FAME} and W_{SO} are the weights of FAME in the FAME phase and the weight of used *Safflower* oil (SO), respectively. M_{FAME} and M_{SO} are the average molecular weights of FAME and SO, respectively. Once the glycerol is separated from biodiesel, additional material should be removed from biodiesel. These materials include soap, some precipitated glycerol and a catalyst, which, if left in the burning process, causes undesirable effects in combustion, resulting in bad odor and smoke in combustion products.

Figure 2. The Schematic of set-up for ultrasonic-assisted biodiesel production process

2.3. Optimization and statistical analysis

The design of the present study follows the box-behnken method. The response surface methodology is a set of mathematical and statistical techniques that are used to develop, promote, and optimize the processes in which the level in question is affected by many variables and the goal is to optimize the response [22,23]. Some phases in the application of RSM as an optimization, modeling and analysis technique is as follows: (1) the selection of independent variables concerning the major effects on the system through screening studies and definition of the experimental region, according to the objective of the study, the experience of the researcher and literature reviews; (2) the selection of the experimental design and implementing the experiments according to the selected experimental matrix; (3) setting the mathematic–statistical orders of the collected experimental data via the fit of a polynomial function; (4) finding the optimum values for all of the studied variables [24]. To derive optimal value, Regression Equation (2) was be used.

$$Y_i = \beta_0 + \sum \beta_i X_i + \sum \beta_i X_i X_j + \sum \beta_{jj} X_i^2 + \varepsilon \qquad (2)$$

where βo, βj, βij and βjj are constant coefficients, xi and xj independent variables in the process and ε are random errors. The levels of independent variables (Table 2) were selected according to the literature review and screening study experiments [5,11]. Finally, according to the curves drawn and the range for the independent variables, the optimal point was obtained and the result was validated by the validation test.

Table 2. Selected independent variables in response surface method

It should be noted that at all phases of the experiment, a power analyzer was used to measure the power consumption of the devices used in the test. Data analysis and optimization were done using the Design Expert software (version 7.0.0, Stat-Ease Company®).

2.4. Engine test

In this study, to investigate the performance characteristics of a diesel engine using biodiesel produced from the safflower oil, different volume ratios of the combination of biodiesel and routine diesel in Iran were prepared and examined. These volume ratios are B (0), B (20), B (50), B (80) and B (100) which were selected according to the latest literature reviews [25,26]. The mixtures were tested in the diesel generator at 50% of the full load and a constant speed of 1530 rpm to derive the required data and compare the performance characteristics of mixed fuels with those of the pure diesel.

2.5. Studied diesel generator

The diesel power generator consists of an engine and a generator, and the engine used in this research is a 4-cycle engine and 12 cylinders (CAT3412 Co.) equipped with supercharge, an indirect spray system with a maximum power of 537 KW at rotational speed of 1,800 rpm. The generator connected to the engine has been manufactured by Caterpillar Co., which is three-phase, powered by 380 V with a maximum power consumption of 300 kW at the rated speed. The generator is connected to a central processing unit that starts processing by using the data from different points and displays the output voltage, power, and engine speed on the control panel. Table 3 presents the technical specifications of the diesel generator.

Table 3. Specification of the test engine

3. Results and discussion

3.1. Biodiesel production

The P-value (0.01) of the model implies its significance. In this case, ultrasonic power, catalyst concentration, molar ratio, time, ultrasonic power × catalyst concentration, ultrasonic power × molar ratio, catalyst concentration × molar ratio, molar ratio × time, catalyst concenteration^2, molar ratio^2, and time^2 are the significant model terms. Values greater than 0.1000 indicate the model terms are not significant. The lack of Fit *F* value of 0.75 implies the Lack of Fit is not significant relative to the pure error. There is a 67.68% chance that a lack of Fit *F* of such value is due to the noise (Table 4).

From the data analysis, Equation (3) was determined. Correction coefficient and error standard for the drawn model are 0.9971 and 0.50, respectively.

$$\text{Yield}=-64.12315-0.012593\times A+141.40000\times B+20.43333\times C+2.18333\times D+0.025000\times A\times B+3.12500\text{E-}003\times A\times C-6.94444\text{E-}004\times A\times D-1.50000\times B\times C+0.33333\times B\times D+0.25000\times C\times D-1.96759\text{E-}005\times A^2-72.53333\times B^2-1.53958\times C^2-0.15648\times D^2 \quad (3)$$

Table 4- The results of reactor performance model by response surface methodology

Based on the results of analysis of variance of regression coefficients, non-significant coefficients were excluded from Equation (3), and the final Equation as well as coding (4) and (5) was drawn to obtain a standard error of 0.75 and a determination coefficient of 0.9907.

Figure 3 illustrates the comparison of the actual data with the predicted data; given the shape and close compatibility of these numbers, there is a strong correlation between the results obtained by the experimental method and the values predicted by the statistical test.

$$\text{Yield}=-64.12315-0.012593\times A+141.40000\times B+20.43333\times C+2.18333\times D+0.25000\times C\times D-72.53333\times B^2-1.53958\times C^2-0.15648\times D^2 \quad (4)$$

$$\text{Yield}=+87.40+1.92\times A-0.92\times B+5.67\times C+5.83\times D+1.50\times C\times D-4.53\times B^2-6.16\times C^2-1.41\times D^2 \quad (5)$$

Where A is the ultrasonic power, B is the catalyst, C is the molar ratio, and D is the reaction time. Regarding the values of the coefficients of Equation (5), it can be argued that the greatest effect in the production of methyl ester, among the studied variables, was obtained for the molar ratio test and the time of reaction, followed by the ultrasonic power and catalyst concentration.

Figure 3. Actual data versus predicted data

As illustrated in Figure. 4a, the effect of ultrasound on the production of biodiesel is greater than that of the catalyst concentration. With an increase in ultrasound power from 160 W to 400 W, the performance increased by 3.83%. Ultrasonic reactors increase the speed of chemical reactions by increasing the mass transfer and creating intermediate phases between the reaction phases, as well as reducing the intensity of reaction conditions such as the temperature and pressure.

The created cavitation leads to the loss of the boundaries between the reaction phases, thus the formation of emulsions that will cause the phases to overlap each other [27].

The reason for such an increase is the increase of ultrasound stirring intensity per increase in the power, which increases the contact of the two formed phases (methoxide and oil). This increased surface reduces the reaction time from 90 min to about 6 min [11]. Other studies have also shown that increasing the power of ultrasound will increase the conversion rates for the above reasons [28]. As illustrated in Figure. 4b, by increasing the molar ratio to a point between the ratios 4 and 6 to 1, the conversion rate first increases to 11.42, and then it remains unchanged from the point 6 to 8. The reason for this observation is the balance of the transesterification reaction which leads to the progression of methyl ester (biodiesel) production by increasing the molar ratio of alcohol to oil [5]. It should be noted that this increase in the rate of methyl ester conversion is limited due to an increase in molar ratio, because if this ratio exceeds a certain value, the purity of the produced biodiesel decreases. The main reason for this observation is that increasing the amount of methanol in the reaction mixture results in the greater dissolution of glycerol and alcohol in biodiesel and will significantly affect its purity. Another study showed that by increasing the molar ratio from 6 to 7, the rate of methyl ester conversion decreased [27]. As Figure. 4c illustrates, increasing the reaction time between the minutes 3 and 9 results in the increase of conversion rate. The reason for such an increase is that with increasing the reaction time, the amount of radiation to which the reaction mixture is exposed increases within a constant duration, and therefore the effect of ultrasound on the reaction environment increases proportionally. Besides that, given that the transesterification reaction is an equilibrium reaction, reducing the amount of reactive material in the reaction environment will cause the reaction to be reversed and the conversion rate of biodiesel reduced. The reason for this is that the physical effect of ultrasound is due to the emulsion preparation in insoluble reactors (oil and alcohol), and the reaction synthetics increases dramatically with increasing the overlapping surface between these reactors through the micro turbulence generated during the cavitation [29]. In a similar experiment, Kumar et al. (2010) used an ultrasound system to produce biodiesel from coconut oil and concluded that the time of ultrasonic reaction was reduced by 15-40 times compared to the conventional reaction [30].

Hosseinzadeh et al. (2015) observed that trends of reaction time and molar ratio differed from those of amplitude and molar ratio on methyl ester content so that they were divided into two parts. As reaction time and molar ratio increased to 5-7 min and 5-6, respectively, methyl ester content increased; however, when these two variables exceeded the ranges, yield decreased. This can be related to the equilibrium of transesterification reaction that progresses with increasing the molar ratio of alcohol to oil, and therefore biodiesel production increases [5].

The study of the effect of catalyst concentration on the conversion rate showed that with increasing the catalyst content from 0.75 to 1, the performance increased by 3.92% and then with increasing its content from 1 to 1.25, the performance decreased by 5.05%. The reason for this reduction can be that further catalyst loading would be inefficient in biodiesel production [31].

Decreased biodiesel yield due to increasing the KOH catalyst concentration is attributed to the formation of soap that contains excess amounts of catalyst [32]. According to the study of Patil et al., (2009), alkalicatalysed transesterification is very sensitive to water, while the existence of water may lead to ester saponification under alkaline conditions. Besides that, excess amounts of catalyst may result in the formation of emulsion, which increases the viscosity of the biodiesel and induces gels formation [33]. In general, the catalyst cost accounts for a large proportion of biodiesel production expense. The ultrasound power enhances the methanol emulsion in oil and furthers production of fine particles. This pattern results in an appropriate distribution and improves the efficiency of the catalyst. In addition, the ultrasound cavitation enhances the mass transfer, and therefore, compared with conventional stirrers, the catalyst consumption decreases by 50% [28].

Figure 4. Figure 4. Response surface plot showing the interaction effects of (a) ultrasonic power (W) versus catalyst concentration (w/w %) (b) ultrasonic power (W) versus molar ratio (c) ultrasonic power (W) versus time (min) (d) catalyst concentration (w/w %) versus molar ration (e) catalyst concentration (w/w %) time (min) (f) molar ratio versus time (min) on biodiesel yield.

Finally, an optimization was performed with regard to the boundary conditions (Table 5), which included the maximum conversion rate of methyl ester and the minimization of energy consumption.

Table 5. Boundary conditions of independent and dependent variable for biodiesel production optimization

The optimization was obtained at ultrasonic power 160, catalyst concentration 0.95, molar ratio 7.02, and reaction time 8.47 min. At these values, reaction yield and energy consumption were obtained 90.97 % and 13547. 6 J, respectively. It should be noted that at the proposed point of the software, the test was repeated, and at the obtained point, the reaction yield was equal to 92% and 13682 J, with an acceptable difference with the point obtained by the model. The yield of reaction reached 96.3 at the optimal point after washing biodiesel.

The main characteristics of safflower methyl ester, including viscosity, density, acid value, flash point, heating value, iodine value, sulfur content, and cetane number were measured by means of the ASTM standards (Table 6). All of these characteristics were then compared with EN 14214 biodiesel standards. The results revealed that some parameters of the biodiesel produced from safflower, including kinematic viscosity, density, acid value, iodine value and flash point fulfilled the acceptable condition according to the EN 14214 standard. Therefore, transesterified safflower could be a potential alternative to petrodiesel. The researchers have investigated several properties of twelve types of biodiesel, including viscosity, specific gravity, cetane number, iodine value, and freezing point. For ten of the 12 studied types of biodiesel, the kinematic viscosity was obtained 4-5 mm^2s^{-1} [34]. The specific gravity of 12 types of biodiesel varied between 0.873 and 0.883. In the present study, safflower fulfilled the range of parameters in another study [34]. All biodiesel fuels are denser and less compressible than the diesel fuel irrespective of the feedstock type [35,36]. Molecular weight of biodiesel is one of the factors that contributes to increasing biodiesel density [35,36].

Regardless of whether the biodiesel is produced from low-cost feedstocks or high-quality vegetable oils, biodiesel's flash point is higher than diesel fuel’s [35]. Various factors influence the change in biodiesel flash point due to the residual alcohol content and the chemical compositions of the biodiesel, including the number of carbon atoms and the number of double bonds [37].

Table 6. Properties of safflower methyl ester in comparison with biodiesel standard (EN 14214) and diesel

3.2. Comparison of conventional methods and ultrasonic system for biodiesel production

The study of biodiesel production using the conventional method (mechanical stirrer, 600 rpm, 60°C) revealed that the greatest biodiesel conversion can be obtained at reaction time of 70–90 min (Figure 5). In the optimal condition, the time of biodiesel production by the ultrasonic system (at molar ratio, catalyst concentration, ultrasonic power, and reaction time of 7, 0.95% and 8.5 min, respectively) was 10.5 times lower than that by conventional method.

Transesterification reactions include the reaction between oil and alcohol in the presence of a catalyst. Oil and methyl alcohol are incompatible liquids and when they react in one tank, two separate layers are formed. Transesterification reactions commercially require continuous mechanical stirring over a long period of time, because the reaction between alcohol and oil can only be carried out at the point of contact between the two liquids (on a molecular scale). When this mixture is exposed to the ultrasonic waves, ultrasonic waves cause cavitation phenomena into the reaction medium. As a result, an emulsion of oil and alcohol is formed that provides a wide surface for reactions. It has been observed that the reaction time is significantly reduced [8].

Some researchers have reported similar results that confirm the suggested experimental data in the current study [11]. In other words, the ultrasonic system decreased the time of reaction to obtain the desired biodiesel conversion.

Figure 5. Comparison of biodiesel conversion rates between ultrasonic method and conventional stirring method

3.3. Biodiesel evaluation

3.3.1. Brake power and brake torque

The effects of different fuel blends on brake power and brake torque are illustrated in Figure 6. The results showed that the brake torque and broke power increased when the amount of biodiesel in fuel increased from B0 to B50. These observations are attributed to the higher oxygen content of biodiesel in combustion region that led to a comparatively more complete combustion. This means that biodiesel of the fuel mixture causes an increase in the oxygen content of the blend that leads to greater combustion efficiency and neutralizes the loss of biodiesel's heating value for these fuel blends [13,15,38]. In addition, the engine delivers fuel based on its volume and biodiesel density is higher than that of diesel, providing larger amounts of biodiesel to compensate the lower heating value [39]. But, when amount of biodiesel in fuel increased from B50 to B100, the brake power and brake torque decreased. The higher brake power and brake torque of B50 than those of B100 could be due to the biodiesel's lower heating value [1,40-42]. The problems with biodiesel fuel flow such as higher density and viscosity, compared to, diesel fuel lead to lower quality of fuel atomization in the combustion chamber, thus resulting in decreased brake power [40,43].

Panwar et al. (2010) investigated the effect of biodiesel production (B5, B10 and B20) from castor on combustion and performance characteristics. At the applied load, brake power of B10 blend was drawn to be 1.5%, 1.76%, and 0.75% higher than those of B0, B5, and B20 blends, respectively. B10 yields lower BSFC than fuel and therefore could serve as a promising alternative to diesel [44]. Aydin and Bayindir (2010) examined the effects of cottonseed oil methyl ester on the performance and emission of a single cylinder engine [43]. The results indicated that the torque of B5 was derived a bit greater than those of other fuels, including diesel. With increasing the biodiesel proportion of the blends, the torque decreased. This effect was produced due to the lower heating value and higher viscosity of cottonseed oil methyl ester [35,45].

Figure 6. Effect of different biodiesel percentage on (a) brake power (b) brake torque

3.3.2.CO and NOx emission

The results indicated that CO emissions decreased when the amount of biodiesel increased (Figure 7a). It is likely that this observation is due to the oxygen inherently presence in the biodiesel, which enhances combustion and burning at higher temperature in the cylinder, leading to decreased CO emission [2,38,46,47]. The trends of NOx were reversed by increasing biodiesel percentage in comparison to those of CO. Notably, NOx formation depends on volumetric efficiency, duration of combustion, and particularly, temperature of high activation energy required for the reactions involved. The increase in NOx emissions was proportional to the amount of biodiesel (Figure 7b). It has been suggested that some injection systems suffer from an unpredictable progression of fuel injection timing caused by the higher bulk modulus of compressibility in the biodiesel-containing fuel blends. This increases sound speed, which leads to a quicker transfer of the pressure wave from the injection pump to the nozzle, resulting in advancing of the needle lift. It has been established that advancing injection timing leads to an increase in NOx emissions [45]. In addition, biodiesels contain comparatively higher oxygen component compared to the diesel fuel, thus it is clear that there is higher oxygen content in biodiesels to react with the nitrogen component in the surrounding air, which leads to larger amounts of produced NOx [2,38,46].

Mofijur et al., (2014) examined the effect of biodiesel production from Moringa Oleifera and diesel mixture in multi cylinder engine. They reported that B5 and B10 blends decreased the CO emissions of diesel by 5.37% and 10.60%, respectively, and reduced the HC emissions of diesel fuel by 3.94% and 9.21%, respectively. However, B5 and B10 caused a slight increase in NOx, compared to diesel fuel, by 3.99% and 8.46%, respectively, and also a slight increase in CO_2 emissions of diesel fuel by 2.25% and 4.96%, respectively [48]. In addition, the use of soybean oil methyl ester in diesel engine has also been investigated, reporting that the smoke, NOx, CO ,and HC decreased by 52.00%, 5.00%, 27.00%, and 27.00%, respectively [35,39].

Figure 7. Effect of different biodiesel percent on (a) CO (b) NOx

4. Conclusion

It can be argued that the greatest effect in the production of methyl ester, among the studied variables, was obtained for the molar ratio test and the reaction time, followed by the ultrasonic power and catalyst concentration. With an increase in ultrasound power from 160 W to 400 W, performance increased by 3.83%. By increasing the molar ratio to a point between the ratios 4 and 6 to 1, the conversion rate first increases to 11.42, and then it remains unchanged from the point 6 to 8. The study of the effect of catalyst concentration on the conversion rate showed that with increasing the catalyst content from 0.75 to 1, the performance increased by 3.92% and then with increasing its content from 1 to 1.25, the performance decreased by 5.05%. The reason for this reduction can be that further catalyst loading would be inefficient in biodiesel production. The optimization was obtained at 160 ultrasonic power, 0.95catalyst concentration, 7.02molar ratio, and, 8.47 min reaction time. At these values, conversion rate and energy consumption were obtained 90.9728 J and 13547.6 J, respectively. The results showed that the brake torque and broke power increased when the amount of biodiesel in fuel increased from B0 to B50. These observations are attributed to the higher oxygen content of biodiesel in combustion region that led to a comparatively more complete combustion. The results showed that CO emissions decreased when the amount of biodiesel increased. The trends of NOx were reversed by increasing biodiesel percentage in comparison to those of CO. The results showed that some of the properties of Safflower methyl ester meet the requirements of EN 14214 biodiesel standards. Therefore, transesterified Safflower could be a potential substitute for petrodiesel.

Acknowledgement

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Figure Captions

Figure 1. A schematic representation of a Soxhlet extractor.

Figure 2. The Schematic of set-up for ultrasonic-assisted biodiesel production process.

Figure 3. Actual data versus predicted data.

Figure 4. Figure 4. Response surface plot showing the interaction effects of (a) ultrasonic power (W) versus catalyst concentration (w/w %) (b) ultrasonic power (W) versus molar ratio (c) ultrasonic power (W) versus time (min) (d) catalyst concentration (w/w %) versus molar ration (e) catalyst concentration (w/w %) time (min) (f) molar ratio versus time (min) on biodiesel yield.

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Figure 7. Effect of different biodiesel percent on (a) CO (b) NOx.

Evaluation of an enhanced ultrasonic-assisted biodiesel synthesized using Safflower oil in a diesel power generator

Authors

Bahram Hosseinzadeh Samani[1], Marziyeh Ansari[1], Alireza Shirneshan[2,3], Ebrahim Fayyazi[4], Gholamhassan Najafi[4], Sajad Rostami[1]

Affiliations

[1]Department of mechanical Engineering of Biosystems, Shahrekord University

[2]Department of Mechanical Engineering, Najafabad Branch, Islamic Azad University, Najafabad, Iran

[3]Modern Manufacturing Technologies Research Center, Najafabad Branch, Islamic Azad University, Najafabad, Iran

[4]Department of Biosystem Engineering, Tarbiat Modares University, Iran

***Corresponding author:**

Bahram Hosseinzadeh Samani

Tel: +983834424403

b.hosseinzadehsamani@gmail.com

"This work was supported by the Shahrekord University."

Table1. Fatty acid profile and properties of used Safflower oil

Properties	Unit	Amount
Density	g cm^{-3}	0.91
Kinematic viscosity	cSt	28.16
Saponification Number	mg K/g oil	211.60
Iodine value	g I_2/100g oil	96.11
Myristic (C14:0)	Wt.%	0.24
Palmitic (C16:0)	Wt.%	7.07
Stearic (C18:0)	Wt.%	2.76
Oleic (C18:1)*	Wt.%	15.22
Linoleic (C18:2)*	Wt.%	74.54
Other fatty acids	Wt.%	0.27

*Carbon atoms number: double bond number.

Table 2. Selected independent variables on response surface method

Independent Variable	Units	Coded level		
		-1	0	1
Molar ratio	x mole Alcohol to y mole Oil	4:1	6:1	8:1
Ultrasonic power	W	160	280	400
Catalyst concentration	weight of catalyst/weight of oil %	0.75	1	1.25
Reaction time	min	3	6	9

Table 3. Specification of the test engine

Engine type	**Diesel power generator CAT3412**
Cylinder number	12
Stroke (mm)	154
Bore (mm)	137
Compression ratio	13:1
Cooling system	Water cooled
Rated Engine Speed (rpm)	1800
Aspiration	Turbocharged-After cooled
Starting Motor	24 V / 7 kW
Governor	Mechanical

Table 4- The results of reactor performance model by response surface method

Source	Sum of Squares	Df	Mean Squar	P-value
Model	1200.34	14	85.74	0.0001<
A-Ultrasonic Power	44.08	1	44.08	0.0001<
B-Catalyst Concenteration	10.08	1	10.08	0.0001<
C-Molar Ratio	385.33	1	385.33	0.0001<
D-Time	408.33	1	408.33	0.0001<
AB	2.25	1	2.25	0.0092
AC	2.25	1	2.25	0.0092
AD	0.25	1	0.25	0.3309
BC	2.25	1	2.25	0.0092
BD	0.25	1	0.25	0.3309
CD	9.00	1	9.00	0.0001<
A^2	0.52	1	0.52	0.1681
B^2	133.30	1	133.30	0.0001<
C^2	246.00	1	246.00	0.0001<
D^2	12.87	1	12.87	0.0001<
Residual	3.45	14	0.25	
Lack of Fit	2.25	10	0.22	0.6768
Pure Error	1.20	4	0.30	
Cor Total	1203.79	28		

Table 5. Boundary Conditions of Independent and dependent variable for biodiesel production optimization

Variable	Goal	Lower Limit	Upper Limit	Weight
Molar Ratio	In range	4	8	1
Catalyst concentration (w/w%)	In range	0.75	1.25	1
Ultrasonic power(w)	In range	160	400	1
Reaction Time (min)	In range	3	9	1
Yield (%)	Maximum	70	93	1
Energy Consumption	Minimum	4800	36000	1

Table 6. Properties of Safflower methyl ester in comparison with biodiesel standard (EN 14214) and diesel

Properties	Units	EN 14214	Safflower methyl ester	Diesel	Test method
Ester content	% (m/m)	Min 96.5	95.9	-	EN14103
Density at 15°C	g/cm^3	0.86–0.90	0.87	0.861	ASTM D4052
Kinematic viscosity	mm^2/s	3.5–5	4.52	2.96	ASTM D445
Acid value	mg KOH/g	Max 0.50	0.37	0.18	ASTM D664
Iodine value	g iodine/100 g	Max 120	117.47	-	AOAC CD1-25
Flash point	°C	Min 120	157	48	ASTM D93
Cetane number	-	Min 51	48	51	ASTM D613
Free Glycerin	%mass	0.02	0.017	-	ASTMD6584
Total Glycerin	%mass	0.24	0.25	-	ASTMD6584

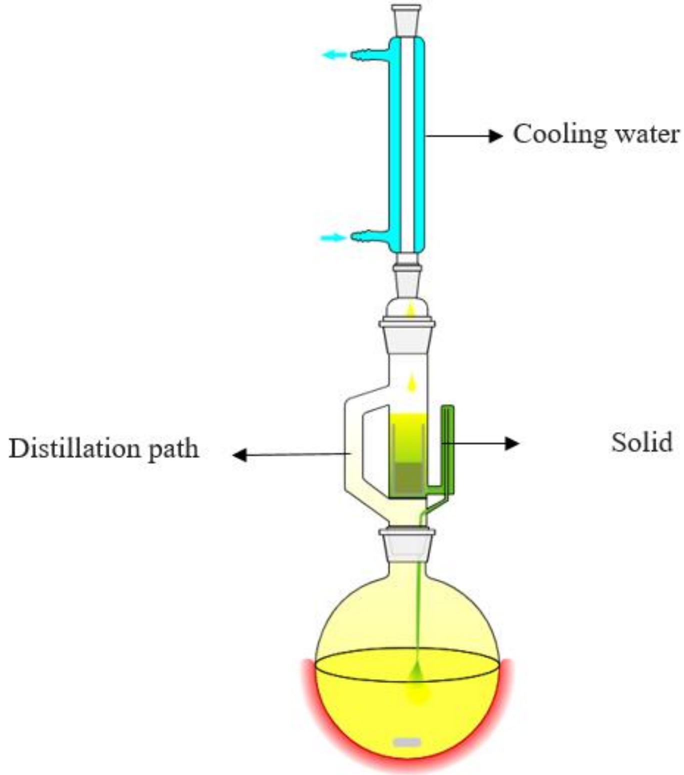


Figure 1. A schematic representation of a Soxhlet extractor

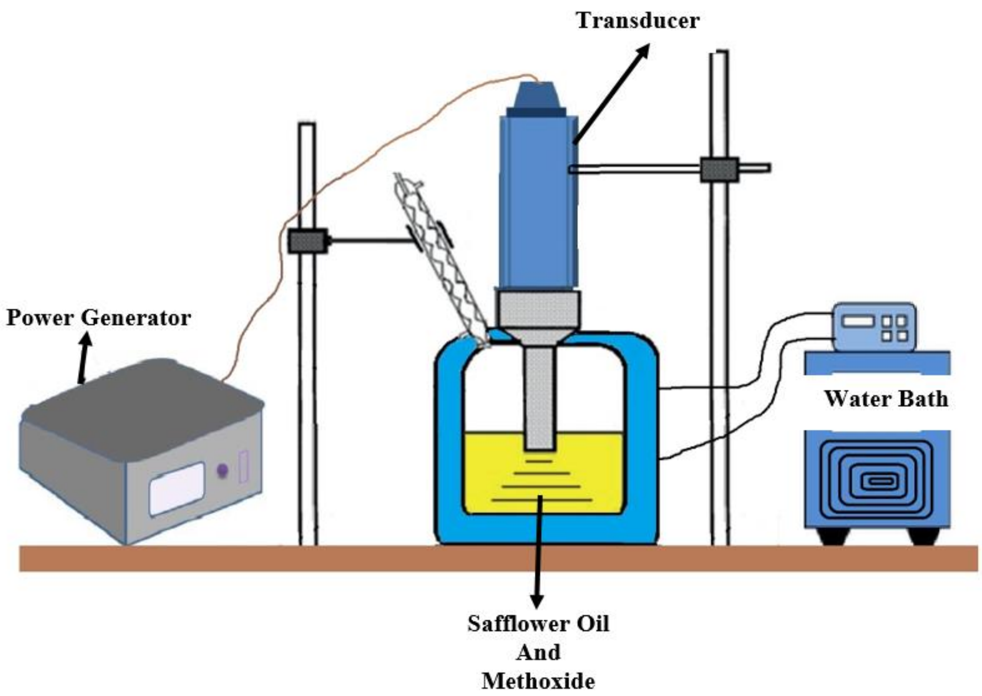


Figure 2. The Schematic of set-up for ultrasonic-assisted biodiesel production process

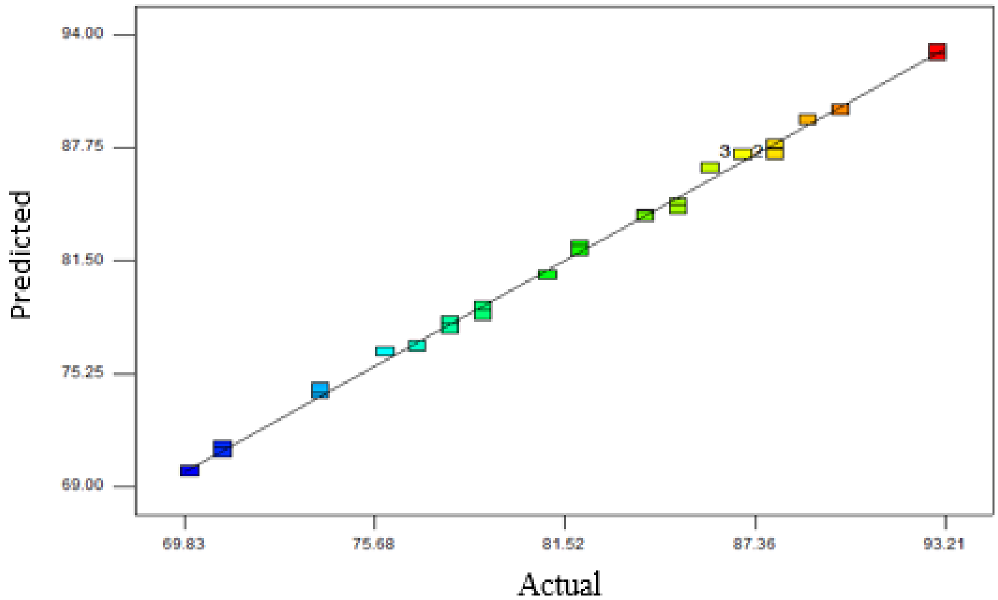
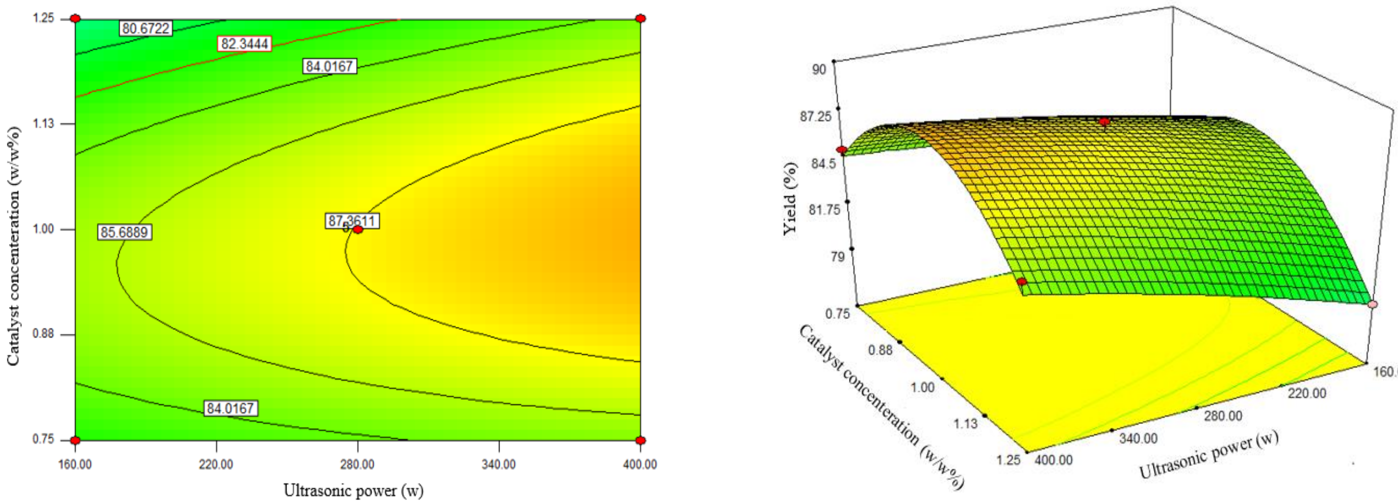
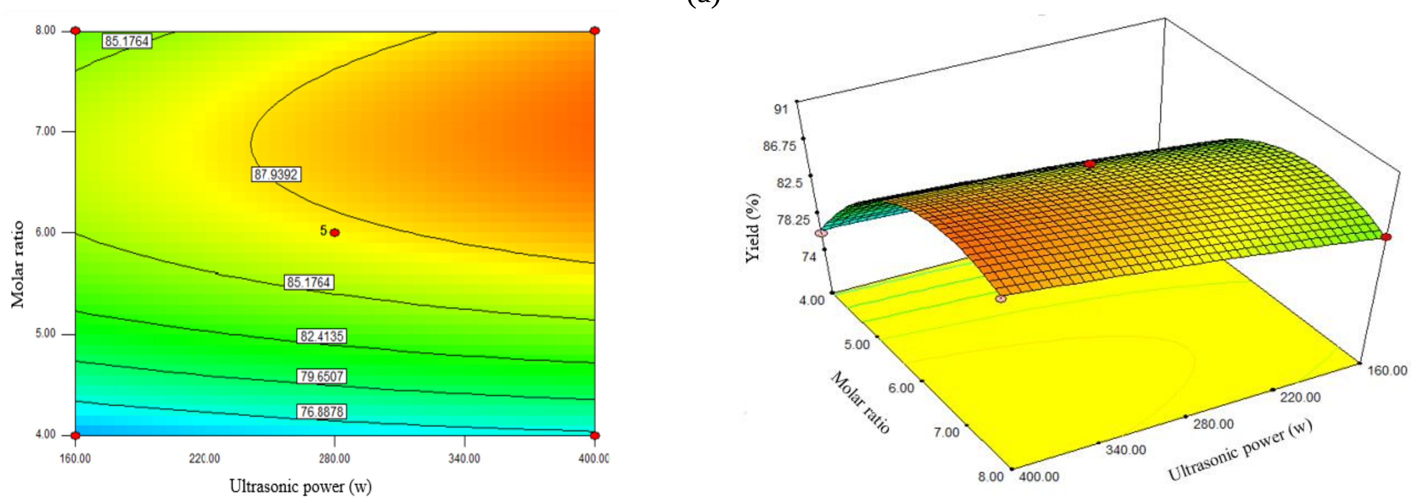


Figure 3. Actual data versus predicted data



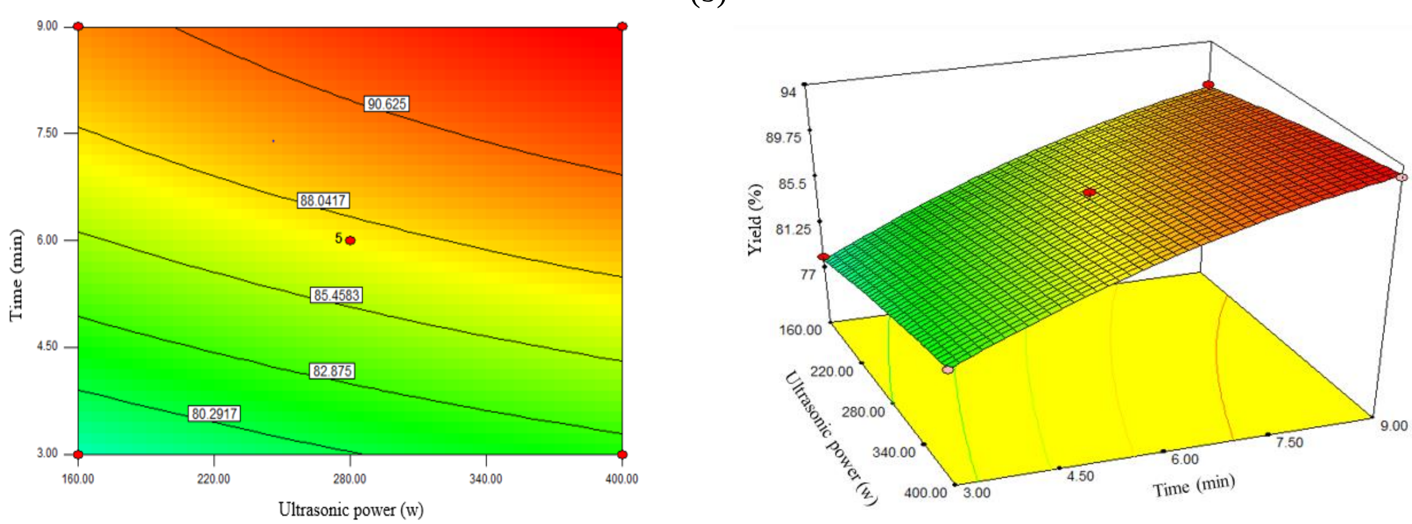
Catalyst concenteration (w/w%)
Ultrasonic power (w)
80.6722
82.3444
84.0167
85.6889
87.3611
Yield (%)
Catalyst concenteration (w/w%)
Ultrasonic power (w)

(a)



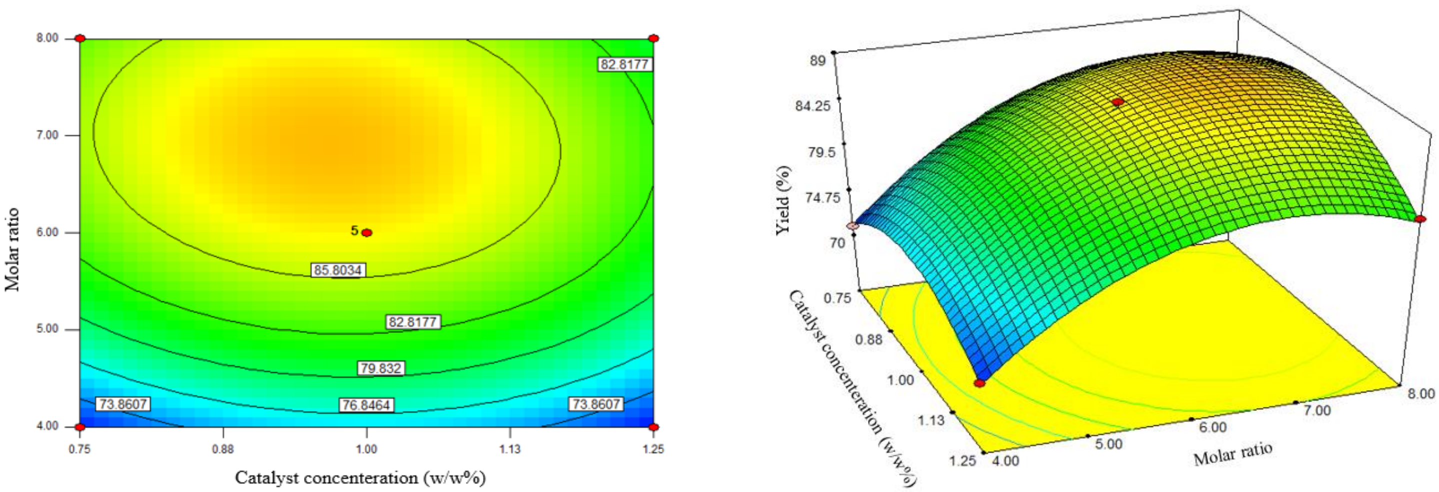
Molar ratio
Ultrasonic power (w)
85.1764
87.9392
82.4135
79.6507
76.8878
Yield (%)
Molar ratio
Ultrasonic power (w)

(b)

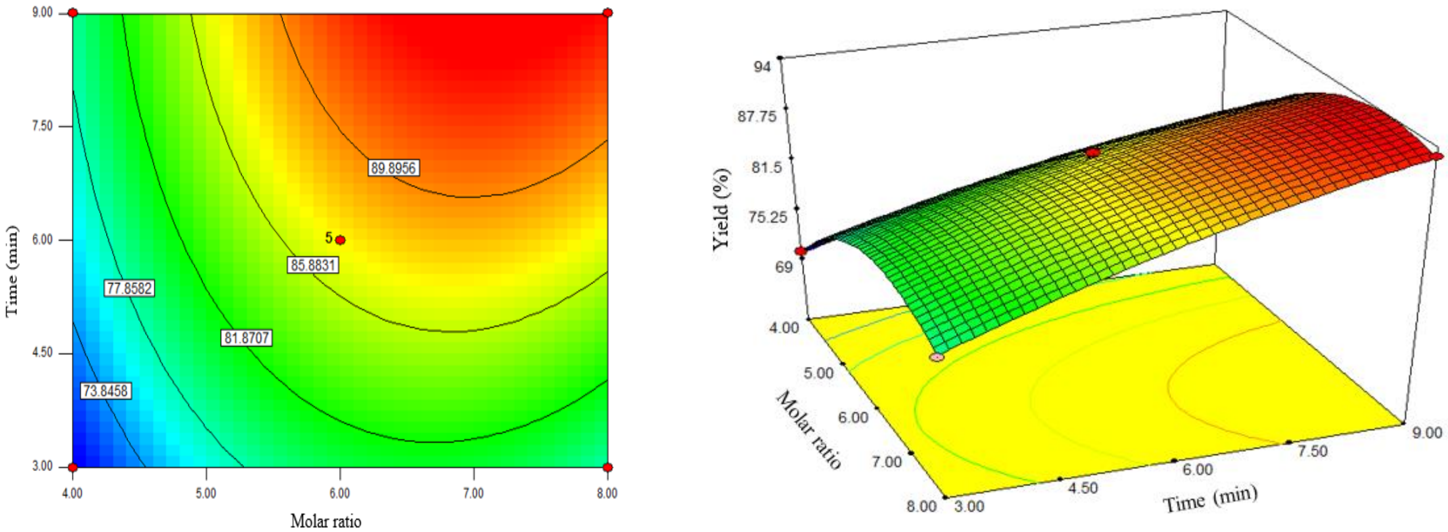


Time (min)
Ultrasonic power (w)
90.625
88.0417
85.4583
82.875
80.2917
Yield (%)
Ultrasonic power (w)
Time (min)

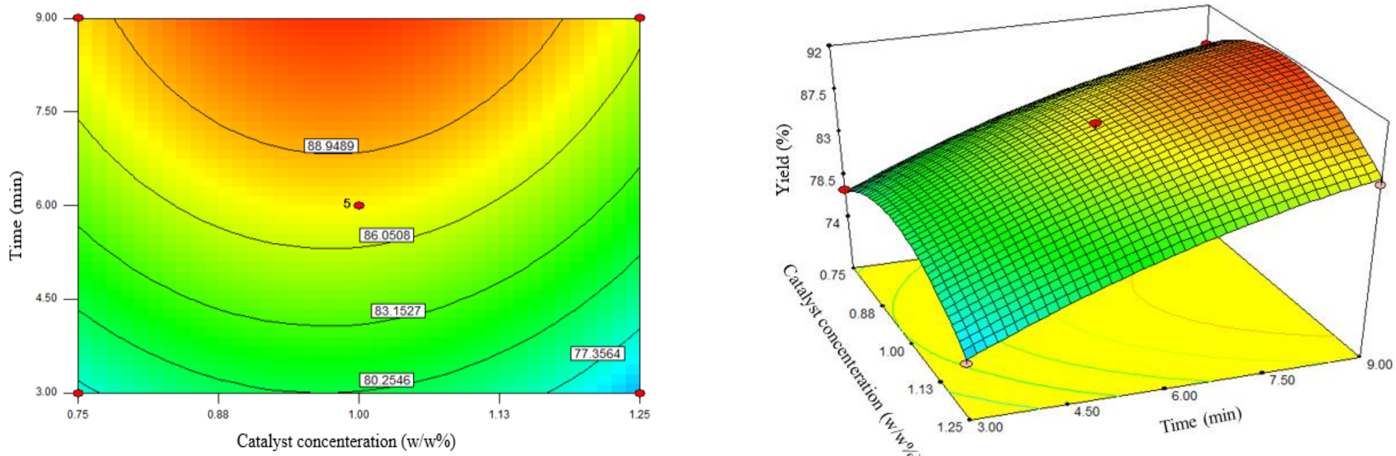
(c)


Molar ratio
Catalyst concenteration (w/w%)
82.8177
85.8034
82.8177
79.832
76.8464
73.8607
73.8607
5
Yield (%)
Catalyst concenteration (w/w%)
Molar ratio

(d)


Time (min)
Molar ratio
89.8956
85.8831
81.8707
77.8582
73.8458
5
Yield (%)
Molar ratio
Time (min)

(e)


Time (min)
Catalyst concenteration (w/w%)
88.9489
86.0508
83.1527
80.2546
77.3564
5
Yield (%)
Catalyst concenteration (w/w%)
Time (min)

(f)

Figure 4. Figure 4. Response surface plot showing the interaction effects of (a) ultrasonic power (W) versus catalyst concentration (w/w %) (b) ultrasonic power (W) versus molar ratio (c) ultrasonic power (W) versus time (min) (d) catalyst concentration (w/w %) versus molar ration (e) catalyst concentration (w/w %) time (min) (f) molar ratio versus time (min) on biodiesel yield.

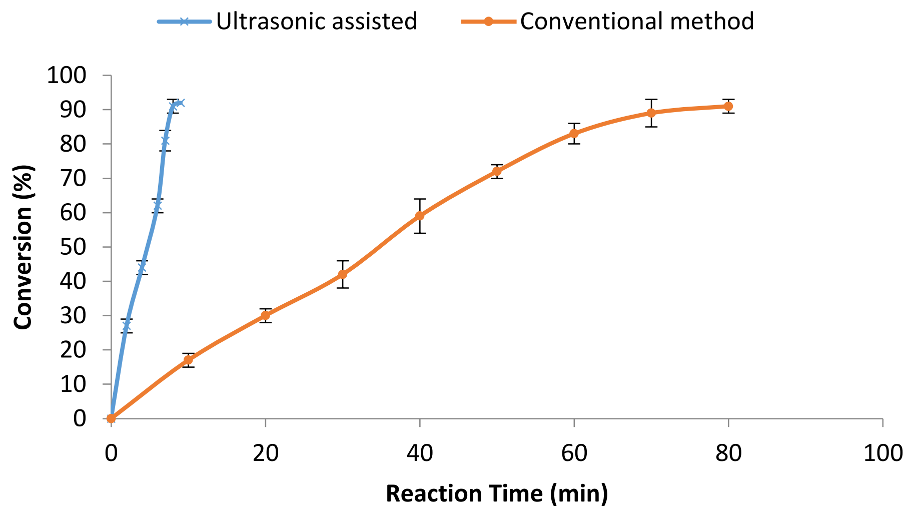
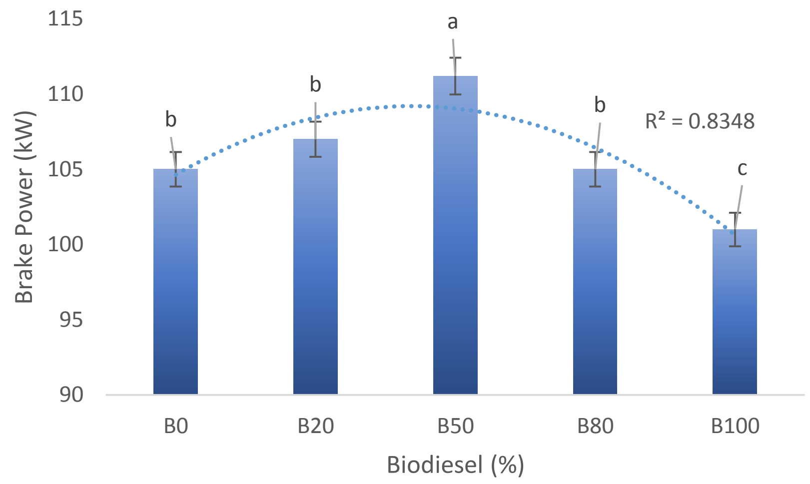
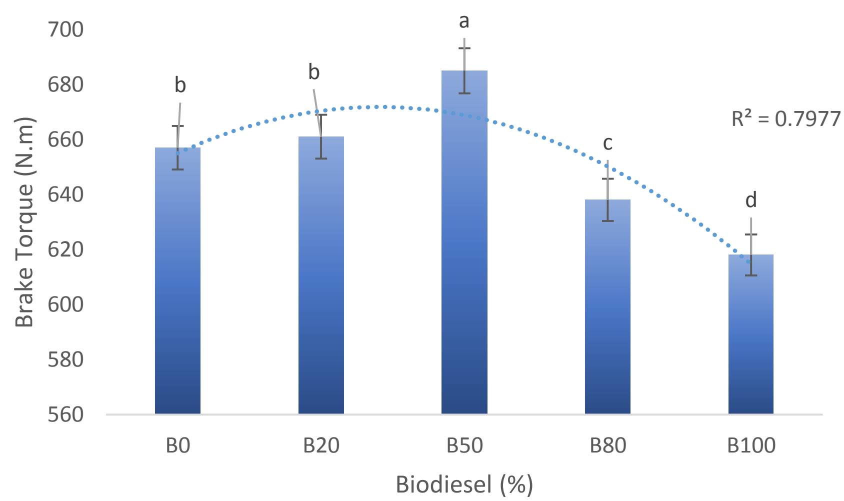


Figure 5. Comparison of extent of biodiesel conversion using ultrasonic method and conventional stirring method

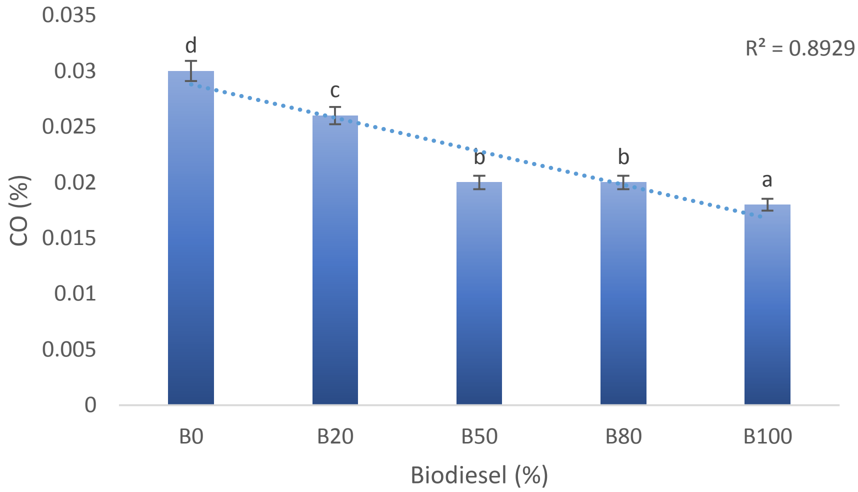


(a)

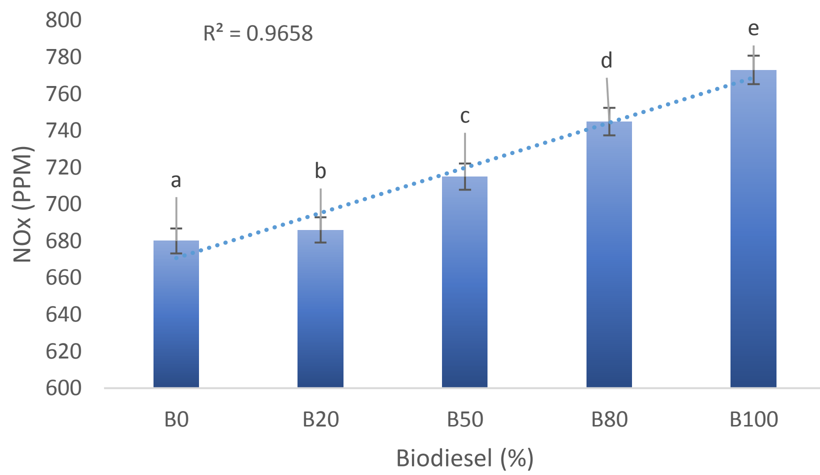


(b)

Figure 6. Effect of different biodiesel percent on (a) brake power (b) brake torque



(a)



(b)

Figure 7. Effect of different biodiesel percent on (a) CO (b) NOx

Response to the honorable referee of the paper entitled:

Evaluation of an enhanced ultrasonic-assisted biodiesel synthesized using Safflower oil in a diesel power generator

Thanking the comments and proposed amendments of the honorable referees, the answers to the referred points are mentioned in separate sections of the paper as follows:

Reviewers' comments:

Reviewers' comments:

Reviewer #3: Full Title: Evaluation of an enhanced ultrasonic-assisted biodiesel synthesized using Safflower oil in a diesel power generator
Manuscript Number: TBFU-2019-0101R1
Article Type: Original Article

Overall the Authors had modified the manuscript based on the suggestion received. However, there are still some small improvements that can be made:

please note, carefully response to the comment one by one and provide the modification made in the manuscript

1. Title: Evaluation of an enhanced ultrasonic-assisted biodiesel synthesized using Safflower oil in a diesel power generator

keywords: should be . Response surface methodology

It was done.

2. abstract and table 2:

Refer to my previous comment to add an appropriate unit in table 2.

It was done. Please check Table 2.

3. "In this study, the effects of alcohol-to-oil molar ratio".
4. Authors mentioned molar ratio? As refer to table 2 "Molar Ratio (Alcohol to Oil) 4:1" means 4 molar over 1 Molar? Please clarify, molar or mole? If a mole, which mole number? It is good it could provide the preparation or calculation.

The coefficients in a balanced chemical equation can be used to determine the relative number of molecules, formula units, or moles of a compound involved in a chemical reaction.

Example:

Triglyceride+ 3Methanol $\longrightarrow$ Glycerol +3 Methyl esters

1 molecule of Triglyceride reacts with 3 molecules of Methanol to form 3 molecules of Methyl esters

OR

1 mole of Triglyceride reacts with 3 moles of Methanol to form 3 moles of Methyl esters

The coefficients in a balanced equation can be used to write a molar ratio. Molar ratios are conversion factors that can be used to relate:

1. moles of product formed from a certain number of moles of reactant
2. moles of reactant needed to form a certain number of moles of a product.
3. the number of moles of a particular reactant needed to completely react with a certain number of moles of a second reactant.

As results:

Safflower mass molar: 910.787 g/mol

Methanol mass molar: 32.04 g/mol

So for the molar ratio of 6: 1 means 910.787 g of safflower oil was mixed with 192.24 g of methanol.

5. Introduction
L79-L82 change to
This study was conducted to investigate the feasibility of biodiesel production from safflower oil using the ultrasonic system, and to evaluate the produced fuel on a diesel power generator to investigate the including engine performance and emission parameters when using different levels of diesel-Safflower biodiesel blends.

It was replaced according to the reviewer comment.

6. As mentioned in the previous comment, the caption should be a stand-alone statement. Please check here https://doi.org/10.1016/j.biortech.2019.03.030 how to write appropriate captions for each figure. Such as Fig 1 in this manuscript.

Thanks for your recommended paper. The authors read the mentioned paper carefully and change the figure caption as reviewer suggestion.

7. Please standardize fig or figure such as figure 4 and fig. 4, both appear in this manuscript. Please follow the Journal format for clarification.

All of figs were converted to figure. So the paper is uniform.

8. Not answer my previous comment on the L200-201: With an increase in ultrasound power from 160 W to 400 W, the performance increased by 3.83%. is the increment is good enough? Please provide a benchmarking value.

The author's statement in Line 200-201 mentions a not significant increase in reaction yield via increasing in ultrasound power. This fact shows the high performance of ultrasound power even in low levels of ultrasound power (160W) which has lower energy consumption in comparison to higher levels (400 W). Also, as it expected, the optimized level for ultrasound power determined by the regression model is in the lowest level of it (please see Line 263).

9. Acknowledgement statement missing?

Acknowledgement was removed in anonymous file according the biofuel journal format. But there is acknowledgement in the final version.

Evaluation of an enhanced ultrasonic-assisted biodiesel synthesized using Safflower oil in a diesel power generator

Bahram Hosseinzadeh Samani[1], Marziyeh Ansari[1], Alireza Shirneshan[2,3], Ebrahim Fayyazi[4], Gholamhassan Najafi[4], Sajad Rostami[1]

Corresponding author's email address: b.hosseinzadehsamani@gmail.com

[1]Department of mechanical Engineering of Biosystems, Shahrekord University
[2]Department of Mechanical Engineering, Najafabad Branch, Islamic Azad University, Najafabad, Iran

[3]Modern Manufacturing Technologies Research Center, Najafabad Branch, Islamic Azad University, Najafabad, Iran
[4]Department of Biosystem Engineering, Tarbiat Modares University, Iran

Abstract

Given the energy crisis, fossil fuel reserves crisis, climate mitigation, and energy efficiency increase, scientists have embarked on producing alternative fuels such as the biodiesel. This study was conducted to investigate the feasibility of biodiesel production from safflower oil using the ultrasonic system, and to evaluate the produced fuel using a diesel power generator. In this study, the effects of alcohol-to-oil molar ratio, ultrasound power (W), catalyst concentration (w/w %), and the reaction time (min) on methyl ester yield were investigated. By increasing the molar ratio to a point between the ratios 4:1 and 6:1, the conversion rate first increases 11.42%, and then it remains unchanged from the point 6 to 8. As the ultrasonic power increases, the rate of conversion increases incrementally. The optimization was obtained at 7.02 molar ratio, 160 W ultrasound power, 0.95 (w/w%) catalyst concentration, and 8.47 min reaction time. The results showed that the brake torque and broke power increased when the amount of biodiesel in fuel increased from B0 to B50. The results showed that CO emissions decreased and NOx increased when there was an increase of amount of biodiesel.

Keywords: Renewable Energy, Optimization, Biodiesel, Safflower Oil, Response surface methodology.

1. Introduction

Alternative fuels refer to substances that share similar characteristics with fossil fuels which also can function effectively as alternative. Biodiesel is ethyl or methyl ester that is produced from vegetable oils or animal fats and used as the fuel in diesel engines or thermal systems [1]. Although the pure biodiesel (B100) can be used directly in standard diesel engines, the problem with using the pure biodiesel is its high viscosity, which weakens the engine's performance. To solve this problem, biodiesel is generally combined with standard diesel fuel [2]. Most of the biodiesel produced in the world is produced by the transesterification of triglycerides (vegetable oils and animal fats) with alcohol (methanol and ethanol) in the stirred-tank reactors (STRs) in the presence of acidic or alkaline homogeneous catalysts [3,4]. The transesterification is performed in a liquid-liquid, two-phase system, the rate of which is limited by the low-mass transfer due to the incompatibility of triglycerides and alcohol. One of the main challenges concerning the conduction of the transesterification using STRs is the limited speed of reaction due to the low mass transfer rates between oil and alcohol (incompatible mixture), the limitation of the upper limit of production efficiency due to lack of separation mechanism of the product during the reversible transesterification, and the discontinuous production of biodiesel. One of the intensification methods which could improve the quality of biodiesel production process is the use of ultrasound [5]. For more agitation and effective surface contact between alcohol and oil molecules, ultrasonic waves can be used. Ultrasound has proven to be a very useful tool in enhancing the reaction rates in a variety of reacting systems. It has successfully increased the conversion, improved the yield, changed the reaction pathway, and/or initiated the reaction in biological, chemical, and electrochemical systems [6]. When the mixture is subjected to ultrasound, ultrasonic waves create cavitation at exposure point [7]. As a result, an emulsion of oil and alcohol is formed that provides a large surface for the reaction, and the response time is significantly reduced [8]. Sonochemistry is generally performed in a liquid medium. During each 'stretching' phase (rarefaction), provided that the negative pressure is strong enough to overcome intermolecular binding forces, a fluid medium can be torn apart, producing tiny cavities (micro bubbles) [6,9]. In succeeding cycles, these cavities can grow and then collapse violently with the release of large amounts of energy. Experimental results have shown that approaching 5000 ^{o}K temperatures and 2000atmpressures are produced during this collapse [10].

Fayyazi et al., (2014) produced biodiesel fuel using an ultrasound system (24 kHz and 400 watts) from the waste oil. Also, other studies reported similar results regarding the increase in biodiesel conversion using ultrasound [11,12].

Hosseinzadeh et al. (2015) sought to reduce the production time of biodiesel from *Pistacia atlantica* oil with the lowest possible energy consumption (process optimization) using ultrasound. They investigated the effects of variables, including molar ratio of alcohol to oil, ultrasound amplitude, ratio of the duration of ultrasound on to that of ultrasound off (pulse), and reaction time on the rate of methyl ester conversion [5].

Moreover, many researchers have investigated the effects of biodiesel fuel blends on engine indicators such as the brake power, brake torque, brake thermal efficiency (BTE), exhaust gas temperature (EGT), Brake-specific fuel consumption (BSFC), NOx, Exhaust particulate matter (PM), CO, CO_2, hydrocarbon emission (HC), and smoke density in comparison to those of diesel. The results of these studies showed that different sources of biodiesel feedstocks led to different engine indicators.

The researchers have also addressed the engine performance and emissions when using biodiesel, and most of them have reported that when using biodiesel, engine power and torque decreases due to the loss of biodiesel heating value [13,14]. Some studies have shown there is no significant difference between B100 and diesel with respect to the engine power [15,16]. However, some researchers have reported that there may be unanticipated increase in power or torque of diesel engines [2,17]. On the other hand, evidence has shown similar trends of engine power performance with load or speed of engines fueled with B100 and B0 [18].

Carthamus tinctorius L., commonly known as safflower, is one of the world's oldest crops belonging to the Asteraceae family and is native to the Middle East. Safflower is a tap-rooted annual crop that can withstand environmental unpleasant conditions (drought, salinity), the production of which reaches to above 420000 ton annually, distinguishing it as a potential bioenergy crop. Safflower is a highly branched, thistle-like, herbaceous plant. It is commercially cultivated for the oil of its seeds. The seeds contain 27–32% oil, 32–40% crude fiber, 5–8% moisture, 14–15% protein, and 2–7% ash. Safflower is a valuable plant due to the variety of its fatty acid content. The composition of standard safflower oil is 2–3% stearic acid, 16–20% oleic acid, 6–8% palmitic acid, and 71–75% linoleic acid [19]. This study was conducted to investigate the feasibility of biodiesel production from safflower oil using the ultrasonic system, and to evaluate the produced fuel on a diesel power generator to investigate the including engine performance and emission parameters when using different levels of diesel -Safflower biodiesel blends.

2. Material and Methods

2.1. Oil extraction

Soxhlet extraction, which is a conventional method and used for the extraction, was carried out in a classic Soxhlet extractor in the presence of n-hexane as a solvent (Figure 1). 10 g of safflower seeds were milled using a laboratory mill. Subsequently, powdered seed was placed in an extraction thimble and then Soxhlet was extracted for 8 h using 200 ml of n-hexane. After extraction, the solvent was evaporated by rotary evaporator and weighed. This procedure was repeated until a constant value for the extracted weight was obtained [20]. Oil yield was further calculated and presented as a weight of extracted oil per weight of sample. Some of physical and chemical properties of safflower oil are shown in Table 1.

Figure 1. A schematic representation of a Soxhlet extractor

Table1. Fatty acid profile and properties of used Safflower oil

2.2. Transesterification reaction

In this section of the experiment, the oil reacts in the presence of methoxide and results in the production of biodiesel and glycerol. Then, oil to methyl ester conversion (yield of the reaction) was investigated in different levels of desired independent variables. . Methoxide is the mixture of a catalyst and methanol. To prepare the methoxide according to Table 2, at each step, the desired amount of alcohol was poured into a beaker, and after adding the catalyst, the stirring method was used to reduce the dissolution time and evaporation rate of alcohol. The alcohol used in this study was methanol (Merck Co., Germany) with a purity of 99.9%. Potassium hydroxide tablets (Merck Co., Germany) with purity of 99.8% were also used as catalyst.

The pre-heated oil was then mixed with the previously prepared methoxide. Afterward, the mixture (*Safflower* oil and methoxide) was transferred to the reaction chamber to be subjected to ultrasound waves. An ultrasonic processor (Topsonic Model, UP400, Iran) was used to perform the transesterification reaction. The equipment consisted of the processor, sonotrode, and PC controller. The processor operated at 400 W and 20 kHz frequency (Figure 2).

The PerkinElmer-Clarus 580 gas chromatograph (made in the USA) was used in this study which was set up based on the BS EN 14103 standard [21]. The Fatty acid methyl ester (FAME) yields of each transesterification step were calculated from the weight of FAME in the FAME phase and the theoretical material balance of the transesterification reaction (BS-EN 14103 standard), as shown in Equation (1):

$$FAME(\%) = \frac{W_{FAME}/M_{FAME}}{3W_{SO}/M_{SO}} \quad (1)$$

Where W_{FAME} and W_{SO} are the weights of FAME in the FAME phase and the weight of used *Safflower* oil (SO), respectively. M_{FAME} and M_{SO} are the average molecular weights of FAME and SO, respectively. Once the glycerol is separated from biodiesel, additional material should be removed from biodiesel. These materials include soap, some precipitated glycerol and a catalyst, which, if left in the burning process, causes undesirable effects in combustion, resulting in bad odor and smoke in combustion products.

Figure 2. The Schematic of set-up for ultrasonic-assisted biodiesel production process

2.3. Optimization and statistical analysis

The design of the present study follows the box-behnken method. The response surface methodology is a set of mathematical and statistical techniques that are used to develop, promote, and optimize the processes in which the level in question is affected by many variables and the goal is to optimize the response [22,23]. Some phases in the application of RSM as an optimization, modeling and analysis technique is as follows: (1) the selection of independent variables concerning the major effects on the system through screening studies and definition of the experimental region, according to the objective of the study, the experience of the researcher and literature reviews; (2) the selection of the experimental design and implementing the experiments according to the selected experimental matrix; (3) setting the mathematic–statistical orders of the collected experimental data via the fit of a polynomial function; (4) finding the optimum values for all of the studied variables [24]. To derive optimal value, Regression Equation (2) was be used.

$$Y_i = \beta_0 + \sum \beta_i X_i + \sum \beta_i X_i X_j + \sum \beta_{jj} X_i^2 + \varepsilon \quad (2)$$

where βo, βj, βij and βjj are constant coefficients, xi and xj independent variables in the process and ε are random errors. The levels of independent variables (Table 2) were selected according to the literature review and screening study experiments [5,11]. Finally, according to the curves drawn and the range for the independent variables, the optimal point was obtained and the result was validated by the validation test.

Table 2. Selected independent variables in response surface method

It should be noted that at all phases of the experiment, a power analyzer was used to measure the power consumption of the devices used in the test. Data analysis and optimization were done using the Design Expert software (version 7.0.0, Stat-Ease Company®).

2.4. Engine test

In this study, to investigate the performance characteristics of a diesel engine using biodiesel produced from the safflower oil, different volume ratios of the combination of biodiesel and routine diesel in Iran were prepared and examined. These volume ratios are B (0), B (20), B (50), B (80) and B (100) which were selected according to the latest literature reviews [25,26]. The mixtures were tested in the diesel generator at 50% of the full load and a constant speed of 1530 rpm to derive the required data and compare the performance characteristics of mixed fuels with those of the pure diesel.

2.5. Studied diesel generator

The diesel power generator consists of an engine and a generator, and the engine used in this research is a 4-cycle engine and 12 cylinders (CAT3412 Co.) equipped with supercharge, an indirect spray system with a maximum power of 537 KW at rotational speed of 1,800 rpm. The generator connected to the engine has been manufactured by Caterpillar Co., which is three-phase, powered by 380 V with a maximum power consumption of 300 kW at the rated speed. The generator is connected to a central processing unit that starts processing by using the data from different points and displays the output voltage, power, and engine speed on the control panel. Table 3 presents the technical specifications of the diesel generator.

Table 3. Specification of the test engine

3. Results and discussion

3.1. Biodiesel production

The P-value (0.01) of the model implies its significance. In this case, ultrasonic power, catalyst concentration, molar ratio, time, ultrasonic power × catalyst concentration, ultrasonic power × molar ratio, catalyst concentration × molar ratio, molar ratio × time, catalyst concenteration^2, molar ratio^2, and time^2 are the significant model terms. Values greater than 0.1000 indicate the model terms are not significant. The lack of Fit *F* value of 0.75 implies the Lack of Fit is not significant relative to the pure error. There is a 67.68% chance that a lack of Fit *F* of such value is due to the noise (Table 4).

From the data analysis, Equation (3) was determined. Correction coefficient and error standard for the drawn model are 0.9971 and 0.50, respectively.

$$\begin{aligned}\text{Yield}=&-64.12315-0.012593\times A+141.40000\times B+20.43333\times C+2.18333\times D+0.025000\times A\times B+3.12500E\text{-}003\times A\times C\\&-6.94444E\text{-}004\times A\times D-1.50000\times B\times C+0.33333\times B\times D+0.25000\times C\times D-1.96759E\text{-}005\times A^2\\&-72.53333\times B^2-1.53958\times C^2-0.15648\times D^2\end{aligned} \quad (3)$$

Table 4- The results of reactor performance model by response surface methodology

Based on the results of analysis of variance of regression coefficients, non-significant coefficients were excluded from Equation (3), and the final Equation as well as coding (4) and (5) was drawn to obtain a standard error of 0.75 and a determination coefficient of 0.9907.

Figure 3 illustrates the comparison of the actual data with the predicted data; given the shape and close compatibility of these numbers, there is a strong correlation between the results obtained by the experimental method and the values predicted by the statistical test.

$$\text{Yield}=-64.12315-0.012593\times A+141.40000\times B+20.43333\times C+2.18333\times D+0.25000\times C\times D-72.53333\times B^2-1.53958\times C^2-0.15648\times D^2 \quad (4)$$

$$\text{Yield}=+87.40+1.92\times A-0.92\times B+5.67\times C+5.83\times D+1.50\times C\times D-4.53\times B^2-6.16\times C^2-1.41\times D^2 \quad (5)$$

Where A is the ultrasonic power, B is the catalyst, C is the molar ratio, and D is the reaction time.

Regarding the values of the coefficients of Equation (5), it can be argued that the greatest effect in the production of methyl ester, among the studied variables, was obtained for the molar ratio test and the time of reaction, followed by the ultrasonic power and catalyst concentration.

Figure 3. Actual data versus predicted data

As illustrated in Figure. 4a, the effect of ultrasound on the production of biodiesel is greater than that of the catalyst concentration. With an increase in ultrasound power from 160 W to 400 W, the performance increased by 3.83%. Ultrasonic reactors increase the speed of chemical reactions by increasing the mass transfer and creating intermediate phases between the reaction phases, as well as reducing the intensity of reaction conditions such as the temperature and pressure.

The created cavitation leads to the loss of the boundaries between the reaction phases, thus the formation of emulsions that will cause the phases to overlap each other [27].

The reason for such an increase is the increase of ultrasound stirring intensity per increase in the power, which increases the contact of the two formed phases (methoxide and oil). This increased surface reduces the reaction time from 90 min to about 6 min [11]. Other studies have also shown that increasing the power of ultrasound will increase the conversion rates for the above reasons [28]. As illustrated in Figure. 4b, by increasing the molar ratio to a point between the ratios 4 and 6 to 1, the conversion rate first increases to 11.42, and then it remains unchanged from the point 6 to 8. The reason for this observation is the balance of the transesterification reaction which leads to the progression of methyl ester (biodiesel) production by increasing the molar ratio of alcohol to oil [5]. It should be noted that this increase in the rate of methyl ester conversion is limited due to an increase in molar ratio, because if this ratio exceeds a certain value, the purity of the produced biodiesel decreases. The main reason for this observation is that increasing the amount of methanol in the reaction mixture results in the greater dissolution of glycerol and alcohol in biodiesel and will significantly affect its purity. Another study showed that by increasing the molar ratio from 6 to 7, the rate of methyl ester conversion decreased [27]. As Figure. 4c illustrates, increasing the reaction time between the minutes 3 and 9 results in the increase of conversion rate. The reason for such an increase is that with increasing the reaction time, the amount of radiation to which the reaction mixture is exposed increases within a constant duration, and therefore the effect of ultrasound on the reaction environment increases proportionally. Besides that, given that the transesterification reaction is an equilibrium reaction, reducing the amount of reactive material in the reaction environment will cause the reaction to be reversed and the conversion rate of biodiesel reduced. The reason for this is that the physical effect of ultrasound is due to the emulsion preparation in insoluble reactors (oil and alcohol), and the reaction synthetics increases dramatically with increasing the overlapping surface between these reactors through the micro turbulence generated during the cavitation [29]. In a similar experiment, Kumar et al. (2010) used an ultrasound system to produce biodiesel from coconut oil and concluded that the time of ultrasonic reaction was reduced by 15-40 times compared to the conventional reaction [30].

Hosseinzadeh et al. (2015) observed that trends of reaction time and molar ratio differed from those of amplitude and molar ratio on methyl ester content so that they were divided into two parts. As reaction time and molar ratio increased to 5-7 min and 5-6, respectively, methyl ester content increased; however, when these two variables exceeded the ranges, yield decreased. This can be related to the equilibrium of transesterification reaction that progresses with increasing the molar ratio of alcohol to oil, and therefore biodiesel production increases [5].

The study of the effect of catalyst concentration on the conversion rate showed that with increasing the catalyst content from 0.75 to 1, the performance increased by 3.92% and then with increasing its content from 1 to 1.25, the performance decreased by 5.05%. The reason for this reduction can be that further catalyst loading would be inefficient in biodiesel production [31].

Decreased biodiesel yield due to increasing the KOH catalyst concentration is attributed to the formation of soap that contains excess amounts of catalyst [32]. According to the study of Patil et al., (2009), alkalicatalysed transesterification is very sensitive to water, while the existence of water may lead to ester saponification under alkaline conditions. Besides that, excess amounts of catalyst may result in the formation of emulsion, which increases the viscosity of the biodiesel and induces gels formation [33]. In general, the catalyst cost accounts for a large proportion of biodiesel production expense. The ultrasound power enhances the methanol emulsion in oil and furthers production of fine particles. This pattern results in an appropriate distribution and improves the efficiency of the catalyst. In addition, the ultrasound cavitation enhances the mass transfer, and therefore, compared with conventional stirrers, the catalyst consumption decreases by 50% [28].

Figure 4. Figure 4. Response surface plot showing the interaction effects of (a) ultrasonic power (W) versus catalyst concentration (w/w %) (b) ultrasonic power (W) versus molar ratio (c) ultrasonic power (W) versus time (min) (d) catalyst concentration (w/w %) versus molar ration (e) catalyst concentration (w/w %) time (min) (f) molar ratio versus time (min) on biodiesel yield.

Finally, an optimization was performed with regard to the boundary conditions (Table 5), which included the maximum conversion rate of methyl ester and the minimization of energy consumption.

Table 5. Boundary conditions of independent and dependent variable for biodiesel production optimization

The optimization was obtained at ultrasonic power 160, catalyst concentration 0.95, molar ratio 7.02, and reaction time 8.47 min. At these values, reaction yield and energy consumption were obtained 90.97 % and 13547. 6 J, respectively. It should be noted that at the proposed point of the software, the test was repeated, and at the obtained point, the reaction yield was equal to 92% and 13682 J, with an acceptable difference with the point obtained by the model. The yield of reaction reached 96.3 at the optimal point after washing biodiesel.

The main characteristics of safflower methyl ester, including viscosity, density, acid value, flash point, heating value, iodine value, sulfur content, and cetane number were measured by means of the ASTM standards (Table 6). All of these characteristics were then compared with EN 14214 biodiesel standards. The results revealed that some parameters of the biodiesel produced from safflower, including kinematic viscosity, density, acid value, iodine value and flash point fulfilled the acceptable condition according to the EN 14214 standard. Therefore, transesterified safflower could be a potential alternative to petrodiesel. The researchers have investigated several properties of twelve types of biodiesel, including viscosity, specific gravity, cetane number, iodine value, and freezing point. For ten of the 12 studied types of biodiesel, the kinematic viscosity was obtained 4-5 mm^2s^{-1} [34]. The specific gravity of 12 types of biodiesel varied between 0.873 and 0.883. In the present study, safflower fulfilled the range of parameters in another study [34]. All biodiesel fuels are denser and less compressible than the diesel fuel irrespective of the feedstock type [35,36]. Molecular weight of biodiesel is one of the factors that contributes to increasing biodiesel density [35,36].

Regardless of whether the biodiesel is produced from low-cost feedstocks or high-quality vegetable oils, biodiesel's flash point is higher than diesel fuel's [35]. Various factors influence the change in biodiesel flash point due to the residual alcohol content and the chemical compositions of the biodiesel, including the number of carbon atoms and the number of double bonds [37].

Table 6. Properties of safflower methyl ester in comparison with biodiesel standard (EN 14214) and diesel

3.2. Comparison of conventional methods and ultrasonic system for biodiesel production

The study of biodiesel production using the conventional method (mechanical stirrer, 600 rpm, 60°C) revealed that the greatest biodiesel conversion can be obtained at reaction time of 70–90 min (Figure 5). In the optimal condition, the time of biodiesel production by the ultrasonic system (at molar ratio, catalyst concentration, ultrasonic power, and reaction time of 7, 0.95% and 8.5 min, respectively) was 10.5 times lower than that by conventional method.

Transesterification reactions include the reaction between oil and alcohol in the presence of a catalyst. Oil and methyl alcohol are incompatible liquids and when they react in one tank, two separate layers are formed. Transesterification reactions commercially require continuous mechanical stirring over a long period of time, because the reaction between alcohol and oil can only be carried out at the point of contact between the two liquids (on a molecular scale). When this mixture is exposed to the ultrasonic waves, ultrasonic waves cause cavitation phenomena into the reaction medium. As a result, an emulsion of oil and alcohol is formed that provides a wide surface for reactions. It has been observed that the reaction time is significantly reduced [8].

Some researchers have reported similar results that confirm the suggested experimental data in the current study [11]. In other words, the ultrasonic system decreased the time of reaction to obtain the desired biodiesel conversion.

Figure 5. Comparison of biodiesel conversion rates between ultrasonic method and conventional stirring method

3.3. Biodiesel evaluation

3.3.1. Brake power and brake torque

The effects of different fuel blends on brake power and brake torque are illustrated in Figure 6. The results showed that the brake torque and broke power increased when the amount of biodiesel in fuel increased from B0 to B50. These observations are attributed to the higher oxygen content of biodiesel in combustion region that led to a comparatively more complete combustion. This means that biodiesel of the fuel mixture causes an increase in the oxygen content of the blend that leads to greater combustion efficiency and neutralizes the loss of biodiesel's heating value for these fuel blends [13,15,38]. In addition, the engine delivers fuel based on its volume and biodiesel density is higher than that of diesel, providing larger amounts of biodiesel to compensate the lower heating value [39]. But, when amount of biodiesel in fuel increased from B50 to B100, the brake power and brake torque decreased. The higher brake power and brake torque of B50 than those of B100 could be due to the biodiesel's lower heating value [1,40-42]. The problems with biodiesel fuel flow such as higher density and viscosity, compared to, diesel fuel lead to lower quality of fuel atomization in the combustion chamber, thus resulting in decreased brake power [40,43].

Panwar et al. (2010) investigated the effect of biodiesel production (B5, B10 and B20) from castor on combustion and performance characteristics. At the applied load, brake power of B10 blend was drawn to be 1.5%, 1.76%, and 0.75% higher than those of B0, B5, and B20 blends, respectively. B10 yields lower BSFC than fuel and therefore could serve as a promising alternative to diesel [44]. Aydin and Bayindir (2010) examined the effects of cottonseed oil methyl ester on the performance and emission of a single cylinder engine [43]. The results indicated that the torque of B5 was derived a bit greater than those of other fuels, including diesel. With increasing the biodiesel proportion of the blends, the torque decreased. This effect was produced due to the lower heating value and higher viscosity of cottonseed oil methyl ester [35,45].

Figure 6. Effect of different biodiesel percentage on (a) brake power (b) brake torque

3.3.2.CO and NOx emission

The results indicated that CO emissions decreased when the amount of biodiesel increased (Figure 7a). It is likely that this observation is due to the oxygen inherently presence in the biodiesel, which enhances combustion and burning at higher temperature in the cylinder, leading to decreased CO emission [2,38,46,47]. The trends of NOx were reversed by increasing biodiesel percentage in comparison to those of CO. Notably, NOx formation depends on volumetric efficiency, duration of combustion, and particularly, temperature of high activation energy required for the reactions involved. The increase in NOx emissions was proportional to the amount of biodiesel (Figure 7b). It has been suggested that some injection systems suffer from an unpredictable progression of fuel injection timing caused by the higher bulk modulus of compressibility in the biodiesel-containing fuel blends. This increases sound speed, which leads to a quicker transfer of the pressure wave from the injection pump to the nozzle, resulting in advancing of the needle lift. It has been established that advancing injection timing leads to an increase in NOx emissions [45]. In addition, biodiesels contain comparatively higher oxygen component compared to the diesel fuel, thus it is clear that there is higher oxygen content in biodiesels to react with the nitrogen component in the surrounding air, which leads to larger amounts of produced NOx [2,38,46].

Mofijur et al., (2014) examined the effect of biodiesel production from Moringa Oleifera and diesel mixture in multi cylinder engine. They reported that B5 and B10 blends decreased the CO emissions of diesel by 5.37% and 10.60%, respectively, and reduced the HC emissions of diesel fuel by 3.94% and 9.21%, respectively. However, B5 and B10 caused a slight increase in NOx, compared to diesel fuel, by 3.99% and 8.46%, respectively, and also a slight increase in CO2 emissions of diesel fuel by 2.25% and 4.96%, respectively [48]. In addition, the use of soybean oil methyl ester in diesel engine has also been investigated, reporting that the smoke, NOx, CO ,and HC decreased by 52.00%, 5.00%, 27.00%, and 27.00%, respectively [35,39].

Figure 7. Effect of different biodiesel percent on (a) CO (b) NOx

4. Conclusion

It can be argued that the greatest effect in the production of methyl ester, among the studied variables, was obtained for the molar ratio test and the reaction time, followed by the ultrasonic power and catalyst concentration. With an increase in ultrasound power from 160 W to 400 W, performance increased by 3.83%. By increasing the molar ratio to a point between the ratios 4 and 6 to 1, the conversion rate first increases to 11.42, and then it remains unchanged from the point 6 to 8. The study of the effect of catalyst concentration on the conversion rate showed that with increasing the catalyst content from 0.75 to 1, the performance increased by 3.92% and then with increasing its content from 1 to 1.25, the performance decreased by 5.05%. The reason for this reduction can be that further catalyst loading would be inefficient in biodiesel production. The optimization was obtained at 160 ultrasonic power, 0.95catalyst concentration, 7.02molar ratio, and, 8.47 min reaction time. At these values, conversion rate and energy consumption were obtained 90.9728 J and 13547.6 J, respectively. The results showed that the brake torque and broke power increased when the amount of biodiesel in fuel increased from B0 to B50. These observations are attributed to the higher oxygen content of biodiesel in combustion region that led to a comparatively more complete combustion. The results showed that CO emissions decreased when the amount of biodiesel increased. The trends of NOx were reversed by increasing biodiesel percentage in comparison to those of CO. The results showed that some of the properties of Safflower methyl ester meet the requirements of EN 14214 biodiesel standards. Therefore, transesterified Safflower could be a potential substitute for petrodiesel.

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Figure Captions

Figure 1. A schematic representation of a Soxhlet extractor.

Figure 2. The Schematic of set-up for ultrasonic-assisted biodiesel production process.

Figure 3. Actual data versus predicted data.

Figure 4. Figure 4. Response surface plot showing the interaction effects of (a) ultrasonic power (W) versus catalyst concentration (w/w %) (b) ultrasonic power (W) versus molar ratio (c) ultrasonic power (W) versus time (min) (d) catalyst concentration (w/w %) versus molar ration (e) catalyst concentration (w/w %) time (min) (f) molar ratio versus time (min) on biodiesel yield.

Figure 5. Comparison of extent of biodiesel conversion using ultrasonic method and conventional stirring method.

Figure 6. Effect of different biodiesel percent on (a) brake power (b) brake torque.

Figure 7. Effect of different biodiesel percent on (a) CO (b) NOx.