

Biofuels

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

--Manuscript Draft--

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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 NO_x 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

32 of the transesterification using STRs is the limited speed of reaction due to the low mass transfer
33 rates between oil and alcohol (incompatible mixture), the limitation of the upper limit of
34 production efficiency due to lack of separation mechanism of the product during the reversible
35 transesterification, and the discontinuous production of biodiesel. One of the intensification
36 methods which could improve the quality of biodiesel production process is the use of ultrasound
37 [5]. For more agitation and effective surface contact between alcohol and oil molecules, ultrasonic
38 waves can be used. Ultrasound has proven to be a very useful tool in enhancing the reaction rates
39 in a variety of reacting systems. It has successfully increased the conversion, improved the yield,
40 changed the reaction pathway, and/or initiated the reaction in biological, chemical, and
41 electrochemical systems [6]. When the mixture is subjected to ultrasound, ultrasonic waves create
42 cavitation at exposure point [7]. As a result, an emulsion of oil and alcohol is formed that provides
43 a large surface for the reaction, and the response time is significantly reduced [8]. Sonochemistry
44 is generally performed in a liquid medium. During each 'stretching' phase (rarefaction), provided
45 that the negative pressure is strong enough to overcome intermolecular binding forces, a fluid
46 medium can be torn apart, producing tiny cavities (micro bubbles) [6,9]. In succeeding cycles,
47 these cavities can grow and then collapse violently with the release of large amounts of energy.
48 Experimental results have shown that approaching 5000 °K temperatures and 2000atmpressures
49 are produced during this collapse [10].

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

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

58 Moreover, many researchers have investigated the effects of biodiesel fuel blends on engine
59 indicators such as the brake power, brake torque, brake thermal efficiency (BTE), exhaust gas
60 temperature (EGT), Brake-specific fuel consumption (BSFC), NO_x, Exhaust particulate matter
61 (PM), CO, CO₂, hydrocarbon emission (HC), and smoke density in comparison to those of diesel.

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

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

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

84 2. Material and Methods

85 2.1. Oil extraction

86 Soxhlet extraction, which is a conventional method and used for the extraction, was carried out in
87 a classic Soxhlet extractor in the presence of n-hexane as a solvent (Figure 1). 10 g of safflower
88 seeds were milled using a laboratory mill. Subsequently, powdered seed was placed in an
89 extraction thimble and then Soxhlet was extracted for 8 h using 200 ml of n-hexane. After
90 extraction, the solvent was evaporated by rotary evaporator and weighed. This procedure was
91 repeated until a constant value for the extracted weight was obtained [20]. Oil yield was further

92 calculated and presented as a weight of extracted oil per weight of sample. Some of physical and
93 chemical properties of safflower oil are shown in Table 1.

94

95 **Figure 1.** A schematic representation of a Soxhlet extractor

96

97 **Table1.** Fatty acid profile and properties of used Safflower oil

98

99

100 2.2. Transesterification reaction

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

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

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

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

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

125

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

127

128 **2.3. Optimization and statistical analysis**

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

140

$$141 \quad Y_i = \beta_0 + \sum \beta_i X_i + \sum \beta_{ij} X_i X_j + \sum \beta_{jj} X_i^2 + \varepsilon \quad (2)$$

141

142 where β_0 , β_j , β_{ij} and β_{jj} are constant coefficients, x_i and x_j independent variables in the process
143 and ε are random errors. The levels of independent variables (Table 2) were selected according to
144 the literature review and screening study experiments [5,11]. Finally, according to the curves
145 drawn and the range for the independent variables, the optimal point was obtained and the result
146 was validated by the validation test.

147

148 **Table 2.** Selected independent variables in response surface method

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

152

153 **2.4. Engine test**

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

161 **2.5. Studied diesel generator**

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

170

Table 3. Specification of the test engine

171 **3. Results and discussion**

172 **3.1. Biodiesel production**

173 The P-value (0.01) of the model implies its significance. In this case, ultrasonic power, catalyst
174 concentration, molar ratio, time, ultrasonic power \times catalyst concentration, ultrasonic power \times
175 molar ratio, catalyst concentration \times molar ratio, molar ratio \times time, catalyst concentration², molar
176 ratio², and time² are the significant model terms. Values greater than 0.1000 indicate the model
177 terms are not significant. The lack of Fit F value of 0.75 implies the Lack of Fit is not significant
178 relative to the pure error. There is a 67.68% chance that a lack of Fit F of such value is due to the
179 noise (Table 4).

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

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

182
183 **Table 4-** The results of reactor performance model by response surface methodology

184
185 Based on the results of analysis of variance of regression coefficients, non-significant coefficients
186 were excluded from Equation (3), and the final Equation as well as coding (4) and (5) was drawn
187 to obtain a standard error of 0.75 and a determination coefficient of 0.9907.

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

191

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

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

192
193 Where A is the ultrasonic power, B is the catalyst, C is the molar ratio, and D is the reaction time.
194 Regarding the values of the coefficients of Equation (5), it can be argued that the greatest effect in
195 the production of methyl ester, among the studied variables, was obtained for the molar ratio test
196 and the time of reaction, followed by the ultrasonic power and catalyst concentration.

197
198 **Figure 3.** Actual data versus predicted data

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

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

206 The reason for such an increase is the increase of ultrasound stirring intensity per increase in the
207 power, which increases the contact of the two formed phases (methoxide and oil). This increased
208 surface reduces the reaction time from 90 min to about 6 min [11]. Other studies have also shown
209 that increasing the power of ultrasound will increase the conversion rates for the above reasons
210 [28]. As illustrated in [Figure. 4b](#), by increasing the molar ratio to a point between the ratios 4 and
211 6 to 1, the conversion rate first increases to 11.42, and then it remains unchanged from the point 6
212 to 8. The reason for this observation is the balance of the transesterification reaction which leads
213 to the progression of methyl ester (biodiesel) production by increasing the molar ratio of alcohol
214 to oil [5]. It should be noted that this increase in the rate of methyl ester conversion is limited due
215 to an increase in molar ratio, because if this ratio exceeds a certain value, the purity of the produced
216 biodiesel decreases. The main reason for this observation is that increasing the amount of methanol
217 in the reaction mixture results in the greater dissolution of glycerol and alcohol in biodiesel and
218 will significantly affect its purity. Another study showed that by increasing the molar ratio from 6
219 to 7, the rate of methyl ester conversion decreased [27]. As [Figure. 4c](#) illustrates, increasing the
220 reaction time between the minutes 3 and 9 results in the increase of conversion rate. The reason
221 for such an increase is that with increasing the reaction time, the amount of radiation to which the
222 reaction mixture is exposed increases within a constant duration, and therefore the effect of
223 ultrasound on the reaction environment increases proportionally. Besides that, given that the
224 transesterification reaction is an equilibrium reaction, reducing the amount of reactive material in
225 the reaction environment will cause the reaction to be reversed and the conversion rate of biodiesel
226 reduced. The reason for this is that the physical effect of ultrasound is due to the emulsion
227 preparation in insoluble reactors (oil and alcohol), and the reaction synthetic increases
228 dramatically with increasing the overlapping surface between these reactors through the micro
229 turbulence generated during the cavitation [29]. In a similar experiment, Kumar et al. (2010) used
230 an ultrasound system to produce biodiesel from coconut oil and concluded that the time of
231 ultrasonic reaction was reduced by 15-40 times compared to the conventional reaction [30].
232 Hosseinzadeh et al. (2015) observed that trends of reaction time and molar ratio differed from
233 those of amplitude and molar ratio on methyl ester content so that they were divided into two parts.
234 As reaction time and molar ratio increased to 5-7 min and 5-6, respectively, methyl ester content

235 increased; however, when these two variables exceeded the ranges, yield decreased. This can be
236 related to the equilibrium of transesterification reaction that progresses with increasing the molar
237 ratio of alcohol to oil, and therefore biodiesel production increases [5].

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

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

253
254 **Figure 4.** Figure 4. Response surface plot showing the interaction effects of (a) ultrasonic power
255 (W) versus catalyst concentration (w/w %) (b) ultrasonic power (W) versus molar ratio (c)
256 ultrasonic power (W) versus time (min) (d) catalyst concentration (w/w %) versus molar ratio (e)
257 catalyst concentration (w/w %) time (min) (f) molar ratio versus time (min) on biodiesel yield.

258
259
260 Finally, an optimization was performed with regard to the boundary conditions (Table 5), which
261 included the maximum conversion rate of methyl ester and the minimization of energy
262 consumption.

263
264 **Table 5.** Boundary conditions of independent and dependent variable for biodiesel production
265 optimization

266 The optimization was obtained at ultrasonic power 160, catalyst concentration 0.95, molar ratio
267 7.02, and reaction time 8.47 min. At these values, reaction yield and energy consumption were

268 obtained 90.97 % and 13547. 6 J, respectively. It should be noted that at the proposed point of the
269 software, the test was repeated, and at the obtained point, the reaction yield was equal to 92% and
270 13682 J, with an acceptable difference with the point obtained by the model. The yield of reaction
271 reached 96.3 at the optimal point after washing biodiesel.

272 The main characteristics of safflower methyl ester, including viscosity, density, acid value, flash
273 point, heating value, iodine value, sulfur content, and cetane number were measured by means of
274 the ASTM standards (Table 6). All of these characteristics were then compared with EN 14214
275 biodiesel standards. The results revealed that some parameters of the biodiesel produced from
276 safflower, including kinematic viscosity, density, acid value, iodine value and flash point fulfilled
277 the acceptable condition according to the EN 14214 standard. Therefore, transesterified safflower
278 could be a potential alternative to petrodiesel. The researchers have investigated several properties
279 of twelve types of biodiesel, including viscosity, specific gravity, cetane number, iodine value, and
280 freezing point. For ten of the 12 studied types of biodiesel, the kinematic viscosity was obtained
281 4-5 mm²s⁻¹ [34]. The specific gravity of 12 types of biodiesel varied between 0.873 and 0.883. In
282 the present study, safflower fulfilled the range of parameters in another study [34]. All biodiesel
283 fuels are denser and less compressible than the diesel fuel irrespective of the feedstock type
284 [35,36]. Molecular weight of biodiesel is one of the factors that contributes to increasing biodiesel
285 density [35,36].

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

290
291 **Table 6.** Properties of safflower methyl ester in comparison with biodiesel standard (EN 14214)
292 and diesel
293

294 **3.2. Comparison of conventional methods and ultrasonic system for biodiesel production**

295 The study of biodiesel production using the conventional method (mechanical stirrer, 600 rpm,
296 60°C) revealed that the greatest biodiesel conversion can be obtained at reaction time of 70–90
297 min (Figure 5). In the optimal condition, the time of biodiesel production by the ultrasonic system
298 (at molar ratio, catalyst concentration, ultrasonic power, and reaction time of 7, 0.95% and 8.5
299 min, respectively) was 10.5 times lower than that by conventional method.

300 Transesterification reactions include the reaction between oil and alcohol in the presence of a
301 catalyst. Oil and methyl alcohol are incompatible liquids and when they react in one tank, two
302 separate layers are formed. Transesterification reactions commercially require continuous
303 mechanical stirring over a long period of time, because the reaction between alcohol and oil can
304 only be carried out at the point of contact between the two liquids (on a molecular scale). When
305 this mixture is exposed to the ultrasonic waves, ultrasonic waves cause cavitation phenomena into
306 the reaction medium. As a result, an emulsion of oil and alcohol is formed that provides a wide
307 surface for reactions. It has been observed that the reaction time is significantly reduced [8].
308 Some researchers have reported similar results that confirm the suggested experimental data in the
309 current study [11]. In other words, the ultrasonic system decreased the time of reaction to obtain
310 the desired biodiesel conversion.

311
312 **Figure 5.** Comparison of biodiesel conversion rates between ultrasonic method and conventional
313 stirring method
314

315 **3.3. Biodiesel evaluation**

316 **3.3.1. Brake power and brake torque**

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

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

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

340 **3.3.2.CO and NOx emission**

341 The results indicated that CO emissions decreased when the amount of biodiesel increased (Figure
342 7a). It is likely that this observation is due to the oxygen inherently presence in the biodiesel, which
343 enhances combustion and burning at higher temperature in the cylinder, leading to decreased CO
344 emission [2,38,46,47]. The trends of NOx were reversed by increasing biodiesel percentage in
345 comparison to those of CO. Notably, NOx formation depends on volumetric efficiency, duration
346 of combustion, and particularly, temperature of high activation energy required for the reactions
347 involved. The increase in NOx emissions was proportional to the amount of biodiesel (Figure 7b).
348 It has been suggested that some injection systems suffer from an unpredictable progression of fuel
349 injection timing caused by the higher bulk modulus of compressibility in the biodiesel-containing
350 fuel blends. This increases sound speed, which leads to a quicker transfer of the pressure wave
351 from the injection pump to the nozzle, resulting in advancing of the needle lift. It has been
352 established that advancing injection timing leads to an increase in NOx emissions [45]. In addition,
353 biodiesels contain comparatively higher oxygen component compared to the diesel fuel, thus it is
354 clear that there is higher oxygen content in biodiesels to react with the nitrogen component in the
355 surrounding air, which leads to larger amounts of produced NOx [2,38,46].

356 Mofijur et al., (2014) examined the effect of biodiesel production from *Moringa Oleifera* and diesel
357 mixture in multi cylinder engine. They reported that B5 and B10 blends decreased the CO
358 emissions of diesel by 5.37% and 10.60%, respectively, and reduced the HC emissions of diesel
359 fuel by 3.94% and 9.21%, respectively. However, B5 and B10 caused a slight increase in NOx,

360 compared to diesel fuel, by 3.99% and 8.46%, respectively, and also a slight increase in CO₂
361 emissions of diesel fuel by 2.25% and 4.96%, respectively [48]. In addition, the use of soybean oil
362 methyl ester in diesel engine has also been investigated, reporting that the smoke, NO_x, CO, and
363 HC decreased by 52.00%, 5.00%, 27.00%, and 27.00%, respectively [35,39].
364

365 **Figure 7.** Effect of different biodiesel percent on (a) CO (b) NO_x

366 **4. Conclusion**

367 It can be argued that the greatest effect in the production of methyl ester, among the studied
368 variables, was obtained for the molar ratio test and the reaction time, followed by the ultrasonic
369 power and catalyst concentration. With an increase in ultrasound power from 160 W to 400 W,
370 performance increased by 3.83%. By increasing the molar ratio to a point between the ratios 4 and
371 6 to 1, the conversion rate first increases to 11.42, and then it remains unchanged from the point 6
372 to 8. The study of the effect of catalyst concentration on the conversion rate showed that with
373 increasing the catalyst content from 0.75 to 1, the performance increased by 3.92% and then with
374 increasing its content from 1 to 1.25, the performance decreased by 5.05%. The reason for this
375 reduction can be that further catalyst loading would be inefficient in biodiesel production. The
376 optimization was obtained at 160 ultrasonic power, 0.95 catalyst concentration, 7.02 molar ratio,
377 and, 8.47 min reaction time. At these values, conversion rate and energy consumption were
378 obtained 90.9728 J and 13547.6 J, respectively. The results showed that the brake torque and broke
379 power increased when the amount of biodiesel in fuel increased from B0 to B50. These
380 observations are attributed to the higher oxygen content of biodiesel in combustion region that led
381 to a comparatively more complete combustion. The results showed that CO emissions decreased
382 when the amount of biodiesel increased. The trends of NO_x were reversed by increasing biodiesel
383 percentage in comparison to those of CO. The results showed that some of the properties of
384 Safflower methyl ester meet the requirements of EN 14214 biodiesel standards. Therefore,
385 transesterified Safflower could be a potential substitute for petrodiesel.

386 **Acknowledgement**

387

388

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496 **Figure Captions**

497 Figure 1. A schematic representation of a Soxhlet extractor.

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

499 Figure 3. Actual data versus predicted data.

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

504

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

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

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

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510

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

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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	$\text{g I}_2/100\text{g oil}$	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 Concentration	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

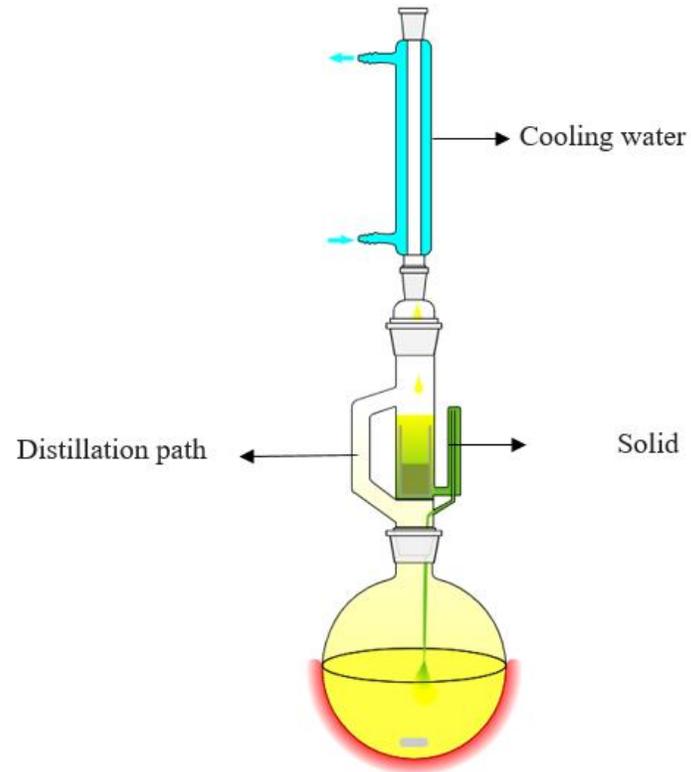


Figure 1. A schematic representation of a Soxhlet extractor

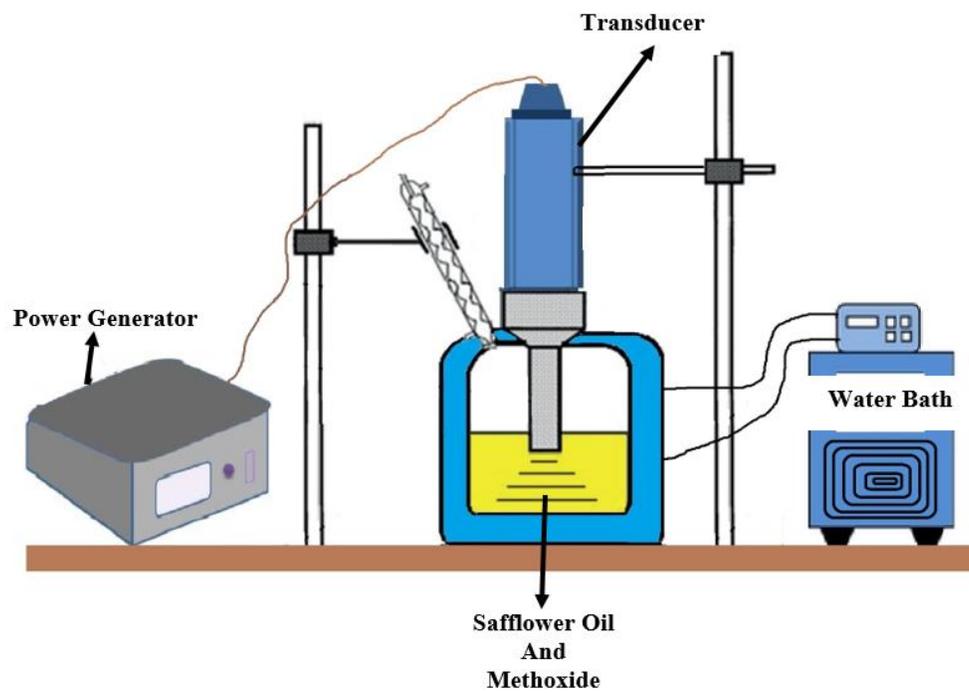


Figure 2. The Schematic of set-up for ultrasonic-assisted biodiesel production process

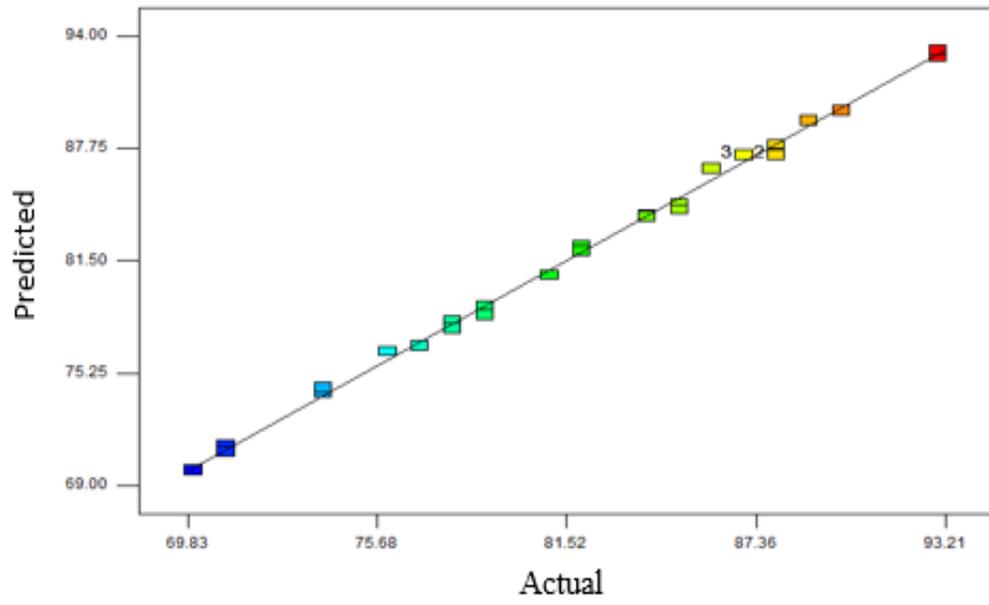
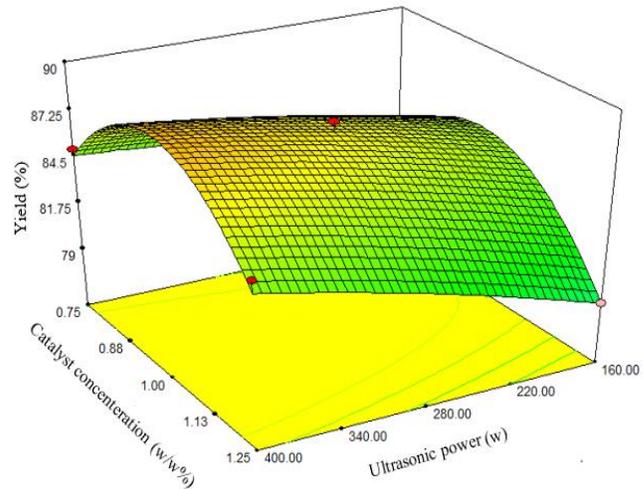
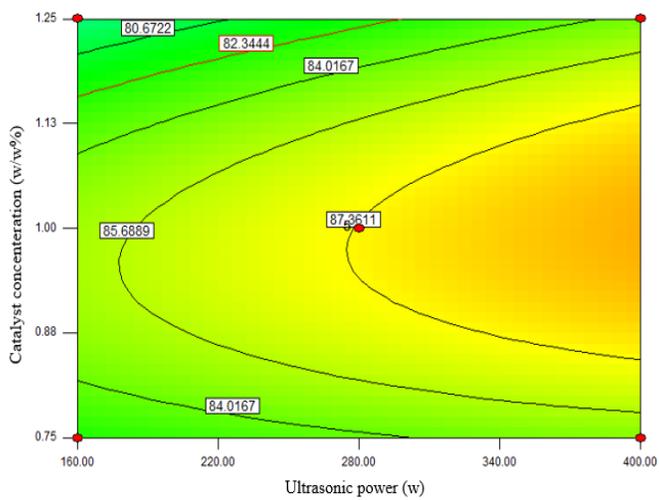
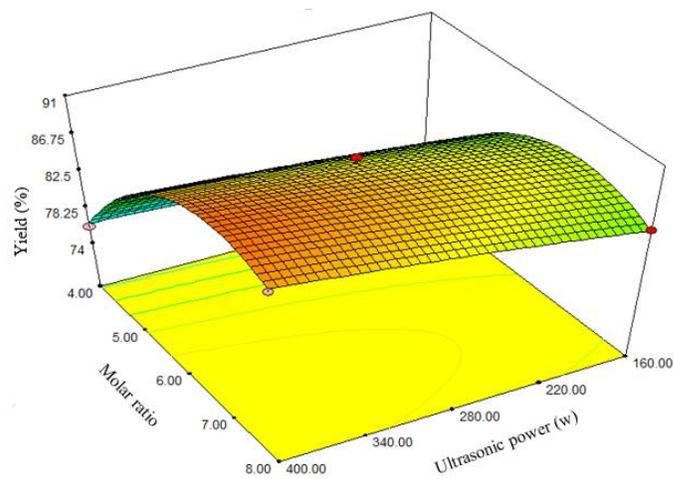
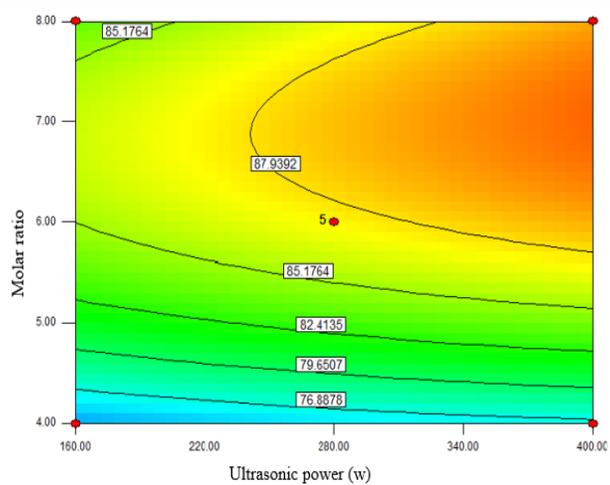


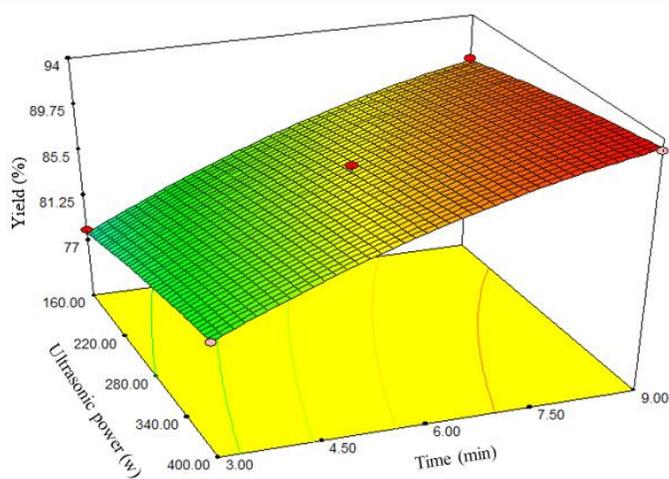
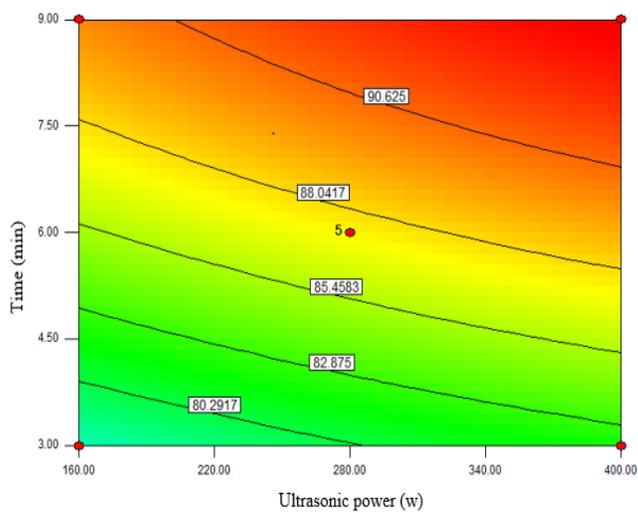
Figure 3. Actual data versus predicted data



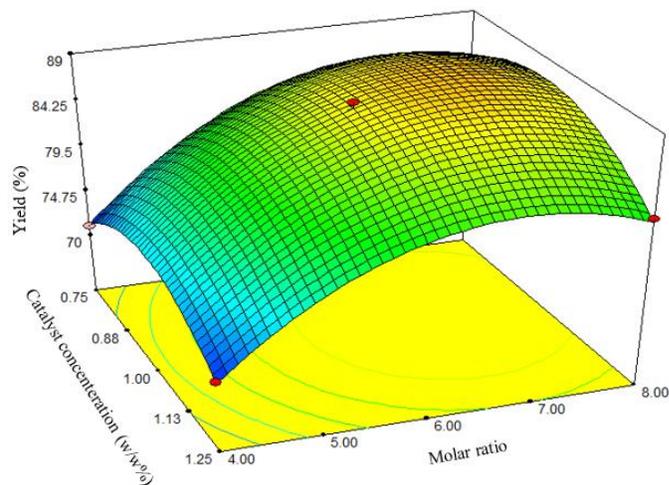
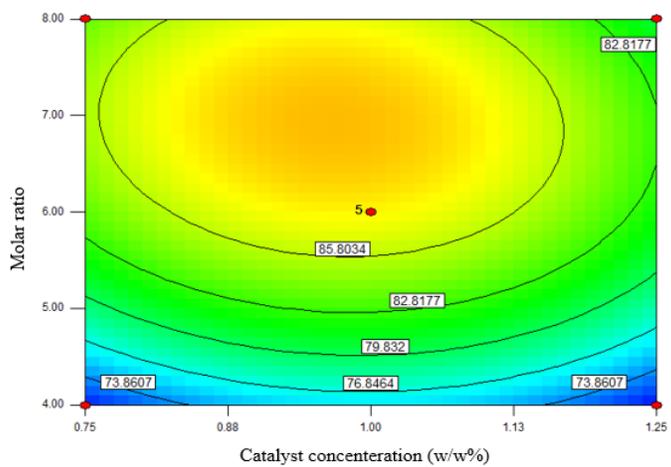
(a)



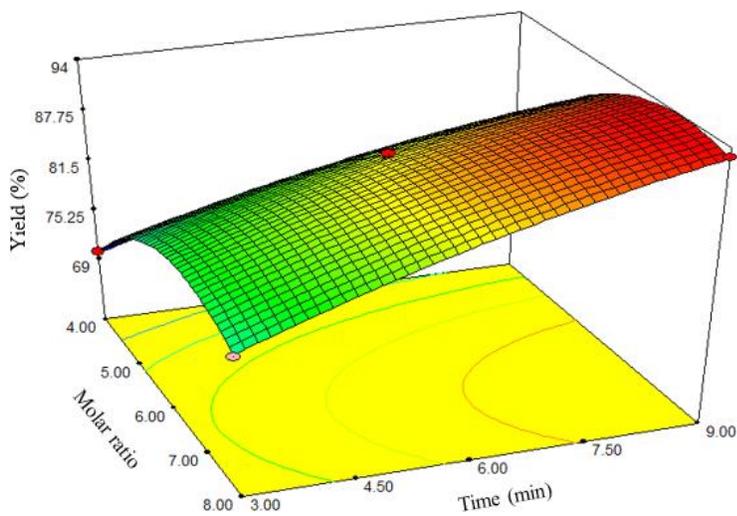
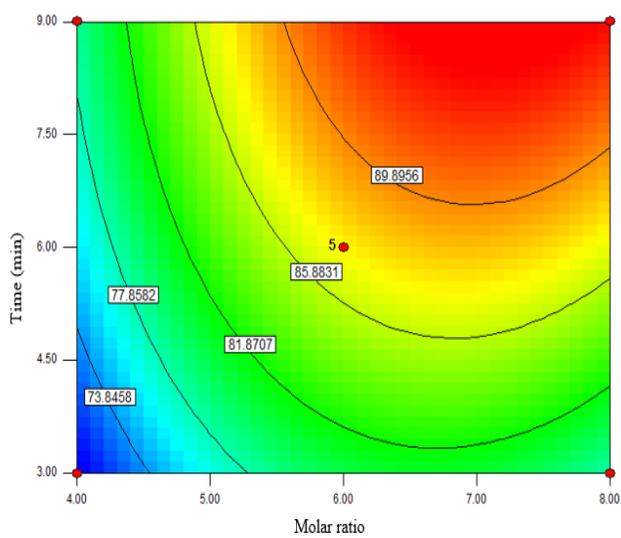
(b)



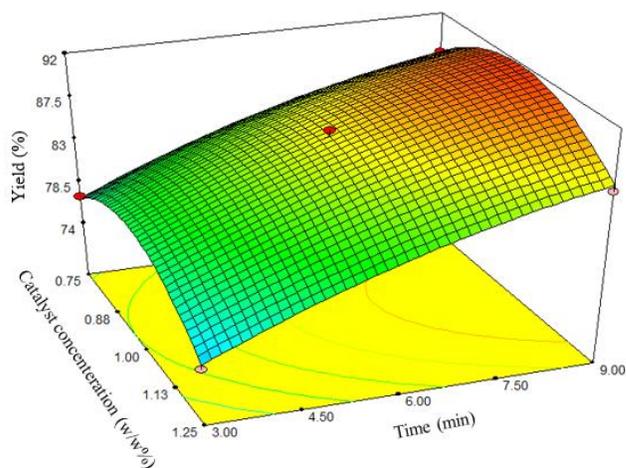
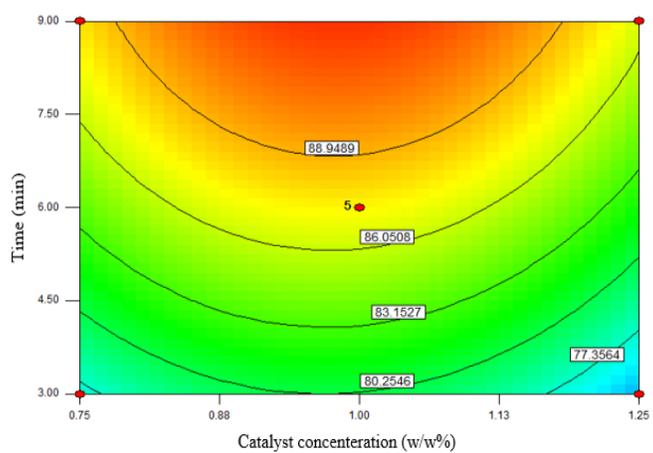
(c)



(d)



(e)



(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 ratio (e) catalyst concentration (w/w %) time (min) (f) molar ratio versus time (min) on biodiesel yield.

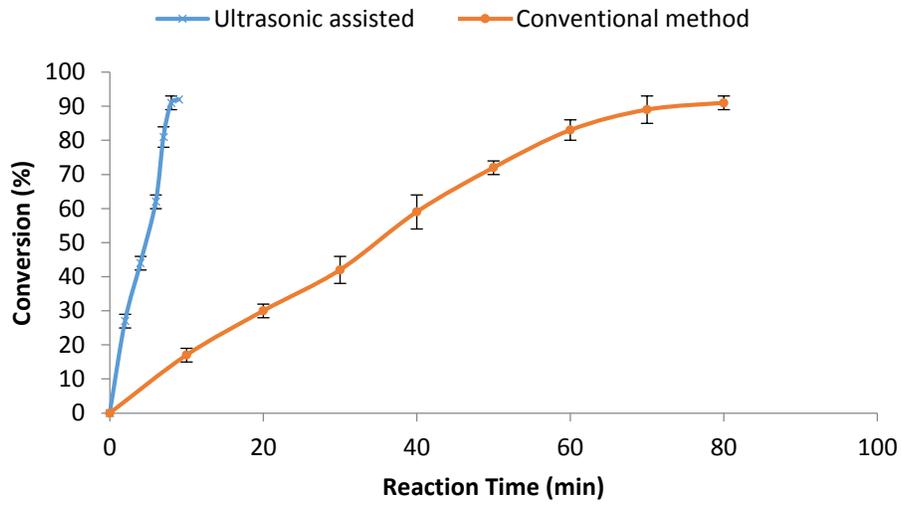


Figure 5. Comparison of extent of biodiesel conversion using ultrasonic method and conventional stirring method

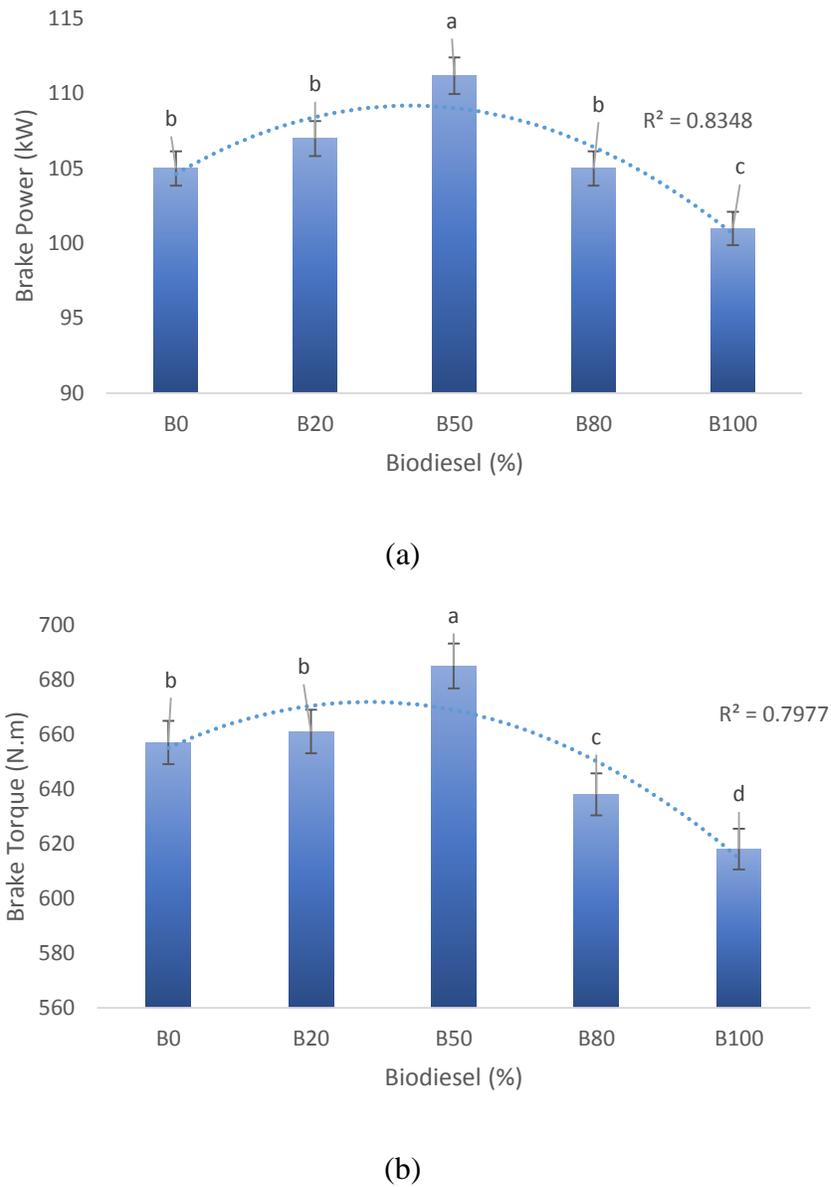
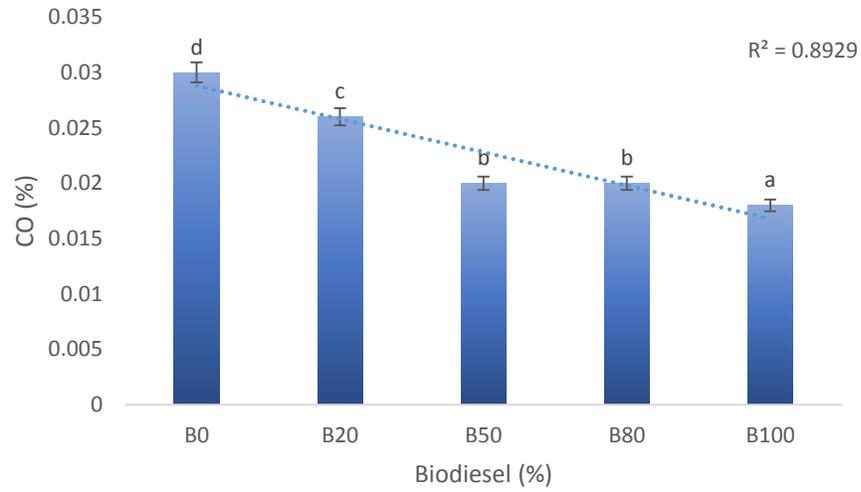
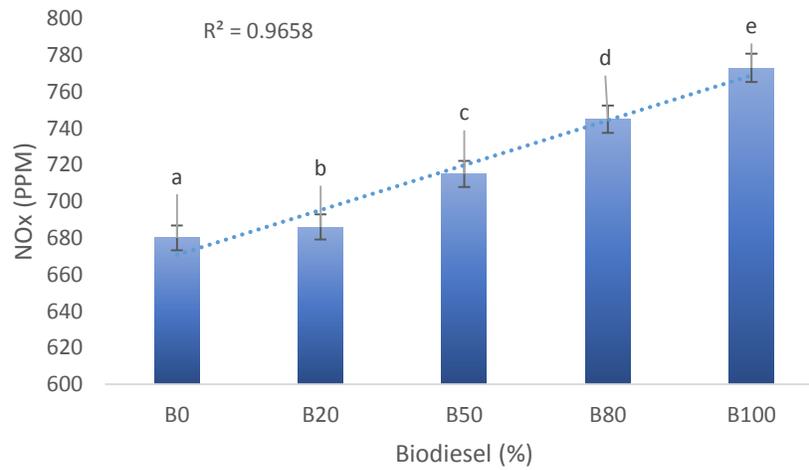


Figure 6. Effect of different biodiesel percent on (a) brake power (b) brake torque



(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:



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

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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.

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

33

34 **1. Introduction**

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

62 release of large amounts of energy. Experimental results have shown that approaching 5000 °K
63 temperatures and 2000atmpressures are produced during this collapse [10].
64 Fayyazi et al., (2014) produced biodiesel fuel using an ultrasound system (24 kHz and 400 watts)
65 from the waste oil. Also, other studies reported similar results regarding the increase in biodiesel
66 conversion using ultrasound [11,12].
67 Hosseinzadeh et al. (2015) sought to reduce the production time of biodiesel from *Pistacia*
68 *atlantica* oil with the lowest possible energy consumption (process optimization) using
69 ultrasound. They investigated the effects of variables, including molar ratio of alcohol to oil,
70 ultrasound amplitude, ratio of the duration of ultrasound on to that of ultrasound off (pulse), and
71 reaction time on the rate of methyl ester conversion [5].
72 Moreover, many researchers have investigated the effects of biodiesel fuel blends on engine
73 indicators such as the brake power, brake torque, brake thermal efficiency (BTE), exhaust gas
74 temperature (EGT), Brake-specific fuel consumption (BSFC), NO_x, Exhaust particulate matter
75 (PM), CO, CO₂, hydrocarbon emission (HC), and smoke density in comparison to those of
76 diesel. The results of these studies showed that different sources of biodiesel feedstocks led to
77 different engine indicators.
78 The researchers have also addressed the engine performance and emissions when using
79 biodiesel, and most of them have reported that when using biodiesel, engine power and torque
80 decreases due to the loss of biodiesel heating value [13,14]. Some studies have shown there is no
81 significant difference between B100 and diesel with respect to the engine power [15,16].
82 However, some researchers have reported that there may be unanticipated increase in power or
83 torque of diesel engines [2,17]. On the other hand, evidence has shown similar trends of engine
84 power performance with load or speed of engines fueled with B100 and B0 [18].
85 *Carthamus tinctorius* L., commonly known as safflower, is one of the world's oldest crops
86 belonging to the Asteraceae family and is native to the Middle East. Safflower is a tap-rooted
87 annual crop that can withstand environmental unpleasant conditions (drought, salinity), the
88 production of which reaches to above 420000 ton annually, distinguishing it as a potential
89 bioenergy crop. Safflower is a highly branched, thistle-like, herbaceous plant. It is commercially
90 cultivated for the oil of its seeds. The seeds contain 27–32% oil, 32–40% crude fiber, 5–8%
91 moisture, 14–15% protein, and 2–7% ash. Safflower is a valuable plant due to the variety of its
92 fatty acid content. The composition of standard safflower oil is 2–3% stearic acid, 16–20% oleic

93 acid, 6–8% palmitic acid, and 71–75% linoleic acid [19]. This study was conducted to
94 investigate the feasibility of biodiesel production from safflower oil using the ultrasonic system,
95 and to evaluate the produced fuel on a diesel power generator to investigate the including engine
96 performance and emission parameters when using different levels of diesel -Safflower biodiesel
97 blends.

98 **2. Material and Methods**

99 **2.1. Oil extraction**

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

108

109 **Figure 1.** A schematic representation of a Soxhlet extractor

110

111 **Table1.** Fatty acid profile and properties of used Safflower oil

112

113

114 **2.2. Transesterification reaction**

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

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

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

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

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

139

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

141

142 **2.3. Optimization and statistical analysis**

143 The design of the present study follows the box-behnken method. The response surface
144 methodology is a set of mathematical and statistical techniques that are used to develop,
145 promote, and optimize the processes in which the level in question is affected by many variables
146 and the goal is to optimize the response [22,23]. Some phases in the application of RSM as an
147 optimization, modeling and analysis technique is as follows: (1) the selection of independent
148 variables concerning the major effects on the system through screening studies and definition of
149 the experimental region, according to the objective of the study, the experience of the researcher
150 and literature reviews; (2) the selection of the experimental design and implementing the

151 experiments according to the selected experimental matrix; (3) setting the mathematic–statistical
152 orders of the collected experimental data via the fit of a polynomial function; (4) finding the
153 optimum values for all of the studied variables [24]. To derive optimal value, Regression
154 Equation (2) was be used.

155

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

156

157 where β_0 , β_j , β_{ij} and β_{jj} are constant coefficients, x_i and x_j independent variables in the process
158 and ε are random errors. The levels of independent variables (Table 2) were selected according
159 to the literature review and screening study experiments [5,11]. Finally, according to the curves
160 drawn and the range for the independent variables, the optimal point was obtained and the result
161 was validated by the validation test.

162

163 **Table 2.** Selected independent variables in response surface method

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

167

168 **2.4. Engine test**

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

176 **2.5. Studied diesel generator**

177 The diesel power generator consists of an engine and a generator, and the engine used in this
178 research is a 4-cycle engine and 12 cylinders (CAT3412 Co.) equipped with supercharge, an
179 indirect spray system with a maximum power of 537 KW at rotational speed of 1,800 rpm. The
180 generator connected to the engine has been manufactured by Caterpillar Co., which is three-

181 phase, powered by 380 V with a maximum power consumption of 300 kW at the rated
 182 speed. The generator is connected to a central processing unit that starts processing by using the
 183 data from different points and displays the output voltage, power, and engine speed on the
 184 control panel. Table 3 presents the technical specifications of the diesel generator.

185 **Table 3.** Specification of the test engine

186 **3. Results and discussion**

187 **3.1. Biodiesel production**

188 The P-value (0.01) of the model implies its significance. In this case, ultrasonic power, catalyst
 189 concentration, molar ratio, time, ultrasonic power × catalyst concentration, ultrasonic power ×
 190 molar ratio, catalyst concentration × molar ratio, molar ratio × time, catalyst concentration²,
 191 molar ratio², and time² are the significant model terms. Values greater than 0.1000 indicate the
 192 model terms are not significant. The lack of Fit *F* value of 0.75 implies the Lack of Fit is not
 193 significant relative to the pure error. There is a 67.68% chance that a lack of Fit *F* of such value
 194 is due to the noise (Table 4).

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

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

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

198
 199
 200 Based on the results of analysis of variance of regression coefficients, non-significant
 201 coefficients were excluded from Equation (3), and the final Equation as well as coding (4) and
 202 (5) was drawn to obtain a standard error of 0.75 and a determination coefficient of 0.9907.

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

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

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

207

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

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

213

214

Figure 3. Actual data versus predicted data

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

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

223 The reason for such an increase is the increase of ultrasound stirring intensity per increase in the
224 power, which increases the contact of the two formed phases (methoxide and oil). This increased
225 surface reduces the reaction time from 90 min to about 6 min [11]. Other studies have also
226 shown that increasing the power of ultrasound will increase the conversion rates for the above
227 reasons [28]. As illustrated in Figure. 4b, by increasing the molar ratio to a point between the
228 ratios 4 and 6 to 1, the conversion rate first increases to 11.42, and then it remains unchanged
229 from the point 6 to 8. The reason for this observation is the balance of the transesterification
230 reaction which leads to the progression of methyl ester (biodiesel) production by increasing the
231 molar ratio of alcohol to oil [5]. It should be noted that this increase in the rate of methyl ester
232 conversion is limited due to an increase in molar ratio, because if this ratio exceeds a certain
233 value, the purity of the produced biodiesel decreases. The main reason for this observation is that
234 increasing the amount of methanol in the reaction mixture results in the greater dissolution of
235 glycerol and alcohol in biodiesel and will significantly affect its purity. Another study showed

236 that by increasing the molar ratio from 6 to 7, the rate of methyl ester conversion decreased [27].
237 As Figure. 4c illustrates, increasing the reaction time between the minutes 3 and 9 results in the
238 increase of conversion rate. The reason for such an increase is that with increasing the reaction
239 time, the amount of radiation to which the reaction mixture is exposed increases within a
240 constant duration, and therefore the effect of ultrasound on the reaction environment increases
241 proportionally. Besides that, given that the transesterification reaction is an equilibrium reaction,
242 reducing the amount of reactive material in the reaction environment will cause the reaction to be
243 reversed and the conversion rate of biodiesel reduced. The reason for this is that the physical
244 effect of ultrasound is due to the emulsion preparation in insoluble reactors (oil and alcohol), and
245 the reaction synthetics increases dramatically with increasing the overlapping surface between
246 these reactors through the micro turbulence generated during the cavitation [29]. In a similar
247 experiment, Kumar et al. (2010) used an ultrasound system to produce biodiesel from coconut oil
248 and concluded that the time of ultrasonic reaction was reduced by 15-40 times compared to the
249 conventional reaction [30].

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

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

260 Decreased biodiesel yield due to increasing the KOH catalyst concentration is attributed to the
261 formation of soap that contains excess amounts of catalyst [32]. According to the study of Patil
262 et al., (2009), alkalicatalysed transesterification is very sensitive to water, while the existence of
263 water may lead to ester saponification under alkaline conditions. Besides that, excess amounts of
264 catalyst may result in the formation of emulsion, which increases the viscosity of the biodiesel
265 and induces gels formation [33]. In general, the catalyst cost accounts for a large proportion of
266 biodiesel production expense. The ultrasound power enhances the methanol emulsion in oil and

267 furthers production of fine particles. This pattern results in an appropriate distribution and
268 improves the efficiency of the catalyst. In addition, the ultrasound cavitation enhances the mass
269 transfer, and therefore, compared with conventional stirrers, the catalyst consumption decreases
270 by 50% [28].

271
272 **Figure 4.** Figure 4. Response surface plot showing the interaction effects of (a) ultrasonic power
273 (W) versus catalyst concentration (w/w %) (b) ultrasonic power (W) versus molar ratio (c)
274 ultrasonic power (W) versus time (min) (d) catalyst concentration (w/w %) versus molar ratio
275 (e) catalyst concentration (w/w %) time (min) (f) molar ratio versus time (min) on biodiesel
276 yield.

277
278
279 Finally, an optimization was performed with regard to the boundary conditions (Table 5), which
280 included the maximum conversion rate of methyl ester and the minimization of energy
281 consumption.

282
283 **Table 5.** Boundary conditions of independent and dependent variable for biodiesel production
284 optimization

285 The optimization was obtained at ultrasonic power 160, catalyst concentration 0.95, molar ratio
286 7.02, and reaction time 8.47 min. At these values, reaction yield and energy consumption were
287 obtained 90.97 % and 13547. 6 J, respectively. It should be noted that at the proposed point of
288 the software, the test was repeated, and at the obtained point, the reaction yield was equal to 92%
289 and 13682 J, with an acceptable difference with the point obtained by the model. The yield of
290 reaction reached 96.3 at the optimal point after washing biodiesel.

291 The main characteristics of safflower methyl ester, including viscosity, density, acid value, flash
292 point, heating value, iodine value, sulfur content, and cetane number were measured by means of
293 the ASTM standards (Table 6). All of these characteristics were then compared with EN 14214
294 biodiesel standards. The results revealed that some parameters of the biodiesel produced from
295 safflower, including kinematic viscosity, density, acid value, iodine value and flash point
296 fulfilled the acceptable condition according to the EN 14214 standard. Therefore, transesterified
297 safflower could be a potential alternative to petrodiesel. The researchers have investigated
298 several properties of twelve types of biodiesel, including viscosity, specific gravity, cetane
299 number, iodine value, and freezing point. For ten of the 12 studied types of biodiesel, the
300 kinematic viscosity was obtained 4-5 mm²s⁻¹ [34]. The specific gravity of 12 types of biodiesel

301 varied between 0.873 and 0.883. In the present study, safflower fulfilled the range of parameters
302 in another study [34]. All biodiesel fuels are denser and less compressible than the diesel fuel
303 irrespective of the feedstock type [35,36]. Molecular weight of biodiesel is one of the factors
304 that contributes to increasing biodiesel density [35,36].

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

310
311 **Table 6.** Properties of safflower methyl ester in comparison with biodiesel standard (EN 14214)
312 and diesel
313

314 **3.2. Comparison of conventional methods and ultrasonic system for biodiesel production**

315 The study of biodiesel production using the conventional method (mechanical stirrer, 600 rpm,
316 60°C) revealed that the greatest biodiesel conversion can be obtained at reaction time of 70–90
317 min (Figure 5). In the optimal condition, the time of biodiesel production by the ultrasonic
318 system (at molar ratio, catalyst concentration, ultrasonic power, and reaction time of 7, 0.95%
319 and 8.5 min, respectively) was 10.5 times lower than that by conventional method.

320 Transesterification reactions include the reaction between oil and alcohol in the presence of a
321 catalyst. Oil and methyl alcohol are incompatible liquids and when they react in one tank, two
322 separate layers are formed. Transesterification reactions commercially require continuous
323 mechanical stirring over a long period of time, because the reaction between alcohol and oil can
324 only be carried out at the point of contact between the two liquids (on a molecular scale). When
325 this mixture is exposed to the ultrasonic waves, ultrasonic waves cause cavitation phenomena
326 into the reaction medium. As a result, an emulsion of oil and alcohol is formed that provides a
327 wide surface for reactions. It has been observed that the reaction time is significantly reduced
328 [8].

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

332

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

335

336 **3.3. Biodiesel evaluation**

337 **3.3.1. Brake power and brake torque**

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

352 Panwar et al. (2010) investigated the effect of biodiesel production (B5, B10 and B20) from
353 castor on combustion and performance characteristics. At the applied load, brake power of B10
354 blend was drawn to be 1.5%, 1.76%, and 0.75% higher than those of B0, B5, and B20 blends,
355 respectively. B10 yields lower BSFC than fuel and therefore could serve as a promising
356 alternative to diesel [44]. Aydin and Bayindir (2010) examined the effects of cottonseed oil
357 methyl ester on the performance and emission of a single cylinder engine [43]. The results
358 indicated that the torque of B5 was derived a bit greater than those of other fuels, including
359 diesel. With increasing the biodiesel proportion of the blends, the torque decreased. This effect
360 was produced due to the lower heating value and higher viscosity of cottonseed oil methyl ester
361 [35,45].

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

363 3.3.2.CO and NOx emission

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

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

388

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

390 4. Conclusion

391 It can be argued that the greatest effect in the production of methyl ester, among the studied
392 variables, was obtained for the molar ratio test and the reaction time, followed by the ultrasonic

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

410 **Acknowledgement**

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525

526 **Figure Captions**

527 Figure 1. A schematic representation of a Soxhlet extractor.

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

529 Figure 3. Actual data versus predicted data.

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

535
536 Figure 5. Comparison of extent of biodiesel conversion using ultrasonic method and
537 conventional stirring method.

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

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