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Research Article

Optimization of Biodiesel Production from *Prunus Scoparia* using Artificial Bee Colony Algorithm

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A B S T R A C T

Renewable energy sources are developed worldwide, owing to high oil prices and in order to limit greenhouse gas emissions. The objective of this research was to study the feasibility of biodiesel production from mountain almond (*Prunus Scoparia)* oil using ultrasonic system and optimization of the process using Artificial Bees Colony (ABC) Algorithm. The results showed that by increasing the molar ratio, the conversion percentage increased and after reaching a certain ratio, further increase in the molar ratio caused decrease in the conversion percentage. Increasing in the ultrasound amplitude resulted in an increase in the conversion percentage which tends to ascend; Furthermore, results of optimization showed that the amount of molar ratio, amplitude, pulse and reaction time were 5.6, 0.90, 0.33 and 5 min, respectively. For independent variables, the values of yield and energy consumption were obtained which were equal to 96.1% and 9912 J, respectively. This finding proves that ABC algorithm can estimate the optimum point in biodiesel production with high accuracy.

1. INTRODUCTION

It is taken for granted that renewable energy sources have captured the attention on global level since they are capable for restricting the amount of emitted greenhouse gases. Among the energy sources used globally, petroleum is believed to be the largest source compared to other energy sources such as coal, natural gas, nuclear, hydro, and renewable.

One can demonstrate the fact that the reserves and resources dealing with petroleum experience their edge of production. To be known as alternative renewable fuel extracted from tree born oils, oils rooted in vegetable, animal fats and waste cooking oil, biodiesel has been reported to have a great role in resolving the issues regarding the depletion of fossil fuel and degradation of environment [1].

When it comes to the construction of biodiesel, it is feasible to define it as constituted by fatty acid alkyl esters which is obtained from triglycerides transesterification within vegetable oils or animal fats. The stoichiometric molar ratio of alcohol to triglycerides is 3:1 in this reaction[1]. Featuring as more highly reactant and cost-effective alcohol, methanol is considered as the widely-used type of alcohol [2]. More often, alkaline, acid, or enzyme catalyst is utilized so as to assist the rapidness of reaction and product yield within the transesterification reaction. From effectiveness perspective, one can mention sodium hydroxide and potassium hydroxide as having great contribution [3]. A number of factors are liable to be considered as having impact on the production of biodiesel i.e. reaction time and temperature, molar ratio of alcohol to oil and catalyst concentration [4].

Trans esterification is categorized by being in to a quite slow process because such a reaction occurs in interfaces among the liquids and that alcohols are immiscible in terms of homogeneity [5]. Consequently, production an emulsion is the solution achieved by enlarging the surface contact between the phases considered as immiscible, by means of a vigorous mixture. When considering the process of base-catalyzing, one can address the fact that some soap is produced by this method and by taking the role of phase-transfer catalyst, assisting the process of reactants mixture [2].

It has been proved through making the experiment that, the trans esterification reaction time can be reduced in

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circumstances where the reactants elements are irradiated with ultrasonic waves at under room temperature condition [6].

One can define ultrasonic waves as types of sound waves that are above normal human hearing range (i.e., above 18-20 kHz) [7]. Suslick has done meticulous study on the impact of ultrasonic waves on liquids. The frequency associated with these waves falls between 20 kHz to l0 MHz, and the pertinent acoustic wavelengths range from 0.15-100mm in liquids. The measuring criteria is not based on the scale of molecular dimensions [3]. It can be added that cavitation is the nonlinear acoustic phenomenon from which chemical effects of ultrasonic are derived. One can address the acoustic cavitation as the production, progression, and collide of bubbles within a liquid to be irradiated with sound or ultrasonic.

The sound passed through a liquid involves two types of waves, namely the expansion waves and compression waves; the former is being negative and the latter is being positive in terms of pressure. Such an action leads to the fact that bubbles assemble and recompose. When the proper conditions are met, the acoustic cavitation can cause implosive compression in such cavities. Thus, local heating, high pressure and very short lifetime are said to be among the outcomes of implosive bubble collide [1, 4].

The last 60 years has seen developed techniques utilized in the structural optimization [8]. What the classical optimization techniques offer is, the imposing of restriction when it comes to resolving the mathematical programming models. To overcome these barriers flexible and adjustable algorithms which pave the way for model a determined mode should be employed; which is highly similar to the reality.

A number of nature-driven algorithm has been developed so far across diverse texts such as Genetic Algorithm (GA) [5] , Simulated Annealing (SA) [6] and Tabu Search (TS) [9].

Swarm intelligence, to be known as a type of inspired algorithm relies heavily on insect-related behaviors in an aim to offer some meta-heuristics which are capable of simulating insect's problem-solving behaviors. Concerning the insect-related interactions, one can say that such a performance is liable to assist the cooperated intelligence dealing with social insect colonies. Ultimately, these interactions have been introduced in scientific problems when the overall goal is optimization.

It is feasible to mention Particle Swarm Optimization (PSO) [10] and Ant Colony Optimization (ACO) [11] among the proper algorithms which are capable to simulate the insect-related patterns in modeling problem. Conducted studies on behaviors and patterns of honey bee have offered optimization algorithms. The review of literature presents both versions of optimization problems, namely, combinational and continuous [8, 12]. To be distinguished as a new member of swarm intelligence, The Artificial Bee Colony (ABC) algorithm attempts to follow the behavior the honey bees do when looking for food. Diverse mechanism are at work when honey bees identify the food resources. Such an ability makes them suitable to be opt for new intelligent search algorithms [13]. Iran is located in a half-dry and dry region of the world. Almond is considered as one of the oldest fruit trees in Iran. *Prunus Scoparia* is a wild species of almond and occupies large areas in many parts of Iran and neighboring countries. Regarding the beneficial effects of almonds, the extraction and use of the oil from the *P. Scoparia kernel* (PSK) could be of interest. The objective of this research is to study the feasibility of biodiesel production from mountain almond (*Prunus Scoparia)* oil using ultrasonic system and optimization of the process using Artificial Bees Colony Algorithm.

2. MATERIALS AND METHODS

2.1. Materials

To ensure the preservation of biodiesel production process, it is essential to prepare oil prior to reaction. In so doing, the methylation process was followed to extract the purified oil using Metcalf et al (1996) method. Followed by the process was the injection of developed sample into the Gas Chromatograph in an attempt to specify the quality of fatty acids and molecular weight of the used oil [1].

The method employed to count the number of free fatty acids was titration [14]. What was obtained through using this method was 2.9% free fatty acid (FFA) content of oil. Two components were used to reduce the FFA esterification reaction; namely, methanol and sulfuric acid which led to less than 1% FFA.

The initiation of oil reaction is beginning with less than 1% FFA in the presence of methanol and the alkaline catalyst trans-esterification [15]. The methanol (99.7%) and KOH (99%) used in this study were provided from Merck company products. The physical and chemical properties of mountain almond oil are shown in Table 1.

TABLE 1. Fatty acid profile and properties of used mountain almond oil.

Properties	Unit	Amount
Density	g cm^{-3}	0.92
Kinematic viscosity	cSt	113.16
Saponification Number	mg K/g oil	98.60
Iodine value	g I_2/100g oil	112.32
Myristic (C14:0)	Wt.%	0.09
Palmitic (C16:0)	Wt.%	8.86
Palmitoleic (C16:1)	Wt.%	0.64
Stearic (C18:0)	Wt.%	2.76
Oleic (C18:1)*	Wt.%	62.81
Linoleic (C18:2)*	Wt.%	23.54
Linolenic (C18:3)*	Wt.%	0.80
Other fatty acids	Wt.%	0.5

*Carbon atoms number: double bond number.

2.2. Equipment A newly developed ultrasonic set-up was used to carry out the research experiments. An ultrasonic processor (Hielscher Model UP400S, USA.) was used to perform the trans-esterification reaction. The equipment consisted of processor, sonotrode, and PC controller (Hielscher Model, UPC400T, USA). The processor operated at 400 W and 24 kHz frequency. The amplitude and the pulse for the reaction were adjustable from 20 to 100%. The titanium sonotrode (H22D) with a diameter of 22 mm and a length of 100 mm was used to transmit the ultrasound wave into the liquid [16].

2.3. Methods

2.3.1. Trans-esterification A mixture of methanol and potassium hydroxide was agitated using a magnetic stirrer for 5 mints to form the methoxide. Mountain almond oil was then mixed with the previously prepared potassium methoxide in a conical flask. Afterwards, the mixture was transferred to the reaction chamber to be subjected to ultrasound waves. The amplitude and time of the reaction were adjusted by a PC controller.

The alcohol to oil molar ratio, catalyst concentration weight, reaction temperature, and probe penetration depth in the mixture were evaluated in the trans-esterification reaction through keeping the pulse, amplitude, and the time of ultrasonic irradiation at a constant value during different experiments. Next, the maximum conversion percent of biodiesel was obtained for each of these conditions.

After completion of the reaction, the solution was treated by concentrating sulfuric acid in order to neutralize the potassium hydroxide and to immediately stop the reaction. The product, a mixture of fatty acid methyl esters (FAMEs) and glycerol, was then put into a refrigerator and kept for gas chromatography (GC) analysis.

The PerkinElmer-clarus580 gas chromatograph made in the USA was used in this study which was prepared based on the BS EN 14103 standard.

The FAME yields of each trans-esterification step were calculated from the weight of FAME in the FAME phase and the theoretical material balance of the trans-esterification reaction (BS-EN 14103 standard), as shown in equation (1):

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

Where W_{FAME} and W_{MA} are the weights of FAME in the FAME phase and the weight of used mountain almond (MA), respectively. M_{FAME} and M_{MA} are average molecular weights of FAME and MA, respectively, and the factor 3 indicates that one mole of triglyceride yields three moles of FAME.

2.3.2. Analysis using response surface methodology In this study, response surface methodology and a Box-Behnken design were used. First, the dependent variables' levels according to Table 2. were coded and based on the selected method. Then, due to the depicted diagrams and the domain for independent variables, the optimal point was found and evaluated using Design Expert 7 software. The software results were then compared with the experimental data.

TABLE 2. Selected independent variables on response surface method.

Independent Variable	Coded level		
	-1	0	1
Molar Ratio (Alcohol to Oil)	4:1	5:1	6:1
Amplitude (%)	24.1	62.5	100
Pulse	24.1	62.5	100
Reaction Time (min)	3	6	9

3. RESULTS AND DISCUTIONS

Analyses of the data showed that the independent variables i.e. molar ratio, amplitude, pulse, and reaction time had a significant effect on the amount of produced methyl ester. Data analysis yields equation (2). Determining factor and standard deviation of the model are measured as 0.99 and 0.22, respectively.

$$Y=-81.2419+51.3197*m+21.6676*A+19.4357*P+4.1246*t+0.5711*m*A+0.6223*m*P+0.2121*m*t+4.9985*A*P+0.1104*A*t-1.0766*P*t-4.7459*m^2-16.01351*A^2-9.1887*P^2-0.4740*t^2 \quad (2)$$

Where m is the ratio of alcohol to oil, A is amplitude, P is the ultrasonic pulse, t is the time of reaction, and Y is the amount of produced methyl ester.

Figure 1. shows the appropriate accuracy of the obtained model to estimate the yielded methyl ester for changes in independent variables. Considering the variance testing of regression coefficients, insignificant coefficients are excluded from equation (2) and the final result (equation 3) is obtained. Determining factor and standard error is 0.91 and 0.58, respectively. Table 3. shows analysis of variance for coefficients of the model.

$$Y=-81.2419+51.3197*m+21.6676*A+19.4357*P+4.1246*t+0.6223*m*P+0.2121*m*t+4.9985*A*P-1.0766*P*t-4.7459*m2-16.01351*A^2-9.1887*P^2-0.4740*t^2 \quad (3)$$

To rank the effectiveness of each variable, normalized equation (4) is obtained as follows:

$$Y=92.38+4.38*m+5.88*A+2.90*P-2.46*t+0.23*m*P+0.64*m*t+0.70*A*P-1.21*P*T-4.75*m^2-2.25*A^2-1.29*P^2-4.27*t^2 \quad (4)$$

TABLE 3. Analysis of variance for coefficients of the model.

Source	df	Sum of Squares	Mean Square
Model	14	1047.84	74.85**
A-molar ratio	1	414.76	414.76**
B-amplitude	1	222.54	222.54**
C-pulse	1	100.72	100.72**
D-time	1	72.40	72.40**
AB	1	0.18	0.18ns
AC	1	0.22	0.22**
AD	1	1.62	1.62**
BC	1	1.98	1.98**
BD	1	0.62	0.62ns
CD	1	5.87	5.87**
A^2	1	146.10	146.10**
B^2	1	32.89	32.89**
C^2	1	10.83	10.83**
D^2	1	118.05	118.05**
Residual	14	0.09	
Lack of Fit	10	0.56	0.68ns
Pure Error	4	0.33	
Cor Total	28	1048.74	

** Significant at 10%, ns non-significant

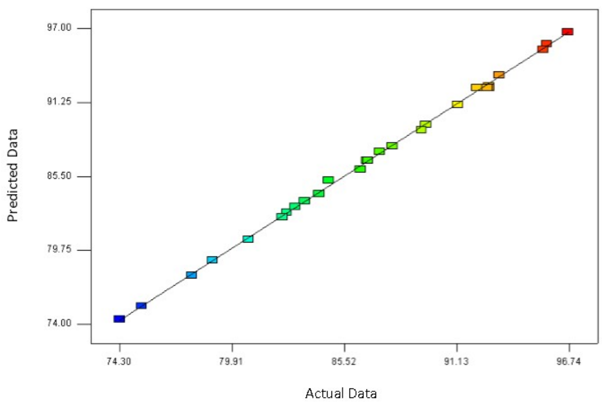

Figure 1. Actual data against model outputs.

Based on the values of equation (4), it is possible to say that molar ratio is the most effective variable among the other variables followed by which, are amplitude, ratio of activation to inactivation time of ultrasonic, and time of reaction, respectively.

As seen in Figure 2. the increase of molar ratio to the range between the ratio of 5 and 6 to 1 leads to increase in conversion percent. Considering the significant status of the second factor coefficient, the conversion percent decreases after a particular ratio. One can contribute the reason to the equilibrium of trans-esterification reaction in which the increase of alcohol to oil ratio leads to increase in methyl ester (biodiesel) production [1].

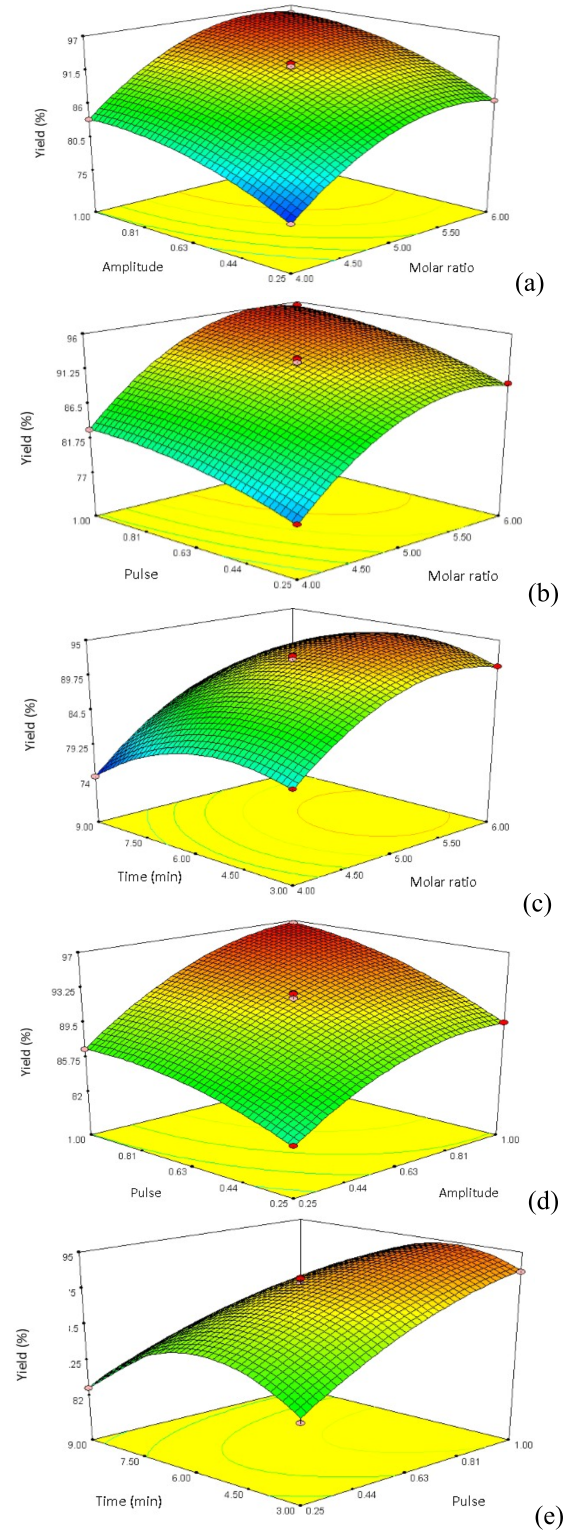

Figure 2. The conversion percentage changes versus the molar ratio, amplitude, pulse and reaction time changes: (a) interaction of the molar ratio and amplitude,(b) interaction of molar ratio and pulse, (c) interaction of the time and molar ratio, (d) interaction of the pulse and amplitude and (e) interaction of the time and pulse.

It is worth noting that the increase of methyl ester conversion percent by the increase of molar ratio has some limitations. The reason is that in case the ratio excesses the determined level, the pure value of produced biodiesel decrease. This can be justified saying that the increase of ethanol share in reaction leads to higher solution of glycerin and alcohol in biodiesel which would impact the purity to some extent. It was found in another study that the increase of molar ratio from 6 to 7 led to decrease in conversion percent of methyl ester [4].

Also, Figure 2. depicts the fact that the increase of amplitude leads to increase in conversion percent and follows an ascending way. Considering the significance of second order coefficient in the assumed model and its negativity, one can say that the increase of conversion percent of methyl ester per increase in amplitude is consistent with second order function which has a downward concave form. The reason of such an increase can be contributed to the increase of ultrasonic stirring per increase of amplitude leading to increase in surface contact of two formed phases (methoxide and oil). It is the surface increase that leads to decrease in reaction time from 90mints to 6mints [1].Other studies have shown that the increase of ultrasonic amplitude increases the conversion percent due to the afore-said reasons [7].

The increase of ratio time, having to do with ultrasonic activation to its inactivation, leads to increase of conversion percent since the time of treatment on the part of the sample under ultrasonic waves increases within a limited time. Such an increase does not progress since the initial vibrate shock is balanced by the integrated wave after switching on the ultrasonic in relation to the sample. Off-switching the ultrasonic leads to decrease in energy consumption which causes that there is an optimum point and this equity is taken an important in this experiment. Fayyazi et al. (2015) and Chand et al. (2010) have reported similar results considering the effect of pulse on the percent of methyl ester conversion [15, 17].

In addition, increasing reaction time up to 5 to 7mints leads to increase in conversion percent followed by the relevant decrease. The reason of increase in former case is that increasing in reaction time increases the radiate status of reaction mix within a constant time which itself gives rises to the effect of ultrasonic waves on the reaction context. Furthermore, the trans-esterification reaction is a type of equilibrium reaction. Reduction of reactive materials in reaction context leads to the reversion of reaction and reduction in biodiesel conversion percent. It is worth noting that reaction time with ultrasonic is reduced by 15 times compared to the conventional reaction time. The reason arises from the fact that the physical effect of ultrasonic lies in the emulsification between insolvent reactors (oil and alcohol), in which the increase of interface between these reactors through the generated micro-turbulence during cavitation, leads to significant increase in kinetics of reaction [15]. In a similar experiment, Kumar et al. (2010) utilized ultrasonic system to produce biodiesel from coconut oil and concluded that the reaction time reduces by 15-40 times using ultrasonic method compared to the conventional method. Also, the conversion percent was obtained more than 98% in 6mints [18].

Another research was to study the feasibility of biodiesel production from *P. atlantica* (Atlas pistache) oil using ultrasonic system. Results showed that the best models for both the yield and energy consumption were full quadric models with suitable coefficients of determination (0.98, 0.99) and least mean squared errors (MSE) (0.351, 17.14). With increasing the amplitude and pulse, the methyl ester content increased. When reaction time and molar ratio increased to range of 5-7 mints and 5-6, respectively, methyl ester content increased, while by increasing these parameters out of range, yield decreased [19].

Finally, the optimization process was performed according to the boundary conditions, which includes maximum yield and minimum energy consumption (Table 4).

TABLE 4. Boundary conditions of dependent and independent variables for optimization of biodiesel production.

Variable	Goal	Lower Limit	Upper Limit	Weight
Molar Ratio	In range	4	8	1
Amplitude (%)	In range	20	100	1
Pulse	In range	20	100	1
Reaction Time(min)	In range	3	11	1
Yield (%)	Maximum	75	97	1
Energy Consumption	Minimum	2250	65000	1

According to boundary conditions, goal function obtained in equation 5:

$$Goal\,function = -\frac{Eq\,(7)}{Yield_{max}} + \frac{Energy\,consumption\,function}{Energy\,consumption_{max}} \quad (5)$$

Algorithm parameters such as colony size, number of Iterations and Acceleration Coefficient were changed to obtain minimal point for equation (5) using try and error method. For example, the effect of colony size on fitness value and trend of fitness value versus iteration are showed in Figures 3. and 4.

The results of optimization showed that the amount of molar ratio, amplitude, pulse and reaction time were 5.6, 0.90, 0.33 and 5 mints, respectively. For independent variables, the values of yield and energy consumption were obtained equal to 95.26% and 25658 J, respectively. At the optimum point obtained by Artificial Bees Colony Algorithm, the yield and energy consumption were equal to 96.1% and 9912 J, respectively, in the laboratory. This finding proves that ABC algorithm can estimate the optimum point in biodiesel production with a high accuracy.

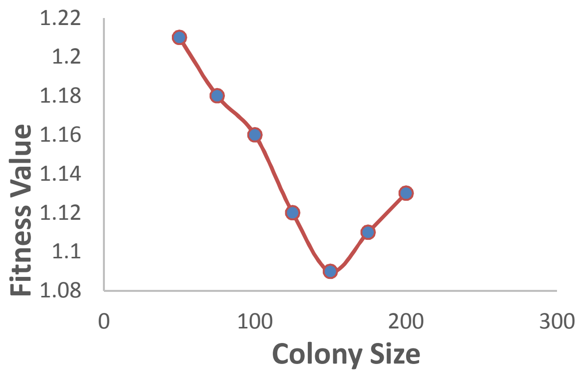

Figure 3. Effect of colony size on fitness value.

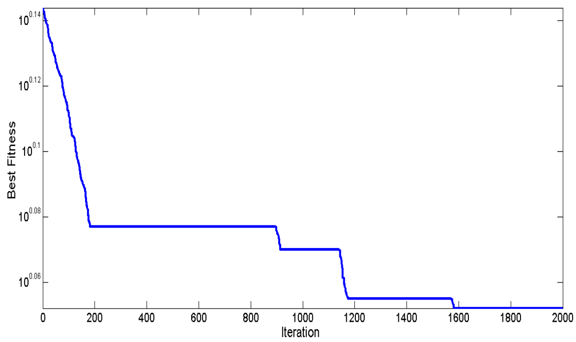

Figure 4. Trend of fitness value versus iteration.

The produced biodiesel must meet the fuel standards to be used as an alternative pure and/or diesel-biodiesel blended fuel in diesel engines. The biodiesel was produced after performing optimization processes using the related software. After washing and purification of the produced biodiesel, several of its important properties were measured based on ASTM D6751. The results are shown in Table 5.
The researchers have reported on several properties of twelve types of biodiesel, including viscosity, specific gravity, cetane number, iodine value, and freezing point. For ten of the 12 assayed types of biodiesel, the kinematic viscosity lay within the narrow range from 4 to 5 mm2s-1[14]. The specific gravity of 12 types of biodiesel varied between 0.873 and 0.883. In the present study, mountain almond meet the range of parameters in other research [14]. Free and bonded glycerin content is an indicator of the biodiesel quality. Low levels of total glycerin ensure high conversion of the oil, while high levels of glycerin and glycerides can cause injector deposits, clogged fuelling systems, and poor cold weather operation. Total glycerin in the produced biodiesel was slightly higher than normal extent. The produced fuel may meet the required standards by a more complete leaching process [19].
The results of experiments on biodiesel production using the conventional method (mechanical stirrer) showed that the maximum biodiesel conversion can be achieved by a reaction time of 55–65 mints. Other researchers have reported similar results which proves the presented experimental data in the current study [1, 15]. In the optimum condition, the biodiesel conversion in the biodiesel produced by ultrasonic system was 12 times greater than that of the conventional method. In other words, the ultrasonic system decreased the time of reaction to achieve the desired biodiesel conversion.

TABLE 5. The Produced Biodiesel Properties in comparison with the ASTM D6751 standard.

Property	Test Method	Limits	Units	Measured Property
Water and Sediment	ASTMD2709	0.05max	%volume	0.05
Kinematic Viscosity at 40°C	ASTMD445	1.9-6.0	mm^2/s	4.3
Sulfated Ash	ASTMD874	0.02max	%mass	0.021
Sulfur S 15 Grade	ASTMD5453	0.0015max	%mass	0.0018
Methanol Content	EN14110	0.20max	%volume	0.14
Cetane Number	ASTMD613	47min.		43
Carbon Residue	ASTMD4530	0.05max	%mass	0.02
Acid Number	ASTMD664	0.50max	mgKOH/g	0.39
Free Glycerin	ASTMD6584	0.02	%mass	0.019
Total Glycerin	ASTMD6584	0.24	%mass	0.23
Oxidative Stability	EN14112	3min	hours	2.3
Cold Soak Filtration	Annex toD6751	360max	seconds	259

4. CONCLUSION

With increasing the molar ratio, the conversion percentage increased, and after reaching to a certain ratio, further increase in the molar ratio caused decrease in the conversion percentage. The increase in the ultrasound amplitude resulted in an increase in the conversion percentage which tends to ascend. The increase in the ultrasonic pulse led to increase in the conversion percentage. The results of optimization showed that the amount of molar ratio, amplitude, pulse and reaction time were 5.6, 0.90 0.33 and 5 mints, respectively. For independent variables, the values of yield and energy consumption were obtained equal to 93.26% and 9322 J, respectively. At the optimum point obtained by Artificial Bees Colony Algorithm, the yield and energy consumption were equal to 96.1% and 9912 J, respectively in the laboratory. This finding proves that ABC algorithm can estimate the optimum point in biodiesel production with high accuracy.

5. ACKNOWLEDGEMENT

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