Research article

Optimization of biodiesel production parameters from *Prosopis julifera seed* using definitive screening design

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ABSTRACT

The concept of waste to valuable products is a hot topic with more explorations going on worldwide to minimize the environmental pollution and wastage of food-based feedstocks. In this work, biodiesel was produced from *Prosopis julifera* seed oil using ethanol as solvent and magnesium nanocatalyst and the process was optimized by employing an advanced statistical optimization method; definitive screening design. The maximum biodiesel yield from *Prosopis julifera* seed was found to be 32.5%. Acid esterification and transesterification were applied to minimize the acidity. Acidity of the *P. julifera* oil was initially reduced to 1.52 mg KOH/g using acid catalyst H_2SO_4, and then to 0.88mg KOH/g by transesterification process using magnesium oxide.

Optimum biodiesel conversion efficiency of 94.83% was achieved under 10:1 ethanol-to-oil ratio, 5% magnesium oxide concentration, 80 min reaction time, 45 °C reaction temperature and 1000 rpm agitation rate. The transesterification reaction was found to be highly affected by the ethanol-to-oil ratio and catalyst concentration. The results showed that the catalytic activity of the magnesium oxide was sufficient for the production of biodiesel from *P. julifera* seed oil.

The fuel properties were evaluated according to ASTM standards. FTIR analysis confirmed the existence of functional groups with respect to the fingerprint region of *P. julifera* ethyl esters. The Definitive screening design method can be suggested as an alternative method for the optimization of process parameters within limited materials and number of experiments. The findings suggest that this method of production of biodiesel from *P. julifera* seed oil shall open up new possibilities for a novel natural biofuel.

1. Introduction

Increasing population growth and rapid economic development are leading to growing energy demand in the world (Nouni et al., 2021). The biggest issue is that a huge part of the energy demand of the world is fulfilled by fossil fuel-based sources such as coal, petroleum, and natural gases (Adepoju, 2020; Kumar et al., 2019). Consequently, the increase in energy demand, natural contamination, and overuse of fossil fuels have constrained countries to look for alternative and eco-friendly energy sources (Aslan and Eryilmaz, 2020). Biodiesel, one of the renewable and alternative energy sources, can be a credible alternative to achieve long-term energy needs (Moshood et al., 2021). Substituting fossil fuels with more feasible energies, increasing the utilization of renewable ones, is imperative, not only to decrease the release of greenhouse gases but also to improve energy supply and security.

Biodiesel is one of the alternative substitutes for nonrenewable fuels and encounters rigorous emissions. It is biodegradable, renewable, nontoxic (Pan et al., 2018) and an eco-friendly resource with various advantages compared to nonrenewable fuels (Bateni and Karimi, 2016; Chhabra et al., 2021). Currently, a huge amount of biodiesel in the world is obtained from food-based plant oils (Chhabra et al., 2021; Dharma et al., 2016). Due to competition from food-based oils for food purposes, the utilization of non-edible plant oils for the production of biodiesel is suitable (Rezania et al., 2019). In addition, there is a chance for soil corruption due to cultivating the same variety of feedstock on an expansive scale, which in turn influences biodiversity. This issue can be settled by using both edible and non-edible oils for renewable fuel production (Mardhiah et al., 2017).

P. julifera is one of the non-edible plant oil sources. It is a member of the Leguminosae family, which is found in tropical and sub-tropical zones all over the world, such as Africa, South America, Asia, India,

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Himalayas, and Pakistan (Rajeshwaran et al., 2018). *P. julifera* plant can cause deterioration of other plant species, soil quality and water supply, with negative implication on local communities (Singh et al., 2020a, b; Kumar and Gupta, 2020). Production of biodiesel from *Prosopis julifera* plants could be used to overcome those issues, as well as environmental management system (Kumar and Sharma, 2011; Kumar and Gupta, 2020).

Biodiesel is a combination of fatty acid alkyl esters produced by transesterification of triglycerides of plant oil or animal fat oil within a short chain of alcohol. Transesterification is the chemical reaction whereby glycerine is expelled from the triglyceride by reacting it with alcohol by incorporating a catalyst to produce biodiesel (Farid et al., 2020). Most of the time, the alcohol that is used to prepare biodiesel is methanol. In such a case, biodiesel production is believed to be partially renewable fuel, since methanol is primarily obtained from natural gas (Adepoju, 2020). The replacement of ethanol for methanol in biodiesel production is considered attractive and interesting since it can be obtained from renewable biomass sources (Muhammad et al., 2021; Stančin et al., 2020).

Heterogeneous and homogeneous catalysts are used for biodiesel production. Heterogeneous catalysts are more suitable compared to homogeneous catalysts, since heterogeneous catalysts; remove the washing step in the biodiesel production step as well as easily separate the catalyst and biodiesel. Additionally, heterogeneous catalysts can be recovered and reused (Rajendiran and Gurunathan, 2020). Currently, heterogeneous catalysts in nano sizes are used to produce biodiesel. Nanocatalyst has a high specific surface area that can be useful in the transesterification step (Rajeshwaran et al., 2018).

To attain the maximum biodiesel yield with bounded raw materials and time, optimization mechanisms are most important (Felix et al., 2019; Elgharbawy et al., 2017). Among them, definitive screening designs (DSD) are the most popular design technique used for industrial experimentation. DSD is the latest optimization technique used to test many variables to identify those variables that have the greatest influence on the process. It detects individual effects as well as interaction effects between parameters (Felix et al., 2019).

Most of the research regarding optimization of biodiesel production is done by response surface methodology from various plant oils and animal fat oils (Chhabra et al., 2021), including process parameters (Felix et al., 2019). However, there is no elaborate work as well as sufficient evidence concerning the production and optimization of biodiesel from *P. julifera seed oil* using magnesium oxide (MgO) nanocatalyst using a definitive screening design method.

Therefore, the objective of this research was to optimize biodiesel production parameters with the use of MgO nanocatalyst using a definitive screening design method from *P. julifera* seed oil. To do so, the effect of parameters such as reaction time, catalyst concentration, reaction temperature, ethanol-to-oil ratio, and agitation rate have been investigated and optimized.

2. Materials and methods

2.1. Materials and chemicals

In this study, the *P. julifera* seeds were collected from Gambella region which is in the southern part of Ethiopia. After collection of the *P. julifera* seeds, it was first sun-dried, washed thoroughly and then dried using hot air oven drier at 103 °C for 24 h to remove moisture content. Using a biomass blender, the *P. julifera* seeds were then ground into powders and the moisture content was confirmed to be below 2 w/w% according to the American Society for Testing and Materials (ASTM) standards method.

Apparatus such as soxhlet extractor, thermometer, stand, pipette, measuring cylinder, separating funnel, magnetic stirrer, electric oven, water bath, hydrometer, conical flask, digital balance, and hot plate were used for this work.

All chemicals and reagents (N-hexane and ethanol; 99.9% purity, NaOH pellet, and H_2SO_4; 98.9% purity) used were of analytical grade and were purchased from chemical product suppliers in Addis Ababa, Ethiopia.

Magnesium oxide (MgO) nanocatalyst with oxygen (O) weight percent of 35.6 and atomic percent of 45.76 and magnesium (Mg) weight percent of 64.80 and atomic percent of 54.64 was obtained from reaction-engineering laboratory, Chemical engineering, Jimma Institute of Technology.

3. Methodology

The prepared *P. julifera* seeds were milled using a laboratory hammer mill to obtain optimum size according to the American Society for Testing and Materials (ASTM) standard method. According to the ASTM standard method, sieve analysis was conducted and the sample was stored for the next analysis. The 250 mL soxhlet apparatus (Model Number: LTSW-35, Capacity: 500 mL, France) was used for the extraction of the oil from the *P. julifera seeds*.

3.1. Oil extraction process

The extraction of oils was performed using 60 mL of n-hexane in a Soxhlet apparatus (Model Number: LTSW-35, Capacity: 500 mL, France). The grounded and dried sample (15 g) was placed in a porous thimble, which was initially dipped into n-hexane so that the solvent diffused completely into the sample. After 10 min, the thimble was subjected to the system that contained n-hexane at 65 °C for 6 h (Hasni et al., 2017). The experiments were done repeatedly and at the end of the extraction process, the oil was collected in the volumetric flask and filtered using a vacuum filter and kept for 48 h to settle any suspended particles. Then, the oils dissolved in n-hexane were recovered using a rotary evaporator at 40 °C. After the optimum *P. julifera seed* oil was obtained, solvent-free oil was left in an airtight container and subjected to characterization as per standard testing method to check its suitability for the production of biodiesel (Felix et al., 2019).

3.2. Oil characterization

First the raw *P. julifera* seed oil was purified (Sánchez-Arreola et al., 2019). Measured volume of the oil was mixed with 2.5% of deionized water and heated to 65 °C, and then 5 wt% of phosphoric acid was added. The decolourized oil of 400 cm^3 was then blended with 10 mL deionized water and once more heated to 65 °C using a mixer for 20 min. The hydrated solute was isolated by enforcing the rinsed oil to clean for 20 min. The oil was then subjected to 103 °C in an oven until the moisture content was removed. Then, the acid value, viscosity, specific gravity, amount of free fatty acid, and moisture content of the oil were determined according to a previous study (Rehan et al., 2018).

3.3. Production of biodiesel

Selection of the type of transesterification process (two steps or one-step transesterification reaction) depends mainly on the amount of free fatty acid (FFA) present in the raw oil (Sánchez-Arreola et al., 2019). If the amount of FFA in the oil is below 2.5%, then a one-step transesterification reaction should be used or if the FFA is above 2.5%, a two-step transesterification reaction should be considered (Rajendiran and Gurunathan, 2020). Since the FFA content of *P. julifera seed* in this study was greater than 2.5%, two step (acid esterification and transesterification) process was considered.

3.4. Pre-treatment (acid esterification)

At present, researchers focus on identifying new and sustainable acid pretreatment method for the transesterification reaction process (Nayak

et al., 2019). The main advantages of the acid pretreatment are their compatibility with high acid value feedstock (Abomohra et al., 2020), enhancing both esterification and transesterification, easier separation of the product with good quality and the elimination of the biodiesel washing step (Mohiddin et al., 2021).

The P. julifera seed oil was found to have an acid value of 6.4 mg KOH/g and thus to bring down the acid value below 2.5 mg KOH/g, to produce biodiesel, an acid pre-treatment was carried out. The esterification process was employed as pre-treatment by using H$_2$SO$_4$ at 1% (v/v) to reduce the *acid value* content below 2.5 mg KOH/g (Jambulingam et al., 2020) and transesterification was carried out by using MgO nano-catalyst. After the completion of the reaction, the alcohol-catalyst was separated from the upper layer. Then, to remove the remaining catalyst, the esterified oil was washed with distilled water and heated to remove the remaining water.

3.5. Transesterification

The transesterification procedure was carried out using a 500 mL volumetric flask. Fifty to sixty grams (50 − 60 g) of oil was used for 18 experimental runs designed by a definitive screening design. For each experiment, oil was carefully transferred into the reaction flask and pre-heated using an oil bath up to the reaction temperature. The MgO nanocatalyst and ethanol mixture were prepared and added to the pre-heated oil, and then the mixture was stirred. At the end of the trans-esterification reaction, the solution is subjected to gravitational settling in a separation flask for 48 h, to separate the ethanol-water and the product. The upper phase containing the biodiesel was collected and mixed with distilled water at 40 °C to remove the remaining impurities. Ethanol and water were removed by using a rotary evaporator at 75 °C (Kumar and Gupta, 2020). In addition, Figure 1 shows the produced biodiesel phase separation process.

The percentage yield of the biodiesel was determined using Eq. (1).

$$\text{Yield } (\%) = \frac{\text{Amount t of biodiesel}}{\text{Amount of oil used}} * 100 \tag{1}$$

3.6. Experimental design and statistical data analysis

The experimental design and statistical data analysis of the process parameters were carried out using the definitive screening design (DSD) of SAS JMP Statistical software version 14 with the aim of parameter optimization for biodiesel production. Selected process parameters were ethanol to oil molar ratio (X_1), catalyst concentration (X_2), temperature (X_3), time (X_4), and agitation rate (X_5). The ranges of parameters were ethanol-to-oil molar ratio (10:1 − 20:1), catalyst concentration (0.5 − 5 %), time (50 − 80 min), temperature (45− 77°C) and agitation rate (750 − 1000 rpm) as shown in Table 1.

3.7. Biodiesel characterization

The fuel properties, such as density, viscosity, acid value, and flash point were characterized according to the ASTM standard methods and its functional groups using Fourier transform infrared (FT-IR) Spectroscopy.

4. Results and discussion

4.1. Characterization of Prosopis julifera seed oil

The proximate property of the *P. julifera* seeds oil is shown in Table 2. The experimental result showed that the moisture content of the *P. julifera* seed oil was in the range ASTM standard (Table 2). A large amount of moisture content than the defined value, induces self-generated hydrolysis, degenerates the oil, and increases the cost of the process (Sánchez-Arreola et al., 2019). The amount of volatile matter and

small ash content indicates that the produced biodiesel from *P. julifera* seed oil can be ignitable with a low amount of ash (Rehan et al., 2018). The *P. julifera* seed oil content was 32.5% and this yield may be due to a change in the particle size and origin of the seeds (Páramos et al., 2020).

The physicochemical property of the oil is very critical since these values influence the transesterification reaction, as well as the yield of biodiesel produced (Kamran et al., 2020). In the ordinary trans-esterification of vegetable oils and fats to biodiesel, high free fatty acid and moisture contents continuously lead to negative impacts because of soap formation (Mukhtar et al., 2021), additional catalyst usage, and produce a lower yield of biodiesel (Rehan et al., 2018).

Pretreatment has been suggested to be the best method to reduce acid values for all non-edible oils, which have acid values greater than 2.5 KOH/g (Sánchez-Arreola et al., 2019). In the acid esterification process using 1% v/v sulfuric acid and 10:1 ethanol-to-oil ratio and 80 min re-action time, the level of acid value of *P. julifera* oil was reduced from 6.4 mg KOH/g to 1.52 mg KOH/g. Since the content of the acid value of the *P. julifera seed* oil, after the pre-treatment was below 2.5 mg KOH/g, the two steps of transesterification reaction are very important for biodiesel production from non-edible oils (Miraculas et al., 2018). The type of seed species, seed maturity, and the extraction technique cause variations in fatty acid concentration in the plants (Dharma et al., 2016).

The peroxide value of seed oil is 163.285 mL/g; the high value of peroxide is suggestive of the high degree of oxidative rancidity of the oils (Charles et al., 2021); additionally, recommend absence or small levels of antioxidants may be utilized to diminish rancidity like propygadlate and butyl hydroxyl anisole (Guerberoff and Camusso, 2019).

The saponification value (SV) is 182 mL/g and it was confirmed with the result of SV for common oil of 210 mL/g. Hence the oils may be utilized for soap making (Adepoju, 2020).

4.2. Experimental data and predicted value of biodiesel yield

The definitive screening design (DSD) was used to design the matrix of the five contributing parameters generated by DSD as indicated in Table1. Depending on the system-generated matrix, 18 runs were con-ducted (Table 3). Table 3 indicates the experimental values and predicted values of biodiesel yield. The maximum yield of biodiesel was found to be 94.2% of yield experimentally and 92.028% of yield at mean points. Using response surface methodology at optimum parameters, a 95.3% yield of biodiesel was reached by Lin et al. (2014), which is corre-sponding to the present study. This difference may be due to the differ-ences in plant origin, duration required for the plant to grow, climate conditions, or variation in material composition (Singh et al., 2020a, b).

Figure 2 indicates the relationship between the experimental value and the predicted value of biodiesel production yield. The variation is quite close between the experimental value and predicted value, which represents that the model employed, is a perfect fit, and the development of correlation meets a substantial level.

4.3. Analysis of variance (ANOVA)

Analysis of variance depends on an approach in which the method utilizes variance to test whether the means are differentiable. It also evaluates the necessity of contributing parameters by linking the response (yield) parameters to different degrees. Depending on the experimental value matrix, the response yield was evaluated and the analysis of variance was generated for the contributing factors as shown in Table 4).

Using p-value and Log-Worth value, the contribution of each factor can be found. The lower the p-value and the higher the Log-Worth value, the higher the significance of the contributing variables in the process. From Table 4, except for the agitation rate, the p-value can be seen as 0.00 in all the cases, which shows that the factors are highly significant. The ethanol to oil ratio and catalyst concentration has the highest sig-nificant contribution to the yield (Log-Worth value of 10.674 and 10.561
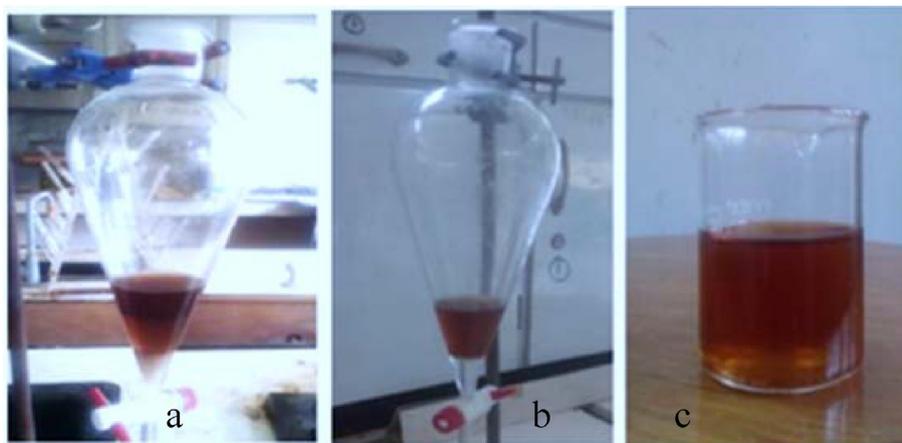
Figure 1. Phase separation (a), washing (b), and purified biodiesel (c).

Table 1. Definitive screening design response and process conditions.

Response	Goal		Lower Limit	Upper Limit
Biodiesel Yield %	Maximize		-	-
Factors	Codes	Roles	Values	
Reaction time (min)	X_1	Continuous	50	80
Ethanol to oil Molar (mol/mol)	X_2	Continuous	10	20
Reaction temperature (^0C)	X_3	Continuous	45	77
Catalyst concentration (%)	X_4	Continuous	0.5	5
Agitation rate (rpm)	X_5	Continuous	750	1000

Chhabra et al. (2021).

Table 2. Physiochemical properties of mesquite seed oil.

Components	Values
Moisture content (%)	5.1
Ash content (%)	2.1
Volatile matter (%)	82.01
Iodine value (g Iodine/100 g oil)	96.5
Viscosity (mm^2/s), 40 $°C$	35.61
Density (g/mL)	0.934
Acid value (mg KOH/g)	1.52
Peroxide value (meq O_2/kg oil)	163.24
Oil contents (%)	32.5
Saponification value (mg/KOH/g of oil)	182

respectively) as shown in Table 4. In addition, Table 4 indicates the co-efficient of determination (R-squared), Root Mean Square Error (RMSE), and adjusted coefficient of determination (R-squared (adj)). The Root Mean Square Error indicates the minimum error between fitted values and the experimental data, whereas the smaller the Root Mean Square Error values, the better the model depicts the response (Hammoudi et al., 2019). The R-squared indicates the percentage of fluctuation in the responses and it also finds out how well the model conforms to the experimental data (Shah et al., 2018).

The model equation was examined by using multiple regression analysis to measure the response by examining the linear and interaction effects between the process parameters suggested by the definitive screening design (Eqn 2). The yield of Biodiesel (Y %), is taken as the dependent variable.

$$Yield = 93.295 + 0.549 \ X_1 + 0.2536 \ X_2 - 0.4714 \ X_3$$
$$- 0.000647 \ X_4 - 0.0025 \ X_2X_4 - 0.003X_1X_3 - 0.0012X_2X_3$$
$$+ 0.001X_1X_4 \tag{2}$$

where, X_1, X_2, X_3 and X_4 are reaction time, catalyst concentration, ethanol to oil ratio, and temperature respectively.

The implications of each coefficient of the process parameters and those of their interactions were analyzed by F-value and p-value using analysis of variance (ANOVA).

4.4. Individual effect of process parameters on the yield of biodiesel

A positive response was observed with the reaction time, since fatty acid conversion into biodiesel enhances with reaction time. The reaction is sluggish at the starting time due to the blending and distribution of alcohol with oil, but afterwards, the reaction proceeds very quickly (Tan et al., 2019). When the reaction time is increased from 50 to 80 min, the yield has also enhanced as shown in Figure 3 (a). Such that, an increase in the reaction time favours the yield of production. When the reaction time is good enough for the completion of the reaction between the reactants, the product yield is very good (Shah et al., 2018).

It indicates that the catalyst concentration of around 5% would produce the maximum yield of biodiesel as indicated in Figure 3 (b). Since triglyceride and ethanol are immiscible, increasing the catalyst concentration can improve the transesterification process and enhance the yield quickly (Kamran et al., 2020). Nevertheless, when the catalyst concentration was very low or very high, soap formation takes place (Athar and Zaidi, 2020), affecting the isolation of glycerol from biodiesel, which may decrease the yield (Chhabra et al., 2021). In contrast, insufficient usage of catalyst concentration could cause uncompleted reactions and decrease the yield of the product (Mukhtar et al., 2021). Hence, the maximum yield could be achieved when a sufficient amount of catalyst concentration is used (Dharma et al., 2016). In this study, the maximum yield of biodiesel was attained at a catalyst concentration of 5%. This result was confirmed by a previous studies that described the influence of catalyst concentration on the yield of biodiesel; an enhancement in catalyst concentration could enhance yield, which may be due to yielding higher alkyl ester in more reactions (Sáez-bastante et al., 2016).

The ethanol to oil ratio is one of the factors that highly influence the biodiesel production process (Figure 3 c). It was observed that too low or too high a value of the ethanol-to-oil molar ratio has undesirable effects. This is indicated by the fact that the transesterification process is an equilibrium reaction in which excessive alcohol could increase the reaction and in turn increase the percentage yield or reduce the percentage

Table 3. Definitive screening design matrix and response for biodiesel yield.

Run	Experimental parameters of Transesterification					Biodiesel Yield		Error	
	(R-T)[1]	(C-C)[2]	(E-O-R)[3]	(R-T)[4]	(A-R)[5]	(A-Y)[6]	(P-Y)[7]	Resid.	Std-Resd.
1	65	5	20	77	1000	92	91.91	-0.005	-0.04
2	65	2.75	15	61	875	92	92.03	0.174	1.27
3	65	0.5	10	45	750	92.4	92.15	0.025	0.23
4	80	0.5	15	77	1000	90.8	91.08	0.002	0.01
5	80	5	10	77	750	94.2	94.24	-0.230	-1.77
6	80	5	10	45	875	93.0	93.41	0.090	0.69
7	50	0.5	20	45	1000	89.66	89.64	-0.015	-0.14
8	50	5	15	45	750	92.8	92.97	-0.038	-0.30
9	50	0.5	20	77	875	89.2	89.23	-0.167	-1.28
10	80	0.5	20	45	750	90	90.09	-0.005	-0.04
11	65	2.75	15	61	875	92	92.03	-0.120	-1.11
12	50	5	20	61	750	91.8	91.63	0.131	1.20
13	80	0.5	10	61	1000	92.7	92.42	-0.296	-2.27
14	50	0.5	10	77	750	91.3	91.52	0.120	0.88
15	50	2.75	10	45	1000	93.2	93.15	0.027	0.21
16	80	5	20	45	1000	92.5	92.54	0.099	0.76
17	50	5	10	77	1000	94.	93.97	0.052	0.38
18	80	2.75	20	77	750	91.04	90.91	0.157	1.15

Resid; Residual, Std-Resd; Standard residual.

[1] Reaction time (min)
[2] Catalyst concentration (w/w %)
[3] Ethanol to oil ratio (g/g)
[4] Reaction temperature (0C)
[5] Agitation rate (rpm)
[6] Actual yield (%)
[7] Predicted yield (%)
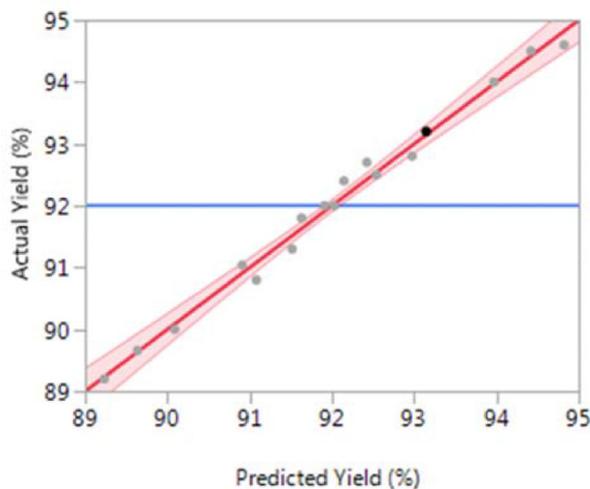
Figure 2. Experimental value Vs Predicted yield of biodiesel produced.

Table 4. Analysis of variance and summary of fit.

Source	DF	Sum of Squares	Mean Square	F Ratio
Model	5	39.760343	7.95207	225.6075
Error	12	0.422968	0.03525	Prob > F
C. Total	17	40.183311		0000*

Parameters effects

Factors	Log-Worth	P-Value
Alcohol to Oil molar ratio	10.674	0.00000
Catalyst concentration	10.561	0.00000
Time	4.173	0.00007
Temperature	2.200	0.00631
Agitation rate	0.764	0.17214

Summary of Fit

R-Squared	0.989474
R-Squared Adj.	0.985088
Root Mean Square Error	0.187743
Mean of Response	92.02778

yield by increasing the solubility of glycerol (Kamran et al., 2020). Excess ethanol resulted in a marginal decrease in biodiesel yield. In addition, phase separation of biodiesel and glycerol is more difficult and increases soap formation (Hasni et al., 2017). In this study, the higher percentage yield of biodiesel produced during the transesterification process was achieved at an ethanol-to-oil molar ratio of 10:1 from the selected range.

The temperature of the reaction determined the transesterification reaction and the yield of biodiesel production. An increase in the reaction temperature was found to reduce the rate of the reaction beyond a certain temperature, the yield of product decreased dramatically (Figure 3 d).

The result showed that when the temperature increased, ethyl ester yield increased, but beyond 45 °C of reaction temperature, a change in the trend was observed and the yield started to decrease. This effect could be defended by utilizing the Arrhenius equation, which states that steady increase in reaction rate constant by temperature might increase the yield of product up to an optimum point (Wu and Leung, 2011). The optimum temperature at which the maximum yield of biodiesel was attained at 45 °C, corresponding to the optimum ethanol-to-oil ratio of 10:1, catalyst concentration of 5%, reaction time of 80 min, and agitation rate of 1000 rpm yielding 94.2% of biodiesel. This optimum temperature was
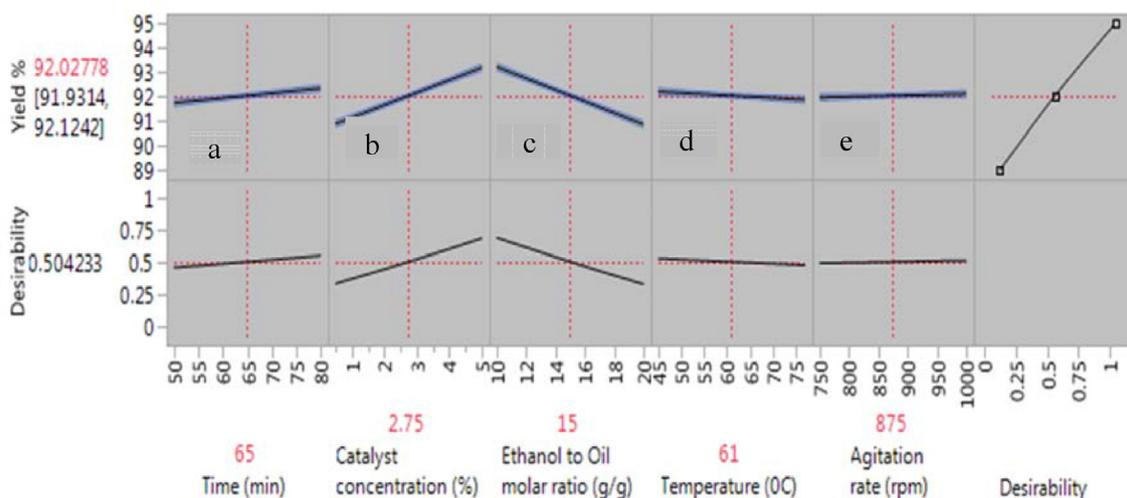
Figure 3. Prediction Profiler for individual effects, (a) time, (b) catalyst concentration, (c) ethanol-to-oil ratio (d) temperature, and (e) agitation rate Vs yield.

confirmed in a previous study where a yield of biodiesel was attained by optimizing factors using a response surface methodology design approach (Rehan et al., 2018).

The agitation rate is an important parameter to increase the homogeneity of the solution when the catalyst is mixed with the oil for the transesterification process (Yadav et al., 2017). Figure 3 (e) indicates the effect of the agitation rate on the percentage yield of biodiesel, in which the agitation rate was studied between 750 − 1,000 rpm. It can be shown that the biodiesel yield was slightly increased by increasing the agitation rate. The increase of the agitation rate hence, blending intensity helps the initiation of the reaction and maximizes the contact area between the solutions (Rehan et al., 2018). In this study, agitation rate has no

significant effect on the yield of biodiesel, since the selected range of parameters is sufficient to make a solution lumped distribution to give the maximum yield of biodiesel. Several researchers have also discovered that a limited range of agitation rates throughout the transesterification process encourages the homogenization of raw materials, which leads to higher yields of biodiesel (Dharma et al., 2016).

4.5. Effect of interaction between process variables on the yield of biodiesel

The effect of reaction time, the concentration of catalyst, ethanol-to-oil molar ratio, and reaction temperature are indicated in Figure 4. The
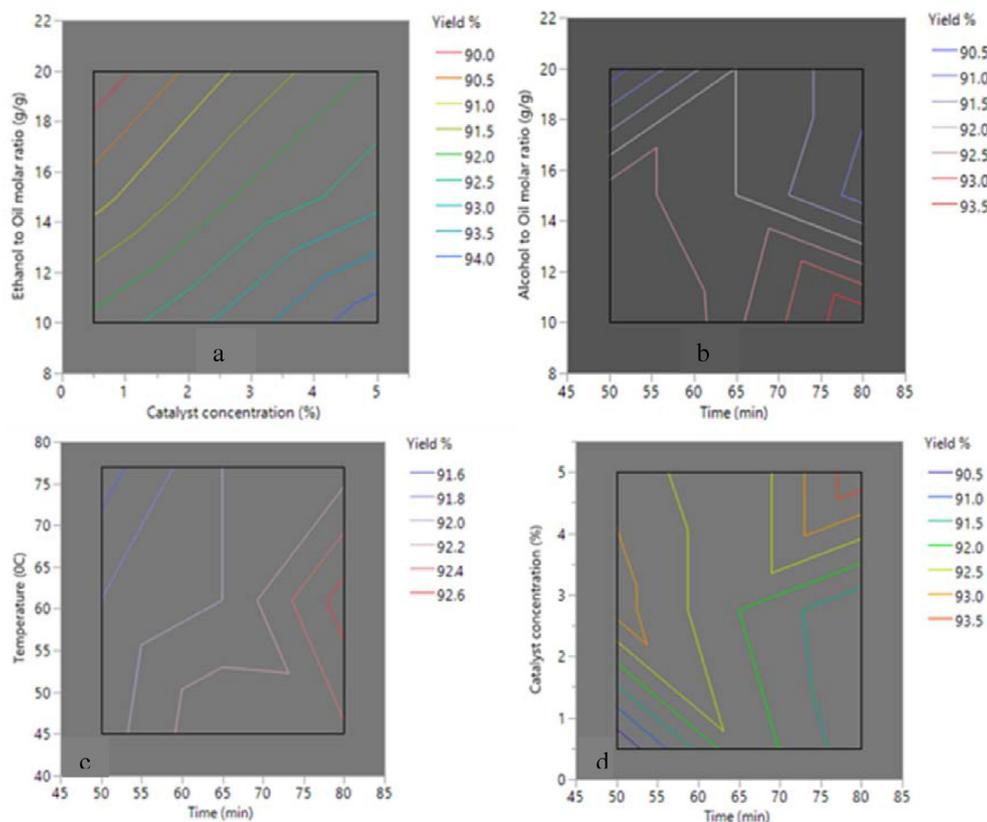
Figure 4. Effect of process parameters on the yield of biodiesel, (a) catalyst concentration Vs ethanol to oil ratio, (b) reaction time Vs ethanol (alcohol) to oil ratio, (c) time Vs temperature, and (d) time Vs catalyst concentration.
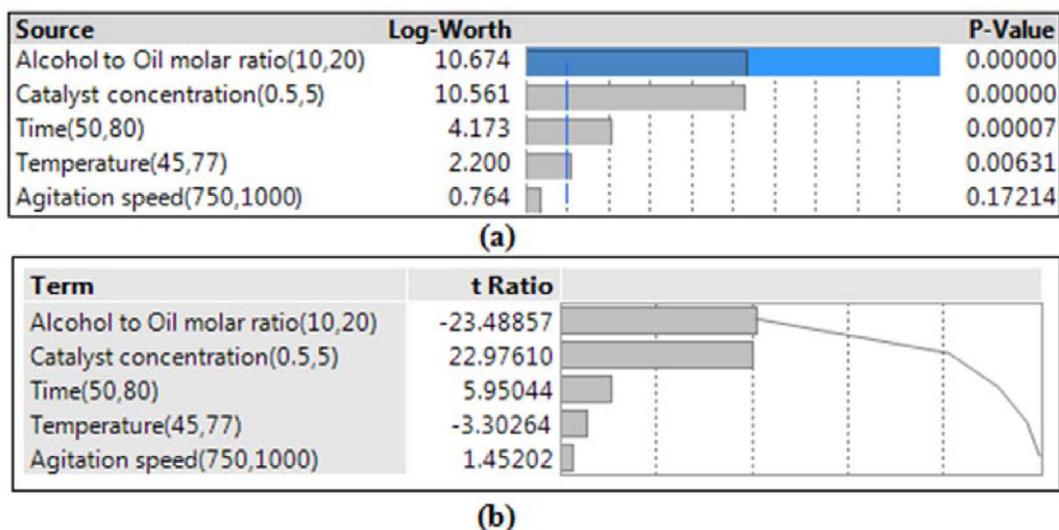
Figure 5. Effect summary plot (a) and Pareto plot of parameter estimates (b).

counterplot curves shown in Figure 4 were drawn to indicate the significance of two independent parameters on the yield of biodiesel.

With an increase in the concentration of catalyst, an increasing trend in the yield of biodiesel was observed. When the concentration of catalysts of 5 w/w% and 10:1 of ethanol-to-oil ratio were used, the maximum yield of biodiesel (94.2%) was attained. Thus, it can be said that a higher amount of catalyst gives a higher yield of biodiesel and an increase in ethanol-to-oil ratio indicates that the yield of biodiesel is starting to decrease. A decreased pattern is seen in the yield when the amount of ethanol to oil ratio is outside of the optimum process parameters (Chhabra et al., 2021). When the reaction is left to take place for the maximum time, the transesterification reaction takes place as well, which is important for the maximum conversion of the biodiesel yield (Baral et al., 2020; Jain et al., 2018; Shah et al., 2018). Therefore, the reaction should be carried out at an optimum time to achieve complete transesterification (Miraculas et al., 2018).

4.6. Effect summary and pareto plot of parameters

The Pareto plot elaborates more about the significance of each parameter. Figure 5 shows, all contributing factors using the reference point, which shows that all parameters cross the blue line, are highly significant with 95% confidence and the null hypothesis can be rejected (Abbasi et al., 2021). The graphs indicate that the ethanol to oil molar ratio and concentration of catalyst has a higher significant effect on the yield of biodiesel, while reaction time and reaction temperature have a lower effect. Figure 5a also shows that the lower the p-value and the higher the log worth values, the more significance on the process. The

blue line is used as the boundary line between the significant and insignificant effects of the process parameters (Miraculas et al., 2018). Figure 5 (b) also shows the positive and negative effect of the different process parameters on the yield.

4.7. Biodiesel production parameters optimization

To find the optimum parameters for the yield of biodiesel production, definitive screening design software was applied. To do so, the definitive screening design model was applied to design the experiments to minimize the number of experiments and time of the experiments. The results of the definitive screening design based on Table 2, are shown in Table 5, which presents the optimized process parameters for the biodiesel production with better yield.

As indicated in Table 5, the optimal parameters for the yield of biodiesel production are 5 wt% of catalyst concentration, 80 min of reaction time, 45 ^{0}c of reaction temperature, 10:1 ethanol-to-oil ratio, and an agitation rate of 1000 rpm. The initial prediction of biodiesel yield was 92.03% at the mean value of the parameters. After optimization of the process parameters, the yield of biodiesel was found to be 94.85%, which was a significant amount. The optimum values of the yields were generated by utilizing desirability maximization in definitive screening design, as indicated in Table 5. In addition, Figure 6 indicates the optimized value of each parameter. Production of biodiesel not only depends on maximum conversion aspects but also depends on the amount of solvent and catalyst usage, temperature, and time profiles (Rajendiran and Gurunathan, 2020).

Table 5. Definitive screening design optimized parameters.

Initial Setting	Factors					Yields (%)			D
	T[8] (min)	CC[9] (%)	ET[10] (v/v)	Tp[11] (^{0}C)	A[12] (rpm)	Yield	Lower CI	Upper CI	
IP.	65	2.75	15	61	875	92.03	91.93	92.13	0.50
Md	80	5	10	45	1000	94.90	94.63	95.17	0.97
EV	80	5	10	45	1000	94.85	94.83	94.9	0.98

IP; Initial prediction, Md; maximizing desirability, EV; Experimental value, D; desirability.
[8] Reaction time
[9] Catalyst concentration
[10] Ethanol to oil ratio
[11] Reaction temperature
[12] Agitation rate
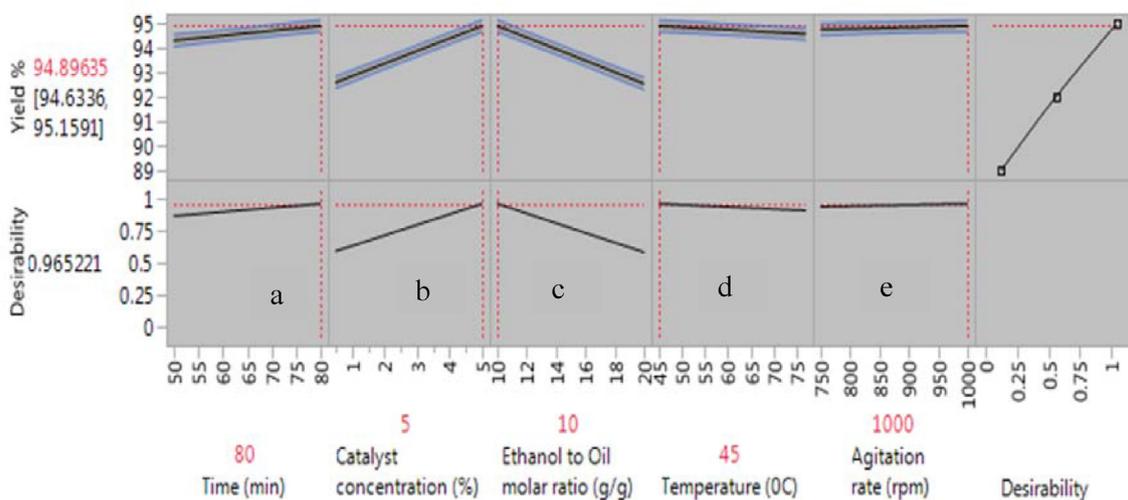
Figure 6. Effect of parameters on the yield of biodiesel (after optimization), (a) time, (b) catalyst concentration, (c) ethanol-to-oil ratio, (d) temperature and (e) agitation rate.

Table 6. Comparison of mesquite biodiesel with standard biodiesel specifications.

Parameter	P. julifera S.B	ASTM D763	EN 1632	Test methods
Specific gravity	0.86	0.87–0.90	0.85–0.90	ASTM D305
Viscosity (mm^2/s)	4.513	3.6–6.5	1.5–6.0	ASTM D545
Acid value (mg KOH/g)	0.88	0.5	≤0.55	ASTM-D774
Free fatty acid (%)	0.42	≤0.41	≤0.35	ASTM-D667
Saponification value (mg KOH/g)	192.54	≤216.8	≤220.9	ASTM-D884
Moisture content (%)	0.054	<0.03	-0.06	- ASTM-D335
Density (g/cm^3)	0.865	0.82–0.95	0.85–0.95	ASTM D395
Flash point (°C)	223	≥125	≥140	ASTM D102
Iodine value (g I$_2$/g 100 oil)	78.51	-	120	EN14214

S = seed, B = biodiesel.

4.8. Model validation

Equation (Eq. 2) generated by regression analysis indicates the theoretical yield and it is validated by carrying out the experiments by using the five process variables. To attain the exact yield of response, experiments were conducted in triplicates and the average yield was determined as 94.83% (Table 5). The result of the experimental yield was in reasonable correspondence with the yield of biodiesel produced from Indian oil sardine fish as feedstock (Anand Kumar et al., 2019). Thus, from the experimental data, it can be concluded that the definitive screening optimization technique is efficient in anticipating the significant response parameters for the biodiesel production process.

4.9. Physicochemical properties of biodiesel

Classification of the physiochemical properties (free fatty acid (FFA), acid value, density, viscosity, specific gravity, moisture content, and Iodine value) of any biodiesel produced from both edible and non-edible oil depend on the plant sources (Adepoju, 2020). These properties are shown in Table 6.

The density of the fuel determines the quality of combustion and fragmentation. Thus, in this study, the produced biodiesel has 0.865 g/cm^3 of density (Table 6), which is in the recommended values of ASTM standard (0.82 − 0.95 g/cm^3). This value is similar to the density of

biodiesel produced from Jatropha seed oil (Kumar Tiwari et al., 2007). Similar to the current value, it was described that biodiesel is qualified by a high density than conventional fuel diesel (Aslan and Eryilmaz, 2020). This means that volumetrically fuel pumps will interpose a higher amount of biodiesel compared to conventional fuel.

The acid value is one common property of biodiesel, which determines the quality of biodiesel produced. The more acid value can contribute to dangerous corrosion in the internal combustion and fuel supply (Chhabra et al., 2021). The ASTM determines a minimum of 0.5 mg KOH/g. In the present study, 0.88 mg KOH/g of acid value and the FFA value of 0.42 % was reported. The more significant amount of acid value than the limited value could be improved by the addition of various additives like fuel stabilizers, cold flow suppliers, and corrosion inhibitors (Kumar et al., 2019).

The properties of the diesel fuel injector, known as spray and droplet size, are determined by the viscosity parameter. The minimum amount of bio-oil viscosity reported by EN 1632 and ASTM D763 were (3.6 − 6.5 mm^2/s 40 °C) and 1.5 − 6 mm^2/s 40 °C) respectively for biodiesel (Ewunie et al., 2021). The current work indicates a viscosity of 4.513 mm^2/s for biodiesel, which is in the range of the specified standard value of biodiesel.

The iodine value is an important parameter to determine the degree of unsaturation, oxidative rancidity and chemical constancy properties of various oil and biodiesel (Sánchez-Arreola et al., 2019). According to EN14214 (European committee for standardization), the iodine value should be less than 120 g I$_2$/100 g of sample for the oil to be desirable as feedstock for biodiesel production (Athar and Zaidi, 2020). In this study, the iodine value of the biodiesel produced from P. julifera seed oil was 78.51 g I$_2$/100 g oil (Table 6). Hence, the value obtained in this is confirmed to the EN14214 recommended value.

Flashpoint is used to determine the flammability of the biodiesel fuel, as an adjustment for prioritizing the transport of fuel (Athar and Zaidi, 2020). This research shows that the P. julifera seed biodiesel activates at 223 °C. In this case, although the result of the flame temperature of biodiesel was greater than the limited value and was not greater than the surface temperature of the combustion chamber, which could achieve up to 2000 °C of combustion in the CI-Engine (Adepoju, 2020).

4.10. FT–IR spectrometry

The functional groups present in the produced biodiesel were analyzed by Fourier Transform Infrared (FTIR) spectroscopy, to distinguish between the existing functional group and the character of

attaching linkages, contributing to respective stretching and bending vibrations in the biodiesel. Esters and oils are noted as substantial absorbers in the infrared area of the electromagnetic spectrum.

It can be seen from Figure 7, that the absorbance peak of the samples were taken at nearly 1745 cm^{-1} where substantial absorption of fatty acid ethyl esters present. The substantial absorption for ethyl esters take place nearly at 3324 cm^{-1}. The FT–IR spectrum for the samples disclosed the functional groups with their respective absorption bands in the spectrum (Rajendiran and Gurunathan, 2020).
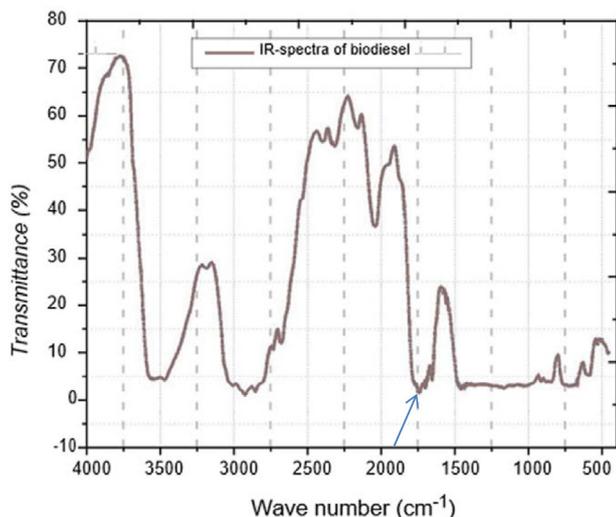
Figure 7. FTIR spectra of biodiesel produced from mesquite seed oil.

5. Conclusion

Production of biodiesel from *P. julifera* seed oil was carried out with MgO nanocatalyst under different process conditions such as ethanol-to-oil molar ratio, reaction time, reaction temperature, agitation rate, and catalyst concentration. The following results were obtained from the above experiments. The oil content of P. juliflora seed was found to be 32.5% w/w. Using definitive screening design (DSD), for the experimental runs, the influences and significance of the parameters were determined and the optimum settings of the parameters were established and validated consequently. The optimum process parameters determined using DSD were: alcohol-to-oil molar ratio (10:1 v/v) MgO concentration (5 w/w %), reaction temperature (45 °C), reaction time (80 min), and agitation rate (1000 rpm) with corresponding to 94.9% of the yield of prediction. To validate the model, experiments were repeated three times and the average yield was computed as 94.83% of biodiesel yield. The experimental yield value was in reasonable correspondence with the predicted yield value of the definitive screening design.

The alcohol to oil molar ratio was found to be the most influencing parameter followed by catalyst concentration. Advanced optimization DSD was successfully used and the results suggest that DSD can be used as an effective optimization method for parameter optimization. The *P. julifera* seed oil can be considered suitable for biodiesel production. FTIR analysis confirmed the existence of functional groups in the fingerprint region of the biodiesel produced from mesquite seed oil. The findings suggest that the produced biodiesel from *P. julifera* seed shall be explored as a novel possible natural biofuel.

Declarations

Author contribution statement

Ketema Beyecha Hundie: Conceived and designed the experiments; Performed the experiments, Analyzed and interpreted the data; Wrote the paper.

Desalegn Abdissa Akuma: Contributed reagents, materials, analysis tools and data.

Data availability statement

Data included in article/supp. material/referenced in article

Declaration of interests statement

The authors declare no conflict of interest.

Additional information

No additional information is available for this paper.

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