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RSM and Artificial Neural Networking based production optimization of sustainable Cotton bio-lubricant and evaluation of its lubricity & tribological properties

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ABSTRACT

Depletion of mineral reservoirs along with health and environmental concerns have led to a greater focus on bio-lubricants. The purpose of this study was to analyze and optimize the reaction conditions of the transesterification process for cotton biolubricant synthesis by using Response Surface Methodology (RSM). In RSM, Rotatable central composite design was selected to examine the effect of reaction input factors on the yield of cotton bio-lubricant during the transesterification process. ANOVA analysis showed that temperature was the most significant factor followed by time, pressure and catalyst-concentration. Optimum reaction conditions obtained by RSM for maximum TMP tri-ester (cotton bio-lubricant) yield of about 37.52% were 144 °C temperature, 10 h time, 25 mbar pressure, and 0.8% catalyst-concentration. RSM predicted results were successfully validated experimentally and by artificial neural networking. About 90%–94% cotton seed oil bio-lubricant was obtained after purification and its physiochemical, lubricity and tribological properties were evaluated and found comparable with ISO VG-46 and SAE-40 mineral lubricant. Hence, cottonseed oil is a potential source for the bio-lubricant industry.

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1. Introduction

The depleting mineral reservoirs and increasing concerns for health and environment *are* becoming critical *for the public. Which* diverted the focus towards bio-based lubricants derived from natural crop seed oils instead of *mineral* lubricants (Heikal et al., 2017; Nagendramma and Kaul, 2012). These crop oil-based lubricants are renewable and eco-friendly (Tamada et al., 2012). Bio-lubricants have good lubrication properties like viscosity index, anti-friction, anti-wear characteristics along with good pour point, flash point and high load carrying capacity (Zainal et al., 2018). But corrosion protection, oxidative and thermal stabilities of the bio-lubricant are not good (Erhan et al., 2006) so their utilization is limited to metal-working, chainsaw, pumps, agricultural two-stroke engines, cutting fluids (Zeman et al., 1995; Shashidhara and Jayaram, 2010), hydraulic oils (Kamalakar et al., 2013) drilling (Jassim et al., 2016).

These drawbacks can be reduced by the chemically modifying crop oils with polyols like NPG (neopentyl glycol), PE (pentaerythritol), and TMP (trimethylolpropane) (Heikal et al., 2017; Yunus et al., 2003; Wang et al., 2014). This two-step chemical modification is a transesterification process (Leung et al., 2010; Gryglewicz

Abbreviations: CSO, Cottonseed oil; CME, Cotton seed oil methyl ester; CBL, Cotton Bio-lubricant; TMP, Trimethylolpropane; VI, viscosity index; RSM, Response surface methodology; RCCD, Rotatable central composite design; ANOVA, Analysis of variance; ANN, Artificial neural networking; ISL, Initial seizure loads; LNSL, Last nonseizure load

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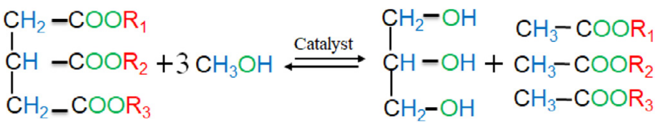
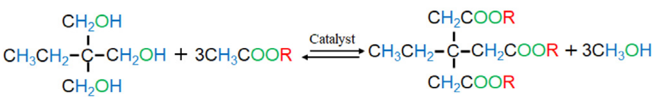
et al., 2003; Ruzaimah NMK, 2010; Kleinaitė et al., 2014). In the first step, methyl ester is produced from the triglyceride of crop oil.



Triglyceride Methanol Glycerol Methyl Ester

(1)

The 2nd step involves the transesterification of polyol (NPG, PE, and TMP) with methyl ester to eliminate β-hydrogen atom of triglyceride, which increases the stability of the bio-lubricant (Gryglewicz et al., 2003; do Valle et al., 2018). TMP is most preferable because of its low melting point and branching structure without β-hydrogen (Ghazi et al., 2009).



TMP Methyl Ester TMP-Ester Methanol

R=alkyl group, C6-C24

(2)

Previous studies showed that TMP based tri-esters developed from vegetable oil exhibit excellent physicochemical characteristics that are comparable with mineral-based lubricants (Sripada et al., 2013). Synthesis of TMP tri-ester (bio-lubricant) from different types of vegetable oils (having different fatty acids compositions) was carried out at different values of input parameters like pressure, temperature, catalyst concentration, and time. So, optimization of the independent input process parameters is essential to get the maximum yield of TMP tri-ester. In the conventional approach, optimization is done by varying one input factor at a time while keeping other parameters constant. But this approach is very time-consuming as well as requires a lot of resources because of many sets of experiments (Chang et al., 2012).

Response Surface Methodology (RSM) uses statistical and mathematical techniques to provides the best optimal reaction conditions with minimum possible runs of the experiment as compared to the single-factor experimental design (Asfaram et al., 2015; Yuan et al., 2008). Moreover, RSM also shows the interaction between the input factors and develops a correlation between them.

Similarly, ANN (Artificial Neural Networking) (Gul et al., 2016, 2019b) is also an efficient way of predicting and validating the results developed from any optimization technique like RSM (Dantas et al., 2020).

Some researchers used response surface methodology (RSM) to optimize bio-lubricant synthesis from sesame oil (Ocholi et al., 2018) Phyllanthus Emblica seed oil (Singh et al., 2018) rapeseed oil (Uosukainen et al., 1999) palm oil (Aziz et al., 2014) canola oil (Sripada et al., 2013). In most of the literature, TMP based bio-lubricants are synthesized at optimal reaction conditions from Palm, Sunflower, Sesame, Canola, Rapeseed, Olive, Jatropha, Waste cooking, and Rubber seed oil. But detailed published work on optimization of biolubricant synthesis from cottonseed oil is not available.

Previously pure cottonseed oil was used as an additive in commercial lubricant (Durak and Karaosmanoglu, 2004) but it cannot be used as a lubricant because of less life. Similarly, cotton seed oil methyl ester along with antiwear additives like MoS_2, hBN and ZDDP (Bajaj and Jahagirdar, 2018) was used to improve tribological properties of lubricants but cottonseed oil and its biodiesel cannot be used purely as biolubricant because these have poor pour point, low thermal and oxidation stability, and poor flash temperature. So further modification by the transesterification process was used to synthesize TMP-triester (biolubricant) from cotton seed oil methyl ester. Siraskar Gulab Dattrao (Dattrao, 2018) synthesize TMP based bio-lubricants and measure lubrication oil temperature only. George S. Dodos et al. (Dodos et al., 2010) also synthesizes TMP-triester from cottonseed oil and evaluate tribological behavior. But no one optimizes and analyzes the process parameters involved in bio-lubricant production from cottonseed oil. Cottonseed oil is one of the potential indigenous oil-producing crops in several countries like Pakistan, China, India, Brazil, the United States, Uzbekistan, and Australia (Gul et al., 2019a). Cotton seed oil has following fatty acids composition: 22%–26% Palmitic acid (C16:0), 2%–5% Stearic acid (C18:0), 15%–20% Oleic acid (C18:1), 49%–58% Linoleic acid (C18:2), and 1% Linolenic Acid (C18:3). Cottonseed oil has a high percentage of linoleic acids (C18:2) and oleic (C18:1) acids which showed that TMP based transesterification process can produce a promising green-lubricant from cottonseed oil for high temperature and pressure applications to replace the conventional mineral lubricants (Gul et al., 2019a). Cotton seed oil has acidic value = 0.21 mg KOH/g, cold filter plugging point = −2.78 °C, iodin value = 118.61, and Saponification Value = 203.02.

The current literature review (Gul et al., 2019a) also showed that cottonseed oil is a potential feedstock to make TMP based cotton bio-lubricant by transesterification.

Therefore, detailed research is required to optimize and analyze the effect of input reaction parameters (like pressure, temperature, catalyst concentration, and time) of the transesterification process to get maximum yield of bio-lubricant (TMP-triester content) from cottonseed oil by using response surface methodology (RSM). In this study RCCD model of response surface methodology (RSM) was selected to develop a correlation between input reaction parameters and output response (yield). Best optimal setting was also predicted from the RCCD model of response surface methodology.

Moreover, physicochemical, lubricity and tribological properties of cotton bio-lubricant were also evaluated to explore the feasibility of cottonseed oil as an alternative potential and renewable feedstock for the global bio-lubricant market.

2. Materials and methodology

2.1. Chemicals and methods

Crude cottonseed oil was purchased from the local market of Lahore, Pakistan. 30 wt % sodium methoxide solution in methanol (ACROS ORGANICS brand) was used as catalyst.

BSTFA: N, O-Bis (trimethylsilyl) trifluoroacetamide (Brand Sigma Aldrich) with ≥ 99% purity,

Ethyl acetate AR+ (EAM brand) Assay (by GC) ≥99.5% and filter papers were purchased from Malaysia. SAE-40 (engine oil: API-5F/CC, AEROIL brand) was purchased from Malaysia.

Cotton seed oil methyl ester (biodiesel) and TMP based cotton bio-lubricant were prepared by the 2-step transesterification process.

In the first step, cotton methyl ester (biodiesel) was produced by reacting triglyceride of cottonseed oil with methanol with 1:6 M ratio at 64 °C and 800 rpm stirring speed in the presence of 1 wt% sodium methoxide catalyst, as shown by above Eq. (1).

In the 2nd step, the reaction of the cotton methyl ester (cotton-biodiesel) with TMP(4:1 molar ratio) was carried out in a 500 ml 3-neck flask at 1000 rpm stirring speed to produce cotton bio-lubricant in the presence of sodium methoxide catalyst.

Other production factors including pressure, temperature, catalyst concentration, and time were changed with different levels as mentioned in Table 1 to get optimum combination of input factors that can give maximum yield of cotton bio-lubricant. Detailed bio-lubricant production procedure was described in author's previous research (Gul et al., 2020). AISI 52100 grade steel balls (having diameter = 12.7 mm, and hardness = 64–66 RC and 210 GPa modulus of elasticity) for tribo-tester.

2.2. Experimental design

Stat-Ease Design-Expert- 10 software with Rotatable' central composite design (RCCD) having 6 center points was used for the DOE (design of experiments) (Montgomery, 2017) for optimizing the synthesis of cotton bio-lubricant and to get maximum cotton TMP tri-ester (bio-lubricant) with less soap formation.

Four numeric input factors (named pressure, temperature, catalyst concentration, and time) and one output response (TMP tri-ester yield) were choose for optimization. Five levels of input factors are mentioned in Table 1. CME to TMP ratio and stirring speed were constant as 4:1 and 1000 rpm respectively. Sodium methoxide (30% solution in methanol) was chosen as a catalyst.

The primary trials were performed to set maximum and lowest ranges of the input levels as described in previous literature of other feedstocks (Hamid et al., 2018).

The maximum temperature was maintained at 145 °C to prevent the escaping of a low boiling point fraction of oleic CME.

Rotatable' central composite design recommended 30 sets of experiments as described by Yi et al. (2010). 6 experimental runs of central point provided enough replication to evaluate the pure experimental error along with 16 factorials and 8 axial experimental runs (Aslan, 2007). All the experiments were conducted randomly to reduce systematic errors.

2.3. Statistical analysis by regression models and ANOVA analysis

Experimental results were analyzed statistically with the help of Stat-Ease Design-Expert-10: RSM software (Rezić, 2011). Statistical polynomial equation, developed by RCCD to predict the dependent response (Y_1) by using experimental data, is as follow.

$$Y = \varphi_\circ + \sum_{i=1}^{4} \varphi_i x_i + \sum_{i=1}^{4} \varphi_{ii} x_i^2 + \sum_{i=1}^{3} \sum_{j=i+1}^{4} \varphi_{ij} x_{ij} + \zeta \tag{3}$$

In Eq. (3) Y represents the responses (Yield of TMP Tri-ester content), x_i and x_{ij} are the ith and jth independent input factors, $\varphi_\circ$ and ζ are intercept and random error. While φ_i, φ_{ii} & φ_{ij} are the regression coefficient for linear 1st order model, quadratic model, and interaction effects between the i and j input factors respectively.

Significance level of the RCCD model was find by using ANOVA analysis in Stat-Ease Design-Expert-10. In ANOVA analysis the values of "Prob > F" determines the significance of model terms. Significant factors have "Prob > F" value less than 0.05. The model should be improved if it has many insignificant factors. "Lack of Fit F-value" should be non-significant for best-fitted model (Montgomery, 2017).

Quality of model fitting is determined from Correlation value i.e R^2 value. R^2 value shows how much variation can occur in observed responses by the experimental independent factors and their interactions. Greater than 90% R^2 value shows a good empirical model fit with actual data, while smaller values of R^2 represent the less significance of the input factors used in the model to explain their behavioral variation (Aziz et al., 2014). If F-value is greater, P-value (i.e Prob > F) of ANOVA analysis is less than 0.05, coefficient of variation (CV) is below 10% and 'lack of fit' comes as 'not significant' than that model is considered acceptable for predicting the optimal combination of input factors (Khorram and Fallah, 2018). Model graphs and response surfaces of all input factors, generated by the regression models, also show the effects of input factors on the output responses and interaction between them. The set of input factors having the highest desirability among all the RSM suggested solutions is considered as an optimal combination.

2.4. Validation of results

The maximum yield of TMP tri-ester (cotton bio-lubricant) suggested by RSM at optimal combination was also validated experimentally and by artificial neural networking (ANN) tool of MATLAB. Mean square error (MSE) was set as performance parameter of the ANN network. The number of neurons is changed in the hidden layer again and again during the training process to get minimum MSE (i.e 0.001). Training of ANN was performed based on experimental data. After successful training, results can be simulated at the optimal combination suggested by RSM.

2.5. Characterization of Bio-lubricant

2.5.1. Preparation of sample

Cotton seed oil based TMP-Triester (cotton bio-lubricant) was prepared at the predicted optimal combination and analyzed by gas chromatography (GC).

For GC analysis, 0.03 ± 0.005 g of bio-lubricant sample was diluted with 1 ml of ethyl acetate (EA) in a 2ml vial. This mixture was swirled to dissolve them well than 0.5 ml of BSTFA was also poured in the vial. After mixing this mixture thoroughly, it was heated at 40 °C for 10 min, then cooled to normal room temperature before injecting it into the GC machine (Jassim et al., 2016).

2.5.2. Gas Chromatography (GC) analysis of Bio-lubricant

CSO based TMP-triester (bio-lubricant) was analyzed by GC (7890A) having DB-5HT (15 m × 0.320 mm ×0.10μ m) column with a (1:1) split ratio.

Carrier gas was He with a flow rate of 26.7 ml/min. Initially, the oven temperature was set at 80 °C for 3 min then further it is ramped at 6 °C/min to reach up to 340 °C and held this 340 °C temperature for 6 min. While temperatures of inlet and detector were kept at 300 and 360 °C (Sripada et al., 2013).

2.5.3. Evaluation of physiochemical, lubricity and tribological properties of CBL

Density, kinematic viscosities at 40 °C and 100 °C, viscosity index (VI) were measured by using Stabinger viscometer SVM:3000 Anton Paar according to ASTM D7042.

Lubricants with high viscosities are considered suitable for extreme conditions like hydraulic and automobile applications. While low viscosity lubricant is preferred for small machinery like chainsaw & small pumps etc. Viscosity index (VI) shows the ability of a lubricant to vary its viscosity with the change in temperature. High VI is required for industrial applications and extreme conditions.

Flash point of cotton bio-lubricant was measured by Anton-Paar according to ASTM standards and pour point was measured by NORMALA B NTE 450 (Normalab, France) according ASTM D97 standard (ASTM, 1991). Low temperature property of the bio-lubricant is important in cold weather. So, bio-lubricant should have the ability to flow at low temperatures (below 0 °C) to provide enough lubricity. While Oxidation Stability of CSO

Table 1
Different levels of all input factors for DOE.

Input factors	Units	Symbols	Levels[a]				
			−alpha	Low	Central	High	+alpha
Pressure	mbar	A	1	9	17	25	33
Temperature	°C	B	85	100	115	130	145
Catalyst concentration	%	C	0.2	0.4	0.6	0.8	1
Time	h	D	3	6	9	12	15

[a]Each input factor has 5 levels: +alpha and −alpha are considered axial points levels, low and high are factorial point levels with one center point.

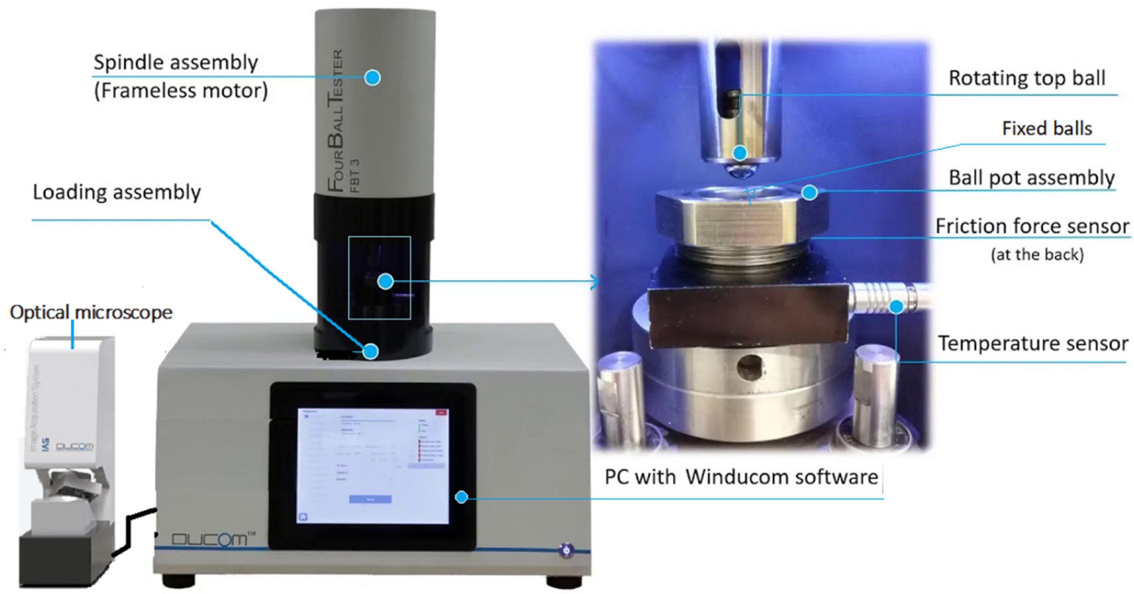


Fig. 1. Four-ball tribo-tester for evaluation of tribological properties.

and CME were determined by 837 Biodiesel Rancimat. Tribological properties (like wear scar diameter and co-efficient of friction) of CBL were measured by using a four-ball tribo-tester (as shown in Fig. 1) according to ASTM-D4172-94, that have following procedure conditions: Load 40 kgf (392 N) at 75 °C (167 °F) temperature with 1200 rpm for 60 min.

While Extreme pressure tribological properties of CBL including initial seizure load (ISL), last non-seizure load (LNSL), weld point (WP), and load wear index (LWI) were also measured by four-ball tribo-tester according to ASTM D2783 standard by varying applied load at 27 °C and 1770 rpm for 10 s and compared with SAE-40 commercial lubricant (D2783-19, 2019).

3. Results and discussion

3.1. Optimization by response surface methodology

3.1.1. Development, fitting and testing of models

The experimental sequence, based on the rotatable central composite design (RCCD) of RSM, was random to eliminate the systematic errors caused by extraneous factors (Raymond H. Myers and Anderson-Cook, 2016).

The cotton bio-lubricant was synthesized by transesterification process according to reaction conditions as suggested in Table 2 DOE. The synthesized cotton bio-lubricant was analyzed by GC to measure percentage of TMP Tri-ester (output response: Y_1) and recorded in Table 2 to optimize the reaction conditions for getting maximum TMP Tri-ester (bio-lubricant).

The results of the response (Y_1) were collected based on the actual design of experiments and presented in Table 2.

The TMP Tri-ester content of cotton biolubricant varied from 27.59 to 39.60% and methyl ester was in excess. Here independent input factors A, B, C, and D represent pressure, temperature, catalyst, and time respectively. The combined effects of all factors on the output response (Y_1) were examined by Stat-Ease Design-Expert- 10 software to develop empirical models.

The obtained experimental results were imported into the software which suggested the quadratic model as best-fitted model to predict the best optimal combination of input factors for producing maximum yield of TMP tri-ester (CSO based biolubricant). RSM developed following 2nd order quadratic equation Eq. (4) to predict responses (Y_1).

$$\begin{aligned} Y_1 = {} & 34.97 + 0.85 * A + 2.39 * B + 0.76 * C + 1.09 * D \\ & - 0.14 * AB + 0.31 * AC + 0.16 * AD - 0.48 * BC \\ & - 0.62 * BD + 0.037 * CD - 0.42 * A^2 + 0.016 * B^2 \\ & - 0.47 * C^2 - 0.70 * D^2 \end{aligned} \tag{4}$$

Here, a positive sign indicates that an increase in factor value will give more yield of TMP tri-ester while a negative sign shows that increase in factor value will give less yield Y_1.

3.1.2. ANOVA Analysis

ANOVA analysis correlates the suggested quadratic model with the experimental data. Table 3 showed the ANOVA (analysis of variance) (Montgomery, 2017) conducted for maximizing the yield of TMP-Tri-ester formation. The factors having "Prob. >F" value below 0.05 are considered as significant model's factors.

In Table 3, $R^2 = 0.9701$ indicated that the models could explain 97.01% of variability for yield with high compatibility of fit and endorsing the adequacy of the adopted regression model.

Table 2
Experimental design and response values obtained after transesterification of TMP with CME.

Std run #	Factor 1	Factor 2	Factor 3	Factor 4	Response 1
	A: Pressure (mbar)	B: Temp (°C)	C: Catalyst concentration (%)	D: Time (h)	Yield: Y_1 (%)
1	9	100	0.4	6	27.59
2	25	100	0.4	6	28.63
3	9	130	0.4	6	34.81
4	25	130	0.4	6	35.38
5	9	100	0.8	6	29.38
6	25	100	0.8	6	31.56
7	9	130	0.8	6	34.69
8	25	130	0.8	6	36.45
9	9	100	0.4	12	30.75
10	25	100	0.4	12	32.45
11	9	130	0.4	12	35.58
12	25	130	0.4	12	36.67
13	9	100	0.8	12	32.61
14	25	100	0.8	12	35.67
15	9	130	0.8	12	35.56
16	25	130	0.8	12	37.87
17	1	115	0.6	9	31.46
18	33	115	0.6	9	34.78
19	17	85	0.6	9	30.12
20	17	145	0.6	9	39.60
21	17	115	0.2	9	31.32
22	17	115	1	9	34.52
23	17	115	0.6	3	30.12
24	17	115	0.6	15	33.84
25	17	115	0.6	9	34.89
26	17	115	0.6	9	35.10
27	17	115	0.6	9	34.85
28	17	115	0.6	9	33.94
29	17	115	0.6	9	35.92
30	17	115	0.6	9	35.10

In Table 3, larger F-value of 90.40 suggested significant model. In this model, A, B, C, D, BD, BC, AC, A^2, C^2, and D^2 are significant terms, having "Prob > F" values below 0.0500 and "lack of fit" is non-significant so the model is acceptable.

Quadratic model terms B, D, A, C, D^2, C^2, BD, A^2, and BC significantly affects the measured response Y_1 (Yield of TMP Tri-ester) in the quadratic model.

ANOVA results of RSM showed that temperature has the highest F value = 755.80 among other single input factors for TMP tri-ester yield. This means among four input factors, the temperature is considered most sensitive and critical factor towards biolubricant synthesis by the transesterification process as supported by early studies also (Sripada et al., 2013). While catalyst (sodium methoxide) concentration is the least effective factor, having low F-values for yield. Although, sodium methoxide accelerates the reaction at faster rate to convert methyl ester into TMP tri-ester (biolubricant) but it causes more soap formation. Early studies also showed that Na^+ of sodium methoxide is converted into fatty soap at very high temperatures (Chang et al., 2012), so optimization is necessary for this purpose.

Plot of Fig. 2 indicated that experimental values and predicted values are closer to each other. Which confirms that RCCD model can develop good correlation between the input factors and predict values of response (Y_1).

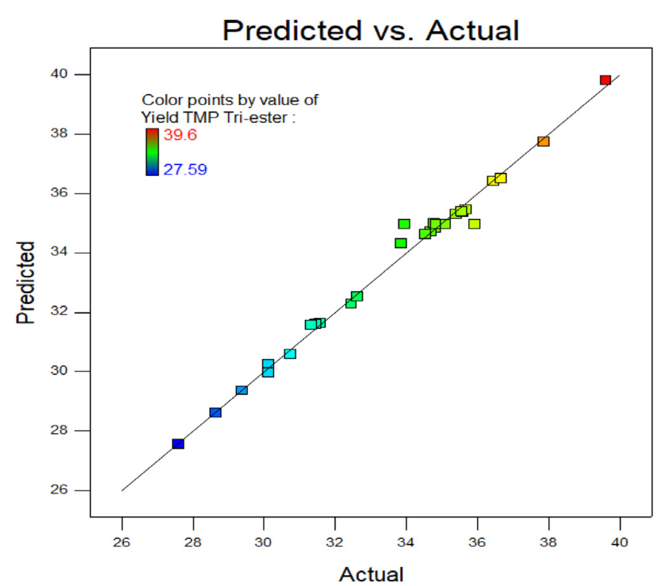


Fig. 2. Correlation between observed and predicted values of CSO based TMP Tri-ester Yield.

3.1.3. Effect of interaction between input factors and output responses

2D response surfaces for CSO based TMP-triester Yield (Y_1) are simulated and presented in Fig. 3. Fig. 3(i). describes the relationship between pressure and temperature while changing catalyst concentration and time. It could be seen that the yield of CSO based TMP tri-ester content increases with the increase in pressure up to a maximum limit of 33 mbar and increase in temperature up to a maximum limit of 145 °C. For high yield time should be set at 10 h and catalyst concentration up to 0.8 should be considered.

High temperature increases the mass transfer rate and improves the conversion of CME to TMP Tri-ester, but very high temperature and prolonged reaction time cause the evaporation of CME and less CME remains in the reaction vessel to convert CME into TMP Tri-ester (Chang et al., 2012). Therefore, optimum conditions are recommended in many cases (Resul et al., 2011).

Fig. 3(ii). explains the interaction between catalyst concentration and pressure by varying temperature and time. The yield

Table 3
ANOVA for CSO based TMP-Tri-ester (Y_1).

Analysis of variance (ANOVA) table for Y_1: Yield						
Source	Sum of squares	df	Mean square	*F* Value	*P*-value prob > *F*	
Model	229.32	14	16.38	90.40	<0.0001	**Significant**
A—Pressure	17.26	1	17.26	95.23	<0.0001	
B—temp	136.95	1	136.95	755.80	<0.0001	
C—catalyst concentration	14.00	1	14.00	77.26	<0.0001	
D—time	28.41	1	28.41	156.77	<0.0001	
AB	0.32	1	0.32	1.75	0.2062	
AC	1.51	1	1.51	8.32	0.0114	
AD	0.43	1	0.43	2.35	0.1461	
BC	3.68	1	3.68	20.29	0.0004	
BD	6.21	1	6.21	34.29	<0.0001	
CD	0.022	1	0.022	0.12	0.7338	
A^2	4.81	1	4.81	26.53	0.0001	
B^2	7.336E−003	1	7.336E−003	0.040	0.8432	
C^2	6.02	1	6.02	33.25	<0.0001	
D^2	13.58	1	13.58	74.95	<0.0001	
Residual	2.72	15	0.18			
Lack of fit	0.70	10	0.070	0.17	0.9907	**Not significant**
Pure error	2.02	5	0.40			
Cor total	232.04	29				
C.V = 1.26%; R^2 = 0.9883; R^2 Adj = 0.9774; Predicted R^2 = 0.9701						

of TMP tri-ester rises with an increase in temperature and time up to 10 hr. Pressure and catalyst concentration is maintained at 25 mbar and 0.8% to get a high yield. Although a high vacuum increases methanol removal from the reaction flask, which accelerates the forward reaction as shown in Eq. (2). But a high vacuum along with high temperature also causes the evaporation of methyl ester from the reaction flask. Therefore, it is necessary to optimize the vacuum pressure rather than creating a high vacuum (Chang et al., 2012).

Fig. 3(iii) explains that with the increase of pressure and time up to 10 hr increases the yield of TMP tri-ester while temperature and catalyst concentration is kept at 145 °C and 0.8% for high yield. Fig. 3(iv). explains that TMP tri-ester yield increases with the increase in temperature and increase in catalyst concentration up to 0.8% with pressure and time as 25 mbar and 10 hr.

Fig. 3(v). explains that high yield of TMP tri-ester is obtained with the increases in temperature and increase in time up to 10 hr while pressure and catalyst concentration is set as 25 mbar and 0.8%. Fig. 3(vi) explains the interaction between time and catalyst concentration by varying pressure and temperature. The yield of TMP tri-ester rises with an increase in time and catalyst. While for high yield, pressure and temperature are maintained at 25 mbar and 145 °C.

3.2. Process optimization

The optimal combination of input factors suggested by RCCD model of RSM for getting a high yield of CSO based TMP tri-ester (bio-lubricant) was as pressure 25 mbar, temperature 144 °C, catalyst concentration as 0.8% of the total weight of mixture and time 10 hr with maximum 98.6% desirability. These optimum conditions suggested 39.43% yield of TMP tri-ester.

3.3. Experimentally and ANN-based validation of results

For validating the predicted results of the RSM models, experiments were conducted on the optimal combination by three times, and averaged was presented in Table 4. Which indicates the effectiveness and high predictability of the response surface methodology (RSM) and artificial neural networking (ANN).

Moreover, ANN (Artificial neural networking) was also used to predict the results at an optimal combination suggested by RSM.

For an artificial neural network, the feedforward backpropagation algorithm was selected with 3 layers of neurons, named input, hidden, and output layers. The transfer functions of input, hidden and output layer are TANSIG, TANSIG, and PURLINE with 4, 15 and 1 neurons respectively. Screenshots of ANN developed model along with network properties and training parameters are mentioned in Fig. 4a. Then the model was trained by exporting experimental data of Table 2 by choosing TRAINLM as the activation function. A detailed procedure on ANN methodology was already explained by the author (Gul et al., 2016, 2019b). When MSE error approaches to 0.001 then results were simulated for RSM suggested an optimal combination of input factors as shown in Fig. 4b.

3.4. Characterization of CSO based Bio-lubricant

The final product was analyzed by GC for CSOME, ME, DE, TE, and TMP as shown in Fig. 5. The CME peak occurred at 15–24 min, monoester peak detected at 24–28 min, di-ester peaks existed at 29–36 min and the tri-ester was appeared at 40–50 min, respectively. The unreacted CME is separated from the obtained mixture by fractionation via vacuum distillation with temperatures as 150–190 °C under very low pressure of about 1–4 mbar. Before fractionation, CME, TMP monoester, TMP di-ester and TMP Tri-ester were 51.19%, 1.35% 9.94%, and 37.52% w/w respectively. But after fractionation less than 2.5% CME was left in the final product, which is acceptable for lubricity. Results show that about 90%–94% of bio-lubricant (TMP Tri-ester) was obtained from CME.

3.5. Physiochemical and tribological properties of CBL

The physiochemical properties of CSO, CME, Cotton biolubricant (Cotton TMP Tri-ester) are measured according to ASTM standard and presented in Table 5. Cotton bio-lubricant has better viscosities, VI (viscosity index), and tribological properties. CBL has comparable pour points with ISO-VG-46 and high flash points which decreases fire hazards.

Cotton bio-lubricant was also tested on extreme pressure conditions at different loads by using 4-ball tribo tester (FBT-3: DUCOM brand) and compared with SAE-40 commercial lubricant as shown in Table 6. Cotton bio-lubricant and SAE-40 showed 16.22 Kgf and 15.411 Kgf load wear index (LWI) respectively.

Microscopic images of worn surfaces of balls tested with bio-lubricant and SAE-40 under initial seizure loads (ISLs) are shown in Fig. 6. SAE-40 showed small wear scar as visualized by shallow

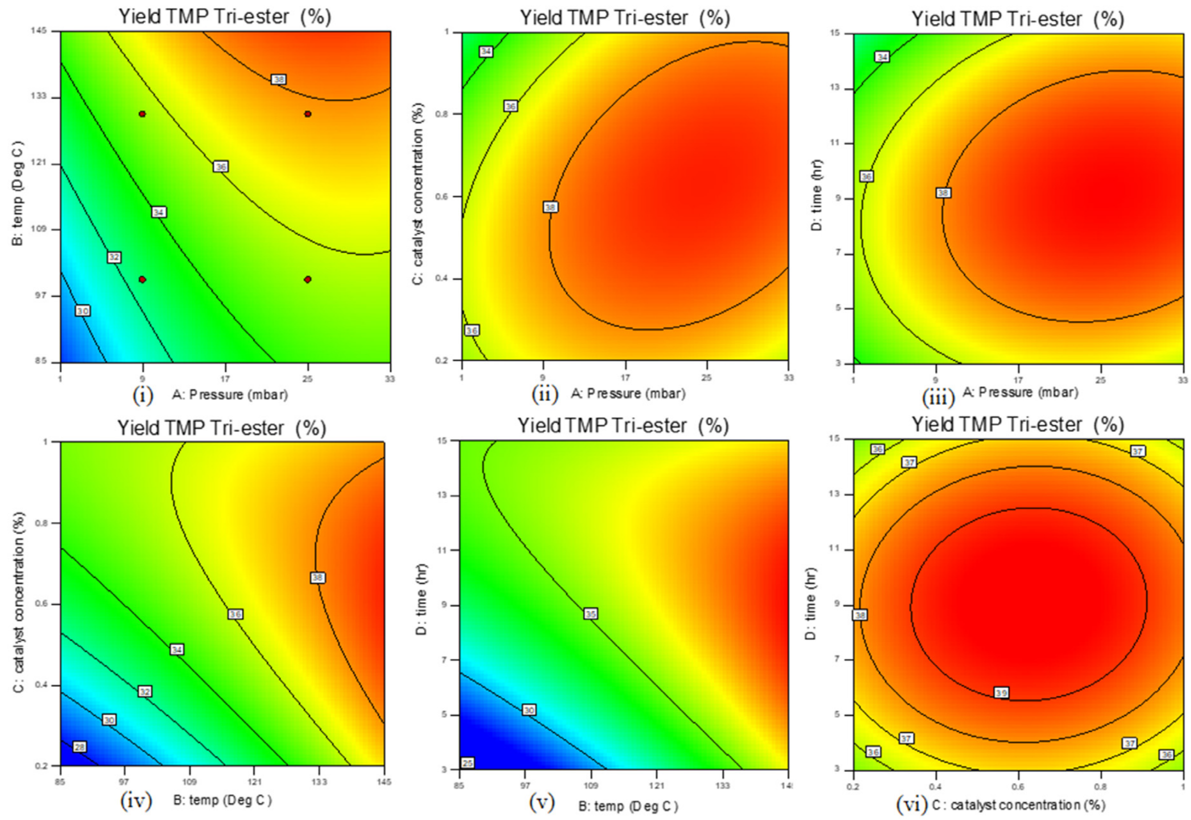


Fig. 3. 2D response surfaces graphs for Cotton-biolubricant Yield (Y_1)

Table 4
Comparison of predicted and experimental results.

Output response	Target	Results obtained at optimal combination (A = 25 mbar, B = 144, C = 0.8%, 10 h)		
		By RSM	By ANN	Experimentally
TMP Tri-ester yield (Y_1)	To maximize	39.43%	39.99%	37.52%

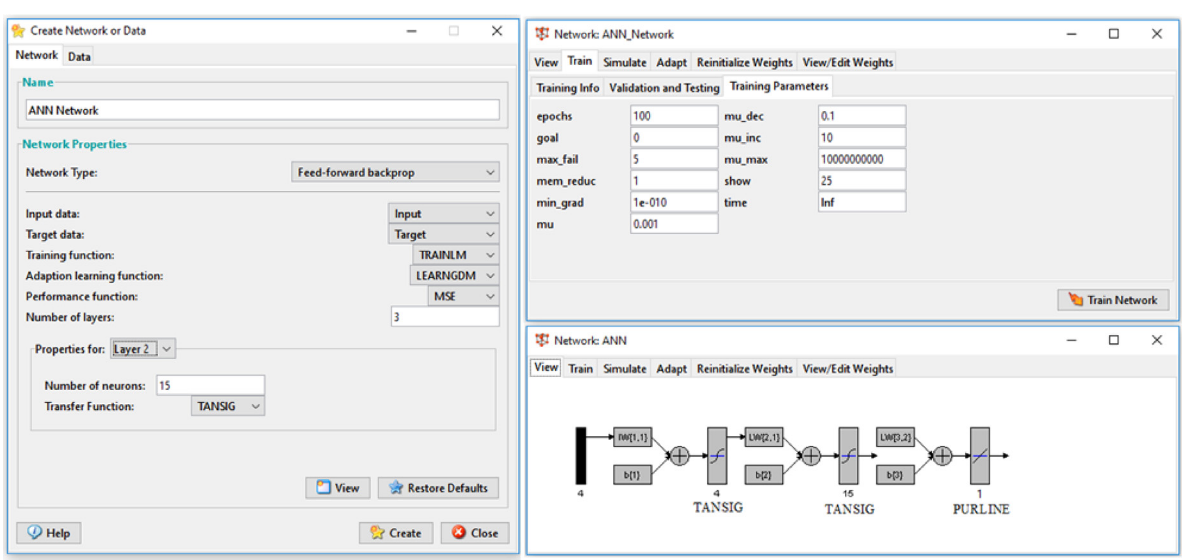


Fig. 4a. ANN network properties with training parameters.

grooves on the ball at 60 kg load because it contained anti-wear and anti-friction additives. Cotton biolubricant showed deep groove wear scratches and high WSD at 70 kg ISL because of the corrosive effects of peroxides and free fatty acids of biolubricant that were produced by oxidation.

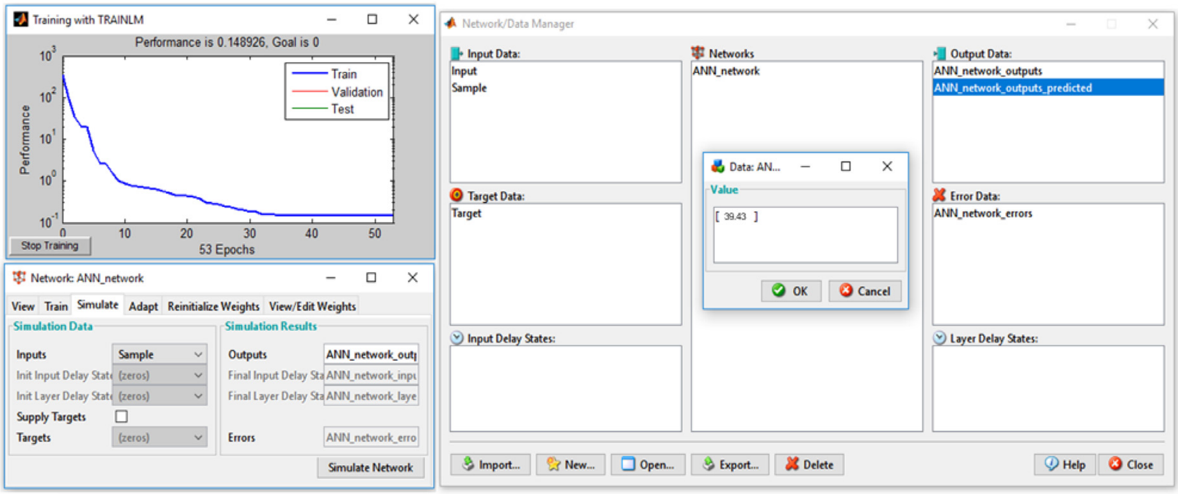


Fig. 4b. Training and simulation of results by ANN model.

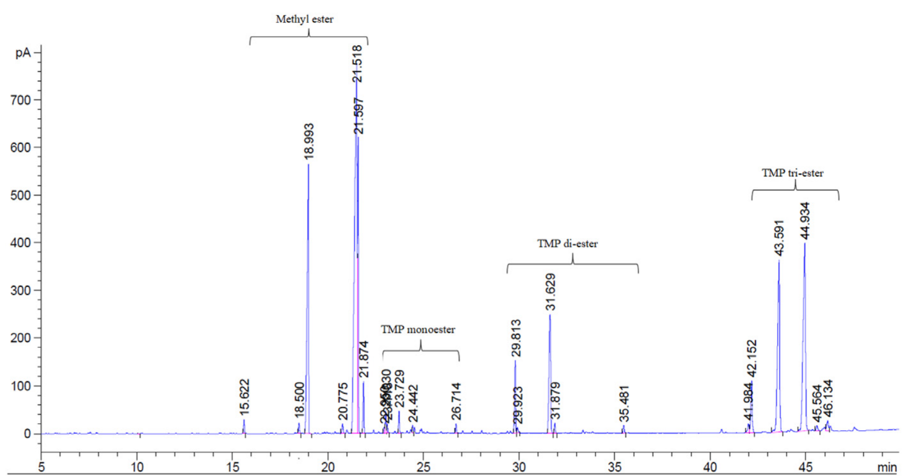


Fig. 5. GC Analysis of Final product at optimum conditions.

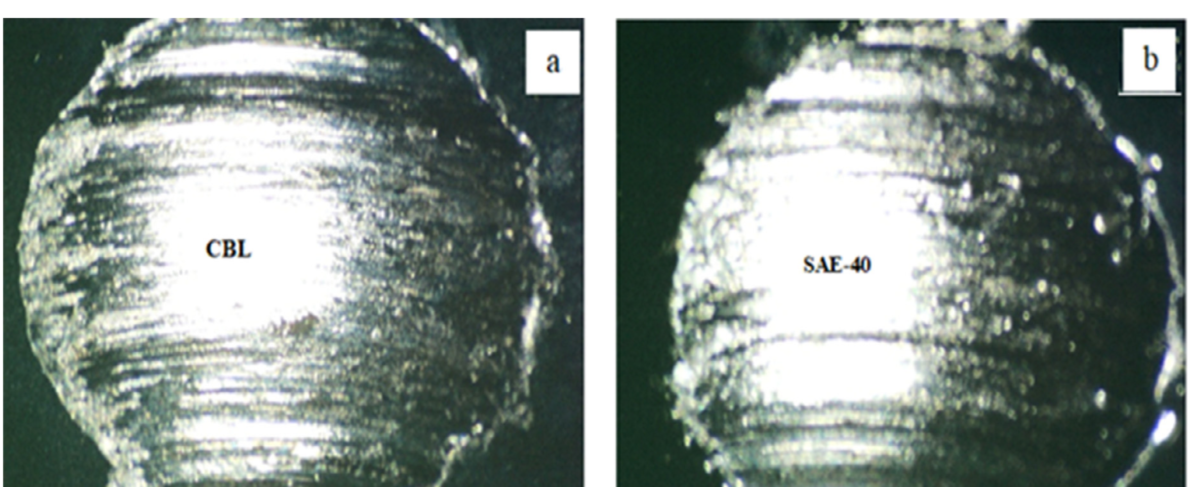


Fig. 6. Microscopic images of worn surfaces of balls tested with CBL and SAE-40 at ISL.

Table 5
Properties of CSO, CME, CBL, and comparison with ISO grade.

Specification	Method	Cottonseed oil	Cotton methyl ester	Cotton TMP-ester	ISO VG46 Ocholi et al. (2018)
Yield, wt.%	–	–	99.74%	**97.5%**	–
Acidic value (mg KOH /g)	ASTM D664	0.21	–	–	–
Density at 15 °C (g/cm^3)	ASTM D7042 by using Stabinger Viscometer SVM:3000 Anton Paar	0.9186	0.8833	**0.9044**	–
Kinematic viscosity cSt @ 40 °C (mm^2/s)		36.162	4.2417	**51.89**	**>41.4**
Kinematic viscosity cSt @ 100 °C (mm^2/s)		8.3566	1.6804	**8.53**	**>4.1**
Viscosity index/ VI		218.5	227.1	**140**	**>90**
Pour point (°C)	ASTM D97	–	1.96	**−6**	**−6**
Flash point (°C)	ASTM D92	–	>160	**296**	**220**
Calorific value (MJ/ kg)	–	37.92	38.67	–	–
Cloud point (°C)	–	6.51	8.09	–	–
Oxidation stability (Hours) @ 110 °C	By using 837 Biodiesel Rancimat	4.67	4.96 hr	–	–
Cetan No (CN)	–	46.50	48.59	–	–
Wear scar diameter (mm)	ASTM- D4172 - 94	–	–	**0.849**	**0.877**
Coefficient of Friction (COF)		–	–	**0.07484**	**0.0884**

Table 6
Average wear scar diameter of test balls at extreme pressure conditions.

Lubricant samples	**WSD (mm) at various loads**												
	40kg	**50kg**	**60kg**	**70kg**	**80kg**	**90kg**	**100kg**	**110kg**	**120kg**	**130kg**	**140kg**	**150kg**	**160kg**
CBL	0.83	0.84	1.12	2.23	2.3	2.51	2.58	2.68	3	3.25	3.42		
SAE-40	0.855	1	1.99	2.12	2.27	2.28	2.34	2.55	2.77	3			
Blue color represents LNSL, Yellow color indicates ISL, and Red color indicates weld point or weld load													

4. Conclusion

- The process parameters of the transesterification process for CBL synthesis were analyzed, optimized, and validated successfully by using RSM and ANN. The optimal combination of input factors suggested by RSM was 25 mbar, 144 °C, catalyst concentration as 0.8% and time 10 hr. At this combination, a maximum TMP tri-ester (cotton bio-lubricant) yield of about 37.52% was achieved in the mixture. After fractionation, 90%–94% pure cotton bio-lubricant was obtained.
- ANOVA results of RSM revealed that temperature and time were the most influencing factors. While catalyst concentration was the least significant factor for cotton biolubricant synthesis.
- RSM and ANN were proved as an effective tool for optimization and validation.
- The physicochemical, lubricity and tribological properties of cotton bio-lubricant were better than ISO VG 46 standard.
- Which shows the potential of cottonseed oil as a new alternative source in the formulation of bio-lubricant for the global lubricant market.
- At extreme pressure conditions CBL has high ISL, weld load, and load wear index (LWI) as compared to mineral SAE-40 lubricant.

CRediT authorship contribution statement

M. Gul: Develop optimization model, Synthesize the bio-lubricant from cottonseed oil by transesterification process, Analysis on artificial neural networking (ANN), Wrote results and discussion portion in this manuscript. **N.W.M. Zulkifli:** Supervise the project/ research, Critically evaluate the technical results (lubricity, tribology), Approve the final version of manuscript. **M.A. Kalam:** Supervise the research, Check overall formatting and bench marking aspects of manuscript. **H.H. Masjuki:** Supervise the research, Statistical analysis. **M.A. Mujtaba:** Synthesize the biodiesel (methyl ester) from cottonseed oil by transesterification process, Characterize the physicochemical properties of cotton biodiesel and cotton bio-lubricant. **Sumra Yousuf:** Worked on methodology of experimentation, Validated the results. **M. Nasir Bashir:** Wrote literature review. **Waqar Ahmed:** Wrote introduction portion of manuscript. **M.N.A.M. Yusoff:** GC analysis of bio-lubricant. **Shazia Noor:** Proof reading of whole manuscript, Wrote the conclusion. **Rauf Ahmad:** Wrote abstract, Draw figures and graphs.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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