



Response Surface Methodology Based Process Optimization for Biodiesel Production using Cottonseed Oil: A Comparative Study

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Present study describes the optimization and comparison of biodiesel production using cottonseed oil as feedstock and NaOH, KOH and NaOCH₃ as catalyst to catalyze transesterification of cottonseed oil. Maximum cottonseed oil fatty acid methyl esters (CSOFAME's) yield (%) obtained using NaOCH₃, KOH and NaOH was 95.41, 94.25 and 91.4 %, respectively. NaOCH₃ was found to be most productive gives best results. GC-MS analysis of CSOFAME's was carried out for compositional analysis. Further fuel properties of CSOFAME's were found compatible with the standards.

Key Words: Optimization, Response surface methodology, Cottonseed oil, Transesterification.

INTRODUCTION

Today, World is facing serious challenges regarding the energy crisis. Drastic situation concerning non renewable petrochemical fuel reserves decline in addition to deleterious environmental and economic concerns have stimulated the researchers worldwide to explore alternative, renewable and environmental friendly fuels like biodiesel^{1,2}. Biodiesel is a biodegradable, nontoxic and clean burning fuel currently being produced from vegetable oils, animal fats and grease by transesterification with short chain alcohol. Chemically biodiesel is fatty acid alkyl esters^{3,4}.

Vegetable oils are the most commonly used feedstock for biodiesel production. Because of the low volatility and high viscosity oils and fats are not recommended for use directly as fuel^{5,6}. Therefore to increase volatility and decrease viscosity oils and fats are subjected to transesterification reaction. Different methods are in use for the production of biodiesel but base catalyzed transesterification is the most abundantly used method⁷. Throughout the world, researchers have renewed interest in biodiesel development and optimization⁸. Different researchers have used cottonseed oil as a feed stock for the production of biodiesel⁹⁻¹³. Response surface methodology (RSM) is compilation of statistical and mathematical techniques

for development, modification and optimization of various processes¹⁴. Current study was carried out with the objective primarily to use response surface methodology for the optimization of reaction parameters including catalyst concentration, alcohol to oil molar ratio, reaction temperature and reaction time for biodiesel production using cottonseed oil as feed stock, NaOH, KOH and NaOCH₃ as alkaline catalysts and secondly to compare optimized biodiesel yield along with other optimized parameters while using different alkaline catalysts.

EXPERIMENTAL

Feedstock and chemical reagents: Cottonseeds were procured from district Gujrat, Pakistan and verified by Dr. Khalid Nawaz (Assistant Prof. Department of Botany, University of Gujrat, Pakistan). Analytical/research grade chemicals were used, NaOH, KOH and methanol were purchased from Merck Chemical Company (Darmstadt, Germany) whereas NaOCH₃ from ACROS (New Jersey USA) while FAMES standards were procured from Sigma Chemical Company (St. Louis, MO, USA).

Extraction of cottonseed oil and quality assessment: Soxhlet extraction method was used for the extraction of cottonseed oil using *n*-hexane as an extracting solvent^{15,16}. Extracted cottonseed oil was subjected to physico-chemical character-

ization for qualitative assessment before transesterification and pre-analyzed for acid value, peroxide value, iodine value, density, saponification and un-saponification value using standard methods.

Experimental design for transesterification: To evaluate the effect of various reaction parameters *i.e.* catalyst concentration (A), reaction time (B), reaction temperature (C) and alcohol : oil molar ratio (D) on % biodiesel yield using cottonseed oil as feedstock central composite response surface design (CCRD) was used for 30 runs. The levels of different reaction parameters used for the current study ranged from 0.25 to 1.25 % for catalyst concentration, 0.5 to 1.5 h for reaction time, 30 to 60 °C for reaction temperature while 3 to 9 for alcohol to oil molar ratio (Table-1). Methanol was used as an alcohol because of its easy availability and low cost, while NaOH, KOH and NaOCH₃ were used as alkaline catalyst to carry out transesterification of cottonseed oil.

TABLE-1
SUMMARY OF CENTRAL COMPOSITE RESPONSE SURFACE DESIGN DIFFERENT LEVELS OF REACTION VARIABLES USED FOR TRANSESTERIFICATION

Factor	Name	Low level	High level
A	Catalyst concentration (%)	00.25	01.25
B	Reaction time (min)	30.00	90.00
C	Reaction temperature (°C)	30.00	60.00
D	Alcohol : oil molar ratio	03.00	09.00

Experimental protocol and FTIR monitoring of transesterification reaction using cottonseed oil as feed stock:

The transesterification of cottonseed oil was executed in a three neck flask furnished with a thermometer, a chiller, condenser, a magnetic stirrer and a heating plate using NaOH, KOH and NaOCH₃ as alkaline catalysts and methanol as alcohol. For each experiment transesterification was conducted at specified reaction conditions according to central composite response surface design and percentage yield of cottonseed oil biodiesel (cottonseed oil fatty acid methyl esters) was calculated for each experiment^{17,18}. Monitoring of transesterification of cottonseed oil was carried out using Interspec 200-X FTIR spectrophotometer fitted with mountable FTIR liquid cells. The spectra were recorded over scanning range of 5000 to 500 cm⁻¹.

Based upon experimental results of transesterification, analysis of central composite response surface design was performed using design expert 7 and second order model for each alkaline catalyst was selected on the basis of lack of fit test and high value of R², further to get optimum yields, the response surface plots were obtained using the estimated equations of selected models. The model can be written as:

$$Y_{\text{yield}} = b_0 + \sum_{i=1}^k b_i X_i + \sum_{i=1}^k b_i X_i^2 + \sum_{i=1}^k \sum_{j=1, j>i}^k b_{ij} X_i X_j + e$$

Compositional analysis of cottonseed oil biodiesel using GC-MS: Qualitative and quantitative analysis of cottonseed oil fatty acid methyl esters (CSOFAME's) was carried out using gas chromatography/mass spectrometry (GC/MS), using Agilent-Technologies (Little Falls, CA, USA) 6890 N network gas chromatographic system, equipped with an inert XL mass

(Agilent-Technologies 5975) and auto injector (Agilent-Technologies 7683 B series). Capillary column (100 m × 0.25 mm with film thickness 0.20 μm) (Agilent-Technologies RT-2560) was utilized for the separation of cottonseed oil fatty acid methyl esters. 1.0 μL sample was injected in the split mode with a split ratio 1:100. Helium was the carrier gas with a flow rate of 1.2 mL/min. The temperature of column oven was programmed from 150 to 250 °C at 4 °C/min while initial and final hold up time 1 and 5 min respectively, whereas the temperature of the injector and MS transfer line was set at 250 and 260 °C, respectively. An electron ionization system (with ionization energy *i.e.* 70 eV) was used for GC/MS detection while scanning mass ranged from 30-550 m/z¹⁹. Unknown CSOFAMES were identified by comparing their relative retention times with the retention times of authentic fatty acid methyl esters (FAMES) standards (Sigma Chemical Co., St. Louis, MO, USA). For further confirmation of CSOFAMES profile MS spectra of the sample was compared with those from the NIST mass spectral library of the GC/MS system, whereas quantification was done by Agilent-Technologies data handling software (Chem Station 6890) and the CSOFAME's composition was reported as relative percentage of the total peak area²⁰.

Fuel properties of cottonseed oil biodiesel: The following fuel properties of the CSOFAME's were ascertained: kinematic viscosity (ASTM D 445), flash point (ASTM D 93), fire point, cloud point (ASTM D 2500), pour point (ASTM D 97) and sulfur content (ASTM D 4294).

RESULTS AND DISCUSSION

Physico-chemical characteristics/quality parameters of cottonseed oil: Cottonseed oil was pre-analyzed before transesterification to evaluate the physico-chemical characteristics and quality of oil, results are presented in Table-2. On the average the acid value, peroxide value and iodine value of cottonseed oil was found to be 0.57 mg KOH/g, 9.30 meq/kg and 105 g I₂/100 g, respectively (Table-2) while density, saponification value and unspoonifiable matter of linseed oil were 0.912, 193 mg KOH/g and 1.10 mg KOH/g, respectively.

TABLE-2
PHYSICO-CHEMICAL CHARACTERISTICS OF COTTONSEED OIL

Property	Values
Acid value (mg KOH/g of oil)	0.570 ± 0.08
Peroxide value (meq/kg of oil)	9.300 ± 0.24
Iodine value (g I ₂ /100 g of oil)	105.000 ± 3.00
Density	0.912 ± 0.01
Saponification value (mg KOH/g of oil)	193.000 ± 2.46
Unspoonifiable matter (mg KOH/g of oil)	1.100 ± 0.09

Note: All the experiments were performed thrice and results are presented as mean ± standard deviation

Comparative CSOFAME's yield using NaOH, KOH and NaOCH₃ as catalyst: Using each alkaline catalyst 30 experiments were executed to assess and compare the effect of specified reaction parameters according to central composite response surface (CCRD) design on transesterification of cottonseed oil to produce cottonseed oil fatty acid methyl esters.

The comparison of cottonseed oil fatty acid methyl esters % yield using three different catalysts *i.e.*, NaOH, KOH and NaOCH₃ for 30 runs is given in Fig. 1. Experimental results regarding the % biodiesel yield clearly summarized the effect of different reaction variables on transesterification reaction and the variation in the % yield of cottonseed oil fatty acid methyl esters.

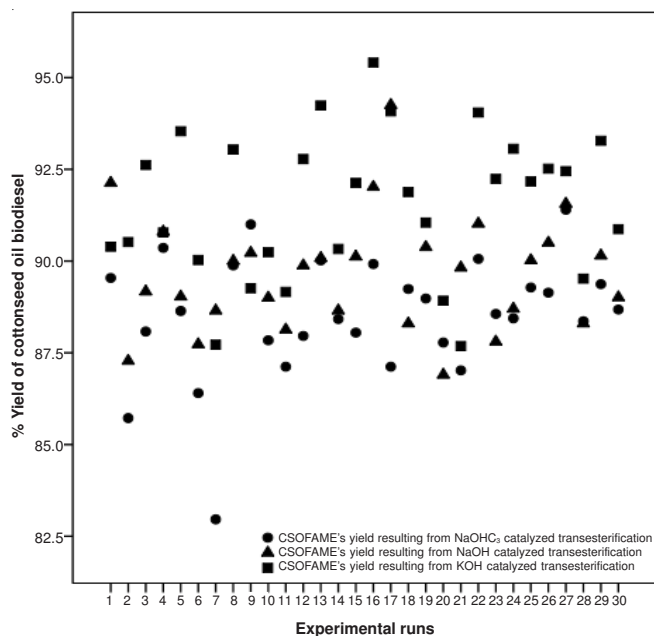


Fig. 1. Comparison of cottonseed oil biodiesel yield using NaOH, KOH and NaOCH₃ as catalysts

FTIR analysis was also performed for monitoring transesterification reaction of cottonseed oil and comparative description was ascertained using FTIR spectrum of cottonseed oil and the cottonseed oil biodiesel. The presence of IR bands in the region 1447-1425 cm⁻¹ for CH₃ asymmetric bending and 1200-1188 for O-CH₃ stretching in cottonseed oil biodiesel IR spectrum clearly depicted the conversion of triglycerides to fatty acid methyl esters, while these IR band were found to be absent in IR spectrum of cottonseed oil. Results were in accordance with the previous studies^{19,21-25}.

Discriptive statistics of biodiesel yield (%) after transesterification of cottonseed oil: When compared the catalytical behaviour of NaOH, KOH and NaOCH₃ toward transesterification of cottonseed oil, NaOCH₃ was found to give best results among the three as for as maximum conversion of cottonseed oil to cottonseed oil fatty acid methyl esters (CSOFAME's) is concerned. The maximum conversion *i.e.* 95.41 % was observed using NaOCH₃ while for KOH and NaOH the maximum % yield of CSOFAME's was 94.25 and 91.40 %, respectively (Table-3). The average % yield of CSOFAME's using NaOH, KOH and NaOCH₃ along with their standard deviation is summarized in Table-3. Based upon maximum conversion of cottonseed oil to cottonseed oil biodiesel, the increasing order of CSOFAME's production using three alkaline catalysts was found to be NaOCH₃ > KOH > NaOH, results were comparable to the findings of Leung and Guo²⁶. Based upon % yield of cottonseed oil biodiesel, NaOCH₃ was found to give better results as compared to NaOH and KOH, this may be because

of the fact that NaOCH₃ usually dissociate into Na⁺ and CH₃O⁻ without water formation as a byproduct, whereas, NaOH and KOH produce sodium/potassium methoxide along with water when dissolved in methanol. In turn, soap formation take place because of the reaction between water and Na⁺ and K⁺ ions while using NaOH and KOH as catalysts for transesterification²⁷.

TABLE-3
DISCRIPTIVE STATISTICS OF BIODIESEL YIELD (%) OBTAINED AFTER EXPERIMENTATION

Name	Analysis	Minimum	Maximum	Mean	SD
Biodiesel yield ^a (%)	Polynomial	82.96	91.40	88.5113	1.67078
Biodiesel yield ^b (%)	Polynomial	86.90	94.25	89.6533	1.58598
Biodiesel yield ^c (%)	Polynomial	87.68	95.41	91.532	1.97232

Biodiesel yield^{a, b & c} represent biodiesel yield using NaOH, KOH and NaOCH₃ as catalysts

Recovery of glycerol was easier when transesterification of cottonseed oil was carried out using NaOCH₃ and KOH as compared to NaOH. The easier recovery of glycerol in case of KOH may be because of softer soap formation than NaOH^{8,26,28,29}.

Based upon the experimental results regarding % yield of CSOFAME's using three catalysts NaOH, KOH and NaOCH₃, analysis of variance ANOVA (Table-4) was carried out to assess the equality of average % yield of CSOFAME's using cottonseed oil as a feedstock.

TABLE-4
TEST OF SIGNIFICANT DIFFERENCE BETWEEN AVERAGE BIODIESEL YIELD ON THE BASIS OF THREE CATALYSTS

Biodiesel yield (%)	Sum of squares	df	Mean square	F	p-value
Between catalysts	139.580	2	69.790	22.765	.000
Within catalysts	266.710	87	3.066	–	–
Total	406.290	89	–	–	–

The *p*-value (0.000 < 0.05) showed that there is significant difference between the average biodiesel yields using three different catalysts. Further post hoc test was applied to check the pairwise significant difference among the average CSOFAME's yields (Table-5). The *p*-values (0.000, 0.000 and 0.013 < 0.05) depicted clearly that significant difference exist between the average CSOFAME's yields while using NaOH & KOH, NaOH & NaOCH₃ and KOH & NaOCH₃ as catalysts.

TABLE-5
PAIR WISE TEST OF SIGNIFICANCE DIFFERENCE BETWEEN AVERAGE CSOFAME'S YIELD (%) USING NaOH, KOH AND NaOCH₃ AS CATALYSTS

Average	Biodiesel yield (%)	Mean difference	Std. error	p-value
1	2	(1-2)		
NaOH	KOH	-1.14200*	.45208	.000
NaOH	NaOCH ₃	-3.02067*	.45208	.000
KOH	NaOCH ₃	-1.87867*	.45208	.013

Optimization study of various reaction parameters was based on selected model and therefore for the selection of suitable model proven fit for the experimental results, Linear, 2F1,

quadratic and cubic models were investigated based upon sequential models testing, lack of fit test and model summary statistics. Among these, quadratic model was suggested fit for the results of present study. The summary statistics of selected quadratic model for three different catalysts NaOH, KOH and NaOCH₃ are given in Table-6.

Quadratic model	C.V. (%)	Press	R-squared	Adj. R-squared
Model ^a	0.68	17.58	0.9320	0.8685
Model ^b	0.77	36.79	0.9027	0.8118
Model ^c	0.44	11.58	0.9781	0.9576

Model^{a,b & c} represent quadratic models used for optimization of biodiesel yield using NaOH, KOH and NaOCH₃ as catalysts

Plot of predicted *versus* actual biodiesel yield (Fig. 2a-c) showed that the difference between the actual and predicted biodiesel yield is very small. It indicates that the model is overall fit for the data. The optimized levels of reaction parameters according to selected quadratic model for optimized/maximum CSOFAME's production are given in Table-7. When NaOH was used as catalyst for base catalyzed transesterification of cottonseed oil, maximum % yield of CSOFAME's was achieved at a catalyst concentration of 0.75 %, when transesterification was performed at 45 °C for 1.5 h using 6:1 methanol to oil molar ratio.

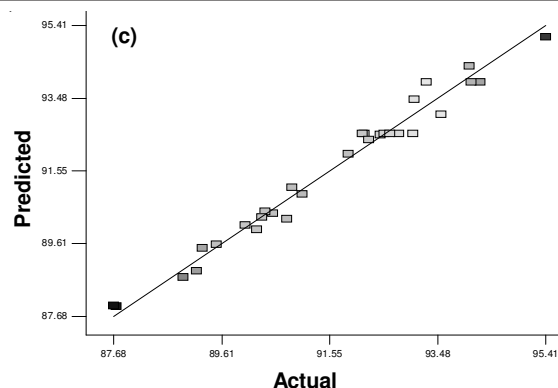
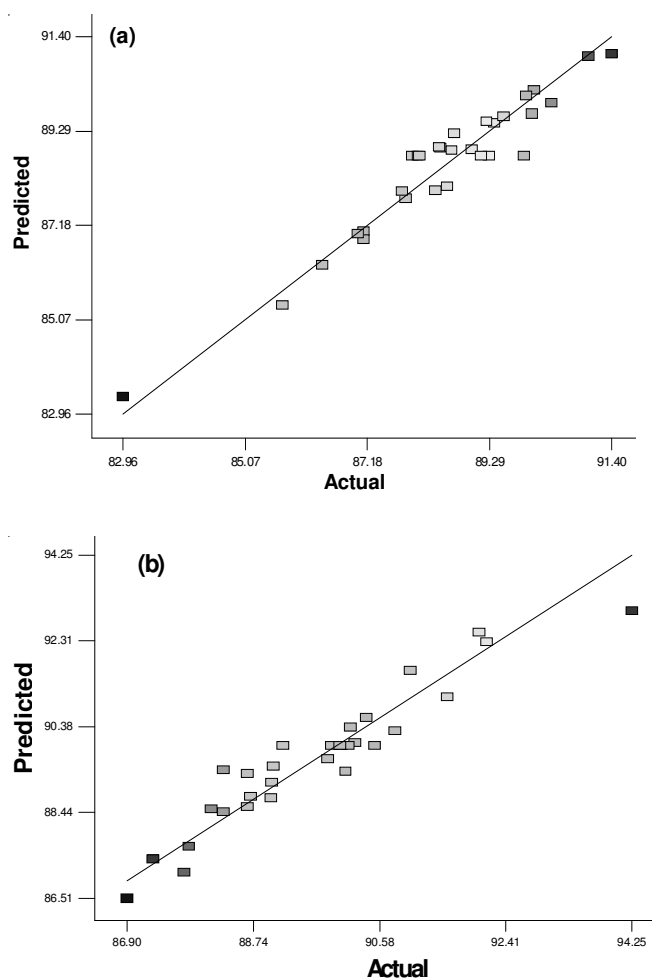


Fig. 2. Plot of predicted *versus* actual values when (a) NaOH (b) KOH and (c) NaOCH₃ was used as catalyst

Catalyst	Catalyst conc. (%)	Reaction time (min)	Reaction temp. (°C)	Methanol: oil molar ratio	Biodiesel yield (%)
NaOH	0.75	90.00	45.00	6.00	91.4
KOH	0.75	60.00	45.00	9.00	94.25
NaOCH ₃	0.50	75.00	52.50	7.50	95.41

On the other hand, when same reaction was executed using KOH as catalyst maximum CSOFAME's yield was obtained at a 0.75 % catalyst concentration, when transesterification was performed at 45 °C for 1 h using 9:1 methanol to oil molar ratio. Whereas the optimized levels of different reaction parameters while using NaOCH₃ as catalyst were found to be 0.50 % catalyst concentration, 75 min reaction time, 52 °C reaction temperature and 7.5:1 methanol to oil molar ratio (Table-7).

Table-8 describes the test of significance of suggested quadratic models a, b and c, main effects, interaction effects and quadratic terms of each model. ANOVA for response surface quadratic model clearly depicts that the *p*-values for testing the model fitness for all three models is less than the level of significance 0.05, means that the quadratic model is fit for the experimental results of transesterification catalyzed by three different alkaline catalysts. For model a, b & c the main effects *i.e.* catalyst concentration, reaction time and methanol:oil molar ratio are found to be significant. Among all first order interaction terms, only catalyst concentration × molar ratio is significant for model a, on the other hand for model b catalyst concentration × molar ratio and reaction temperature × methanol: oil molar ratio are significant, whereas for model c catalyst concentration × reaction time, reaction time × reaction temperature, catalyst concentration × molar ratio and reaction time × methanol: oil molar ratio are found to be significant. Furthermore among quadratic terms only reaction time and methanol: oil molar ratio for model a, catalyst concentration and methanol to oil molar ratio for model b and all quadratic terms for model c are found to be significant.

Response surface plot (Fig. 3a) summarized the effect of catalyst *i.e.* NaOH concentration and methanol: oil molar ratio on the % yield of CSOFAME's. For an increase in levels of catalyst (NaOH) concentration up to 0.75 % while methanol to oil molar ratio up to 6:1, the conversion of cottonseed oil to cottonseed oil fatty acid methyl esters increases and has

TABLE-8
RESPONSE SURFACE QUADRATIC MODEL ANALYSIS OF VARIANCE (ANOVA)TABLE

Source	df	SS (MS) ^a	SS (MS) ^b	SS (MS) ^c	F value (p-value) ^a	F value (p-value) ^b	F value (p-value) ^c	
Model	14	75.45 (5.39)	65.84 (4.70)	110.34 (7.88)	14.68 (0.0001)	9.94 (0.0001)	47.77 (0.0001)	significant
A-catalyst conc.	1	13.67 (13.67)	18.48 (18.48)	0.90 (0.90)	37.24 (0.0001)	39.04 (0.0001)	5.48 (0.0334)	
B-Reaction Time	1	6.50 (6.50)	9.23 (9.23)	7.19 (7.19)	17.71 (0.0008)	19.49 (0.0005)	43.61 (0.0001)	
C-Reaction temp.	1	0.89 (0.89)	0.48 (0.48)	0.33 (0.33)	2.41 (0.1412)	1.02 (0.3291)	1.98 (0.1798)	
D-alcohol: oil molar ratio	1	18.60 (18.60)	20.09 (20.09)	53.28 (53.28)	50.69 (0.0001)	42.45 (0.0001)	322.97 (0.0001)	
AB	1	0.27 (0.27)	0.56 (0.56)	7.45 (7.45)	0.73 (0.4064)	1.17 (0.2960)	45.18 (0.0001)	
AC	1	0.54 (0.54)	0.000 (0.0009)	0.0056 (0.0056)	1.46 (0.2453)	0.001 (0.9658)	0.034 (0.8560)	
AD	1	2.47 (2.47)	2.34 (2.34)	1.03 (1.03)	6.74 (0.0203)	4.95 (0.0419)	6.24 (0.0246)	
BC	1	0.74 (0.74)	0.71 (0.71)	1.50 (1.50)	2.00 (0.1774)	1.49 (0.2410)	9.10 (0.0087)	
BD	1	0.64 (0.64)	0.21 (0.21)	9.83 (9.83)	1.73 (0.2078)	0.45 (0.5139)	59.57 (0.0001)	
CD	1	0.31 (0.31)	4.10 (4.10)	0.004 (0.0049)	0.83 (0.3762)	8.66 (0.0101)	0.030 (0.8655)	
A ²	1	0.89 (0.89)	4.87 (4.87)	20.19 (20.19)	2.44 (0.1395)	10.28 (0.0059)	122.37 (0.0001)	
B ²	1	2.64 (2.64)	0.034 (0.034)	2.20 (2.20)	7.21 (0.0170)	0.071 (0.7935)	13.31 (0.0024)	
C ²	1	0.54 (0.54)	1.25 (1.25)	2.18 (2.18)	1.48 (0.2432)	2.65 (0.1245)	13.23 (0.0024)	
D ²	1	22.56 (22.56)	2.49 (2.49)	4.51 (4.51)	61.48 (0.0001)	5.26 (0.0367)	27.33 (0.0001)	
Residual	15	5.50 (0.37)	7.10 (0.47)	2.47 (0.16)				
Lack of Fit	10	2.23 (0.22)	6.15 (0.61)	1.86 (0.19)	0.34 (0.9303)	3.23 (0.1039)	1.50 (0.3431)	not significant
Pure Error	5	3.27 (0.65)	0.95 (0.19)	0.62 (0.12)				
Cor Total	29	80.95	72.94	112.81				

maximum value 91.4 %, while beyond these levels of NaOH concentration and methanol:oil molar ratio, a decreasing trend in % yield of CSOFAME's is observed. Almost similar trend is observed from response surface plots (Fig. 3b) showing the effect of catalyst (KOH) concentration and methanol to oil molar ratio on % yield of CSOFAME's. Difference was just in the levels of methanol: oil molar ratio and maximum % yield was observed at somewhat higher levels of methanol: oil molar ratio *i.e.* 9:1 while using KOH as a catalyst than NaOH. On the other hand when NaOCH₃ was used to catalyze transesterification of cottonseed oil lesser amount of catalyst *i.e.* 0.5 % was used as compared to NaOH and KOH. Response surface plots (Fig. 3c) also depicts that maximum % yield was achieved at intermediate levels of methanol: oil molar ratio *i.e.* 7.5:1.

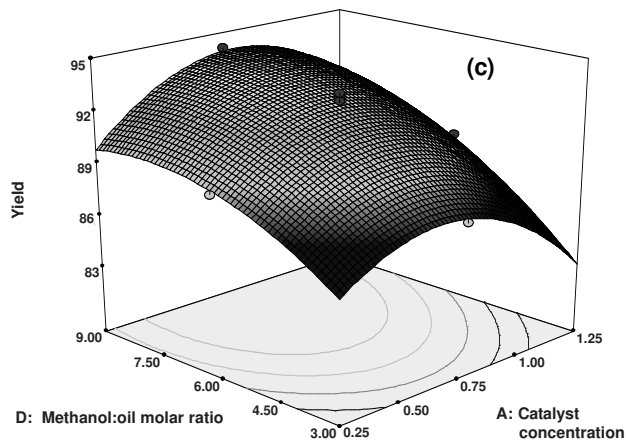
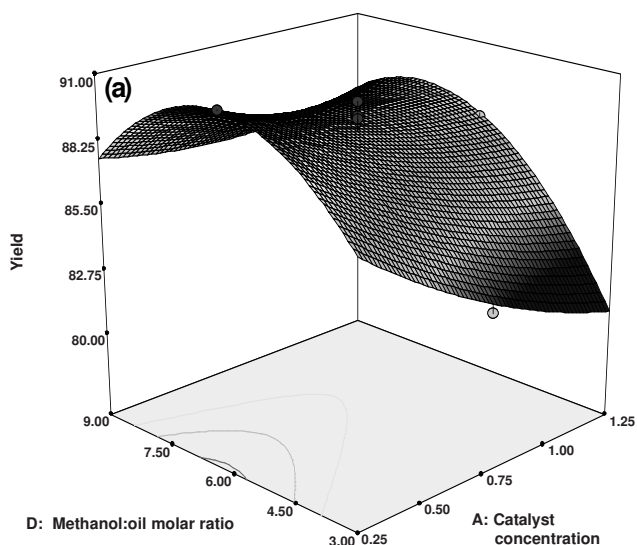
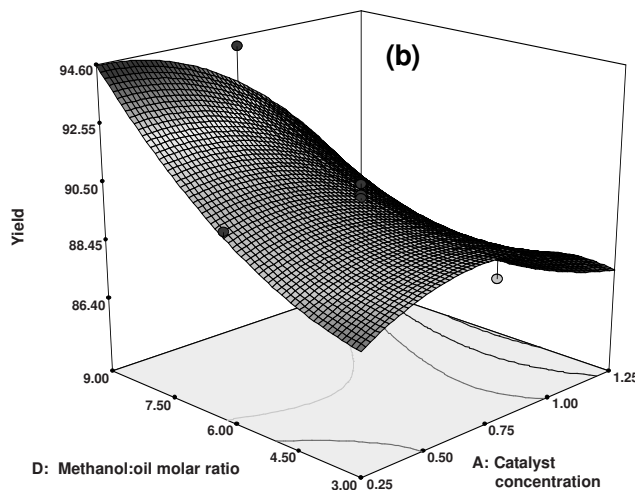


Fig. 3. Response surface plots of CSOFAE'S yield predicted from the model showing the effect of (a) NaOH & methanol: oil molar ratio (b) KOH & methanol: oil molar ratio (c) NaOCH₃ & methanol: oil molar ratio on % yield of CSOFAE'S

TABLE-9
COMPARISON OF FATTY ACID METHYL ESTERS (g/100 g) PROFILE OF COTTONSEED OIL BIODIESEL WITH OTHER BIODIESELS

Fatty acid methyl ester	Retention times	CSOME's	LOME's ²⁹	RSOME's ⁸	RBOME's ¹⁶	SOME's ³⁰
C16:0	14.91	24.0 ± 0.17	4.50	3.50	18.8	11.0
C18:0	18.16	2.39 ± 0.02	4.40	0.90	1.40	4.00
C18:1	19.11	21.2 ± 0.11	17.0	64.4	43.1	22.0
C18:2	20.67	50.0 ± 1.03	15.5	22.3	32.2	53.0
C18:3	-	-	58.6	8.20	1.80	8.00
Others	-	2.39 ± 0.08	-	-	-	-

The values for cottonseed oil methyl esters (CSOME's) are given as mean ± S.D and are compared with other oil FAME's; CSOME's for cottonseed oil methyl esters; LOME's for linseed oil methyl esters; RBOME's for rice bran oil methyl esters; SOME's for Soybean oil methyl esters; RSOME's for rapeseed oil methyl esters

TABLE-10
FUEL PROPERTIES OF COTTONSEED OIL FATTY ACID METHYL ESTERS

Property	Test method	CSOFAME's	Reference value [Ref. 30]
Kinematic viscosity (mm ² /s; 40 °C)	ASTM D 445	5.26 ± 0.12	6.1
Flash point (°C)	ASTM D 93	195 ± 2.75	200
Fire point (°C)	ASTM D 92-05a	201 ± 3.89	-
Cloud point (°C)	ASTM D 2500	-1.0 ± 0.01	-2
Pour point (°C)	ASTM D 97	-3.4 ± 0.04	-5
Sulfur content (%)	ASTM D 4294	traces (< 0.002)	< 0.004

Note: All the experiments were performed thrice and results are presented as mean ± standard deviation.

Final equations in terms of actual factors

Biodiesel yield^a = 82.82094 – 15.96583 (A) + 0.033875 (B) – 0.23181 (C) + 4.61708 (D) – 0.034500 (AB) + 0.097667 (AC) + 1.04833 + 3.25167 (AD) – 0.00190556 (BC) – 0.00886111 (BD) + 0.012278 (CD) + 2.88833 (A²) + 0.00138009 (B²) + 0.00249815 (C²) – 0.40310 (D²).

Biodiesel yield^b = 81.41458 + 9.56 (A) + 0.13742 (B) + 0.19989 (C) – 1.95 (D) + 0.049667 (AB) + 0.004 (AC) – 1.02 (AD) – 0.00187 (BC) – 0.0051 (BD) + 0.045 (CD) – 6.74 (A²) – 0.000156 (B²) – 0.0038 (C²) + 0.13389 (D²).

Biodiesel yield^c = 90.35875 + 26.22333 (A) – 0.00761 (B) – 0.59728 (C) + 0.62806 (D) – 0.18200 (AB) + 0.67667 (AC) + 0.010000 + 0.52000 (AD) + 0.00722 (BC) + 0.034833 (BD) – 0.00156 (CD) – 13.72667 (A²) – 0.001257 (B²) + 0.00501 (C²) – 0.18019 (D²).

Note: Biodiesel yield^{a, b & c} represent biodiesel yield using NaOH, KOH and NaOCH₃ as catalysts, respectively.

GC-MS compositional analysis of cottonseed oil biodiesel: GC/MS analysis of cottonseed oil fatty acid methyl esters (CSOFAME's) is given in Table-9. Major fatty acid methyl esters investigated in cottonseed oil biodiesel (CSOFAME's) mainly consist of palmitic acid methyl ester (C16:0), stearic acid methyl ester (C18:0), oleic acid methyl ester (C18:1) and linoleic acid methyl esters (C18:2) with % composition 24.0, 2.39, 21.2 and 50 %, respectively. GC/MS of cottonseed oil fatty acid methyl esters (CSOFAME's) described that the biodiesel is rich in linoleic acid methyl esters (C18:2) content. For comparison fatty acid esters composition of various biodiesel fuels including linseed oil methyl esters (LOME's), rice bran oil methyl esters (RBOME's), rapeseed oil methyl esters and soybean oil methyl esters is given in Table-9.

Fuel properties of cottonseed oil biodiesel: Experimental results regarding the fuel properties of cottonseed oil fatty acid methyl esters are presented in Table-10. Kinematic viscosity

of the cottonseed oil methyl esters was found to be 5.26 ± 0.12 mm²/s while the average values of flash point, fire point cloud point and pour point were 195 ± 2.75, 201 ± 3.89, -1.0 ± 0.01 and -3.4 ± 0.04 °C respectively, where as sulfur content in cottonseed oil biodiesel was found to be < 0.002 mg/Kg. The fuel properties of the cottonseed oil biodiesel were compared with the findings of Siva Kumar *et al.*¹⁰ given in Table-10. Further the estimated fuel properties of cottonseed oil fatty acid methyl esters were found to be compatible with ASTM biodiesel standard (D 6751a) and European biodiesel standards (EN 14214).

Conclusion

Results of response surface methodology based optimization and comparative studies of biodiesel yields depicted that cottonseed oil is an excellent feedstock for biodiesel production and optimized conversion of triglycerides of cottonseed oil to cottonseed oil fatty acid methyl esters is achieved during 0.5 % NaOCH₃, 75 min reaction time, 52.5 °C reaction temperature and 7.5:1.0 methanol:oil molar ratio.

REFERENCES

1. N. Saifuddin, and B.K.H. Chua, *Malaysian J. Chem.*, **6**, 77, (2004).
2. C.C. Akoh, S.-W. Chang, G.-C. Lee and J.-F. Shaw, *J. Agric. Food Chem.*, **55**, 8995 (2007).
3. P.T. Vasudevan and M. Briggs, *J. Ind. Microbiol. Biotechnol.*, **35**, 421 (2008).
4. W. Du, W. Li, T. Sun, X. Chen and D. Liu, *Appl. Microbiol. Biotechnol.*, **79**, 331 (2008).
5. F. Ma and M.A. Hanna, *A Rev. Bioresour. Tech.*, **70**, 1 (1999).
6. M.H. Chakrabarti and R. Ahmad, *J. Bot.*, **40**, 1153 (2008).
7. A. Singh, B. He, J. Thompson and J. Van Gerpen, *Appl. Eng. Agric.*, **22**, 597 (2006).
8. Y.C. Sharma, B. Singh and S.N. Upadhyay, *Fuel*, **87**, 2355 (2008).
9. U. Rashid, F. Anwar and G. Knothe, *Fuel Proces. Technol.*, **90**, 1157 (2009).
10. A.S. Kumar, D. Maheswar and K.V.K. Reddy, *Jordan J. Mech. Indust. Eng.*, **3**, 190 (2009).
11. D. Royon, M. Daz, G. Ellenrieder and S. Locatelli, *Bioresour. Technol.*, **98**, 648 (2007).

12. S.C. Capareda, J. Powell and C. Parnell, Engine Performance and Exhaust Emissions of Cottonseed oil Biodiesel. Beltwide Cotton Conferences, Nashville, Tennessee, January 8-11 (2008).
13. F. Karaosmanoglu, M. Tuter, E. Gollu, S. Yanmaz and E. Altintig, *Energy Sources*, **21**, 821 (1999).
14. R.H. Myers and D.C. Montgomery, Response Surface Methodology Process and Product Optimization using Designed Experiments, John Wiley & Sons, Inc., edn. 2. (2002).
15. U. Rashid and F. Anwar, *Energy Fuels*, **22**, 1306 (2008).
16. U. Rashid, F. Anwar, T.M. Ansari, M. Arif and M. Ahmad, *J. Chem. Technol. Biotechnol.*, **84**, 1364 (2009).
17. J.M. Encinar, J.F. Gonzalez, J.J. Rodriguez and A. Tejedor, *Energy Fuels*, **16**, 443 (2002).
18. U. Rashid and F. Anwar, *Fuel*, **86**, 265 (2008).
19. M.A. Dube, S. Zheng, D.D. McLean and M.A. Kates, *J. Am. Oil Chem. Soc.*, **8**, 599 (2004).
20. F. Anwar, R. Naseer, M.I. Bhangar, S. Ashraf and F.N. Talpur, *J. Am. Oil Chem. Soc.*, **85**, 321 (2008).
21. N. Siatis, G.C.S. Kimbaris, P.A. Tarantilis and M.G. Polissiou, *J. Am. Oil Chem. Soc.*, **83**, 53 (2006).
22. I.T. Soares, F.R. Thais, C.S. Renzo, C.E. Fortes and C.P. Isabel, *Energy Fuels*, **22**, 2079 (2008).
23. J.S. Oliveira, R. Montalvao, L. Daher, P.A.Z. Suarez and J.C. Rubim, *Talanta*, **69**, 1278 (2006).
24. G.F. Zagonel, P.G. Peralta-Zamora and L.P. Ramos, *Talanta*, **63**, 1021 (2004).
25. M. Younas, Organic Spectroscopy and Chromatography, Ilmi Kitab Khana, Lahore, Pakistan, edn. 2, p.73 (2007).
26. D.Y.C. Leung and Y. Guo, *Fuel Proc. Technol.*, **87**, 883 (2006).
27. N. Ellis, F. Guan, T. Chen and C. Poon, *Chem. Eng. J.*, **138**, 200 (2008).
28. Y.C. Sharma and B. Singh, *Fuel*, **87**, 1740 (2008).
29. J.W. Czerkawski, K.L. Blaxter and F.W. Wainman, *Br. J. Nutr.*, **20**, 485 (1966).
30. B.R. Moser, M.J. Haas, J.K. Winkler, M.A. Jackson, S.Z. Erhan and G.R. List, *Eur. J. Lipid. Sci. Technol.*, **109**, 17 (2007).