Electronic Supplementary Material (ESI) for RSC Advances.

Successive optimisation of waste cooking oil transesterification in a continuous microwave assisted reactor

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Supplementary data

A microwave oven, LG wavedom model (MS-2384B, 900W 2450Hz, 220V South Korea) was adapted as reactor (Fig. 1). The output microwave power is adjustable from 180 to 900 watts. Two holes (12 mm diameter) were made on top of the microwave oven for inlet and outlet connection of Teflon tube. The reactor is made of a 5 m Teflon tube with inner diameter of 9 mm, outside diameter of 12 mm. The volume of the reactor inside the microwave oven is 318 ml. Fig. 2 shows the Teflon coil arrangement inside the microwave chamber. One temperature sensor was placed in the middle of the microwave chamber. The other two temperature sensor was installed in inlet and outlet of the reactor.

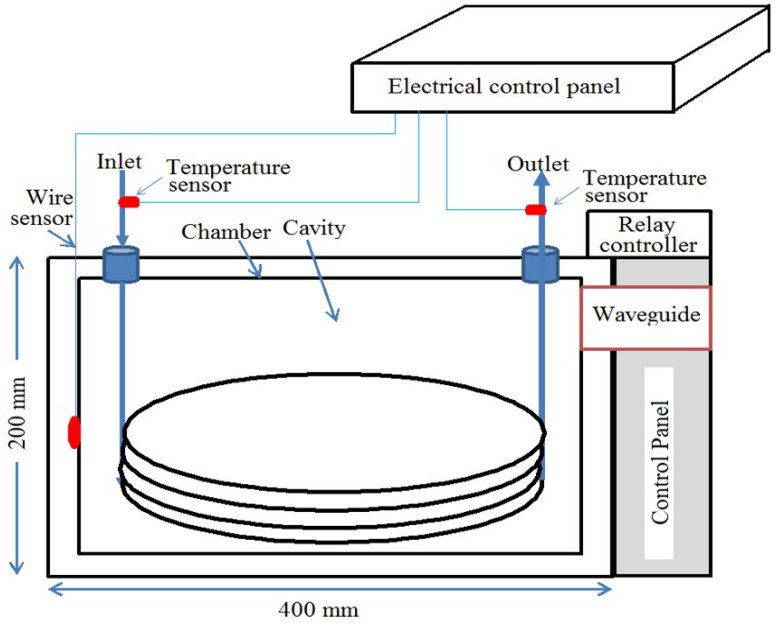

Fig. 1. Schematic of LG microwave cavity, waveguide and Teflon position

Fig. 2. Teflon coil tube inside microwave cavity

The output range of the solenoid metering pump is 1.94 ml/stroke with a back pressure of 1 bar. The Beta ® b BT4b pump was operated at 180 strokes/minute using 100% stroke length. To ensure the accuracy of liquid pumping rate the pump was calibrated from 1 to 6 minute. The calibration plot in Fig. 2 shows a perfectly linear line with $R^2 \approx 1$, indicating that the pumping rate is stable and accurately measured.

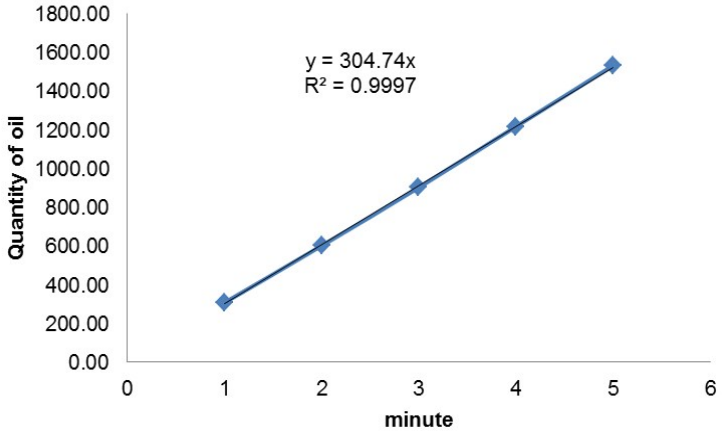

Fig. 3. Calibration of Prominent b4 metering pump

The WCOME composition was determined according to ASTM D6584 method. The fatty acid methyl esters content in the sample was quantified by comparing the peak areas percentage obtained by GC-MS. The most common FAME and the systemitic name were found in WCO are Lauric (Dodecanoic), Myristic (Tetradecanoic), Palmitic (Hexadecanoic), Palmitoleic (Cis-9- Hexadecanoic), Stearic (Octadecanoic), Oleic (Cis-9-Octadecenoic), Linoleic (Cis-9-cis-12-Octadecadienoic, Linolenic (Cis-9-cis-12-cis-15 Octadecatrienoic) and Arachidic (Eicosanoic). The methyl esters standard from Sigma-Aldrich was prepared in the concentration ranging from 0.6 – 47.2 µl ml^{-1} to develop a calibration curve. The sample was prepared by mixing 50 µL of methyl ester diluted with 950 µL of n-hexane. The syringe and vial was rinsed thoroughly with clean n-hexane before use to avoid sample contamination. The sample was mixed thoroughly by shaking before use. Then, use the dispensed syringe and filtered the sample through 0.45 µm nylon into the GC vial before analysis by GCMS. The sample of 0.1 µL was injected in the GC-MS for analysis the methyl ester. The GC chromatogram of WCOME is shown in Fig. 4 and the calibration curve is shown in Fig. 5. The GC calibration shows $R^2 > 0.986$.

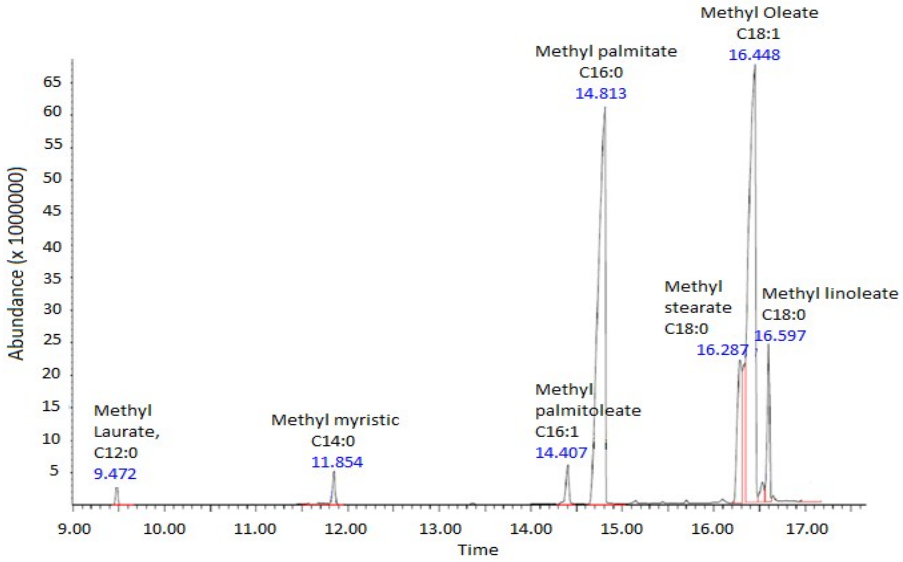

Fig. 4. GC chromatogram of WCOME

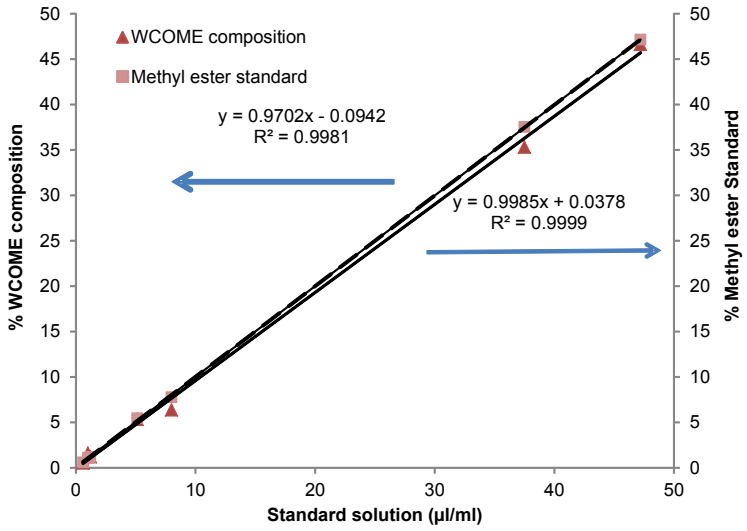

Fig. 5. Calibration curve of WCOME by GC-MS

Table 1: Calibration data from GC

Fatty acid	Systematic Name	Short Name	Amount Standard solution (µL) dilute in n-Hexane	% WCOME Composition	% Standard solution in GC
Lauric	Dodecanoic	C12:0	0.60	0.53	0.59
Myristic	Tetradecanoic	C14:0	1.40	1.22	1.2
Palmitic	Hexadecanoic	C16:0	42.40	35.32	37.53
Palmitoleic	Cis-9- Hexadecanoic	C16:1	1.90	1.59	1.07
Stearic	Octadecanoic	C18:0	5.13	5.32	5.45
Oleic	Cis-9-Octadecenoic	C18:1	47.50	46.62	47.14
Linoleic	Cis-9-cis-12-Octadecadienoic	C18:2	10.00	6.37	7.76
R^2 = 0.994				96.97	100.74

Most of the fatty acids in the WCO are made up of 12 to 24 carbon atoms with different atomic bonding. In this work the most abundance fatty acid are 12 to 20 was obtained using GCMS. The molecular weight of WCO was calculated using equation [MW = 14.027C – 2.016d + 31.9988], where; C is the number of carbon and d is the amount of bonding.

Table 2: Fatty acid in standard vegetable oil.

Fatty acid	**Short name**	**Chemical structure**	**Molecular weight**
Lauric	C12:0	$CH_3(CH_2)_{10}COOH$	200.32
Myristic	C14:0	$CH_3(CH_2)_{12}COOH$	228.38
Palmitic	C16:0	$CH_3(CH_2)_{14}COOH$	256.43
Palmitoleic	C16:1	$CH_3(CH_2)_5CH=CH(CH_2)_7COOH$	254.41
Stearic	C18:0	$CH_3(CH_2)_{16}COOH$	284.48
Oleic	C18:1	$CH_3(CH_2)_7CH=CH(CH_2)_7COOH$	282.47
Linoleic	C18:2	$CH_3(CH_2)_4CH=CHCH_2CH=CH(CH_2)_7COOH$	280.45
Linolenic	C18:3	$CH_3CH_2CH=CHCH_2CH=CHCH_2CH=CH(CH_2)_7COOH$	278.44
Arachidic	C20:0	$CH_3(CH_2)_{18}COOH$	312.54

The density value (ASTM D5002) was determined using DA-130N Kyoto Electronic at room temperature (25 ^oC). Triplicate experiment was run of each sample. Viscosity bath, Cole-Parmer with cannon glass capillary viscometer was used to measure the kinematic viscosity at 40 °C (ASTM D445). The kinematic viscosity is expressed as follows:

$$KV\left(\frac{mm^2}{s}\right) = (Average\ of\ effux\ time, s)\ x\ (Viscosity\ Constant, \frac{mm^2}{s^2})$$

Cloud point and pour point (ASTM D2500) was measured using Spark-proof freezer (Koehler model). Pensky-Martens Flash Point Tester: PM 4 closed cup model was used to measure the flash point according ASTM D93. The acid value was obtained using Potentiometric titrators, 785 DMP titrino (metrohm) according to ASTM D664.

Table 3: Properties of WCO methyl esters

Properties	Units	ASTM	Limits	This work
Density	(g/cm^3)	D5002	0.82 - 0.9	0.893
Kinematic Viscosity, 40°C	mm^2/s	D445	1.9 - 6.0	4.52
Cloud point	^{o}C	D2500	-3 to 12	12
Pour point	^{o}C	D97	-15 to 10	-2
Flash point	°C	D93	> 130	128
Acid value	(mg KOH/g)	D664	< 0.50	0.87

The OFAT experiment is a traditional method and most commonly used. The experiment was carried out by changing one factor while fixing the others at the certain time level. In this work, the effect of five independent variables, namely the catalyst loading, methanol to oil molar ratio, reaction time, temperature and microwave irradiation power on the yield and conversion of biodiesel was studied. The conditions studied were the ratio of methanol to WCO (from 4:1 to 12:1 mol/mol), $NaOCH_3$ catalyst loading (from 0.5 to 1.5 wt.%), reaction temperature (from 60 °C to 70 °C), microwave irradiation power (from 180 W to 900 W) and reaction time (from 4 to 8 min). The range of variable was selected based on the literature review. Results from the OFAT study are shown in Fig. 6.

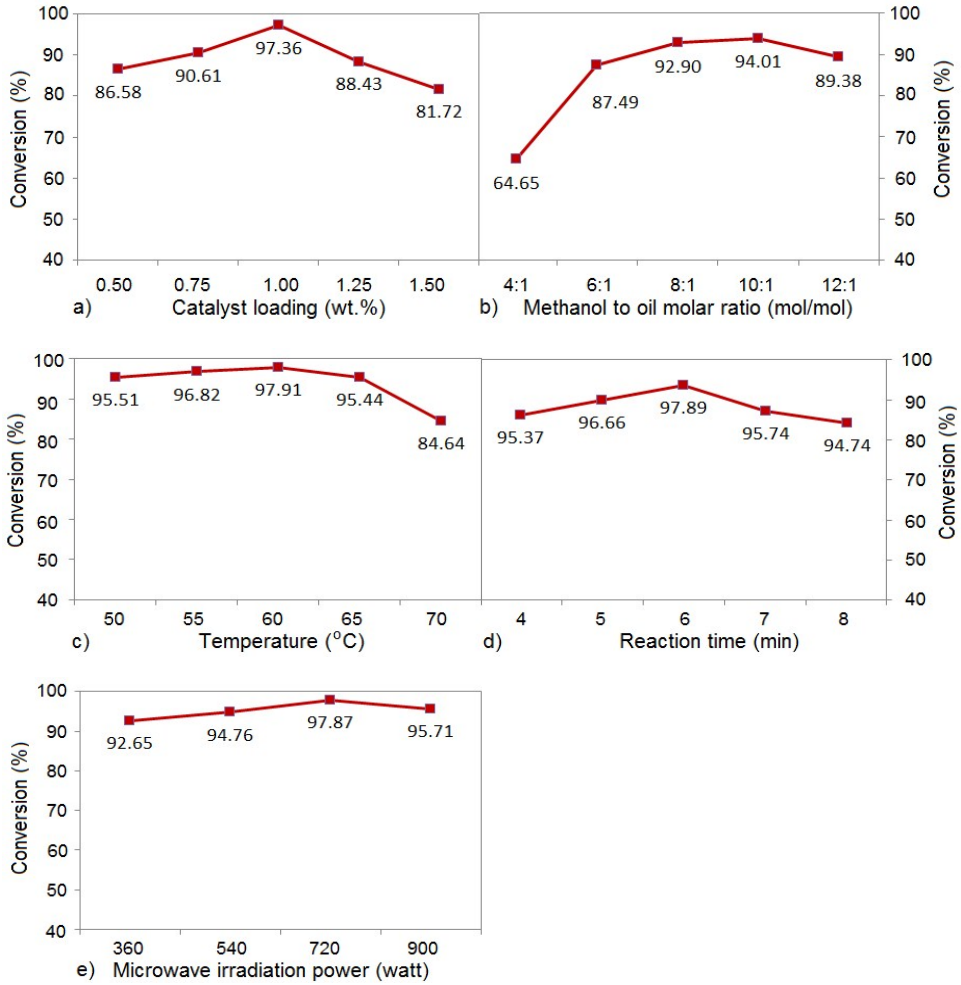

Fig. 6. Effects of a) catalyst loading, b) methanol to oil molar ratio, c) temperature, d) reaction time, and e) microwave irradiation power on biodiesel conversion under nominal parametric settings

Two level factorial (2LF) data

The independent variables such as catalyst loading, x_1 (from 0.75 to 1.25 wt.%), methanol to oil molar ratio, x_2 (from 8:1 to 12:1), reaction time, x_3 (from 5 to 7 min), temperature, x_4 (from 55 to 65 °C) and microwave irradiation power, x_5 (from 540 to 900 W) in this work were chosen based on One Factor at One Time (OFAT) studies.

Table 4: Independent variable and code for two-level factorial

Variable	Unit	Symbol	Coded levels		
			α = -1	α = 0	α = +1
Catalyst loading	wt. %	x_1	0.75	1.00	1.25
Methanol to oil molar ratio	mol	x_2	8	10	12
Reaction time	min	x_3	5	6	7
Temperature	^oC	x_4	55	60	65
Irradiation power	Watt	x_5	540	720	900

Table 5: Experimental matrix for two-level factorial design

Run	x_1 Catalyst Loading	x_2 Methanol to Oil Molar Ratio	x_3 Reaction Time	x_4 Temperature	x_5 Microwave Irradiation Power	Y, Conversion
	(wt. %)	(mol/mol)	(min)	(^oC)	(Watt)	(wt. %)
1	0.75(-1)	8(-1)	5(-1)	55(-1)	900(+1)	94.40
2	1.25(+1)	8(-1)	5(-1)	55(-1)	540(-1)	93.07
3	0.75(-1)	12(+1)	5(-1)	55(-1)	540(-1)	97.26
4	1.25(+1)	12(+1)	5(-1)	55(-1)	900(+1)	92.67
5	0.75(-1)	8(-1)	5(-1)	65(+1)	540(-1)	93.04
6	1.25(+1)	8(-1)	5(-1)	65(+1)	900(+1)	94.26
7	0.75(-1)	12(+1)	5(-1)	65(+1)	900(+1)	97.44
8	1.25(+1)	12(+1)	5(-1)	65(+1)	540(-1)	93.61
9	0.75(-1)	8(-1)	7(+1)	55(-1)	540(-1)	88.64
10	1.25(+1)	8(-1)	7(+1)	55(-1)	900(+1)	89.29
11	0.75(-1)	12(+1)	7(+1)	55(-1)	900(+1)	96.68
12	1.25(+1)	12(+1)	7(+1)	55(-1)	540(-1)	95.26
13	0.75(-1)	8(-1)	7(+1)	65(+1)	900(+1)	89.29
14	1.25(+1)	8(-1)	7(+1)	65(+1)	540(-1)	93.31
15	0.75(-1)	12(+1)	7(+1)	65(+1)	540(-1)	97.25
16	1.25(+1)	12(+1)	7(+1)	65(+1)	900(+1)	94.71

Box-Behnken design model

Following the result from 2LF study, the most significant effects were chosen for the response surface method to determine the optimum biodiesel conversion. The chosen range for parameters x_1, x_2 and x_3 were 0.60 to 0.90 wt.%, 11:1 to 13:1 and 4 to 6 min respectively. The quadratic model was suggested in sequential model sum of squares.

Table 6: Sequential model sum of squares

Source	Sun of squares	df	Mean square	F value	p-value	
Mean	128000	1	128000			
Linear	41.29	3	13.76	1.98	0.1750	
2FI	2.31	3	0.77	0.083	0.9673	
Quadratic	70.30	3	23.43	31.41	0.0011	Suggested
Cubic	1.53	3	0.51	0.46	0.7384	Aliased
Residual	2.20	2	1.10			

Total	128100	15	8538.09

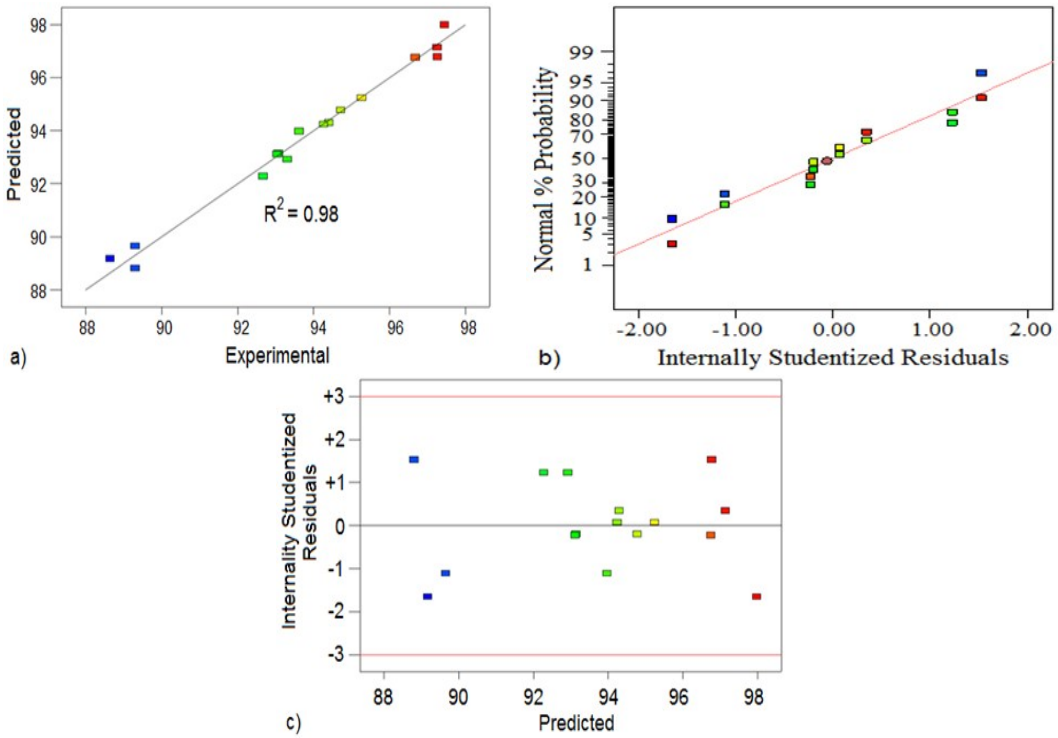

Fig 7. Two-level factorial design model a) Experimental versus predicted values b) Normality probability plot of residual for percentage conversion and c) Plot of residual versus predicted response

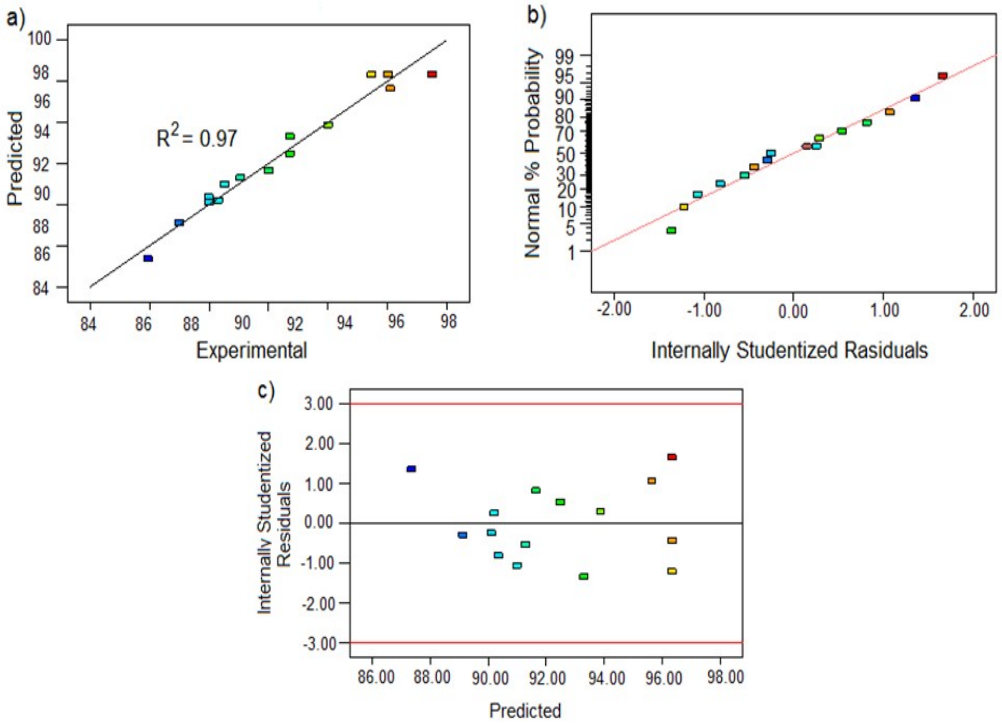

Fig 8. Box Behnken design model a) Experimental versus predicted values b) Normality probability plot of residual for percentage conversion and c) Plot of residual versus predicted response

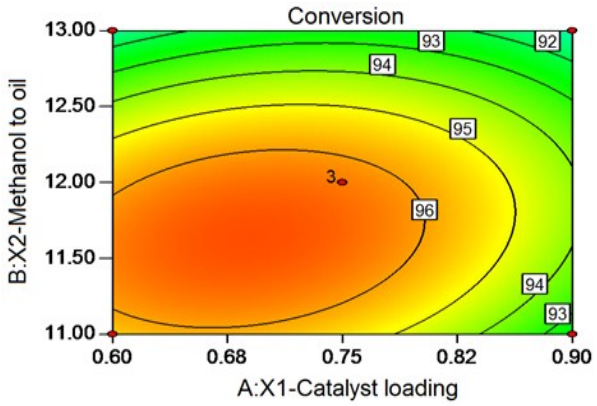

Fig. 9. 2D contour plot on effect of catalyst loading (X_1) versus methanol to oil (X_2) molar ratio at fixed reaction time 4.47 min

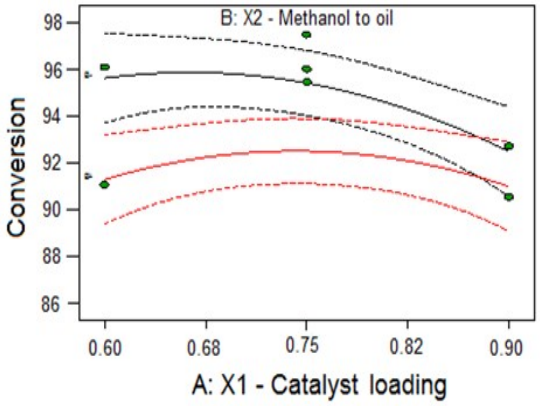

Fig. 10. Interaction on effect of catalyst loading (X_1) versus methanol to oil (X_2) molar ratio at fixed reaction time 4.47 min.

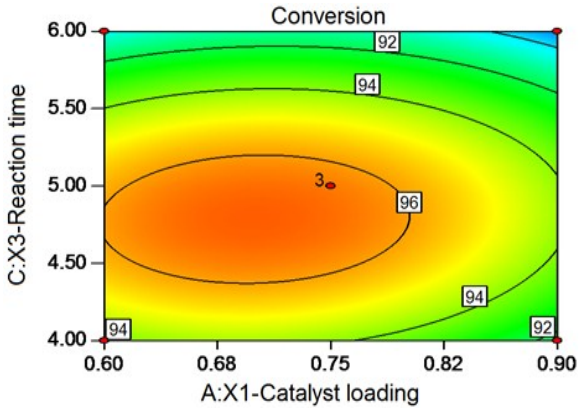

Fig. 11. 2D contour plot on effect of catalyst loading (X_1) versus reaction time (X_3) at fixed methanol to oil molar ratio, 11.62:1

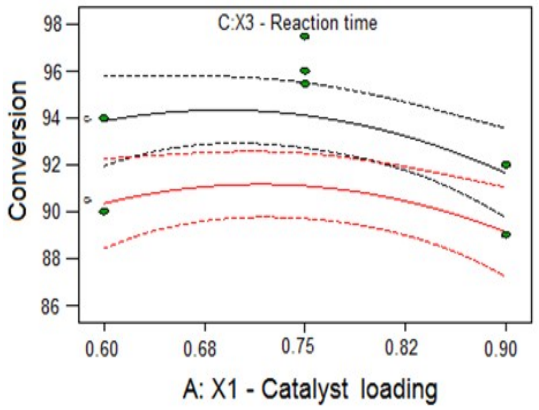

Fig. 12. Effect of catalyst loading (X_1) versus reaction time (X_3) at fixed methanol to oil molar ratio, 11.62:1; a) 2D contour plot and b) Interaction of catalyst and reaction time

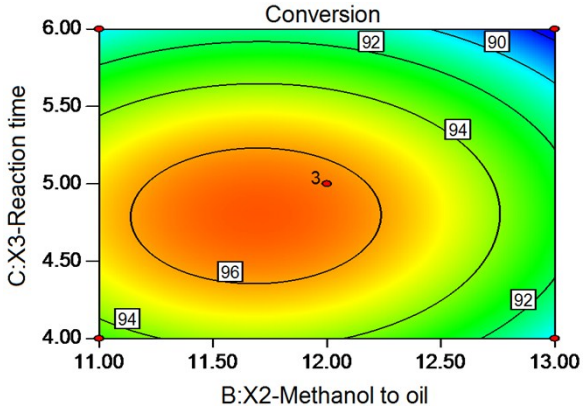

Fig. 13. 2D contour plot on effect of methanol to oil molar ratio (X_2) versus reaction time (X_3) at catalyst loading, 0.68 wt. %.

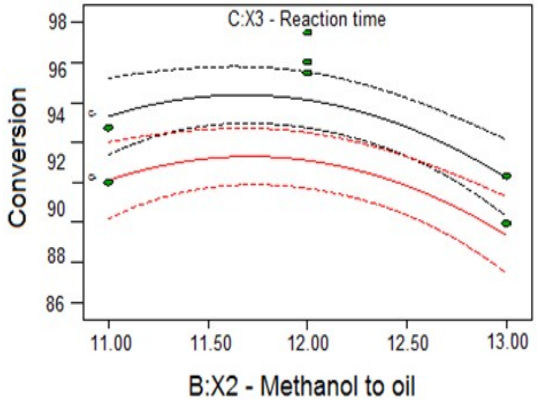

Fig. 14. Effect of methanol to oil molar ratio (X_2) versus reaction time (X_3) at catalyst loading, 0.68 wt. %.; a) 2D contour plot and b) Interaction of methanol to oil and reaction time

Fig. 15 is generated from Box-Behnken data shown in Table 3 of the manuscript. The optimisation target was to obtain the maximum WCO conversion to biodiesel.

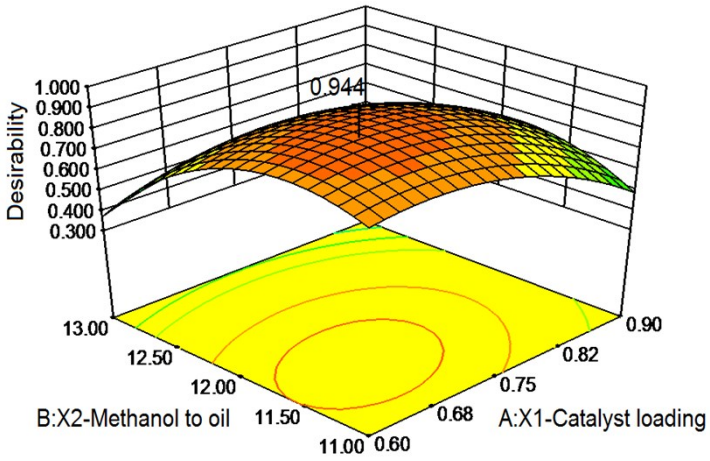

Fig. 15. Optimization surface plot