MICROWAVE ASSISTED BATCH AND CONTINUOUS TRANSESTERIFICATION OF KARANJA OIL: OPTIMIZATION OF PROCESS PARAMETERS

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ABSTRACT:

Biodiesel or fatty acid methyl ester has been used as alternative fuel to mineral diesel. Use of microwave energy for biodiesel synthesis is a new technology and is reported to offer several advantages over other techniques. In the present investigation, a non-Edible oil, Karanja or Pongamia oil was selected as feed stock for biodiesel synthesis under microwave irradiation. Based on the literature optimized process parameters of catalytic oil ratio and irradiation time for the fixed volume, Karnja Biodiesel was successfully synthesized in a microwave assisted batch process. Further the effect of volume of the reaction mixture on irradiation time and irradiation power on the yield of biodiesel were investigated and discussed in detail. Response surface methodology (RSM) was applied for the optimization of the variables. Biodiesel was also successfully synthesized in a continuous reactor having the hold up of 160ml. The effect of different process parameters like irradiation time, irradiation power and methanol to oil ratio were studied in detail and optimization studies were carried out by using Box-bhenken experimental design. The important properties of the biodiesel like Ester content, density, viscosity, Acid value and Cetane index were analysed and found to be within the limits of ASTM D6751-09 standards.The results showed that the reaction time was reduced to a great extent (up to 6.4 min.) when compare to conventional heating methods (60 min), which enable the continuous conversion process under Microwave irradiation.

Keywords: Biodiesel, Microwave irradiation, Continuous Transesterification, Response Surface Methodology (RSM)

INTRODUCTION

Biodiesel is a mixture of mono alkyl esters of long chain fatty acids, an alternative fuel which resembles the diesel fuel that is derived from triglycerides found in the oils, animal fats or used cooking oils. By transesterification [Shay, 1993; Agarwal, 2004) of these triglycerides with alcohol (methanol or ethanol) in the presence of a homogeneous or heterogeneous catalyst (alkali or acid) or without catalyst to chemically break the molecule of Triglyceride, the biodiesels are produced. Major feed stocks used for the production of biodiesel include the edible oils like rapeseed (Jeong and Park, 1996) sunflower (Vicente et al., 2004) , palm oil (Darnoko and Cheryman, 2000) and soybeans (Oliveira et al., 2005). To make the production inexpensive and for better food security, low cost oils like waste vegetable oils (Felizardo et al., 2005) and non-edible oils like Jatropha, Pongamia pinnata (Karmee and Chadha, 2005) and tigernut oil (Ugheoke et al. 2007) have been intensively investigated as potential low priced biodiesel sources. Biodiesel made from these feed stocks was predicted to be more economical than the biodiesel produced from refined vegetable oil. In India, Karanja (Pongamia pinnata) is a forest based non-edible oil plant, with an annual production potential of 135,000 million tones (Srivastava and Prasad, 2000) makes it a good feed stock for the biodiesel production. The problem with the usage of karanja oil for biodiesel synthesis is its high free fatty acid content (FFA) which requires a pretreatment step (esterification) in order to reduce the FFA content below 1%, so that the alkali transesterification can be utilized to synthesize the end product (biodiesel), which is capable of meeting the ASTM standards.

Normally biodiesel is synthesized in conventional mode (Meher et al., 2005) both in batch wise and continuous manner but there are problems with the mass transfer limitations, equilibrium nature of the reaction and costs associated with the production. In order to avoid those problems different technologies were used for the synthesis of biodiesel which includes lipase catalyzed method (Lai et al., 2005), supercritical methanol (Demirbas, 2005), ultrasonic method (Fan et al., 2010), static mixers(Thompson and He, 2007), micro channel reactors (Kobayashi et al., 2006), oscillatory flow reactors (Harvey et al., 2003), cavitational reactors (Mancosky et al., 2007), rotating/spinning tube reactors (Lodhar and Jachuck, 2007), membrane reactors (Dube et al., 2007), reactive distillation (Omota et al., 2003), centrifugal contactors (Kraai et al., 2008) and application of microwave irradiation (Breccia et al 1999; Barnard et al., 2007). Application of Microwave irradiation for biodiesel synthesis is more efficient in reducing the time required for the reaction and separation of the products and offers a better way to synthesize biodiesel when compared to conventional mode of heating(Hernando et al., 2007; Refaat et al., 2008).

Major factors of the biodiesel production are %FFA, moisture content, reaction time, temperature, methanol to oil ratio, catalyst type and concentration, and intensity of mixing. The alkali-catalyzed transesterification reaction may able to give the

product when the feed oil's free fatty acid (FFA) value is lower than 3% [Dorado et al, 2002). Non edible oils in general will have a higher percentage of free fatty acids (FFA). Before the non edible oil having higher FFA considered for the transesterification process; the free fatty acids must be pretreated with alkaline or acid catalysts to form esters (Van Gerpen, 2005). In presence of water (> 0.06% w/w), hydrolysis of formed ester takes place and it forms the soap, which reduces the catalyst efficiency and also makes the downstream recovery difficult (Guo and Leung, 2003). Because of their low cost and ease of handling in transportation and storage, KOH and NaOH are used as homogenous alkali catalyst. Both the catalysts KOH (Jeong and Park, 1996; Darnoko and Cheryman, 2000; Ugheoke et al., 2007) and NaOH (Vicente et al., 2004; Oliveira et al., 2005; Felizardo et al., 2006) had given the biodiesel with the best properties. In the conventional method, reaction time in the order of 30 minutes to 2 hours need to be maintain at the temperatures around methanol boiling point. However, higher temperatures decrease the time required to reach maximum conversion (Pinto et al., 2005). Stoichiometric methanol to oil ratio is 3:1, but in general excess alcohol is used in order to shift the equilibrium towards forward direction (product side). For maximum conversion to the ester, a molar ratio of 6:1 was mostly used (Vicente et al., 2004; Darnoko and Cheryman, 2000; Ugheoke et al., 2007). Vigorous mixing is required in order to overcome mass transfer limitations.

The present work describes the microwave assisted batch synthesis of biodiesel by varying the parameters like time of irradiation, catalyst concentration, volume of the reaction mixture, methanol to oil ratio and parameter optimization through central composite design to get maximum yield. Further the continuous studies were performed using PTFE tubular reactor having the hold up of 160 ml, by varying parameters like irradiation power, residence time, catalyst concentration, methanol to oil concentration. The parameters were optimized for maximum yield through Box–Behnken experimental design.

MATERIALS AND METHODS

Materials

Karanja oil was purchased from a local departmental store. Analytical grade methanol (99.8%), KOH pellets and anhydrous sulfuric acid was purchased and they were used as purchased without any further purification.

Experimental setup

Batch studies

Entire batch experiments were conducted in a modified domestic microwave oven (Samsung M183DN), which can be operated with power ranging from 100 to 800W. A round bottom flask of 500ml capacity with a Teflon agitator connected to a motor was used as the batch reactor. Carousel plate was replaced with a Teflon base in such a way that the carousel axis can rotate freely. A hole of 10mm was made at the top of the oven to accommodate the condenser to aid in the reflux of methanol vapors. The experimental setup is as shown in figure 2.1

Karanja oil with 0.8% FFA was used for transesterification. Anhydrous potassium hydroxide(1.2 wt% based on oil weight) was dissolved in methanol (40 wt% based on oil weight) depending on the amount of oil so that the total reaction mixture would be 100ml, 200ml, 300ml, 400ml, and 500ml respectively. The reaction mixture was mechanically agitated at 300 rpm for better dispersion of reactants and it was irradiated for different time periods at an irradiation power of 180W. Immediately after the reaction is over oxalic acid is added to neutralize the remaining potassium hydroxide. The product obtained was allowed to settle into two phases in a separating funnel, upper layer was biodiesel and the lower layer was glycerol. The biodiesel layer was washed with warm water for 3-4 times then dried over anhydrous sodium sulfate and filtered. The quality of biodiesel and triglyceride in karanja oil were analyzed through thermogravimetry (Priyanka et al., 2008; Venkatesh et al., 2011).

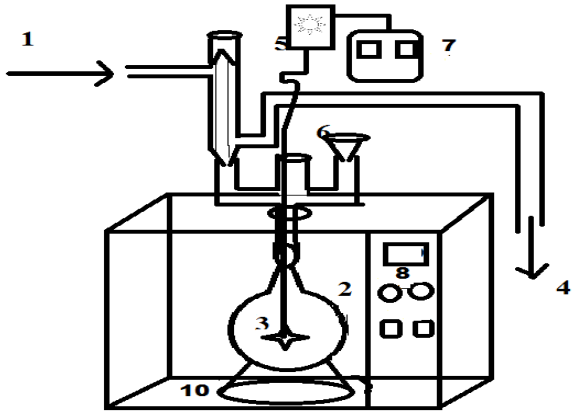

Fig.1 Schematic diagram of domestic microwave oven modified for batch experiments.(1: water inlet, 2: microwave oven, 3:Teflon stirrer, 4: water outlet, 5: motor, 6: three neck adopter: 7: power supply, 8: operating buttons)

In order to optimize the yield a standard RSM (Montgomery, 2001) design called, central composite design (CCD) was applied to study the transesterification reaction variables. This method is suitable for fitting a quadratic surface and it helps to optimize the effective parameters with a minimum number of experiments, as well as to analyze the interaction between the parameters. A five level-four factor central composite design (CCD) consisting of 31 experiments (16 factorial points, 8 axial points and 7 center points), was applied to study the transesterification reaction variables (Usta, 2005; Jeong and Park, 2006). Catalyst amount, volume of the reaction mixture, irradiation time and Methanol/oil ratio was chosen as independent variables in the experiment and the response optimized is yield.

Table 1: Independent variables and levels used for experimental design in batch transesterification step.

Variables	Levels				
	-2	-1	0	+1	2
KOH concentration, C'	1	1.3	1.6	1.9	2.2
Volume of the reaction mixture, V'	100	200	300	400	500
Irradiation time, T'	2	4	6	8	10
Methanol –oil ratio, M'	30	35	40	45	50

Transformation of variables from coded (X) to uncoded is as follows: C'=1.6+0.3X; V'=300+100X; T'=6+2X; M'=40+5X; where X can be -1, 0 or +1

The experimental data obtained by following the above procedures were fit to second order polynomial equation

$$y = \beta o + \sum_{i=1}^{4} \beta_i x_i + \sum_{i=1}^{4} \beta_{ii} x_i^2 + \sum_{i=1}^{3} \sum_{j=i+1}^{4} \beta_{ij} x_i x_j \quad (1)$$

Where y is the response (%FAME Yield); x_i and x_j are uncoded independent variables and β_0, β_i, β_{ii} and β_{ij} are intercept, linear, quadratic and interaction constant coefficients, respectively. The aim was to maximize percentage yield of FAME in transesterification step. Minitab v15 software package was used for regression analysis and analysis of variance (ANOVA). Stepwise elimination of insignificant terms was carried out to obtain statistically significant reduced fit models. Optimal conditions obtained were validated by conducting experiments.

Continuous studies

Continuous experiments were conducted in a modified domestic microwave oven (Samsung TRIO, which can be operated with power ranging from 100W to 900W.The glass plate on the carousel was removed and a stationary ceramic tile cut to the size of the oven was fit into the oven slightly above the carousel axis such that it can rotate freely. The surface on the top of the carousel axis was covered with aluminum foil to avoid randomly reflecting microwave radiation. A hole of 10mm was made at the top of the oven. A poly-tetra-fluoro-ethylene (Teflon) tubing (0.4 cm ID X 1300 cm) was coiled into the oven and connected to the inlet pumps and the outlet reservoir at the back of the oven (as shown in Fig. 2).

Anhydrous potassium hydroxide was dissolved in methanol (based on oil weight) and the solution is transferred in to an oil containing vessel equipped with an agitator, in which the agitation of reactants was done at an rpm of 1200 by means of a mechanical agitator in order to prevent the phase separation. Then the reactants were continuously pumped in to the Teflon tubular reactor situated inside the microwave oven with different flow rates so that irradiation time can be varied. The product is collected continuously for different flow rates at an irradiation power of 180W. The detail procedure may found else were (Venkatesh et al., 2011).

A three level-three factor Box-Behnken design (Montgomery, 2001) consisting of 15 experiments, was applied to study the transesterification reaction variables. Catalyst amount, flow rate and Methanol/oil ratio were chosen as independent variables in the experiment, the coded and un-coded levels of all variables are given in Table 2.

Table 2: Independent variables and levels used for experimental design in continuous transesterification step.

Variables	Levels		
	-1	0	+1
KOH concentration, K	1	1.2	1.4
Flow rate, F (ml/min)	25	50	75
Methanol –oil ratio, M'	30	40	50

Transformation of variables from coded (X) to uncoded is as follows: C=1.6+0.2X; F =50+25X; M=40+10X; where X can be -1, 0 or +1

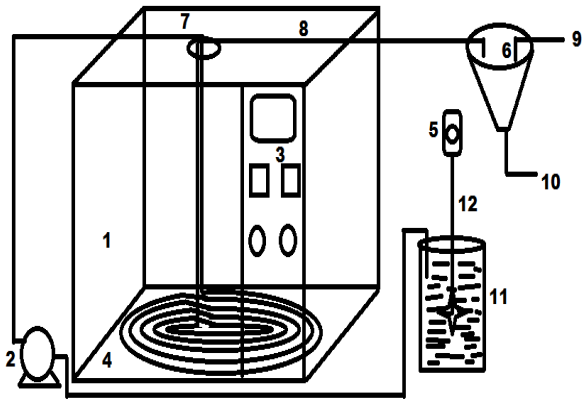

Fig. 2: Schematic diagaram of domestic microwave oven modified for continuous experiments. (1: microwave oven, 2: Pump, 3: operating buttons: 4: PTFE tubular reactor, 5: motor, 6: Separator: 7: inlet, 8: outlet, 9: biodiesel outlet, 10:glycerol outlet, 11:tank, 12: agitator)

RESULTS AND DISCUSSION

Batch studies

Initially the batch studies were performed to understand the effect of various parameters like *irradiation time and power, and volume* on the biodiesel. The process parameters like methanol to oil ratio and KOH concentration were not considered in the present study, since these parameters were extensively studied in the literature (venkatesh, 2011).

Effect of irradiation time for different power

In order to fix the power level for batch studies, reactants volume of 500ml was studied by irradiating it under microwave for different irradiation times and powers (Fig. 3). From the results it was observed that the yield is increasing with increasing irradiation time for all the power levels (180 to 450W) and reached to a saturation yield at around 8 minutes of irradiation time. But the increase in the yield is not that much significant on comparison with the energy supplied to the system. When the power level was increased to 450 Watt, the yield was slightly decreased because of the fact that higher powers drastically increase the reaction temperature, which favors accelerated the saponification reaction of triglycerides (Dorado et al. 2002). Further the yield curve at 180W and 300W are approaching each other during all the irradiation time.

Based on the above results, the further experiments were conducted at a power level of 180 W.

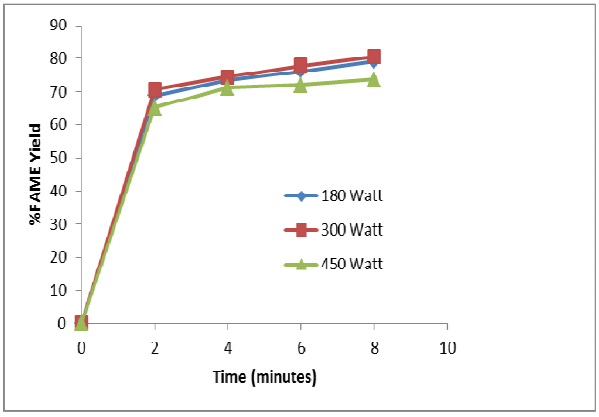

Fig. 3: Effect of irradiation time at different power level for 500ml of the reaction mixture at a fixed methanol to oil ratio of 40% w/w, catalyst concentration 1.2% w/w.

Effect of Volume and Irradiation time

The effect of irradiation time on different volume of reactants were studied in batch mode on the yield of biodiesel at a fixed KOH concentration of 1.2% w/w, methanol to oil ratio of 40% w/w and at an irradiation power of 180W. From the fig. 4 it was observed that the increase in the volume of reactant at a particular irradiation time and power (180W) may reduce the biodiesel yield. Since the microwave heating is a bulk heating process, the required temperature cannot be generated for the whole volume of the reactants due to the limitations in the penetration characteristics and intensity of the microwave, besides the physical properties of the contents of the reaction vessel, both the volume of the contents and geometry of the reaction vessel are crucial to provide uniform and reproducible heating. As the volume increases, whole the reaction mixture is not been effected by the microwave irradiation which decreased the net dielectric heating so that the yield. On the other hand as the irradiation time increases the reaction temperature increases to the required level by convection, which, in turn increases the yield of biodiesel to a maximum of 94.47% for an irradiation time of 8 minutes at 180W. Further it decreased the viscosity of reaction mixture, which makes the entire reaction mixture being exposed to the irradiation. Further increasing the irradiation time didn't improve the yield significantly.

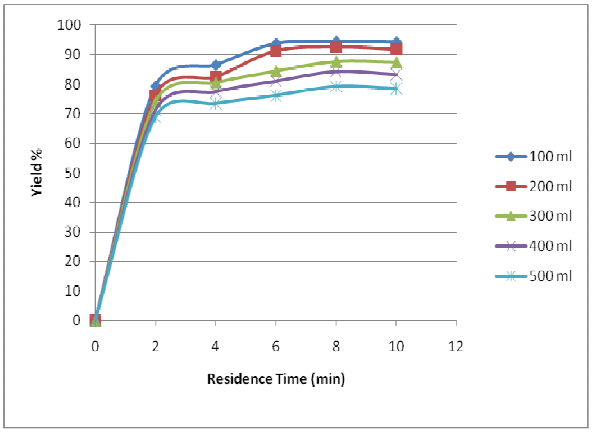

Fig. 4: Effect of irradiation time for different volumes of the reaction mixture at 180W

Continuous studies

As mentioned in the experimental section; a tubular continuous reactor was considered for the production of biodiesel. Based on the batch studies the irradiation time, microwave power, volume of the reactor and catalyst concentrations were fixed for the continuous reactor to study the effect of methanol to oil ratio. Since the dispersion of alcohol into the oil is difficult for the production, the authors expected that the higher methanol to oil ratio may required to obtain a high yield.

Effect of methanol to oil ratio

The effect of methanol to oil ratio is studied on the yield of biodiesel at a fixed KOH concentration of 1.2% w/w in a PTFE tubular reactor of hold up 160ml, for an irradiation power of 100W (Fig. 5) and 180W (Fig.6) respectively. Analysis of the both the Fig. 5 and Fig.6 indicated that, at lower methanol to oil ratio the yield was less due to low quantity of alcohol available. In general, the transesterification reaction is a reversible reaction and excess alcohol is required in order to drive the reaction in the forward direction (product side). Hence the methanol to oil ratio increases the yield increases and it reached a maximum yield of 91.82% at an irradiation time of 8 minutes, power of 180W and methanol to oil ratio of 40% w/w (11:1 molar ratio). Increasing methanol to oil ratio beyond 40% didn't improve the yield. As the residence time increases the yield also increases, due to the lower flow rate.

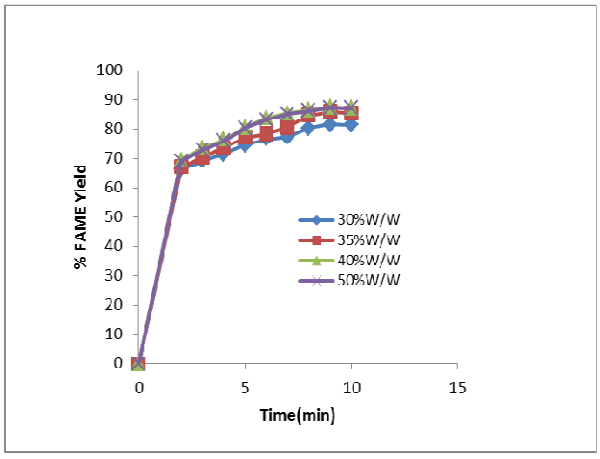

Fig. 5: Effect of methanol to oil ratio at an irradiation power of 100W.

At lower residence time (higher flow rate) the reaction mixture is not allowed to expose to the microwave irradiation for sufficient time in order to get the required dielectric heating to achieve the good yield. As the flow rate decreases or the residence time increases the mixture is well irradiated so that yield increased and got a maximum yield at 8 minutes residence time and increasing the residence time beyond this point didn't improve the yield significantly (Fig. 5 and 6).

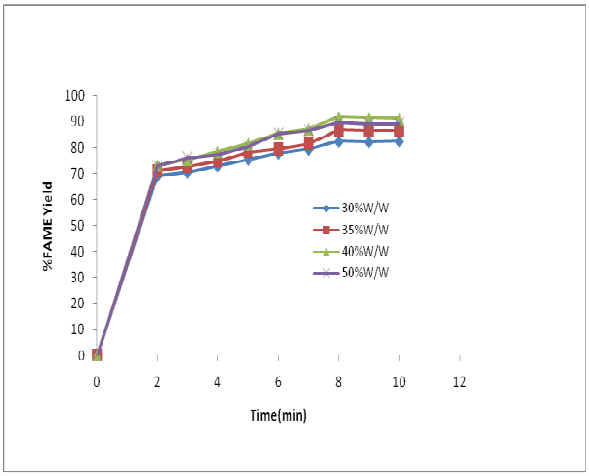

Fig. 6: Effect of methanol to oil ratio at an irradiation power of 180W.

Optimization of Process Parameters

Batch Process

The complete design matrixes together with both the experimental as well as predicted values obtained for yield as response at the design points for batch experimentation by using CCD method are given in Table 3. All the variables are shown in both coded and un-coded (actual) form. Biodiesel yield obtained ranged from 57.49 to 91.47% in batch studies. The experimental data were fit to quadratic polynomial equation through least square technique and statistical analyses were carried out. Upon stepwise elimination of insignificant terms, the significant terms were fit to reduced model.

Regression coefficients of predicted quadratic polynomial after step wise elimination shows (Table: 4) that linear and quadratic term of C, M, V and T are significant model terms in optimizing the yield. Interaction terms have no effect on yield of biodiesel. High coefficient of determination 0.984 shows that model is highly significant. The predicted model can be represented by Eq. (2).
Quadratic polynomial equation developed for batch transesterification is,

$$\%FAMEYield=110.175–37.903C–0.256M–0.086V +6.059T+8.140C^2+0.017M^2+0.00V^2–0.127T^2 \quad (2)$$

The Contour plots are further plotted to study the interaction effect of process parameters on the biodiesel yield in batch process using the eq. (2). The 0 level values for each variable were kept constant to draw the contours between the other variables. Fig. 7 shows the Contour plots for the present system.
In figures 7a, 7b and 7c; as the catalyst concentration increases the yield decreased with decrease in methanol ratio (Fig 7a) with increase in volume of the reaction mixture (Fig.7b) and with decrease in irradiation time (Fig.7c) due to the fact that higher catalyst concentration is more susceptible to soap formation. From the figures 7a, 7d and 7e it was observed that the lower methanol ratios gives less yield with increase in volume (Fig 7d) and with decrease in irradiation time (Fig.7e) due to the equilibrium nature of the reaction. Lower irradiation times are not sufficient to provide the necessary dielectric heating for higher volume, lower methanol ratio, which was evident from Fig.7e and Fig 7f respectively. Further, when the irradiation time was increased for the higher volume of reactant, there will be conventional currents developed in the reaction mixture which makes the system to tend to be homogeneous in terms of heat transfer. Hence the biodiesel yield was improved for larger volumes at higher irradiation times.

Table 3: Central composite experimental design and response for yield obtained through batch transesterification of karanja oil

Std. order	Levels of variable uncoded (coded)				Yield	
	C	M	V	T	Exp.	Predicted
1	1.3(-1)	35(-1)	200(-1)	4(-1)	77.46	76.02
2	1.9(1)	35(-1)	200(-1)	4(-1)	62.47	62.65
3	1.3(-1)	45(1)	200(-1)	4(-1)	82.53	82.52
4	1.9(1)	45(1)	200(-1)	4(-1)	69.16	67.82
5	1.3(-1)	35(-1)	400(1)	4(-1)	71.32	70.54
6	1.9(1)	35(-1)	400(1)	4(-1)	57.49	56.48
7	1.3(-1)	45(1)	400(1)	4(-1)	78.12	77.28
8	1.9(1)	45(1)	400(1)	4(-1)	62.54	61.86
9	1.3(-1)	35(-1)	200(-1)	8(1)	85.27	85.40
10	1.9(1)	35(-1)	200(-1)	8(1)	72.66	71.26
11	1.3(-1)	45(1)	200(-1)	8(1)	91.47	90.24
12	1.9(1)	45(1)	200(-1)	8(1)	74.52	74.75
13	1.3(-1)	35(-1)	400(1)	8(1)	79.54	78.64
14	1.9(1)	35(-1)	400(1)	8(1)	64.35	63.80
15	1.3(-1)	45(1)	400(1)	8(1)	84.47	83.75
16	1.9(1)	45(1)	400(1)	8(1)	68.32	67.54
17	1.0(-2)	40(0)	300(0)	6(0)	87.57	89.07
18	2.2(2)	40(0)	300(0)	6(0)	58.24	59.52
19	1.6(0)	30(-2)	300(0)	6(0)	66.45	67.91
20	1.6(0)	50(2)	300(0)	6(0)	78.86	78.16
21	1.6(0)	40(0)	100(-2)	6(0)	81.27	82.34
22	1.6(0)	40(0)	500(2)	6(0)	67.86	69.60
23	1.6(0)	40(0)	300(0)	2(-2)	60.27	61.82
24	1.6(0)	40(0)	300(0)	10(2)	75.63	76.86
25	1.6(0)	40(0)	300(0)	6(0)	71.43	71.36
26	1.6(0)	40(0)	300(0)	6(0)	70.52	71.36
27	1.6(0)	40(0)	300(0)	6(0)	72.67	71.36
28	1.6(0)	40(0)	300(0)	6(0)	71.89	71.36
29	1.6(0)	40(0)	300(0)	6(0)	69.82	71.36
30	1.6(0)	40(0)	300(0)	6(0)	72.43	71.36
31	1.6(0)	40(0)	300(0)	6(0)	70.80	71.36

The optimization was carried out through response surface methodology and optimized values

of independent variables were found to be as follows: catalyst concentration (C) of 1.13% w/w, methanol to oil ratio (M) of 36.72 % w/w, 100 ml of the reaction mixture (V) and a residence time (T) of 6.4 minutes.

Table 4: Regression coefficients of predicted quadratic polynomial equation for yield of biodiesel in batch process.

Terms	Regression coefficient	SE
Intercept		
βo	+110.175*	30.35
Linear		
$\beta 1$	-37.903*	14.86
$\beta 2$	-0.256*	1.02
$\beta 3$	-0.086*	0.04
$\beta 4$	6.059*	2.03
Quadratic		
$\beta 11$	8.140*	3.06
$\beta 22$	0.017*	0.011
$\beta 33$	0.000*	0.000
$\beta 44$	-0.127*	0.069
F value = 69.63	Lack of fit (P = 0.125)	$R^2 = 0.984$

* Significant at 95% confidence level

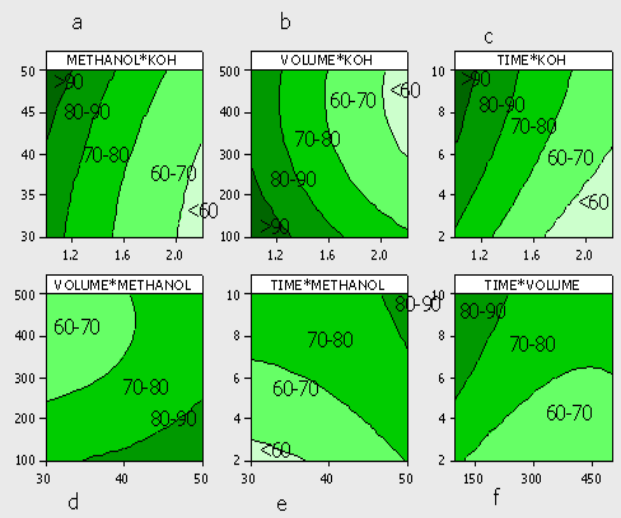

Fig 7: Contour plots of Yield predicted from the batch process quadratic model equation

Few experiments were conducted at optimal condition to validate the model. The final yield value at this condition was determined to be 90.14 ± 0.57%. This value is reasonably close to the predicted yield of 90.14%.

Continuous Process

The Box-Behnken method was applied to design the experimental points for the optimization of the continuous process through response surface methodology. The complete design matrixes together with both the experimental as well as predicted values obtained for yield as response at the design points for continuous experimentation was given in Table 5.

Biodiesel yield obtained ranged from 64.12 to 83.57%. The experimental data were fit to quadratic polynomial equation through least square technique and statistical analyses were carried out. Upon stepwise elimination of insignificant terms, the significant terms were fit to reduced model and found to be

$$\%FAMEYield = -128.273 + 278.875K - 0.414F - 2.768M - 118.792K^2 + 0.004F^2 - 0.03M^2 \quad (3)$$

Table 5: Box–Behnken experimental design and response for continuous process

Std. order	Levels of variable un coded (coded)			Yield (%)	
	C	**F**	**M**	**Exp**	**Predicted**
1	1.0 (-1)	25 (-1)	40 (0)	83.57	82.6
2	1.4 (1)	25 (-1)	40 (0)	79.48	79.12
3	1.0 (-1)	75 (1)	40 (0)	72.28	72.63
4	1.4 (1)	75 (1)	40 (0)	65.38	66.35
5	1.0 (-1)	50 (0)	30 (-1)	68.49	68.85
6	1.4 (1)	50 (0)	30 (-1)	64.12	63.87
7	1.0 (-1)	50 (0)	50 (1)	74.57	74.82
8	1.4 (1)	50 (0)	50 (1)	70.41	70.04
9	1.2 (0)	25 (-1)	30 (-1)	78.42	79.02
10	1.2 (0)	75 (1)	30 (-1)	69.54	68.82
11	1.2 (0)	25 (-1)	50 (1)	85.54	86.26
12	1.2 (0)	75 (1)	50 (1)	74.32	73.72
13	1.2 (0)	50 (0)	40 (0)	77.27	77.12
14	1.2 (0)	50 (0)	40 (0)	76.54	77.12
15	1.2 (0)	50 (0)	40 (0)	77.56	77.12

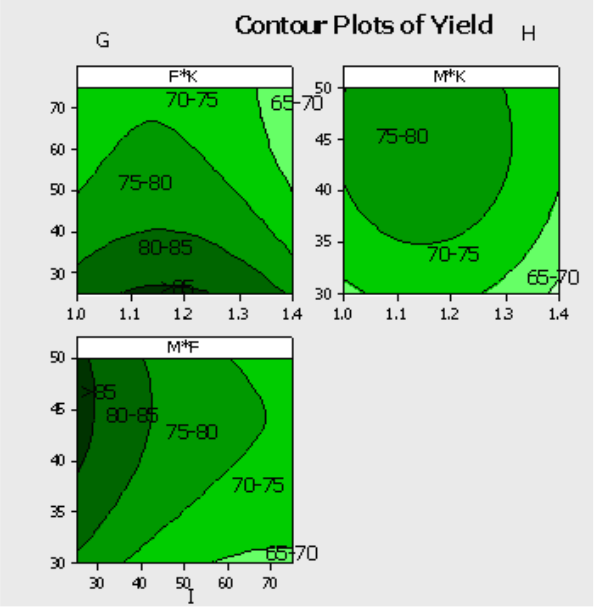

Fig. 8: Contour plots for continuous process

At a fixed methanol to oil ratio (Fig. 8g), as the flow rate is decreases yield is increasing, since the reaction mixture is not well irradiated due to the lower residence times. Further if the catalyst concentration is increased beyond 1.2% w/w, the yield is not

significantly increasing because of the soap formation. At a fixed flow rate (Fig. 8h), increasing the methanol to oil ratio with lower concentrations of catalyst didn't show good yields. Since transesterification reaction is a reversible reaction which requires excess alcohol in order to get good yields, but as the catalyst concentration is increased in the range of 1.1 to 1.3% w/w, the required amount of methanol to oil ratio decreased for higher yield. Further increment in catalyst concentration with both higher and lower methanol to oil ratio decreased the yield. At a fixed catalyst concentration (Fig. 8i) as the flow rate decreases yield increased for higher methanol to oil ratios. The variables are optimized through response surface methodology and the optimized values of independent variables were found to be as follows: KOH concentration (K) 1.22 (w/w) %, methanol–oil ratio (M) 39.49 and a flow rate of 25.21ml/minute. Few experiments were conducted at optimal condition to validate the model. The final yield value at this condition was determined to be 84.97±1.46%.

Properties of Biodiesel

The biodiesel synthesized through microwave assisted batch/continuous transesterification process were analyzed for its physical and chemical properties. The result is summarized and compared with the ASTM D6751-08 (ASTM, 2009) standards (Table 6). The density, viscosity, acid value and FFA are within the limits of ASTM standard, which confirms suitability of the microwave assisted biodiesel as engine fuel. The cetane index has not changed much as a result of unchanged iodine value and saponification number. The FAME content or ester content is also with in the limits of ASTM standars, which confirms the purity of the oil.

Table 6: Properties of Karanja biodiesel synthesized through microwave assisted transesterification

Properties	Karanja biodiesel	ASTM D6751-08
Density (Kg/m^3)	885	860-900
Kinematic viscosity (mm^2/s)	4.3	1.9 – 6.0
Acid value (mg KOH/g)	0.42	<0.5
Saponification No. (mg KOH/g)	227	-
Iodine value (g I_2/ 100g)	82.6	-
Cetane index	56.5	>47
Ester content	96-98	>96.4

CONCLUSIONS

Karnja Biodiesel was successfully synthesized in a microwave assisted batch/ continuous process. Effects of volume of the reaction mixture, irradiation time and irradiation power on the yield of biodiesel were discussed. A standard RSM design called central composite design was applied for optimization of reaction variable like catalyst concentration (C), volume of the reaction mixture (V), irradiation time (T) and methanol to oil ratio (M) for the batch process. Statistical analysis was carried out and insignificant terms were eliminated and the terms which are having the strong effect on the yield of biodiesel were included. With the inclusion of these terms a quadratic polynomial equation is developed to predict the yield of biodiesel. The results of the optimization were catalyst concentration(C) of 1.13% w/w, methanol to oil ratio (M) of 36.72 % w/w, 100 ml (V) of the reaction mixture and a residence time (T) of 6.4 minutes.

Biodiesel was successfully synthesized in a continuous reactor of hold up160ml. The effect of different process parameters like irradiation time, irradiation power and methanol to oil ratio were explained in detail. Optimization studies were carried out by using Box-bhenken experimental design and after carrying out the statistical analysis the response was fitted to a quadratic polynomial. Optimized values of independent variables were found to be as follows: KOH concentration (K) 1.22 (w/w) %, methanol–oil ratio (M) 39.49 %w/w and a flow rate of 25.21ml/minute. An optimum yield of more than 90% was achieved at a residence time of 11 minutes. Increasing the residence time beyond this point didn't improve the yield significantly. This data would be helpful for scaling up the reactor further.

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