

Optimization of Microwave Mediated *In Situ* Transesterification for Biodiesel Production from *Simarouba glauca* using Response Surface Methodology

Pankaj Dinesh Javalkar
Dept. of Chemical Engineering
Nirma University
Ahmedabad, India
pankaj.dj.2008@gmail.com

Venkatesh Kamath H.
Dept. of Biotechnology Engineering
NMAM Institute of Technology
Nitte, India
venkibt29@gmail.com

Abstract—Biodiesel has become more attractive recently because of its environmental friendly benefits and being made from renewable resources. Integration of oil extraction from seed with transesterification using microwaves i.e. microwave mediated *insitu* transesterification is a relatively new technique and offers several advantages. Parameters such as power, time of irradiation, catalyst concentration, methanol concentration, co-solvent type and concentration are studied and compared. Central composite rotatable design was used to optimize the reaction variables to arrive at best conditions for higher and economical yield by *insitu* transesterification of *Simarouba glauca* seeds. A yield based on seed weight of 43.52% was predicted using response surface methodology. This was validated experimentally and a yield of 38.5% was achieved. Quality analysis were carried out and Thermogravimetric analysis (TGA) was used to confirm biodiesel production.

Index Terms—Biodiesel, *Simarouba glauca*, transesterification, response surface methodology.

I. INTRODUCTION

Energy is the most fundamental requirement for human existence. Majority of the world's energy needs are supplied through petrochemical sources, coal and natural gases. Diesel fuels have an essential impact over the industrial economy of a developing country and used for transport of industrial and agricultural goods and operation of diesel tractor and pump sets in agricultural sector. An alternative fuel must be technically feasible, economically competitive, environmentally acceptable and readily available. One possible alternative to fossil fuel is the use of oils of plant origin like vegetable oils and tree borne oil seeds. This alternative diesel fuel can be termed as biodiesel or fatty acid methyl ester (FAME) [1]. It is biodegradable and non-toxic, has low emission profiles and so is environmentally beneficial. Chemically, biodiesel is a mixture of methyl esters with long-chain fatty acids and is typically made from resources such as vegetable oils, animal fats, or even used cooking oils (UCO).

Vegetable oils include edible and non-edible oils. The yield and properties of biodiesel products produced from different feed stocks would be quite different from each other [2].

The production of biodiesel from different non-edible oilseed crops has been extensively investigated over the last few years. Some of these non-edible oilseed crops include jatropha tree (*Jatropha curcas*), karanja (*Pongamia pinnata*), tobacco seed (*Nicotiana tabacum L.*), rice bran, mahua (*Madhuca indica*), neem (*Azadirachta indica*), rubber seed tree (*Hevea brasiliensis*) [3]. *Simarouba glauca* is a newer and a promising feedstock for biodiesel production. *Simarouba glauca* belongs to the family of Simaroubaceae. Common names include Paradise Tree and Bitterwood. Seeds contain 60-75% oil that can be extracted by conventional methods. Each well-grown tree yields 15 to 30 kg nutlets equivalent to 2.5-5 kg oil and about the same quantity of oilcake. This amounts to 1000-2000 kg oil/ha/year (400-800 kg/acre/year) and about the same quantity of oilcake. The average per hectare yield of *Simarouba* is 4 tons of seed, 2.6 tons of oil and 1.4 tons of cakes [4]. A number of methods are currently available for the production of biodiesel fuel. Primarily they are direct blend, micro-emulsions, thermal cracking and transesterification. Transesterification (also called alcoholysis) is the reaction of a fat or oil with an alcohol to form esters and glycerol. In transesterification of vegetable oil, the triglyceride reacts with three molecules of alcohol in the presence of catalyst, producing a mixture of fatty acid alkyl esters and glycerol. The overall process is a sequence of three consecutive reactions, on which di- and mono glycerides are formed as intermediates [5]. A catalyst is usually used to improve the reaction rate and yield. Because the reaction is reversible, excess alcohol is used to shift the equilibrium to the products side. Microwaves, a non-ionizing radiation incapable of breaking bonds, are a form of energy and not heat and are manifested as heat through their interaction with the medium or the materials wherein they can be reflected (metals), transmitted (good insulators that will

not heat) or absorbed (decreasing the available microwave energy and rapidly heating the sample). Several organic reactions have been carried out under microwave irradiation and are well documented [6]. Thermal effects are caused by the presence of polar molecules (alcohol) in the reaction system and their changing alignment under oscillating electromagnetic field. Because the mixture of vegetable oil, methanol, and potassium hydroxide contains both polar and ionic components, rapid heating is observed upon microwave irradiation, and because the energy interacts with the sample on a molecular level, very efficient heating can be obtained [7]. A catalyst is usually used to improve the reaction rate and yield. In order to understand and control the transesterification reaction it is necessary to know the reaction mechanism. Two types of mechanisms describing the base-catalyzed transesterification reactions have been proposed by various research groups. The first mechanism proposes the formation of two tetrahedral intermediates [8]. Other mechanism suggests the formation of only one tetrahedral intermediate which, in a subsequent step, rearranges to form the products [9, 10]. Base-catalyzed transesterification of glycerides can be explained by means of the following reaction mechanism, which includes a pre-step followed by three steps as shown in Fig.1:

- Pre-step: Quick formation of methoxide anion from methanol and alkaline catalyst.
- Step One: Nucleophilic attack of the alkoxide anion on the carbonyl group of the glycerides to form a tetrahedral intermediate.
- Step Two: Breaking of the tetrahedral intermediate to form the alkyl ester and the glyceride anion.
- Step Three: Regeneration of the active catalyst, which may start another catalytic cycle.

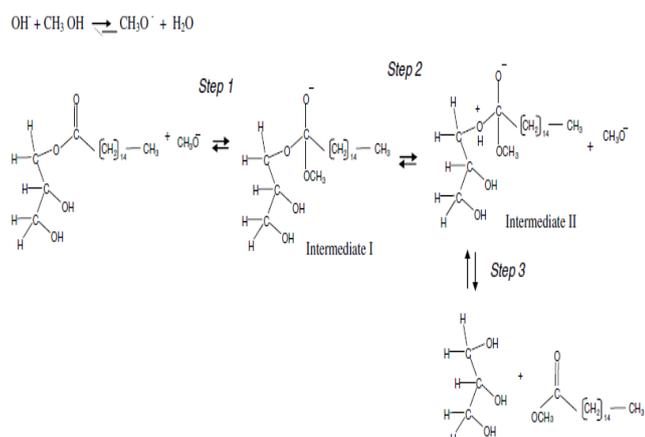


Figure 1: Base transesterification of glycerides

The *in situ* biodiesel production for converting oil to biodiesel developed by Harrington and D'Arcy-Evans in 1985. In this method, to achieve transesterification of its acyglycerols, the oilseeds are directly treated at ambient temperature and pressure with a methanol solution in which the catalyst has been previously dissolved. That means that the oil in the

oilseeds is not isolated prior to transesterification to fatty acid esters. To reduce the alcohol requirement for high efficiency during *in situ* transesterification, the oilseeds need to be dried before the reaction takes place. Milled oilseeds are mixed with alcohol in which the catalyst had been dissolved and the mixture is heated under reflux for 1–5 h. Two layers are formed around the time of the completion of the reaction. The lower layer is the alcohol phase and can be recovered. The upper layer, including the crude biodiesel, is washed with water to remove the contaminants until the washing solution is neutral. After the washing step, the upper layer is dried over anhydrous sodium sulfate then filtered, and the residual product is biodiesel [11]. A standard RSM design called a central composite rotatable design (CCRD) is the most popular technique. 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.

II. MATERIALS AND METHODS

A domestic microwave oven (Onida) 700W, 2450 MHz is used with modification as shown in Fig.2 for all microwave mediated batch experiments. A thermocol base is provided as support by replacing carousel plate in such a way that carousel axis rotates freely. A 100ml round bottom (RB) flask with a Teflon agitator connected to a motor is used as a batch reactor. A three neck glass adapter is connected externally through a hole made to the top of oven. The agitator through the glass adapter is connected to a motor externally and a rpm indicator is used to measure the speed of agitator. A condenser is provided through glass adapter to aid refluxing of methanol vapors [13].

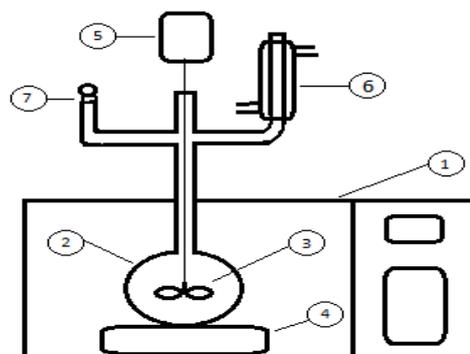


Figure 2: Schematic diagram of domestic microwave oven modified for batch experiments [13].

(1: Microwave oven, 2: Round Bottom flask, 3: Teflon Stirrer, 4: Base, 5: Motor, 6: Condenser, 7: feed neck).

The seeds in good condition were selected, cleaned, de-shelled and then dried at a temperature of 100–105°C for 35 min. Seeds were ground to fine particles using a grinder-mixer. Soxhlet extraction of these seeds was carried out to determine the oil content of seeds. The dry powdered seeds were directly used in microwave reactor for *in situ*

transesterification without any further modification or treatment.

A sample run of in situ transesterification was carried out to check the feasibility of reactive extraction. Parameters selected were 60% microwave power (420W), 200% (methanol), 400% (chloroform), 2% (KOH) and 2 minutes reaction time. Percentage of chemicals is based on weight of seeds. Qualitative and Quantitative analysis of biodiesel was evaluated using Thermogravimetry [12,13]. Yield of biodiesel produced using in situ transesterification is calculated as in Equation 1.

$$\% \text{ Yield} = \frac{\text{Weight of biodiesel (g)}}{\text{Weight of seed (g)}} \times 100 \quad \text{Eq.1}$$

III. OPTIMIZATION OF REACTIVE EXTRACTION

The factors affecting reactive extraction or *in situ* transesterification were optimized using response surface methodology. The independent variables selected were catalyst concentration (A), time of irradiation (B), methanol concentration (C), chloroform concentration (D). KOH was used as catalyst for transesterification step. The coded and uncoded levels of all variables are given in Table 1. The range for catalyst concentration (0.5-2.5%), time of irradiation (2-10min), methanol concentration (0-400%), chloroform concentration (0- 800%) were used based on literature [12]. Speed of stirring and microwave power were kept constant at 350 rpm and 420W respectively [12,13]. A CCRD experimental design was used to optimize the process variables for *in situ* transesterification step. A 5 level 4 factor design consisting of 27 experiments was employed, which include 3 centre points. Table 2 provides detail of experimental combinations in standard order with coded as well as uncoded levels. The experiments were carried out in a randomized order. Statistical analysis was carried out using Minitab v15. Each experiment was carried out with 5g of sieved seed kernel. To the 5g of sieved seed, methanolic KOH and chloroform was added and irradiated by microwave power. The product was filtered, separated glycerine and then washed with warm water. The dried biodiesel was analyzed using TGA for yield.

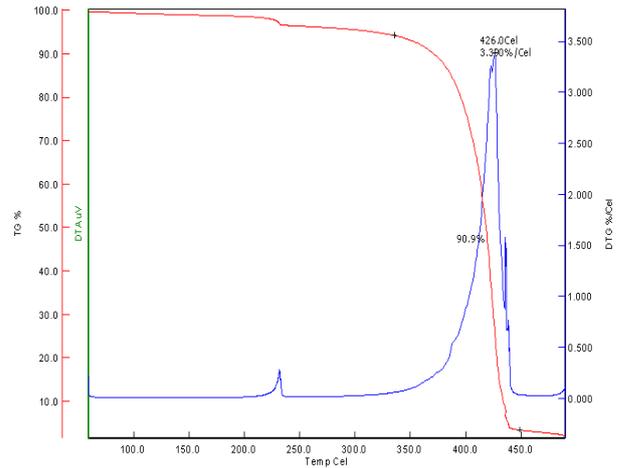


Figure 3: TG and dTG curves for *S. glauca* oil.
Table 1: Independent variables and levels used for experimental design in *in situ* transesterification.

Variables		Levels				
		-2	-1	0	+1	+2
A	KOH (w/w)%	0.5	1.0	1.5	2.0	2.5
B	Time min	2	4	6	8	10
C	Methanol (v/w)%	0	100	200	300	400
D	Chloroform (v/w)%	0	200	400	600	800

Note: % is based on weight of powdered seed

IV. RESULTS AND DISCUSSION

Oil of *S. glauca* was extracted using Soxhlet apparatus. An oil yield of 56 (v/w of seeds)% was obtained. A sample run of insitu transesterification was conducted using *S. glauca*. TGA and dTG of oil extracted by Soxhlet apparatus and biodiesel produced by insitu method for *Simarouba glauca* is shown in Fig. 3 and Fig. 4 respectively. In Fig. 3 the dTG curve at the temperature of 426°C is close to the peak maximum of oil; there is a mass loss of 90.9% from the TG graph. This means the sample analyzed has 90.9% oil. In Fig. 4 the dTG curve at 239.2°C close to the peak maximum of 233°C for FAME; there is a mass % loss of 24.95%. This means the sample has 24.95% FAME [13]. The yield of biodiesel is calculated to be 13.1% based on Eq. 1. The theoretical maximum yield of biodiesel is calculated to be about 51% based on seed weight. In order to increase the biodiesel yield a solvent can be added to facilitate extraction of oil from seed.

Response surface method of experimental design is employed to improve the biodiesel yield. The CCRD experimental design matrix for independent variables; experimental and predicted % biodiesel yield are given in Table 2. The experimental data was fit to the quadratic model through stepwise elimination of insignificant terms. Equation 2 represents the best quadratic fit for the experimental data. The coefficients of significant terms are shown in Table 3. Coefficient of determination ($R^2 = 82.81\%$) and standard error, 0.401141, indicates the predicted model fits the experimental data [12]. Insignificant lack of fit data (F statistic: 8.52, P statistic: 0.263) also support the predicted model.

Figure 4: TG and dTG curves for *S. glauca* biodiesel.

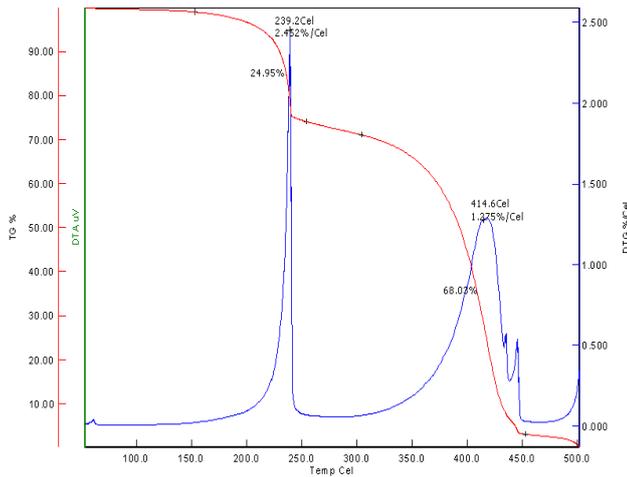


Table 2: CCRD experimental design and response for *in situ* transesterification reaction of *S. glauca*.

Run Order	Std. Order	Levels of variables Uncoded (coded)				Response: %FAME Yield	
		A	B	C	D	Experimental	Predicted
1	14	2(1)	4(-1)	300(1)	600(1)	36.0	39.1
2	1	1(-1)	4(-1)	100(-1)	200(-1)	27.2	28.7
3	10	2(1)	4(-1)	100(-1)	600(1)	27.4	28.6
4	15	2(1)	8(1)	300(1)	600(1)	21.6	20.7
5	5	1(-1)	4(-1)	300(1)	200(-1)	26.0	21.1
6	13	1(-1)	4(-1)	300(1)	600(1)	15.2	21.8
7	6	2(1)	4(-1)	300(1)	200(-1)	28.0	31.9
8	7	1(-1)	8(1)	300(1)	200(-1)	22.6	21.7
9	11	1(-1)	8(1)	100(-1)	600(1)	31.2	28.4
10	2	2(1)	4(-1)	100(-1)	200(-1)	19.6	21.3
11	4	2(1)	8(1)	100(-1)	200(-1)	24.4	22.0
12	18	1.5(0)	6(0)	200(0)	400(0)	36.0	35.2
13	3	1(-1)	8(1)	100(-1)	200(-1)	31.0	29.4
14	8	2(1)	8(1)	300(1)	200(-1)	33.6	32.5
15	17	1.5(0)	6(0)	200(0)	400(0)	38.0	35.2
16	16	2(1)	8(1)	300(1)	600(1)	36.0	38.0
17	9	1(-1)	4(-1)	100(-1)	600(1)	32.6	29.5
18	12	2(1)	8(1)	100(-1)	600(1)	26.1	27.5
19	22	1.5(0)	10(2)	200(0)	400(0)	28.4	34.2
20	19	0.5(-2)	6(0)	200(0)	400(0)	8.0	11.6
21	27	1.5(0)	6(0)	200(0)	400(0)	37.0	34.4
22	21	1.5(0)	2(-2)	200(0)	400(0)	37.0	34.7
23	20	2.5(2)	6(0)	200(0)	400(0)	26.0	21.5
24	25	1.5(0)	6(0)	200(0)	0(-2)	28.0	31.3
25	23	1.5(0)	6(0)	0(-2)	400(0)	18.1	20.6
26	26	1.5(0)	6(0)	200(0)	800(2)	40.0	37.6
27	24	1.5(0)	6(0)	400(2)	400(0)	27.0	23.5

Fig. 5 shows the parity plot which represents the difference between predicted and experiment values. Ideally all the points should fall on the line passing through origin. However, in real cases it shows the rate of deviation observed. Experimental data is satisfactorily linear with predicted data.

Table 3 shows that the linear, two of the quadratic terms and three of the interaction terms of A, B, C, D are significant model terms in increasing the % yield. Three interaction terms and two quadratic terms have no effect on increasing the % yield. The goodness of fit of model was checked by the coefficient of determination (R^2). In this case, high coefficient of determination, 82.81%, and small standard error 0.4011, shows that model is highly significant. In addition, the value of

adjusted coefficient of determination is also very high to advocate for a high significance of the model.

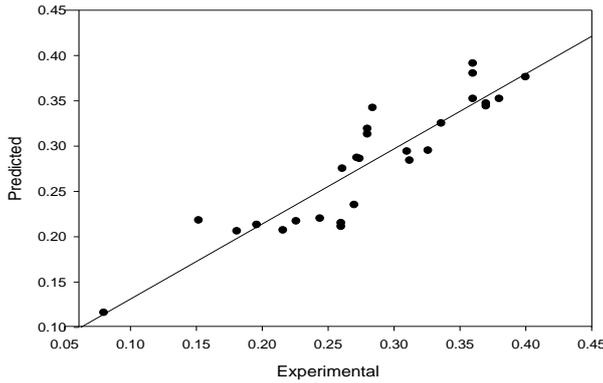


Figure 5: Parity plot for *in situ* transesterification of *S. glauca*.

Table 3: Regression coefficients of predicted quadratic polynomial after stepwise elimination for *in situ* transesterification of *S. glauca*.

Terms	Regression coefficient	Std. Error
Intercept β_0	0.3482	0.0136

experimental yield was determined to be $38.5 \pm 0.5\%$. The experimental yield at optimal point is statistically comparable with predicted yield. An yield of 96% was achieved on the basis of oil extracted using Soxhlet method.

Table 4: Optimum values of parameters for *in situ* transesterification of *S. glauca*

Variables	Optimum values	% FAME Yield	
		Experimental	Predicted
A KOH (w/w)%	2.222	38.5 ± 0.5	43.5
B Time min	2.0		
C Methanol (v/w)%	285		
D Chloroform (v/w)%	800		

Fig. 6 suggests a high yield at (i) low values of time and high catalyst concentration (ii) higher values of both methanol and catalyst (iii) higher values of chloroform and catalyst (iv) less time and higher values of chloroform (v) less time higher concentrations of chloroform (vi) high values of methanol and chloroform in order from left to right.

Linear		
β_1	0.0249	0.0081
β_2	-0.0011	0.0081
β_3	0.0072	0.0081
β_4	0.0157	0.0081
Quadratic		
β_{11}	-0.0447	0.0079
β_{33}	-0.0309	0.0079
Interaction		
β_{13}	0.0454	0.0100
β_{14}	0.0163	0.0100
β_{24}	-0.0044	0.0100

Regression coefficient = 82.81% ; Standard error = 0.4011;
Lack of fit analysis (95%): F statistic = 8.52;
 P (Lack of fit) = 0.263 (>0.05)

$$\begin{aligned} \% \text{ FAME yield} = & [0.3482 + 0.0249 \times A - 0.0011 \times B \\ & + 0.0072 \times C + 0.0157 \times D - 0.0447 \times A^2 \\ & - 0.0309 \times C^2 + 0.0454 \times A \times C \\ & + 0.0163 \times A \times D - 0.0044 \times B \times D] \times 100 \end{aligned} \quad \text{Eq.2}$$

The optimized values of independent variables were found to be as given in Table 4. The experiments were conducted in triplicate at optimal condition to validate the model. The

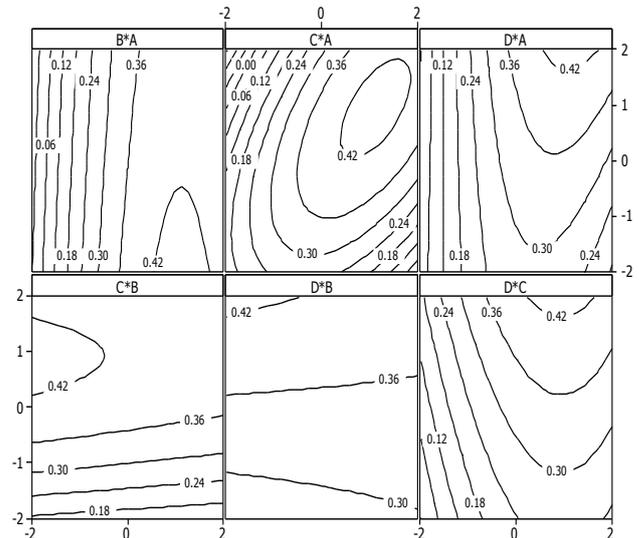


Figure 6: Contour plots of *in situ* transesterification of *S. glauca*.

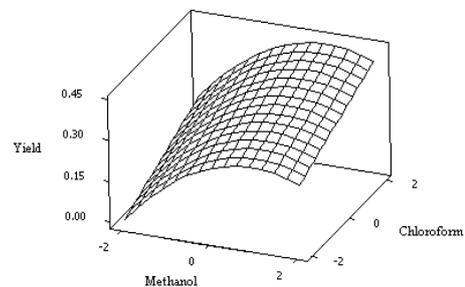


Figure 7: 3D Surface plot; *in situ* method.
Constant values are A= 2.222%, B=2min

3D surface plot for optimization is shown in Fig. 7 which gives a 3 dimensional view of the contour plot. Results interpretation will give same result as that of contour plot. However a surface plot aid the imagining the variations when two parameters are varied simultaneously, keeping the other values on hold. Properties of biodiesel tested are represented in Table 5. Values obtained fall within the range of ASTM standards. The solvents methanol and chloroform could be reused by distillation when carried out commercially. However, commercialization of this technique is only possible if an oven for industrial purposes would be brought into market rather than the domestic one (where parameter settings could be varied locally rather than globally). Once this is achieved process can be operated at exact conditions obtained after optimization rather than rounding off the values which would not yield the best results as predicted. The scope of commercialization of this process largely depends on an industrial microwave oven. Research conducted on microwave penetration can be used as reference to study its maximization based on the material of container, alignment of it etc. Also, more comprehension needs to be acquired in the direction of intensifying the microwave penetration further and optimization of variable of a continuous reaction system. Any work at its earliest stage seems ludicrous as the distance of moon from the earth was once. However, scientific knowledge combined with required levels of imagination will make it seem like an invention that was never one; but simply another existence in nature.

Table 5: Properties of *Simarouba glauca* biodiesel.

Kinematic Viscosity (mm ² /s)	Density (kg/m ³)	Saponification value (mgKOH/g)	Acid value (mgKOH/g)	Iodine value (gI ₂ /100g)
5.7	861.33	168.81	1.552	48.57

V. CONCLUSION

In situ transesterification proves to be a reliable and economical method for production of biodiesel. *Simarouba glauca* is excellent non- edible feedstock for biodiesel production. Base catalyzed *in situ* transesterification reaction was optimized using Central Composite Rotatable Design (CCRD). The values 2.222% KOH, 2 minutes, 285%

methanol, 800% chloroform are optimum solutions predicted for transesterification of *S. glauca*. Results showed up to 96% conversion i.e. *in situ* transesterification was achieved.

ACKNOWLEDGMENT

Authors would like to thank Dr. C. Vaman Rao, HOD, Biotechnology Dept. NMAMIT, Nitte for inspiring us and initiating awareness program regarding biofuels.

REFERENCES

- [1] Meher L.C., Vidya Sagar D. and Naik S.N. (2006). Technical aspects of biodiesel production by Transesterification. *Renew Sustain Energy Rev*, 10: 248-268.
- [2] Dennis Y.C., Wu X. and Leung M.K.H. (2010). A review on biodiesel production using catalyzed transesterification. *Appl Energy*, 87: 1083-1095.
- [3] Balat M., H.B (2010). Progress in biodiesel processing. *Appl Energy*, 87: 1815-1835.
- [4] Joshi S. and Joshi S. (2008). *Simarouba glauca* DC (Paradise Tree) - Brochure. AgEcon Search Database, University of Agril. Sciences, Bangalore. [<http://purl.umn.edu/43624>]
- [5] Srivastava A. and Prasad R. (2000). Triglycerides-based diesel fuels. *Renew Sustain Energy*, 4:111-133.
- [6] Varma R.S.(2001).Solvent-Free accelerated organic synthesis using microwaves. *Pure Appl Chem*, 73: 193-198.
- [7] Lidstorm P., Tierney J., Wathey B., and Westman J.(2001). Microwave assisted organic synthesis – A review. *Tetrahedron*, 57:9225-9283.
- [8] Ma F. and Hanna M.A.(1999). Biodiesel production: A Review. *Bioresour. Technol*, 70: 1-15.
- [9] Freedman B. and Pryde E.H. (1984). Variables affecting the yields of fatty esters from transesterified vegetable oils. *J Am Oil Chem Soc*, 61: 1638-1643.
- [10] Ulf S., Serchelia R., and Vargas R.M. (1997). Transesterification of vegetable oils : A review . *J. Braz. Chem. Soc.* , 9: 199-210.
- [11] Qian J.F., Wang F. and Liu S. (2008). *In situ* alkaline transesterification of cottonseed oil for production of biodiesel and nontoxic cottonseed meal. *Bioresour Technol*, 99: 9009-9012.
- [12] Regupathi I., Kamath H.V., Reddy S.Y., and Saidutta M.B. (2013). Microwave assisted batch and continuous transesterification of karanja oil: process variables optimization and effectiveness of irradiation. *Biomass Conv Biorefiner*. (Published online first) DOI 10.1007/s13399-013-0080-8.
- [13] Kamath V., Regupathi I., and Saidutta M.B. (2010). Microwave-assisted batch synthesis of *Pongamia* biodiesel. *Biofuels* 1(6): 847-854.