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Use of Microwave Irradiation to Produce Biodiesel from *Simarouba glauca* Oil Seed: Rapid Extractive Transesterification Approach.

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ABSTRACT

Biodiesel, a non-renewable energy source, is gaining popularity due to its environmental friendly benefits, also, its commercialization possibilities. The use of non-edible oil has been one the key factor while choosing the feedstock. The most common method producing biodiesel involves extraction of oil, transesterification of oil to biodiesel and further purification. In this work, an integrated processing approach using microwave to simultaneously extract oil and its transesterification to biodiesel from *Simarouba glauca* seeds is reported. Several advantages such as, lower use of solvent, higher extraction efficiency, and most importantly, a rapid process was reported. Parameters such as microwave irradiation time, catalyst (KOH) concentration, methanol concentration, co-solvent chloroform concentration were studied and analyzed. A central composite rotatable design was used to optimize the extractive reaction variables at 420W microwave power with 5g powdered seed. At an optimal condition of 2.2%(w/w-seed) KOH, 285%(v/w-seed) methanol, 800%(v/w-seed) chloroform and irradiation time 2 min, a biodiesel yield of 43.52%, based on seed weight, was predicted. A validation experiment produced a yield of 39.9%, corresponding to 72.5% conversion of oil in the seed to biodiesel. Quality analysis of purified biodiesel were carried out and purity of biodiesel was confirmed using thermogravimetric analysis (TGA).

Keywords: Biodiesel, *Simarouba glauca*, reactive extraction, transesterification, response surface methodology.

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INTRODUCTION

Energy is the most fundamental requirement for human existence. The energy demand is majorly met through fossil fuels such as, coal, petrochemical sources, and natural gases. An alternative fuel must be renewable, technically scalable, economically viable, environmental friendly, and readily available [1, 2]. In this regard, biodiesel produced from plant based oil is promising. The biodiesel, or fatty acid methyl ester (FAME), is biodegradable, non-toxic, and emits less green-house gases [2]. Several feedstocks to produce biodiesel have been reported including *Pongamia* and *Jatropha*. But, the yield and biodiesel properties varies based on the feedstock and catalyst used. Recently, use of non-edible oilseed crops for biodiesel production are extensively investigated, owing to their economic advantages. This includes *Jatropha curcas*, *Pongamia pinnata*, neem, rice bran, *Madhuca indica*, rubber seed tree, *Scleropyrum* etc. [3–8]. However, *Simarouba glauca*, a promising feedstock, is less studied for its potential to produce biodiesel.

S. glauca belongs to the family Simaroubaceae, and its seeds or the kernel contain 50-60% of oil. About 15 to 30 kg of nutlets equivalent to 3-5 kg oil is produced in a well grown tree. On an average *Simarouba* yields 4 tons of seed, 1.4 tons of oil cake, and 2.6 tons of oil per hectare [9, 10]. Usually biodiesel is produced from oil through a transesterification process using an alcohol, catalyzed by acid or base catalyst. In transesterification reaction, the triglyceride in the oil reacts with 3 molecules of alcohol (usually methanol), in the presence of a catalyst, and produces biodiesel (mixture of FAMEs) and glycerol. The overall transesterification reaction is a sequence of three consecutive reactions, where, di-glycerides and mono glycerides are formed as intermediates [11]. Since this reaction is reversible in nature, an excess alcohol is used to drive the equilibrium for completion. The most preferred homogeneous catalyst is base, usually hydroxides of sodium or potassium [12]. The reaction is brought about using heat to overcome the activation energy requirements. But, the reaction needs about 1 to 2 hours of heating, thus consuming high energy. Use of microwave irradiation for this purpose have reported consuming less energy, owing to rapid heating [13]. Thermal and non-thermal effects are the main cause for rapid reactions under microwave irradiation, due to the presence of dielectric materials, like polar molecules, in the reaction system. These effects bring down the reaction barriers by decreasing their activation energy which is not seen in the case of conventional heating mechanism [3].

The common process used in biodiesel production is to extract the oil from seeds, use them in biodiesel production and then purify the biodiesel. The extraction is normally carried out through a mechanical expeller, but the efficiency of extraction is very low [14, 15]. The efficiency of, an alternative extraction, solvent extraction is high, but, the it is not economical at industrial scale. An integration of oil expulsion along with biodiesel production is termed as *in situ* biodiesel production, and expected to overcome these hurdles [14]. To achieve higher efficiency, the moisture content of oilseeds need to be reduced before reaction. *In situ* biodiesel from feedstocks such as, coffee wastes [16], cotton seeds [17], Jatropha [18] have been reported. But, they used conventional heating method. In this current work, microwave has been used as a rapid technique to economically improve biodiesel production from *Simarouba glauca* through process integration. Further, this process was optimized, and, quality and purity of biodiesel were tested.

MATERIALS AND METHODS

All the chemicals used in the experiments were of either Merck reagent grade or Lobachemie reagent grade and used without modification.

Microwave reactor setup

A domestic microwave oven (Onida) 700W, 2450 MHz was used with modification as shown in Fig. 1 for all microwave (MW) mediated batch experiments. A thermocol base was provided as support by replacing carousel plate, in such a way that carousel axis rotated freely. A 100ml round bottom (RB) flask with a teflon agitator connected to a motor was used as a batch reactor. Three-neck glass adapter was connected externally through a hole (1cm) made to the top of oven. The agitator, through the glass adapter, was connected to an external motor. A condenser was provided through glass adapter to aid refluxing of methanol vapors [3, 13].

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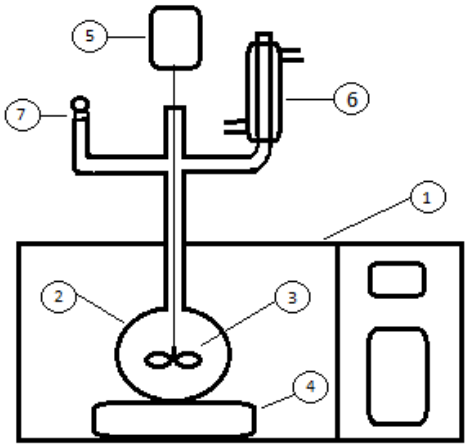

Fig 1: Schematic diagram of domestic microwave oven modified for batch experiments[3].

Microwave extractive transesterification

The seeds in good condition were selected, cleaned, de-shelled and then dried at a temperature of 100–105^{0}C for 2 hours. Seeds were ground to fine particles using a grinder-mixer. Using Soxhlet extraction based gravimetric method was employed to estimate oil content in the seeds. The dried and powdered seeds were directly used in MW reactor for in situ transesterification without any further modification or treatment. A typical MW experiment for reactive extraction was as follows. A solution of 200%(v/w) methanol, 400%(v/w) chloroform and 1%(w/w) KOH, based on weight of powder, was prepared. In the reaction vessel, 5g of powder was added with the solution and irradiated for 2 min. The biodiesel produced was separated gravimetrically and washed with warm water. The biodiesel was quantified using Eq.1.

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

Response surface method based optimization

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), and 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 a set of preliminary experiments. Speed of stirring and microwave power were kept constant at 350 rpm and 420W respectively. A 5 level 4 factor central composite design, consisting of 27 experiments including 3 center points, was employed. The experiments were carried out in a randomized order and statistical analysis using Minitab v15 at 95% confidence level.

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

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Biodiesel quality analysis

The biodiesel, after washing and purification, was tested for its quality. The physico-chemical properties such as viscosity, density, saponification value, acid value and iodine value were measured as per ASTM D6751 [19]. The purity of biodiesel was measured using thermogravimetric analyzer [20].

RESULTS AND DISCUSSION

Gravimetric analysis of oil seed

Oil from *S. glauca* was extracted using Sohxlet apparatus followed by gravimetric measurement. An oil yield of 60.5 (w-oil/w-seeds)% was obtained, in good agreement with reported values [9, 10]. TGA and dTG curves obtained through gravimetric analyzer is shown in Fig. 2. for the oil extracted by Soxhlet apparatus. The dTG curve at the temperature of 426°C is close to the peak maximum of oil with a mass loss of 90.9% as shown in TG curve. This means the sample contained 90.9% of oil as triglyceride. To measure the effectiveness of MW process, 55% triglyceride (60.5x0.909) was considered as theoretical maximum oil content in the seed.

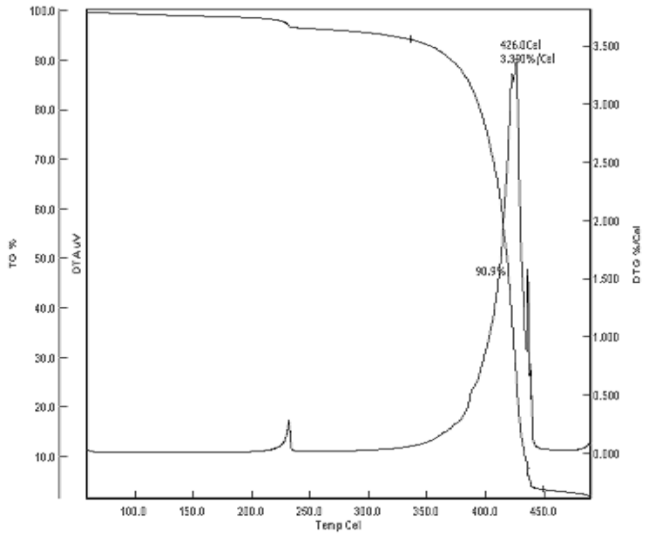

Fig 2: TG and dTG curves for *S. glauca* oil.

Optimization of MW reactive extraction process

Response surface method of experimental design was 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 based on 95% confidence level. Eq. 2 represent the best quadratic fit for the experimental data. The coefficients of significant terms with their standard error are shown in Table 3. The correlation between experimental data and quadratic model showed a statistically significant coefficient of regression (R^2 = 82.81%) and model standard error (0.401). Insignificant lack of fit test ($F_{13,3}$=8.52, p=0.263) also supported the predicted model. All the linear terms, two of the quadratic terms and three of the interaction terms of A, B, C, D are significant in increasing the biodiesel yield.

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

Using the statistical model, the process conditions were optimized to obtain higher biodiesel yield. The predicted result is shown in Table 4. Experiments were conducted in triplicate at optimal condition to validate this predicted result. The experimental biodiesel yield was determined to be 39.9±0.5%. The experimental yield at optimal point was statistically comparable with predicted yield at 95% confidence level. Considering 55% triglyceride content in the oil seed, 72.5% efficiency was achieved using MW assisted process.

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Table 2: Experimental design and response for *in situ* transesterification of *S. glauca* seeds.

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

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

Terms	Regression coefficient	Std. Error
Intercept		
β_o	0.3482	0.0136
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

R^2 = 82.81%; Std. error = 0.4011; Lack of fit $F_{13,3,\alpha=0.05}$= 8.52; P_{LoF} = 0.263 (>0.05)

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Table 4 Optimum values of parameters for *insitu* transesterification of *S. glauca* seed.

Variables			Optimum values	% Biodiesel Yield	
				Experimental	*Predicted*
A	KOH	(w/w)%	2.22	39.9±0.5	43.5
B	Time	min	2.0		
C	Methanol	(v/w)%	285		
D	Chloroform	(v/w)%	800		

Table 5: Properties of *S. glauca* biodiesel

Kinematic Viscosity (mm^2/s)	Density (kg/m^3)	Saponification value (mgKOH/g)	Acid value (mgKOH/g)	Iodine value ($gI_2/100g$)	Ester content (%)
5.2	861.3	168.8	0.52	48.5	99.5

Physico-chemical properties of biodiesel

Properties of biodiesel tested using ASTM D6751 standards are shown in Table 5. The properties were found to conform to the ASTM standards. The solvents, methanol and chloroform, used in the process 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). The purified biodiesel was tested for its ester content using thermogravimetry (Fig. 3). A peak at 231^{0}C with 99.5% mass drop indicated the purity of ester.

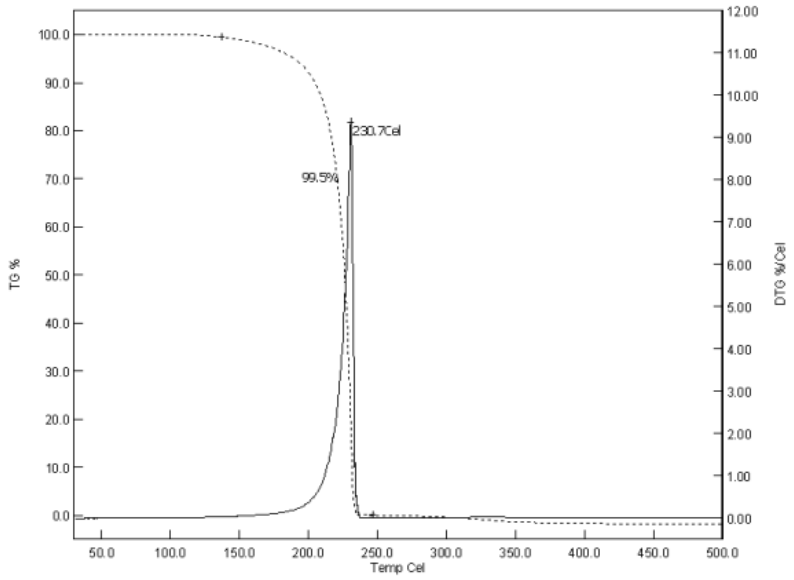

Fig 3: TG and dTG curves for *S. glauca* biodiesel.

CONCLUSION

In situ transesterification proves to be a reliable and economical method for production of biodiesel from *Simarouba glauca* seeds. Base catalyzed in situ transesterification reaction was carried out and the process was optimized using Central Composite Rotatable Design (CCRD). Under an optimal condition of 2.22% KOH, 2 min irradiation time, 285% methanol, and 800% chloroform, biodiesel yield of 39.5%, corresponding to 72.5% process efficiency was achieved. The purity and quality of biodiesel were tested and found to be within ASTM standard limits.

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