Application of Response Surface Methodology for Optimization of Biodiesel Production by Transesterification of Hydnocarpus Wightiana Seed Oil with Methanol

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Abstract- Response surface method and Central Composite design was used in order to optimize the process parameters of transesterification reaction during the production of biodiesel from Hydnocarpus Wightiana seed oil and investigation of reaction time, methanol quantity and reaction time was done. Prediction of biodiesel yield was done by generating a quadratic model by keeping temperature of reaction constant (55ºC to 60ºC) for all the experiments. 87.53% of the volume of oil was the maximum yield predicted by model for optimized parameters of duration of reaction (75 minutes), methanol quantity (35% volume of oil) and alkaline catalyst concentration (0.46% weight of oil). And 93.6% was the maximum experimental yield obtained for same parameters.

Keywords Response surface method, Central Composite design, transesterification, Hydnocarpus Wightiana, biodiesel.

1. Introduction

Fossil fuel depletion and the environmental degradation are the two main crises of today's world and mean time, demand for the petroleum products are increasing in line with the increase in population and the industrialization. It is also predicted that, global demand for the petroleum will increase by 30% by 2035[1]. Countries like India are certainly depending on foreign countries for the petroleum products as the domestic supply is not meeting the requirements. The money invested by the government in importing the crude oil is huge as the price of crude oil is increasing exponentially with increase in demand. Thus, the world is in search of alternative fuel sources in order to overcome the scarcity of petroleum fuels. Many renewable fuel sources have already been found which includes solar energy, wind energy, hydro energy, ocean energy and tidal energy etc. Even though there are many renewable sources available, the economical factor and ease factor restricts them from their abundant usage.

Diesel engines are in use since 18th century and the first diesel engine was made to run with peanut oil. Fossil fuels replaced the vegetable oil with advancement in technology. The concept of biodiesel starts from the early 1912 when Rudolf Diesel who is the inventor of Diesel engine stated that "The use of vegetable oil for engine fuels may seem insignificant today but such oil may become in the course of time, as important as petroleum and the coal tar products of present time" [2]. In reality, words of Rudolf Diesel are proving true because of the globalization, industrialization and environmental concerns like preventing the depletion of Ozone layer. However, neat vegetable oil is not suitable for existing diesel engine as it causes many practical problems like injector choking, clogging, carbon deposition, etc [3]. It is reported that there is a drop in power and efficiency when neat vegetable oil is used in unmodified diesel engine [4]. Hence,many researchers[5] have made attempts to modify vegetable oil into a fuel that is suitable for unmodified diesel engine without compromising power and efficiency.

Transesterification process is generally and globally used method to modify vegetable oil into respective esters (biodiesel).

Low Sulphur and aromatic content, higher flash point, biodegradability, lubricity, cetane number and non-toxicity are some of the advantages of the biodiesel and on the other hand, higher viscosity, pour point, lower volatility calorific value and oxidation stability are some of the disadvantages of biodiesel. As a result of all these factors biodiesel seems to be one of the promising fuel which can replace diesel fuel in automobile sector in phase wise.

2. Materials and Method

In this research, a new feedstock Hydnocarpus Wightiana (HW) is selected to produce biodiesel. HW trees having local name Marotti are found mainly in Western Ghats of Karnataka, Kerala and also in some parts of Maharashtra. It is an evergreen tree which grows up to a height of 10m with elliptical leaves. Flowering of trees takes place between January to April and they bear fruits between August and September. Each fruit contains 10 to 16 black seeds which accounts for 20% of fruits weight. On an average, 20kg of seeds can be obtained from a typical HW tree. The kernels of HW seeds make up 60-70% of seed weight and they contain 63% of oil with pale yellow colour[6].

In this work, oil was extracted by using conventional method of mechanical press extraction which yielded around 43.5% of oil. Chemicals required like methanol (99.3%) and Sodium Hydroxide pallets were purchased from VASA scientific company Bangalore. Free Fatty Acid (FFA) level of HW seed oil was found to be 1.72%. Table 1 shows the Fatty acid composition of HW oil determined from Gas Chromatography (GC) analysis. It is found that, the oil contains 45.9% of Hydnocarpic acid, 13.94% of Lauric acid and 11.2% of Gorlic acid as major contents and it also contains other acids like Caproic acid, Palmitic acid, Oleic acid and etc.

2.1 Procedure or method used for production of biodiesel from HW oil

Filtered HW crude oil is shown in Fig. 1 and as determined FFA level of HW crude oil was below 4%, single stage transesterification method was used for production of biodiesel[7].

Sodium Hydroxide (NaOH) was used as catalyst during transesterification process as it is one of the cheapest, readily available and one of the most efficient catalyst available today [8].

3. Experimental design

3.1 Parameter design methodology

In order to get the maximum yield of methyl ester during the transesterification procedure, optimization of the process parameters has been done and five level three factors CCD is used. Three process parameters such as quantity of methanol (A) in ml, quantity of NaOH (B) in grams and reaction time (C) in minutes were selected and each of them was treated at five levels. The details of Independent parameter level used in CCD are given in Table. 2.

Table. 1. Fatty acid composition of HW oil

Sl. No.	Parameters	Results
1	Caproic acid	0.13%
2	Caprillic acid	2.29%
3	Capric acid	1.69%
4	Lauric acid	13.94%
5	Myristic acid	5.96%
6	Hydnocarpic acid	45.90%
7	Gorlic acid	11.19%
8	Palmitic acid	4.80%
9	Stearic acid	1.42%
10	Oleic acid	3.63%
11	Linoleic acid	1.36%
12	Linolenic acid	0.23%
13	Archaidonic acid	7.34%
14	Behenic acid	0.11%

Fig. 1. HW crude oil

Table. 2. Independent parameter and level used in CCD

Parameter	Unit	Symbol	Level				
			-1.68	-1	0	1	+1.68
CH_3OH	ml	A	21.6	25	30	35	38.4
NaOH	grams	B	0.16	0.5	1.0	1.5	1.84
Reaction time	minutes	C	34.8	45	60	75	85.2

3.2 Design of Experiments

Experimental matrix for CCD is shown in Table 3. Biodiesel yield of twenty experiments conducted using alkaline catalyzed transesterification with keeping reaction temperature (55^{o}C to 60^{o}C) and RPM (500 rpm) constant is also given.

3.3 Transesterification process

Filtered HW crude oil is taken initially in a 250ml flat bottom flask and is heated to around 70^{o}C using pre heater in order to remove moisture content present and it was cooled down to room temperature. The oil sample was again heated to 55^{o}C to 60^{o}C by using magnetic stirrer. Meantime, sodium methoxide solution is prepared by dissolving required amount of NaOH pallets in calculated amount of methanol. Half of the prepared sodium methoxide solution is added to oil taken on magnetic stirrer after 15 to 20 minutes and remaining half is added after 15 more minutes.

Heating and stirring is continued till required amount of time for particular experiment. During whole process, stirring is at low RPM (500 to 600) and heating at constant temperature (55^{o}C to 60^{o}C) is maintained by using magnetic stirrer with hot plate. Same procedure is followed for all 20 experiments and is given in Table. 3. After the completion of Transesterification reaction, mixture was allowed to settle in conical settling tank for about 17 to 20 hours and by gravity separation method.

During settling, biodiesel or methyl ester of golden yellow colour will be floating as top layer and light brown colour glycerol will be settled at bottom. Glycerol will be drained off leaving the biodiesel with excess methanol and some moisture content. Water washing of biodiesel is carried out in order to remove excess catalyst present and then it is heated to 105^{o}C to remove the moisture content present.

3.2 Statistical Analysis

The experimental data's were analyzed by using RSM DX7 software and ANOVA analysis was also carried out by using the same software.

4. Result and Discussion

In order to optimize the process parameters of transesterification reaction to obtain maximum methyl ester yield RSM method is used. Experimentally observed and analyzed yields of methyl ester are shown in Table 3. The predicted model for % of HW methyl ester yield in terms of coded factors is given in Eq. (1).

$$R1=+81.91 + 2.44 * A - 1.22 * B + 4.07 * C - 1.30 * A * B - 3.45 * A * C - 7.35 * B * C + 0.55 * A^2 - 6.55 * B^2 - 1.30 * C^2 \quad (1)$$

Interaction of factors affecting the HW methyl ester yield was understood by using RSM method. It was observed that, quantity of methanol used was one of the limiting factor and specific interaction between quantity of methanol used, amount of catalyst used and reaction time noticed.

According to the model obtained, maximum yield of 87.53% was obtained when 35ml of methanol with 0.5grams of NaOH catalyst was made to react with 100ml of filtered HW oil for duration of 75 minutes. But experimentally, yield of 93.6% was obtained for same process parameters. Variation of 6.48% is obtained between predicted and experimental yield and which is in an acceptable limit.

Table. 3. Experimental matrix and result for CCD

Exp NO	A	B	C	CH_3OH (%v/v of oil)	NaOH (%w/v of oil)	Reaction Time (min)	Yield %	
							Experimental	Predicted
1	-1	-1	-1	25	0.5	45	62.7	57.22
2	-1	-1	1	25	0.5	75	91.1	86.96
3	-1	1	-1	25	1.5	45	75.6	72.09
4	-1	1	1	25	1.5	75	78.8	72.43
5	1	-1	-1	35	0.5	45	74.8	71.59
6	**1**	**-1**	**1**	**35**	**0.5**	**75**	**93.6**	**87.53**
7	1	1	-1	35	1.5	45	86.7	81.26
8	1	1	1	35	1.5	75	71.9	67.80
9	0	0	-1.68	30	1.0	34.8	65.5	71.38
10	0	0	+1.68	30	1.0	85.2	77.4	85.07
11	0	-1.68	0	30	0.16	60	58.8	65.42
12	0	+1.68	0	30	1.84	60	54.4	61.33
13	-1.68	0	0	21.6	1.0	60	72.4	79.38
14	+1.68	0	0	38.4	1.0	60	81.0	87.57
15	0	0	0	30	1.0	60	82.3	81.93
16	0	0	0	30	1.0	60	82.3	81.91
17	0	0	0	30	1.0	60	82.3	81.91
18	0	0	0	30	1.0	60	82.3	81.91
19	0	0	0	30	1.0	60	82.3	81.91
20	0	0	0	30	1.0	60	82.3	81.91

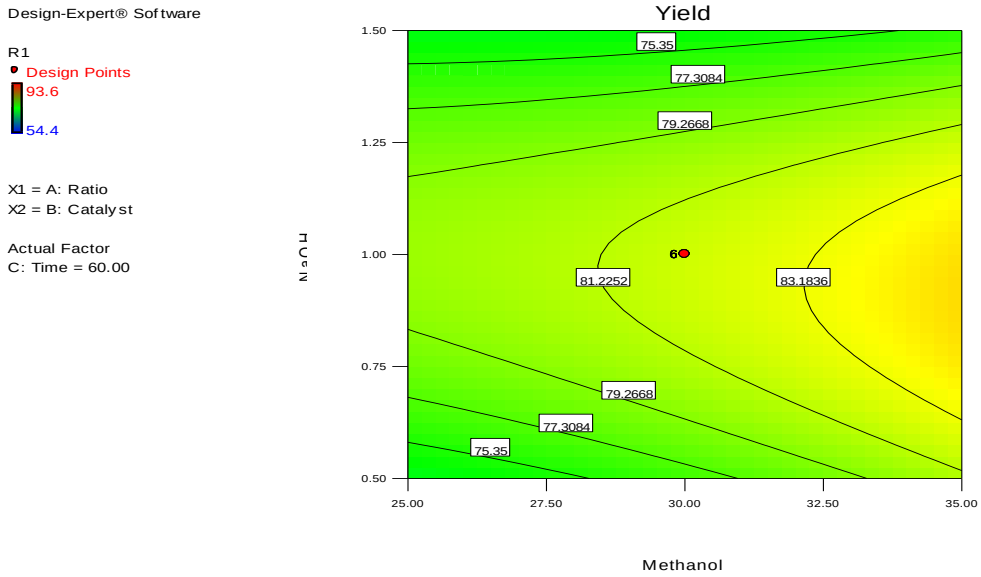

Fig. 2a. 2D counter plot representing the Effect of methanol quantity and catalyst concentration on Experimental yield

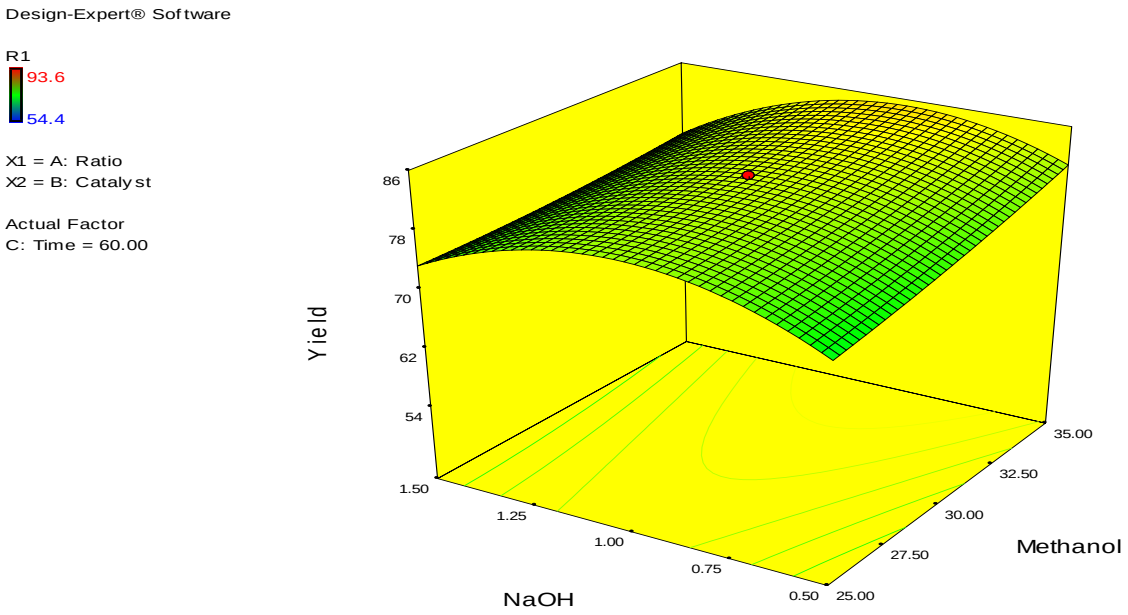

Fig. 2b. 3D surface plots representing the Effect of methanol quantity and catalyst concentration on Experimental yield

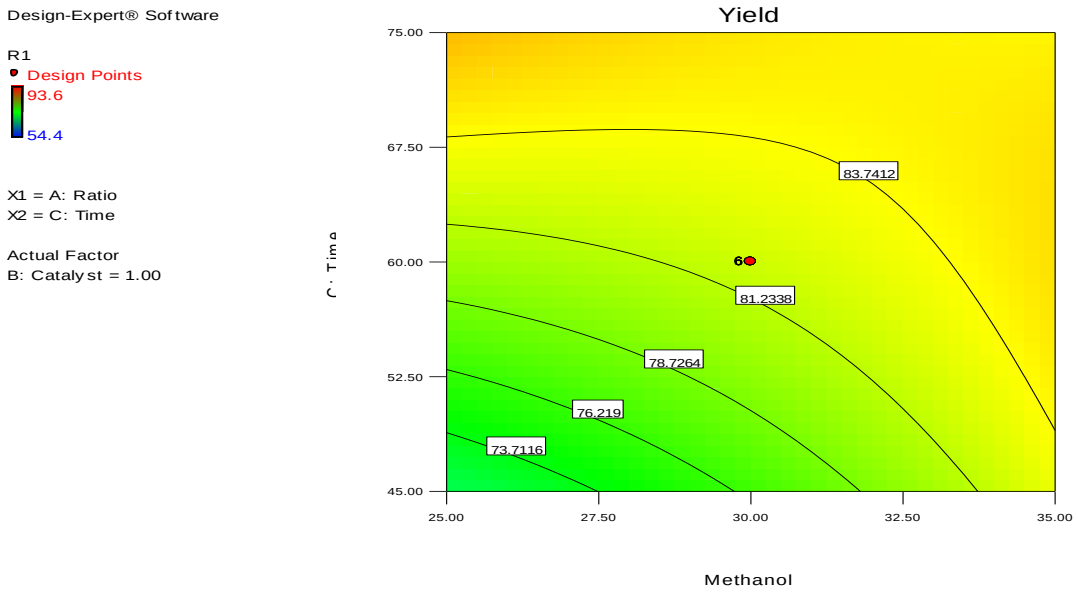

Fig. 3a. 2D counter plot representing the Effect of methanol quantity and reaction time on Experimental yield

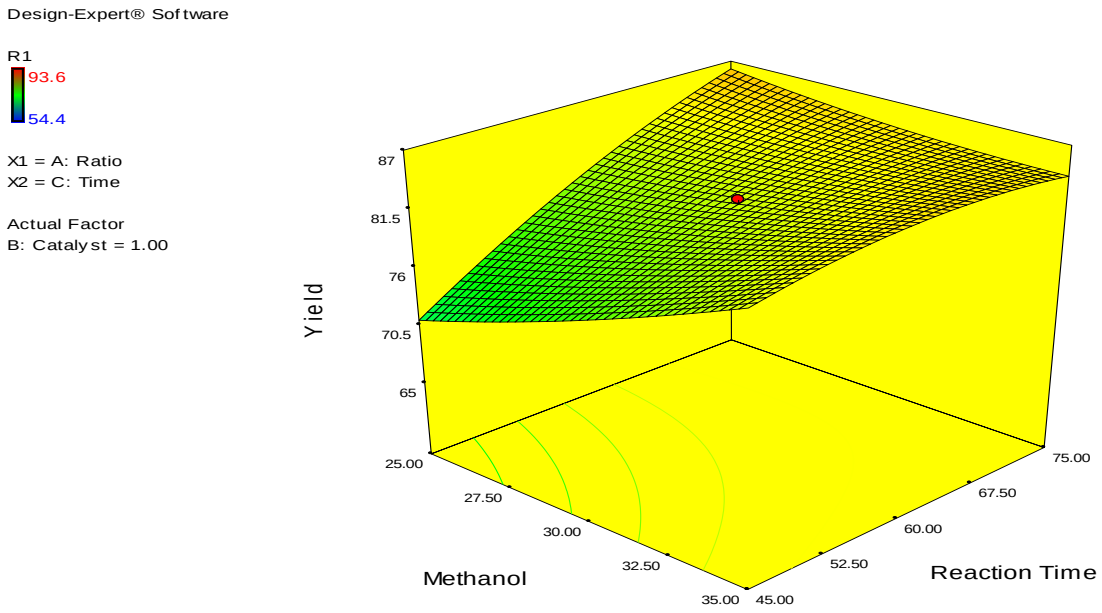

Fig. 3b. 3D surface plots representing the Effect of methanol quantity and reaction time on Experimental yield

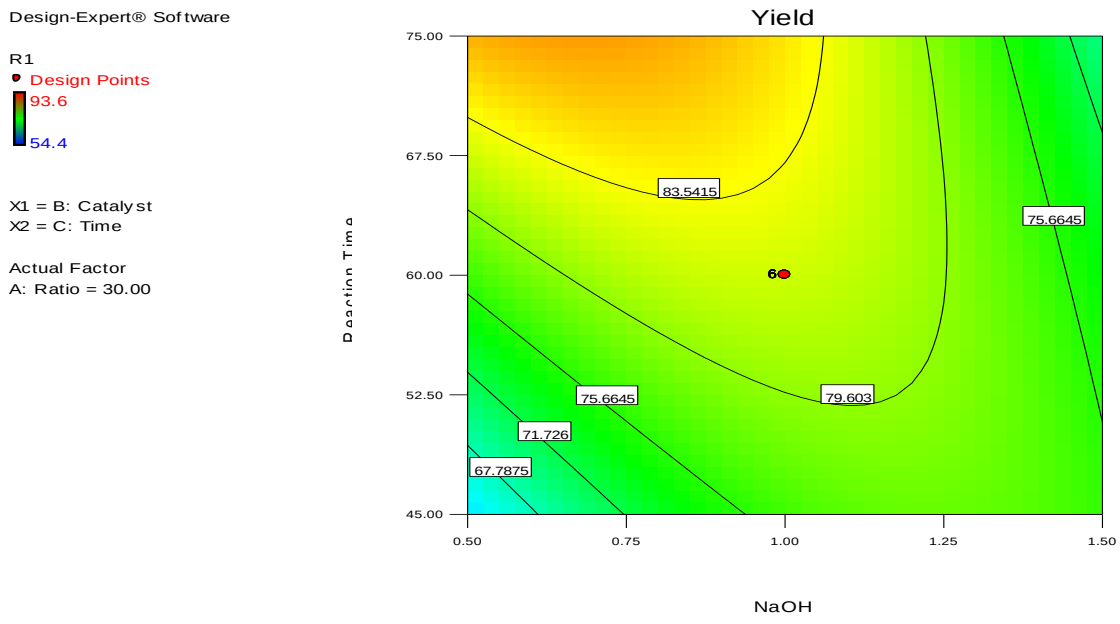

Fig. 4a. 2D counter plot representing the Effect of catalyst concentration and reaction time on Experimental yield

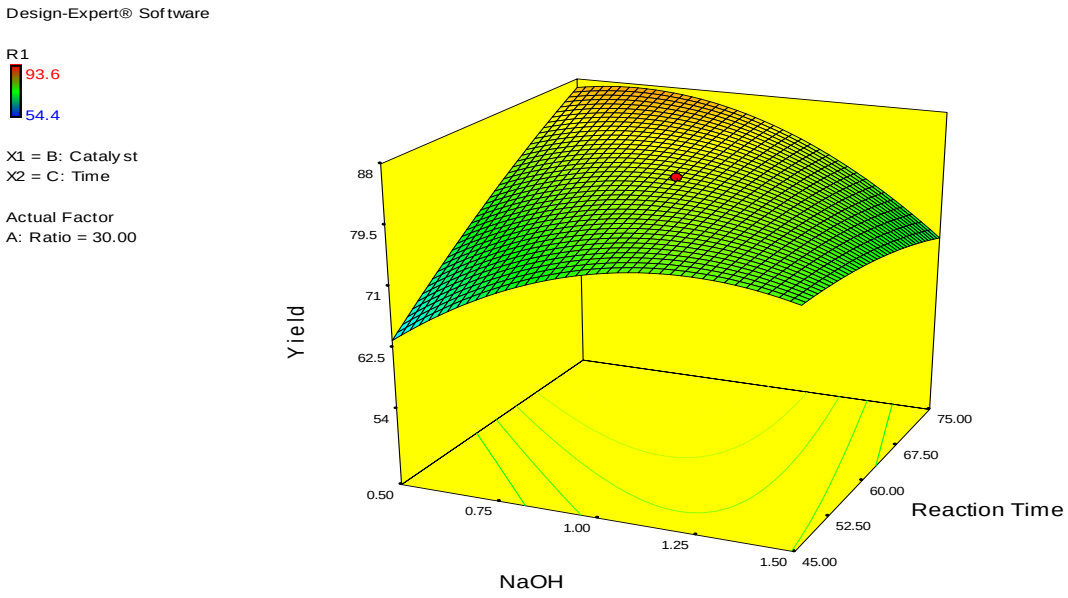

Fig. 4b. 3D surface plots representing the Effect of catalyst concentration and reaction time on Experimental yield

Fig. 2a and Fig. 2b shows 2D counter plots and 3D response plot between quantity of methanol used and catalyst concentration for constant temperature and RPM. From Fig. 2a and Fig. 2b, it is observed that, for given catalyst concentration, biodiesel yield is increasing slightly with increase in quantity of methanol used. But, yield is varying drastically with variation in catalyst concentration. For given quantity of methanol, lower yield of biodiesel yield was obtained for very high as well as very low catalyst concentration.

Fig. 3a shows the counter plot representing the Effect of methanol quantity and reaction time on experimental yield and Fig. 3b shows the 3D surface plot of effect of quantity of methanol and reaction time on experimental yield. From Fig. 3a and Fig. 3b it is observed that, when reaction time was less with less quantity of methanol reacting, the biodiesel yield was very less as there was incomplete reaction and thus for given methanol quantity, the yield found to be increase with increase in reaction time till maximum yield was reached for that particular parameters and it found to decrease with further increase in reaction time. And for given reaction time, yield was found to increase with increase in quantity of methanol.

Fig. 4a shows the 2D counter plot representing the effect of catalyst concentration and reaction time on biodiesel yield and Fig. 4b shows the 3D surface plot representing the effect of catalyst concentration and reaction time on biodiesel yield. It can be observed from the Fig. 4a and Fig. 4b that, yield obtained is very low when both catalyst and reaction time available is very less. For given reaction time, biodiesel yield found to increase with increase in reaction time till optimum time was reached after which yield found to decrease due to conversion of reaction methyl ester into soap molecules. But, for optimum amount of catalyst available, the biodiesel yield obtained increased at higher rate.

5. Conclusion

Present work carried out concludes that, Response Surface Methodology and Central Composite design can be successfully applied to optimize the process parameters of Transesterification reaction to get maximum biodiesel yield. Optimum point can be easily located by using graphical 3D surface plots. From model it is predicted that, when methanol quantity is 35% volume of oil, catalyst concentration is 0.5% weight of oil and when reaction time is 75 minutes, maximum yield for HW methyl ester (87.53% of oil) is obtained. And experimentally, maximum yield of 93.6% was obtained at same parameters. Variation of 6.48% observed between experimental and predicted maximum yield is in allowable limit. And thus, it can also be concluded that, Hydnocarpus Wightiana seed can be a potential source for biodiesel in future.

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