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Optimization and Biodiesel Production from *Prosopis Julifera* Oil with High Free Fatty Acids

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ABSTRACT

Prosopis julifera is a non-edible feedstock found in the arid and semi-arid regions was used for the production of biodiesel. Solvent extraction technique was used for oil extraction from *Prosopis julifera* .The present work mainly concentrates on the three step process of biodiesel production from *Prosopis julifera* oil .The acid value of *Prosopis julifera* oil was reduced below 1% using acid catalyst 1% v/v H_2SO_4 followed by esterification process using alkaline catalyst (KOH).Transesterification reaction is found to be affected by the reaction variables namely methanol to oil molar ratio, amount of catalyst used, reaction time and reaction temperature. Gas chromatography was used to analyse the Fatty acid methyl esters. The methyl ester obtained from the previous step was refined to produce biodiesel. The fuel properties of *Prosopis julifera* methyl ester (PJME) such as viscosity, cetane number, flash point, acid value, etc were determined and compared according to the ASTM standards. The optimum reaction conditions of Methanol/oil molar ratio of 9:1v/v, reaction temperature of 55^0C, reaction time of 2 hrs and 0.75% w/v of KOH usage were determined. Response surface Methodology (RSM) technique was used to optimize the maximum yield of *Prosopis julifera* methyl ester.

Keywords: *Prosopis julifera*; Acid Esterification; Transesterification; Process optimization.

I. INTRODUCTION

As the world is moving towards modernization and industrialization, there is the escalation in the usage of conventional fuels for transportation and also there is the hike in their price. The usage of fossil fuels increases the emission of greenhouse gases and environmental pollution which leads to global warming. Since fossil fuels are exhaustive and the ecological changes that happen in the world, there is the need to find the best substitute for conventional fuel Mambully (2009). Due to its inherent features such as renewable, biodegradable, lesser NO_x emission, Biodiesel is found to be the most promising alternative source. Though various researches, evaluations, tests and certifications from large number of countries, researchers have confirmed Biodiesel as clean alternative fuel having self combustion properties with lower carbon emission, no sulfur and no aromatics .As Biodiesel have got similar properties like Diesel, it can be blended easily and also it has good flash point and combustion properties Palash (2013). Vegetable oils (edible and non-edible) and animal fat are the main raw materials used for the Biodiesel production. The use of edible oil for Biodiesel production causes imbalance of food supply and arises the food vs. fuel conflict Balat (2011). Exploring new methods to produce biodiesel other than vegetable oils will help to reduce the usage of edible oils. As Non-edible oils do not contribute towards human nutrition, and the cost of biodiesel production is less, it can be replaced for edible oils. Non edible oils like Jatropha, Pongamia, Tobacco, Rubber seed, Mahua, *Camelina sativa*, Rice bran etc. are found to be the cheapest feedstock for biodiesel production Atabani (2013).

Prosopis julifera, a non-edible feedstock found in arid and semi-arid zones of India can grow even in the saline areas.The species *Prosopis julifera* is widespread all over the world. It consists of 44 species, having mostly thorny trees and shrubs. Pragnesh N. Dave (2013).The species of *Prosopis julifera* have been predicted to occupy some 3.1million sq.km in the world Deepak Rajagpoal. India covers an area of about 3.29 million sq.km. Over 40% of the country's total land surface constitutes the arid and semi-arid regions. According to the Department of land resources (DOLR), GOI

about 63.9 million hectare of land is lying waste in India are unsuitable for cultivation, are termed as "Waste lands". These lands are said to be characterized by sandy soils, rocky soils, saline soils etc. About 23 million hectare land (10 million hectare salt affected region and 13 hectare arid and semi arid region) is found to be lying waste in India Jennifer Baka (2013). The current strategy is cultivation of non-edible plants Jatropha, sweet sorghum, and castor, Pongamia in these waste lands. Although these plants grow in diverse agro-climate conditions, withstand pest attack and drought, the yield of the seed, oil content and nutrient requirements are found to be critical. This leads to the less chance for plantation of these plants in the waste lands [9]. *Prosopis julifera* is found to be abundantly used in various fields and new research is going on in making new drugs and pesticides from the same (A Technical manual on Managing *Prosopis julifera*). Hence, *Prosopis julifera* plantation instead of other plants will be more reliable.

Oils obtained from non edible feedstock can be converted into Biodiesel using four standard techniques namely Blending, Pyrolysis, Transesterification and micro-emulsification. Among these four methods, Transesterification resolves the problem of oils having high viscosity. This process has the advantage of reducing the viscosity of oil thereby increasing the fuel properties. Transesterification is a chemical reaction to produce mono ester by reacting triglycerides with short chain alcohol in the presence of catalysts. Methanol, ethanol, propanol, butanol are the commonly used short chain alcohols. Methanol is widely used alcohol due to its lowest price Ivana *et al.* (2012).The triglyceride in the vegetable oil or animal fat react with alcohol to form a mixture of glycerol and methyl ester called biodiesel.

Transesterification reaction can be a carried out with the help of one or more than one catalyst. Depending on the FFA content, the reaction is either one step or two step process. When comparing edible oils with non-edible oils, edible oils are found to contain large amount of FFA. Base catalysed transesterification of non edible oils produces high quality biodiesel in a shorter reaction time. This usage of base catalyst has the disadvantage of reduction in the yield of biodiesel due to soap formation Lin *et al.* (2009). NaOH and KOH are the catalysts used in most of the processes. The use of acid catalyst in the transesterification process has the advantage of tolerance and less sensitivity towards high FFAs. However the rate of reaction using acid catalyst is slow. Commonly used acid catalysts are H_2SO_4 and. The advantages of both acid and base catalysts are combined to form 2 step acid (acid/base) process for biodiesel production from non edible oils having high FFA content Milan D. Kosti (2014). In the first step, using acid catalysed transesterification the FFA value was reduced below 1% . In the next step, biodiesel from the feedstock *Prosopis julifera* is produced with the help of an alkaline catalyst. This two step transesterification is influenced by reaction time, reaction temperature, and quantity of catalyst. In acid catalysed and base catalysed reactions,to get the faster yield of FAME, methanol was used as the alcohol when compared with ethanol.

By two step transesterification process using 1% v/v H_2SO_4 acid catalyst, the acid value was reduced below 1% Rajeshwaran (2016).Lin Lin *et al*. has reported a three step Transesterification process in producing biodiesel. In that, initially the acid value was reduced and then esterification process was done with alkaline catalyst. An experimental investigation was done by Ramadass *et al*. on the Biodiesel production from high FFA Rubber seed oil.FFA was reduced by acid catalysed transesterification in the first step followed by alkaline catalysed transesterification.

In the conventional optimization process only a single variable can be changed at a time and the others will be kept constant. Response surface methodology is a suitable tool which provides desired response. Also RSM is found to be cost effective and very fast with a shorter time period. The extent of biodiesel extraction based on various optimum conditions can be analysed using RSM. The explanatory variables use an experimental design like central-composite design (CCD) to fit full second-order polynomial model. In general, a CCD coupled with a full second-order polynomial model, is considered to be a very powerful combination providing an adequate representation of most incessant response surfaces. For the investigation of complex processes, RSM is proved to be the effective statistical technique giving enough information in the reduced number of experimental runs. Most of the research regarding optimization of Biodiesel production is done by the method of RSM only Melvin Jose (2011).RSM based D-Optimal design was used to analyse the influence of various process parameters on the yield of Biodiesel from Waste cooking oil. (GR. Kannan). Alok Kumar Tiwari *et al*. optimized the Biodiesel production from high FFA *Jatropha curcas* oil using RSM based Central composite design. That process gave a yield of about 99%. The optimum reaction conditions of Methanol/oil molar ratio of 9:1v/v, reaction temperature of 60^0C, reaction time of 2 hrs and 1% w/v of NaOH usage were determined by Response surface methodology Rajeshwaran (2016). RSM was used to optimize and to study the maximum biodiesel conversion of *Prosopis julifera* in this present work.

There is no detailed work regarding the extraction of oil from the non edible feedstock-*Prosopis julifera.* Also literature has no evidence of biodiesel production from *Prosopis julifera* oil. Optimization of Biodiesel production parameters of *Prosopis julifera* was not yet reported so far.

1.1 Materials and Methods

Materials

Prosopis julifera belongs to the Botanical family Fabaceae (Pragnesh and Dave). The nature of the tree and its size vary between the species. The tree has thorns which vary in number and size. It may be present in some branches or may be absent. The

Table 1 Properties of Oil produced from non-edible feedstocks

Properties	Jatropha oil	Rubber seed oil	Rice Bran oil	Mahua oil	Karanja oil	*Camelina Sativa* oil	Tobacco oil	*Prosopis julifera* oil
Density,Kg/m^3	913	910	922	960	909	910	923	967-971
Viscosity at 40^{0}C(mm^2/sec)	40.4	76.4	43.5	24.9	27.84	14.03	27	38-41.2
Calorific value(MJ/kg)	38.65	37.5	--	36	--	44.5	--	38-41
Flash point(^{0}C)	240	198	316	232	232	--	--	202-212
Acid value (mg KOH/g of oil)	28	34	40	38	12.27	3.163	36.6	39-43.7
Saponification value (mg KOH/g of oil)	195	206	--	--	165.5	193.31	--	180-186
Iodine value (I_2g100/g of oil)	101	135.3	108	--	89	--	130.2	102-112

flowers are small which are densely gathered together on cylindrical, spike-like inflorescences. Flowers are 4-6mm long and are generally straw yellow in colour Jennifer (2013). The plant flowers almost any time of the year except the summer season.

The pod (fruit) of *Prosopis julifera* are found to be flattened and straight with 6-30cm long, 5-16mm wide and 4-9mm thick. The aged pods will swell and become pulpy and will look yellowish brown in colour. Seeds are upto 6.5mm long and weigh approximately 0.25 to 0.3g (25000-30000 seed/kg) Pragnesh N. Dave,(2013).The production of pods approximately vary from 5 kg to 40 kg/tree depending on the climatic conditions and habitat.

Pods (dried fruits) were gathered from the waste lands of Ramnad district in Tamil Nadu. Prosopis julifera collected during the seasonal period were then cleaned and dried for removal of moisture content. The dried pods are crushed and powdered. From the powdered pods, PJO was extracted using the soxhlet apparatus. Polar and non-polar solvents such as Petroleum Ether (68.7^{0}C), n-Pentane (35-37^{0}C), Ethyl acetate (76-78^{0}C), Iso-propanol (81-83^{0}C), Hexane (60-80^{0}C), Methanol (65^{0}C), and Ethanol (78.36^{0}C) were used and the amount of oil extracted with these solvents ranged from 10-37%. Since, maximum oil yield was obtained with methanol, oil from *Prosopis julifera* was obtained using the solvent methanol.

The unrefined *Prosopis julifera* oil was dark brown in colour. Fatty acid composition was obtained Gas chromatography analysis. Based on Triglycerides, the vegetable oil has different grades of Fatty acid and variation in fatty acid is based on hydrocarbon chain length and number of double bonds. Percentage compositions of fatty acids differ based on the flora species and growth conditions. Table 1 provides the properties of oils produced from non edible feedstock.

The saturated (palmitic, stearic) fatty acids and unsaturated (oleic, linoleic) fatty acids present in PJO was 23% and 68% respectively. The PJO had an acid value of about 39 to 43.7 mg KOH/gm, which corresponds to a fatty acid value of 19.5 to 21.85%.For the agreeable transesterification reaction using acid catalyst, the FFA value should be 1%.Since the FFA value obtained was far away from the limits, the transesterification process became complicated forming soap .The formation of soap prevented the separation of Biodiesel from Glycerin. Hence, the FFAs were initially converted into ester in a pre-treatment process, using an acid catalyst like 1% v/v H_2SO_4.In this pretreatment process, the acid value of PJO can be reduced below a FFA value of 1%.

Apparatus

Figure 1, the apparatus used for transesterification consists of constant temperature water bath, reaction flask with condenser and digital rpm. Digital rpm is used for controlling the Mechanical stirrer. The agitation speed of the mechanical stirrer was kept as 600rpm for all the transesterification processes. The glass reactor consists of three necks, one for stirrer, and others for condenser. The volume of the glass reactor measured 500ml.The reaction temperature was measured using a temperature indicator.

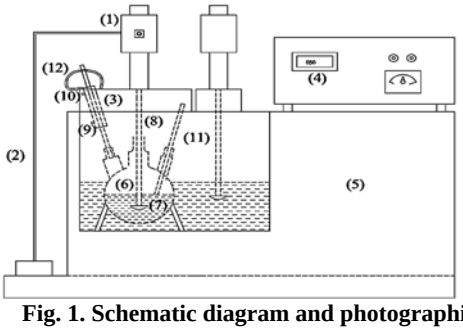

Fig. 1. Schematic diagram and photographic view of constant temperature water bath.

Pretreatment

Prosopis julifera oil pretreatment consists of two steps. The effect of methanol /oil molar ratio,(3,5,6,7and 9) v/v, and reaction time

Table 2 Fatty Acid composition of Prosopis Julifera Oil

Fatty Acids	Formula	Systematic name	Structure	Net (%)
Lauric acid	$C_{12}H_{24}O_2$	Dodecanoic acid	C_{12}	0.2
Myristic acid	$C_{14}H_{28}O_2$	Tetradecanoic acid	C_{14}	0.1
Palmitic acid	$C_{16}H_{32}O_2$	Hexadecanoic acid	C_{16}	10.6
Stearic acid	$C_{18}H_{38}O_2$	Octadecanoic acid	C_{18}	5.2
Oleic acid	$C_{18}H_{34}O_2$	Cis-9- Octadecanoic acid	$C_{18:1}$	34.7
Linoleic acid	$C_{18}H_{32}O_2$	Cis-9-cis12-Octadecanoic acid	$C_{18:2}$	43.4
Arachidice acid	$C_{20}H_{40}O_2$	Eicosanoic acid	C_{20}	0.13
Behenic acid	$C_{22}H_{44}O_2$	Docosanoic acid	C_{22}	0.1

(0.5, 0.75, 1, 1.25, 1.5, 2 hours) on the acid value of PJO in each step of pretreatment were studied. In this pretreatment process, whatever may be the methanol/oil molar ratio and reaction time, the amount of H_2SO_4 used was 1% v/v only Milan D. Kosti (2014). 100gm of PJO was taken and poured into a flask which was kept in a water bath. The water bath was retained hot by keeping at the temperature 110^0C for 30 minutes to eliminate moisture and the PJO was preheated. To this preheated oil, sulfuric acid, methanol solution was added and the mixture was stirred at the same rate for few minutes. After the completion of this reaction, the end product was poured into a separating funnel to separate the excess methanol. The excess methanol along with H_2SO_4 and impurities moved to the top surface and it was then removed .Using standard ASTM method, the acid value of the product separated at the bottom surface was measured at standard intervals. In a minimum reaction time, the product having an acid value of 8.6mg KOH/gm and very little amount of methanol was utilized as raw material for the second step. For to investigating the influences of methanol/oil molar ratio and reaction times and the acid value of the raw material obtained the same experimental procedure as above was repeated. For the transesterification reaction, the product having 2.7mg KOH/gm and with lowest amount of methanol in minimum reaction time was used. Rubber seed oil having acid values of 35mg KOH/gm was reduced to 3.8mg KOH/gm and 40mg KOH/gm was reduced to 0.9 mg KOH/gm in Rice bran oil Milan D. Kosti (2014). Similarly in Rubber seed oil an acid value of 34mg KOH/gm was reduced to 0.12mg KOH/gm Lin *et al.* (2009). The final reaction mixture was poured into a separating funnel. The mixture was separated by centrifugal process was then washed with distilled water and then dried with anhydrous sodium sulphate and was used for additional processing.

Transesterification

The experimental setup utilized in the pretreatment process was the same for this process. Before starting the reaction, PJO was preheated to the desired temperature to maintain the catalytic activity and to avoid the moisture absorbance, KOH-methanol solution was prepared newly. The methanolic solution was then added to the already present PJO in the reaction flask and from that point, time was noted. The product obtained after transesterification was poured into a separating funnel. The esters present in the lower aqueous glycerol were then separated by gravity. The esters thus separated were then washed twice with distilled water. In a rotary evaporator, the washed esters were dried under vacuum and were stored for further analysis.

1. Motor	5. Constant temperature water bath	9. Water in
2. Motor stand	6. Three neck round bottom flask	10. Water out
3. Lie beg condenser	7. Stirrer blade	11. Thermo-couple
4. Temperature controller	8. Stirrer rod	12. Tube

Gas chromatography analysis was performed in Central Electrochemical Research Institute (*CECRI*) - *CSIR* Lab, located at *Karaikudi*, in Tamil nadu. Gas Chromatograph used was *Agilent Technologies*, model 7980A with split-spiltless injector. This Gas chromatograph used a capillary column of dimension (30 x 250µm x0.25 µm) Helium was used as a carrier gas at velocity of 36.445 cm/s .The split ratio was maintained at 1:10.The initial temperature of the oven was kept at 50^0C for 1 minute reaction time and then, 10^0C for 1minute to 300^0C for a reaction time of 3 minutes and the run time as a total of 28 minutes. The lipids and other components composed in extracted oils were quantitatively and qualitatively analyzed using AOAC norms. Fatty acid and Methyl esters were analysed. Methyl esters obtained from *Prosopis julifera* contain 16% saturated fatty acids like Palmitic and stearic acids. Table 2 shows the *Prosopis julifera* oil fatty acid composition. The percentage of fatty acids such as Oleic, Linoleic and linolenic acids present in oil was 78.1% .The proportion of fatty acid present in the Biodiesel extracted from *Prosopis julifera* pods is as follows: Palmitic acid (10.6%), Behenic acid (0.1%) ,oleic acid(34.7%),linoleic acid(43.4%) , Lauric acid (0.2%), Myristic acid (0.1%), Arachidice acid(0.13%), and Stearic acid (5.2%)

Table 3 Experimental design with process data and the response for transesterification process model

Std	Run	Methanol/oil	KOH	Temperature	Time	Yield of Methyl Ester
		(v/v)	(w/v)	deg C	(min)	(%)
27	2	7.5	0.875	60	75	67.8
29	3	7.5	0.875	60	75	67.8
30	4	7.5	0.875	60	75	67.8
14	5	12	0.25	65	120	53
22	6	7.5	0.875	65	75	48
26	7	7.5	0.875	60	75	67.8
18	8	12	0.875	60	75	54
20	9	7.5	1.5	60	75	64
1	10	3	0.25	55	30	33
6	11	12	0.25	65	30	43.8
8	12	12	1.5	65	30	41
15	13	3	1.5	65	120	43
13	14	3	0.25	65	120	45.8
2	15	12	0.25	55	30	43.7
23	16	7.5	0.875	60	30	58
16	17	12	1.5	65	120	50.2
3	18	3	1.5	55	30	33.6
7	19	3	1.5	65	30	36
9	20	3	0.25	55	120	38.8
12	21	12	1.5	55	120	52.8
17	22	3	0.875	60	75	34.7
24	23	7.5	0.875	60	120	72
25	24	7.5	0.875	60	75	63.6
5	25	3	0.25	65	30	29
28	26	7.5	0.875	60	75	63.6
4	27	12	1.5	55	30	42.5
11	28	3	1.5	55	120	35.7
19	29	7.5	0.25	60	75	53
21	30	7.5	0.875	55	75	55.7

2. EXPERIMENTAL DESIGN-RSM MODEL

Central composite design (CCD) was performed to analyse the effect of the various process variables on the conversion of Fatty acid methyl esters. The percentage of biodiesel conversion was considered as the dependent variable and the independent variables were temperature, reaction time, methanol/oil molar ratio. Table 3 shows the limits of the process variables affecting the methyl ester conversion. The influence of dependent variables on the biodiesel conversion efficiency was evaluated. The investigation of process parameters methanol/oil volume ratio (factor A), amount of sodium hydroxide (factor B), reaction temperature (factor C) and reaction time (factor D) with respect to methyl ester yield(Y) was analysed with the help of the following equation.

$$Y=63.61 + 6.08A + 0.039B - 0.22C + 4.93D - 0.86AB - 1.36AC + 0.71AD + 0.47BC - 1.09BD + 0.61CD - 15.88A^2 + 1.73B^2 - 8.38C^2 + 4.77D^2 \quad (1)$$

Where, Y is the dependent variable and A, B, C, D are independent variables. The statistical analysis of experimental data was done using Deign expert 7.1.5 trial software

3. RESULTS AND DISCUSSION

Pretreatment

Pretreatment is found to be the best method for the reduction of acid values below 1mg KOH/gm as all the non-edible oils have an acid values in the range 20-45mg KOH/gm Ramadhas (2005).Important variables which affect the acid value were type of feedstock and alcohol, alcohol: oil molar ratio, concentration of catalyst, reaction time and reaction temperature. From Fig. 2, it can be seen that the reaction was rapid in the initial stage and became very slow in the later on stage. In this research, the rate of reaction was affected by molar ratio and reaction time. With the increase in molar ratio, the acid value decreased steadily and the reaction rate were found to be approximately same since due to the effect of water produced during esterification of FFA, the supplementary reaction may be put off and the reaction rate was nearly identical Lin *et al.* (2009). FFA of 5% should be obtained in the first Pretreatment step so that less than 1%FFA will be obtained after second pretreatment step Kosti (2014).The optimum condition of 9:1v/v methanol/oil ratio and 2 hours minimum reaction time was selected for reducing the acid value from 43.7mg KOH/gm to 8.6mg KOH/gm. In the second step pretreatment also, the same tendency was followed similar to the first step. This can be shown from the Fig. 3.The combination of 9:1v/v methanol/oil molar ratio and reaction time of 2 hours was found to be optimum value which reduced acid value from 8.6mg KOH/gm to 2.7mg KOH/gm. Further reduction in acid value was found to be very much complicated. With the increase in the Methanol/oil ratio and the reaction time, there was a decrease in the acid value. Transesterification of PJO with methanol was performed after this pre-treatment process.

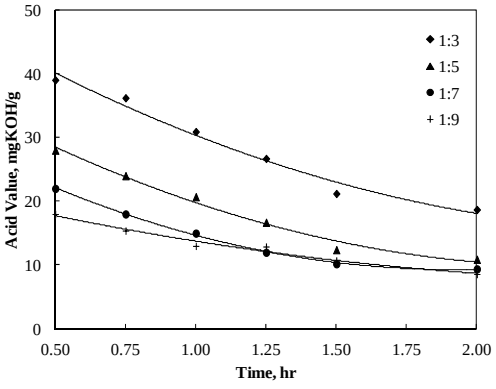

Fig. 2. Effect of methanol /oil molar ratio and reaction time on reduction of acid value of PJO during the first step pretreatment of biodiesel production. Initial acid value was 43.7mg KOH/g of oil.

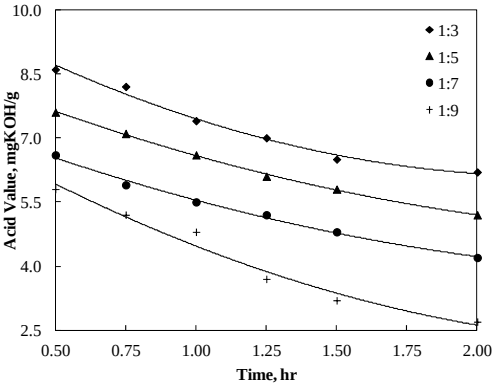

Fig. 3. Effect of methanol /oil molar ratio and reaction time on reduction of acid value of PJO during the second step pretreatment of biodiesel production. Initial acid value was 8.6mg KOH/g of oil.

Alkaline Catalysed Transesterification

The reaction product obtained from acid catalyzed pretreatment was used for this alkali catalysed transesterification. The experiments were carried out at different molar ratios, catalyst amount, reaction temperature and reaction time and optimum condition was noted down.

Effect of Molar Ratio on Conversion Efficiency

Three moles of alcohol and one mole of triglyceride reacts to yield 3 moles of fatty acid alkyl esters and one mole of glycerol. Methanol to oil ratio is an important parameter in the conversion of fatty acid alkyl esters Atapour (2011). Surplus amount of alcohol is needed to impel reaction products to right side of equilibrium reactions.

In the present work, molar ratios of 3:1, 5:1, 7:1, 9:1, 12:1 v/v were used. From the test, it was found that the molar/oil ratio had no effect on acid, peroxide, saponification and iodine values of methyl ester Kosti (2014). Fig. 4 shows the conversion efficiency at different molar ratios. With the increase in the addition of methanol, the conversion efficiency showed proportional increase in the initial stage and the increment in conversion efficiency was very less when the methanol/oil molar ratio was above 9:1v/v. High molar ratio interfered with the separation of glycerine due to its increased solubility. Amount of glycerine remained in the solution drove the reaction products back to the left side of equilibrium, and thus resulted in the yield of low amount of esters. An optimum value of methanol was chosen carefully.

From the literatures, the methanolysis reaction of non-edible oils was carried out with the molar ratio from 6:1 to 18:1 for both the steps irrespective of the catalyst. The molar ratio increased from 3:1 to 6:1, showed improved results on the ester yield. In the first step, when the methanol/oil molar ratio increased, the acid value reduced stridently, then slowly decreased and was constant at the final step Ramadhas (2005). More amount of triglycerides would be produced if the molar ratio was increased further and the reaction will also be incomplete if the

molar ratio is less than 6:1.Aslo mixing of the reactants during transesterification will be insufficient for molar ratio < 6:1. The end product will be diluted if the molar ratio is greater than 6:1 and if it is increased further than 6:1, the methanol added will not have any effect on the yield of esters Atapour (2011). The present study revealed that the better yield of methyl esters of about 72% was at an optimum methanol/oil molar ratio of 9:1.Also, it was inferred that the yield of methyl esters gradually increased from 37 % to 72%.This gradual increase was noticed for the ratios from 3:1 to 9:1.After that methyl ester yield decreased. The transparency of biodiesel and the oil yield decreases if the molar ratio is increased from 7:1 to11:1. Abundant quantity of methanol used for the reaction leads to the difficulty in the separation of glycerol from biodiesel. For the molar ratio above 13:1, unreacted methanol in the top level, ester in the middle level and glycerin at the bottom will be obtained Shashikant Vilas Ghadge (2005).

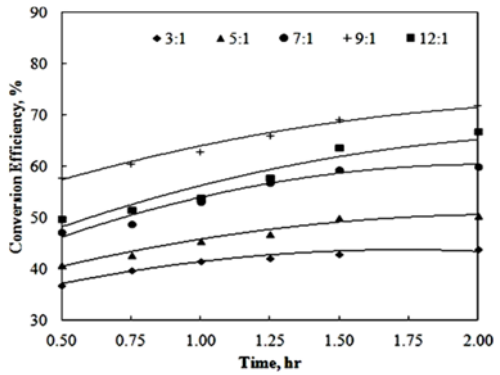

Fig. 4. Influence of molar ratio (methanol /oil) on the yield of PJME (KOH 0.75%, temperature 55^{0}C, rate of stirring 600 rpm).

Effect of Catalyst Amount on Conversion Efficiency

A set of experiments were conducted by changing the amount of KOH from 0.25%to 1.5% w/v Fig. 5 shows the conversion efficiency with different catalyst amounts. The maximum yield of ester was obtained during the esterification of PJO with the catalyst 0.75% w/v KOH. It was observed that the lowest catalytic concentration (0.25%) was not sufficient to complete the reaction. Increasing the amount of catalyst above 1.25% w/v did not increase the conversion efficiency. With the enhancement in the concentration of catalyst beyond 1.25% w/v, the methyl ester yield diminished and the quality of ester yield was based on the formation of glycerol and soap. The ester yield efficiency reduced with the increase in the amount of catalyst added. Excess amount of catalyst used led to the formation of emulsion which increased the viscosity and formation of gels and at last the reaction ceased. From the experimental work, it was found that, for an efficient transesterification reaction, 0.75% w/v of KOH was the optimum amount of catalytic concentration. The yield of methyl esters were 95-96% ,98% and 97-98% using 1% KOH for Rapseed oil, Tobacco seed oil and *Pongamia pinnata* Atabani (2013).Catalytic concentration of 1.33% yielded 89.9% of Karanja oil and 86.2% *Jatropha curcas* oil was obtained using 1% KOH Ramadhas (2005).

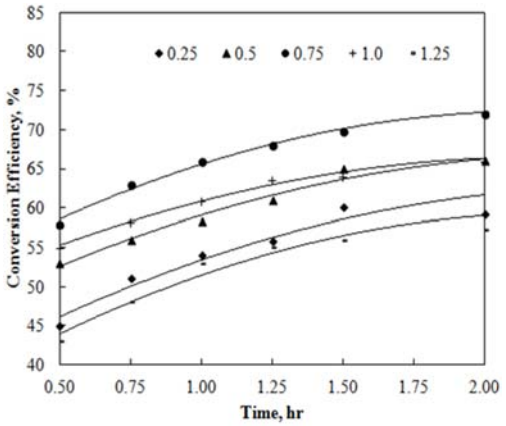

Fig. 5. Influence of the amount of Catalyst on the yield of PJME (KOH 0.75%, temperature 55^{0}C, rate of stirring 600 rpm).

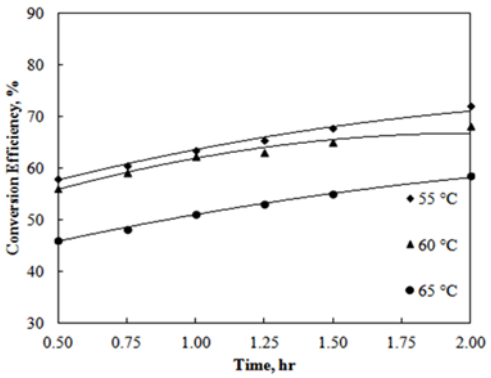

Fig. 6. Influence of Reaction Temperature on the yield of PJME (methanol /oil) 9:1, Catalyst KOH 0.75%, rate of stirring 600 rpm).

Effect of Reaction Temperature on Conversion Efficiency

The influence of reaction temperature on conversion efficiency is shown in the Fig. 6 keeping 9:1 molar ratio and 1% w/v KOH catalytic concentration. For the yield of esters, reaction temperatures of 55^{0}C, 60^{0}C, 65^{0}C were used. The maximum ester yield of 72% was noticed for a reaction temperature of 55^{0}C, and 2 hrs reaction time. Similar results have been reported by earlier researchers using non edible oils. In general for the base catalysed transesterification reaction, the temperature was set based on the type of alcohol used Ramadhas (2005). The methyl ester yield efficiency reduced when there was the rise in temperature. When the temperature was further increased from 65^{0}C -65^{0}C, *Prosopis julifera* methyl esters yield and purity was decreased. At the high reaction temperature, loss of methanol accelerates saponification of glycerol by alkaline catalyst and the

Table 4 Properties of Biodiesel produced from non-edible feedstocks

Properties	Test Procedure	Biodiesel-standard ASTM D6751-02	DIN EN 14214	Diesel	Diesel Prosopis Julifera oil-Biodiesel(PJME)
Density,Kg/m^3	ASTM D4052	875-900	860–900	847	893
Viscosity at 40^{0}C(mm^2/sec)	ASTM D445	1.9–6.0	3.5–5.0	2.85	4.9
Calorific value(MJ/kg)	ASTM D240			43.4	39
Cetane number	D613	47 min	51 min	46	49
Flash point(^{0}C)	ASTM D4052	>130	>120	68	120
Cloud point (^{0}C)	ASTM D2500	-3 to 12	--	--	4
Acid value (mg KOH/g of oil)	ASTM D4052	>0.8	>0.50	0.35	2.7
Saponification value (mg KOH/g of oil)	--	--	--	--	92
Iodine value (I_2g100/g of oil)	--	--	--	--	87

ester yield will be attained earlier than the completion of alcoholysis. Bubbles produced due to the vaporization of methanol obstructed the alcoholysis reaction though condensation system was used in the experiment. Hence the reaction temperature must not exceed the boiling point of methanol (65^{0}C) and reaction at higher temperature must be avoided. The findings from the experimental results of most of the researchers conclude that almost all the experiments were conducted near the boiling point of methanol and the maximum ester yield was observed between the temperature range 50 to 60^{0}C. Ester yield obtained for Rice bran oil was 95-99% Milan D. Kosti (2014), Mahua Indica oil Barbosa DC (2010), Rubber seed oil at a reaction temperature of 45±5^{0}C Lin *et al.*(2009).

Effect of Reaction Time on Conversion Efficiency

The ester conversion was carried out at the reaction time such as 0.5, 0.75, 1, 1.25, 1.5, 1.75 and 2 hours. This was done by keeping 9:1v/v molar ratio, 0.75% w/v KOH catalytic concentration and 55^{0}C reaction temperature. The conversion efficiency can be improved by stirring the chemical reagents and oil at constant rate. It was observed that reaction time extremely influenced the yield of esters. When the reaction time was enhanced from 0.75 to 2 hrs, there was the rise in the conversion efficiency of Methyl esters *Prosopis julifera* oil. The conversion procedure is considered to be the best if it achieves maximum conversion within a shortest time period. The data obtained from the current experiments indicate that the reaction time of 2 hours was sufficient for the completion of the reaction and also it was found to be the optimum value. *Prosopis julifera* oil ester conversion with this time was found to be 72%. If the oil is kept too long under the reaction time than the optimal value, the appearance of the oil becomes dark in colour. The yield of Jatropha biodiesel was 95% and 98% for Soybean and castor oil for a reaction time of 2 hours Shashikant Vilas Ghadge (2005).In general, on edible oils can be analysed by further increasing the reaction time above 2 hours. Neem oil when reacted at 6.5to 8 hrs yielded 88 to 94% biodiesel and Mahua oil produced 99% of ester yield after undergoing a chemical reaction of 3 hours Ramadhas (2005).

Fuel Properties of Methyl esters of *Prosopis julifera* oil

Based on the Biodiesel ASTM standards, the fuel properties of methyl esters *Prosopis julifera* oil are summed up in Table 4. Most of the properties of Prosopis julifera Biodiesel match the values as prescribed in the ASTM standard D6751-02 and DIN EN 14214 standards.

Oxygen content present in Biodiesel helps in complete combustion. The calorific value of *Prosopis julifera* Biodiesel was lower than that of diesel and that is due to the presence of oxygen content in Biodiesel. The Cetane number was found to be slightly greater than the regular diesel fuel. Also viscosity value was noticed to be a little bit greater than diesel. This implies that the biodiesel is having good ignition properties and there is the need to do slight engine modification. Density was very much greater than the diesel. The flash point and cloud point observed was confined as per the ASTM D6751-02.

4. DESIGN OF EXPERIMENT-AN OVERVIEW

The evaluation of the effect of process variables on the *Prosopis Julifera* Methyl ester was done by constructing RSM based Central Composite Design. The benefit of using this method is that the dependent process variables can be evaluated with lesser number of experiments. The different process parameters taken for analysis are methanol-oil molar

Table 5 Process parameters level for the optimization of transesterification process

Factors	Process Parameters	Lower level (-1)	Middle level (0)	Upper level (+1)	Std. Dev.
A	Methanol/oil (v/v)	3:1	7.500	12:1	3.486
B	KOH (w/v)	0.25	0.875	1.5	0.484
C	Ext.temperature (^{0}C)	55^{0}C	60.000	65^{0}C	3.873
D	Extraction time (min)	30	75.000	120	34.857

Table 6 ANOVA result for methyl ester yield by transesterification method a statically significant at the confidence level of 95%

	Sum of		Mean	F	p-value	
Source	Squares	Df	Square	Value	Prob > F	
Model	4214.823	14	301.0588	13.3061	< 0.0001	significant
A-METHONAL/OIL(v/v)	664.9089	1	664.9089	29.38744	< 0.0001	
B-KOH	0.027222	1	0.027222	0.001203	0.9728	
C-Temperature	0.888889	1	0.888889	0.039287	0.8455	
D-Time	437.0939	1	437.0939	19.31854	0.0005	
AB	11.73063	1	11.73063	0.518467	0.4826	
AC	29.43063	1	29.43063	1.300766	0.2720	
AD	7.980625	1	7.980625	0.352725	0.5614	
BC	3.515625	1	3.515625	0.155383	0.6990	
BD	19.14063	1	19.14063	0.845972	0.3722	
CD	5.880625	1	5.880625	0.25991	0.6176	
A^2	653.0578	1	653.0578	28.86365	< 0.0001	
B^2	7.72134	1	7.72134	0.341265	0.5678	
C^2	181.7851	1	181.7851	8.034482	0.0126	
D^2	59.04179	1	59.04179	2.609511	0.1271	
Residual	339.3842	15	22.62561			
Lack of Fit	315.8642	10	31.58642	6.7148	0.0242	Significant
Pure Error	23.52	5	4.704			
Cor Total	4554.207	29				

ratio, reaction temperature and time taken for the reaction. A face centered design was modeled using RSM based central composite design which was created using Design expert 7.1.5 version.

Optimization of Transesterification Process

To evaluate the effect of process parameters on acid value in the first step of Transesterification, Central composite design (CCD) was used. The model significance and suitability was tested by analysis of variance (ANOVA) based on the alkaline value (response).The process parameters level for the optimization of transesterification process is given in Table no 5.

Optimization of Alkaline-Esterification Process Parameters

After reducing the FFA value of the *Prosopis julifera* oil by Acid transesterification process, Biodiesel was produced by Alkaline Transesterification. Analysis of variance was then carried out to test the model significance. The ANOVA table is given in Table no 6.

The model using Response surface methodology with central-composite design (CCD) for the methyl ester yield had an F-value of 13.31 and a very low p-value of <0.0001.The above mentioned values indicate that the model is significant with a

Table 7 R-squared results for methyl ester yield

Factor	Optimum value	Factor	Optimum value
Std.Dev.	4.756639	R-Squared	0.925479
Mean	50.59	Adj R-Squared	0.855926
C.V. %	9.40233	Pred R-Squared	0.697989
Press	1375.423	Adeq Precision	12.85999

The percentage of yield can be given by the empirical formula

Yield of Methyl Ester = - 1202.54 +16.73 x Methanol/oil(v/v) +3.99 x KOH+40.28062 x Temperature -0.39 x Time -0.30 x Methanol/oil (v/v) x KOH-0.060 x Methanol/oil(v/v) x Temperature+3.48765E-003 x Methanol/oil (v/v) x Time+0.15 x KOH xTemperature-0.038KOH x Time+2.69444E-003 x TemperaturexTime-0.78402xMethanol/oil(v/v)^2-4.41x KOH^2-0.33505 x Temperature^2+2.35737E – 003 x Time^2

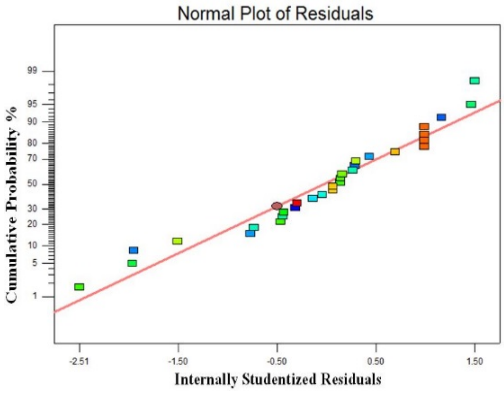

Fig. 7. Normal probability plot of residuals.

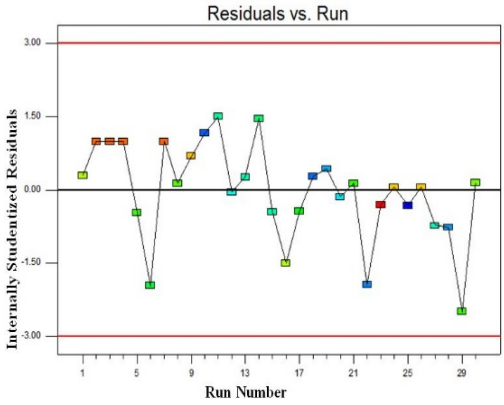

Fig. 8. Residuals Vs Run.

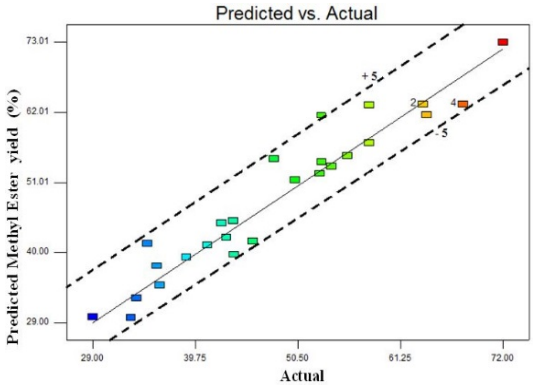

Fig. 9. Predicted and Actual Methyl Ester Yield.

chance of 0.01% and Model-F value happened due to noise. In this RSM model, the main aim is to increase the yield of methyl ester. For that methanol/oil volume ratio (factor A) was the important resolving factor. This was confirmed by the high F-value of 29.39 for factor A. The other process parameter, factor B (amount of Potassium hydroxide) also had a considerable impact on the biodiesel yield. The influence of temperature on ester yield was less significant. The two process variables namely methanol/oil volume ratio (factor A) and amount of Potassium hydroxide (factor B) had an interactive effect as observed from the p-value of 0.9728 which was less than 0.0500. R squared & adj R squared values found using RSM were 0.9255 and 0.8559 respectively is shown in Table 7. Lack of fit value 6.71 indicates that the lack of fit is significant. Signal to noise ratio can be evaluated by means of Adequate precision. In this present model a

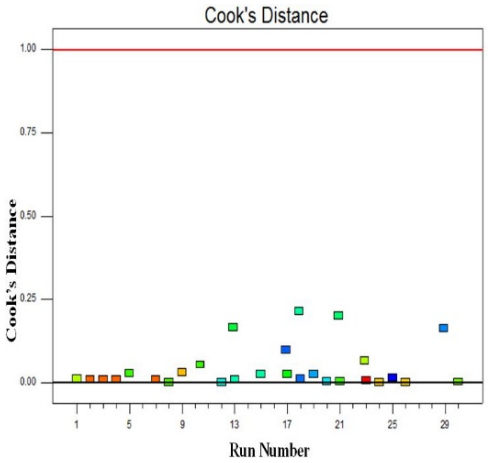

Fig. 10. Cook's Distance Vs Run.

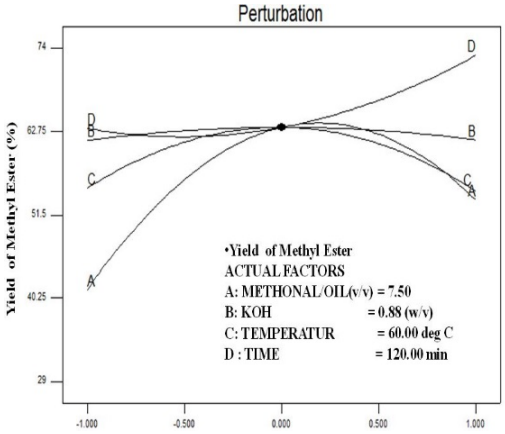

Fig. 11. Pertubation of Transesterification for Percentage Yield of Methyl Ester.

desirable value of 12.86 (value greater than 4) was found. This value indicates that the signal to noise ratio is low and this model could be applied to navigate the design space. The scattered points around the diagonal help in the comparison of Actual and Predicted values of methyl ester yield.+2.5% was the mean relative percent deviation (MRPD) value . Fig. 7 shows the normal distribution of the data which help to confirm the ANOVA results.

The RSM based predicted and actual methyl ester yield and perturbation chart is shown in the Fig. 8 and [9]. Cooks distance Vs Run number Fig. 10, was less than 0.2 was far low from the limits of 0.18. A negative non-linear steep curvature was found for methanol/oil volume ratio and the methyl ester yield in the Perturbation chart Fig. 11.The chart showed the ester yield for actual factors methol/oil 7.50 v/v,KOH 0.88 w/v,temperature 60^0C and time 60 mins Also, it was inferred that the (factor A) was the most important process parameter when comparedwith other variables. The other process variables like amount of alkaline catalyst, time and temperature showed a plateau shaped curves which indicate their less significance in the methyl ester yield. The response surface model for the ester yield comparing (factors AB, AC, AD) and (BC, BD, CD) is shown in Figs. 12 and 13 .The biodiesel yield was maximum when the methanol/oil volume ratio was kept minimum3:1v/v and the Potassium hydroxide added were also minimum.

5. CONCLUSION

In India, there is 10 million hectare of salt affected land and 13 million hectare of arid and semi-arid zones and this 23 million hectare of waste land available can be utilized for *Prosopis julifera* plantation. An average amount of 6.3 million litres of oil can be produced from about 1 million hectare plantation of *Prosopis julifera.* By the conversion of this *Prosopis julifera* oil to methyl esters, an approximate amount of 5 million litres of biodiesel can be produced. Hence, the species Prosopis julifera found abundant in our country can do wonders if utilized in a useful manner.

Biodiesel from *Prosopis julifera* oil was obtained by acid catalysed transesterification reaction using various catalyst concentration, methanol/oil molar ratios, reaction temperature and reaction time. The following points are concluded from the present work.

- In a two step acid esterification process using 1% v/v H_2SO_4 and9:1v/v methanol/oil ratio and 2 hours minimum reaction time, *Prosopis julifera* oil FFA level was decreased from 43.7mg KOH/gm to 8.6mgKOH/gm and then finally it was reduced to 2.7mg KOH/gm.
- The optimum condition for transesterification was found to be using KOH as catalyst, 0.75% w/v catalytic concentration, 9:1v/v molar ratio, 55^0C reaction temperature and 2 hours reaction time.
- The ester conversion efficiency with these parameters is 72%.
- Using Response surface methodology, optimum conditions of 7.5:1v/v methanol/oil molar ratio, 0.88% w/v sodium hydroxide, at an extraction temperature of 60^0C and an extraction time of 120 min produced 73.01% of methyl ester yield.
- The properties of refined biodiesel such as cetane number, kinematic viscosity, Acid value, calorific value after transesterification agrees well with the ASTM standards.
- The biodiesel obtained in this process could be the best suitable alternative fuel for direct injection diesel engines.

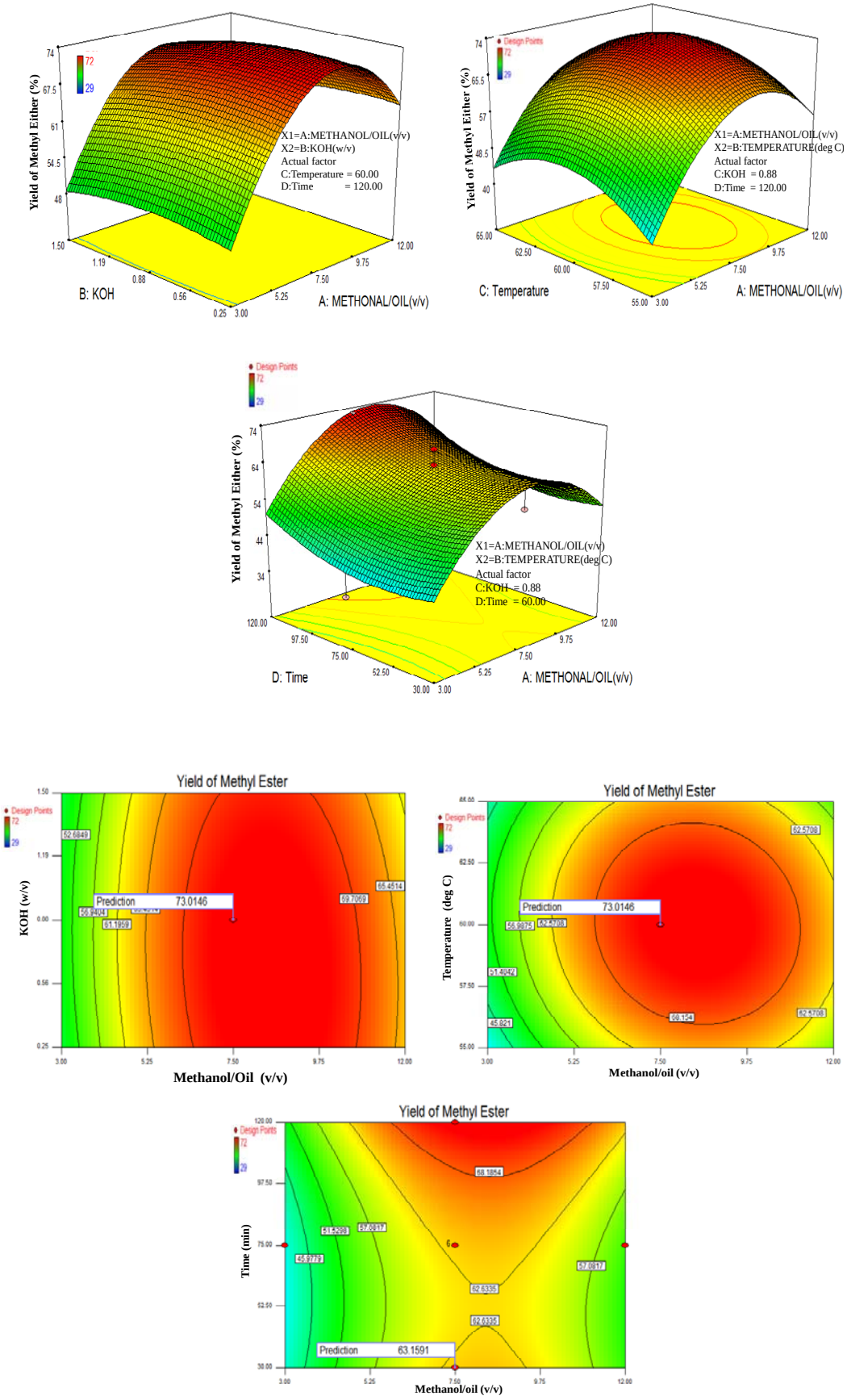

Fig. 12. Response Surface (3D) and contour plots of methyl ester as function.

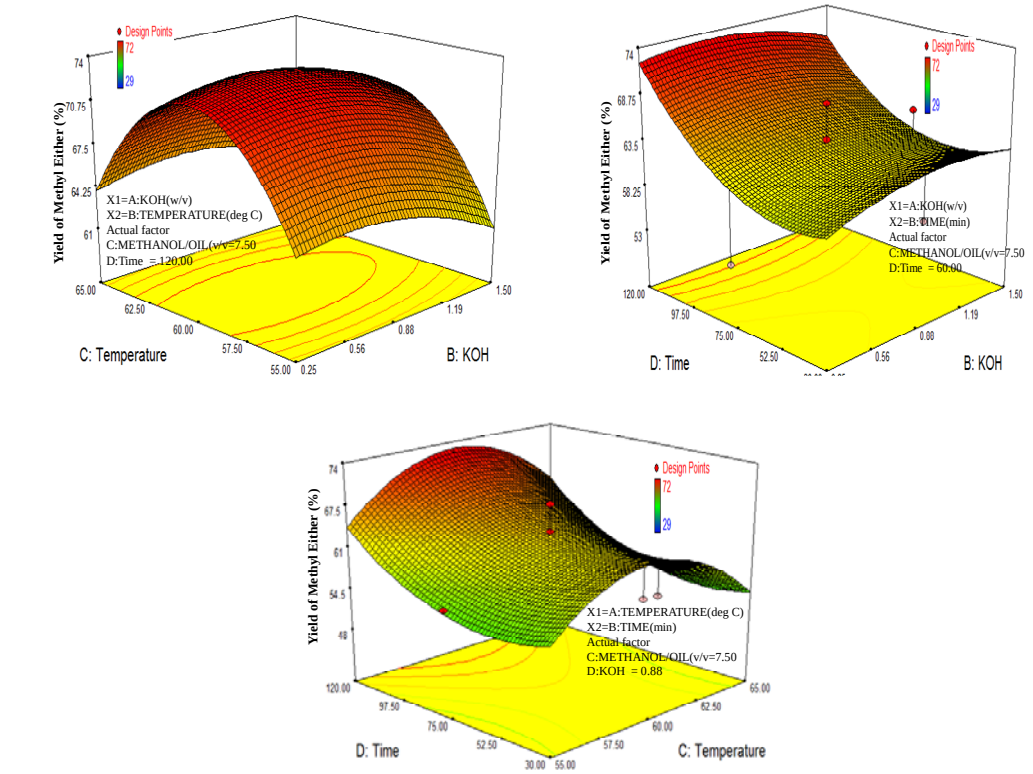

Fig. 13. Response Surface (3D) and contour plots of methyl ester as function relationship of BC, BD, CD base on the second order polynomial equation.

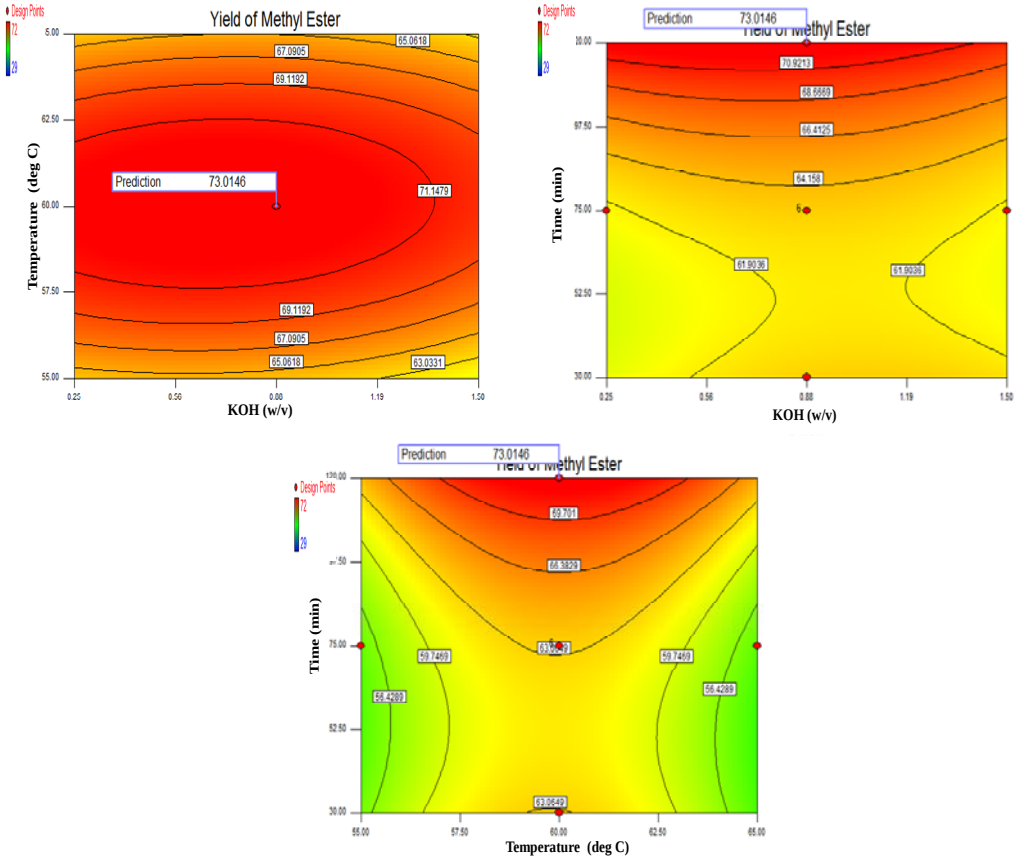

Fig. 13. Response Surface (3D) and contour plots of methyl ester as function relationship of BC, BD, CD base on the second order polynomial equation.

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