Journal of Mines, Metals and Fuels, 71(6): 743-750; 2023. DOI: 10.18311/jmmf/2023/32047

Print ISSN : 0022-2755

Journal of Mines, Metals and Fuels

Contents available at: www.informaticsjournals.com/index.php/jmmf

Palm Oil Sludge Biodiesel Production and Optimization using Box Behnken Design

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Abstract

Palm Oil Sludge (POS) was used to make biodiesel with HCl as an acidic catalyst along with methanol, followed by a transesterification reaction. The high Free Fatty Acid (FFA) content was reduced from 18.96% to 1.4% in the POS using 5% wt. of HCl, 7.5:1 molar ratio of Methanol to Palm Oil Sludge (POS) waste, 60 min stirrer and 400 rpm. The effect of reaction duration was also studied and found that 97.53% of FFA removal was achieved at 90 min of esterification process. The transesterification reaction yielded 94.66% biodiesel at catalyst loading 0.25%wt of NaOH for a reaction duration of 60min, at 60°C and 400 RPM. The properties of biodiesel produced was analyzed as per IS 1448 standards and was found comparable to ASTM D6751 petroleum diesel standards and ASTM D6751 biodiesel standards. This study also involves the optimization of process parameters for the removal of excess FFA using Response Surface Methodology (RSM) and Box-Behnken Design (BBD).

Keywords: *Palm oil Sludge (POS), Box-Behnken Design (BBD), Response Surface Methodology (RSM)*

1.0 Introduction

The feedstock utilized for biodiesel production contributes 75% of the overall cost of biodiesel production[2]. Biodiesel is a safe, clean, and disposable bio-based fuel and alternative fuels that had become necessary since there is a reduction in oil field reserves along with a high number of emissions produced during the combustion reaction[7,10]. Also, the Biomass and agricultural wastes also serves as renewable energy sources that can partially replace petroleum-based fuels. Biodiesel production depends on the climate, local soil conditions, and availability of crops/agricultural wastes.[16] Malaysia, as one of the world's foremost exporters and producers of palm oil, does have the potential to lead the palm oil biodiesel business[1]. Only 10% of the total biomass obtained from palm oil farms is transformed into edible oil, with around 90% of total biomass produced as waste materials[19]. The effective utilization of palm oil sludge (POS) and acidic crude palm oil (ACPO) have been mentioned as a viable feedstock for biodiesel synthesis[5]. However, because POS waste typically contains a large proportion of Free Fatty Acids (FFAs), it is impractical to convert it to biodiesel using the standard alkaline transesterification process. Crude palm oil after milling is inedible due to excessive FFA and impurity concentration. The POS produced by palm oil mills is a promising feedstock for the biodiesel production.

In the present study acid esterification of POS waste for biodiesel production was explored using process parameters including acid catalyst concentration, reaction time: and methanol to POS waste ratio. The transesterification reaction was carried out at 60°C. for a duration of 60min and NaOH concentration was optimized. The fuel properties of biodiesel were calculated.

Statistical based experimental designs like RSM are found

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to be more effective, since the variables are tested simultaneously. As the experimental studies are sensitive and time consuming for the purpose of optimizing the production parameters, it is essential to reduce the total number of experimental trials by using the design of experiments[6]. The current study deals with the application of Box–Behnken (BB) design to optimize the production parameters for biodiesel production by using POS waste sample in the presence of HCl as a catalyst.

2.0 Material and Methods

2.1 Preparation of POS waste and chemicals used

POS waste was obtained from Kalpavriksha Oil Palm Private Limited, a local mill located in Davangere, Karnataka, India. The POS waste used in the present work is the oil that has leached off during milling process, recovered from the large settling tanks kept for the separation process. The collected samples of POS waste were semisolid at room temperature. These samples were preheated to 60°C in an electrical heater and further filtered through a sieve of 2mm mesh, in order to remove the suspensions. The Laboratory Grade Methanol 99.8%, Hydrochloric acid and Sodium Hydroxide pellets, were brought from Sigma-Aldrich for the present work.

2.2 Characterisation of POS Waste sample

The characteristics of POS waste was determined according to standards methods of Pharmocopia USP-35 and Sadasivam (1996)[13]. The several Free fatty acid compositions of POS waste were analysed using GC. Clarus 500 Perkin Elmer along with Column Elite-5MS (95% Dimethyl oly siloxane/5% Diphenyl), with dimensions 30×0.25 mm × 0.25 m df along with mass detector Turbo Mass Gold-Perkin Elmer using Software Turbomass).

2.3 Esterification of Palm Oil Sludge (POS) using acid catalyst

The production of biodiesel from POS waste is a two-step process viz. the first step is acid-catalysed esterification process which reduces the FFA level of POS to lesser than 1% and the second step includes base-catalysed transesterification which yields biodiesel, followed by separation and refinement. The process variables in esterification step were optimised by varying HCl catalyst loading (2 to 6 % wt), molar ratio of methanol to POS (3.5:1 to 9.5:1), and reaction time (30 to 120 min) in a multiple batch process at a temperature of 60°C and stirrer speed of 400 rpm in order to convert excess FFA into Fatty Acid Methyl Ester (FAME) using the experimental set up shown in Figure 1. The experiments were performed in 500 ml independent batch reactor consisting of 100g of POS with methanol reflux condenser connected in series. The coolant was circulated using circulating pump from the coolant tank. The temperature of the reaction was regulated using a heater attached with PID controller.

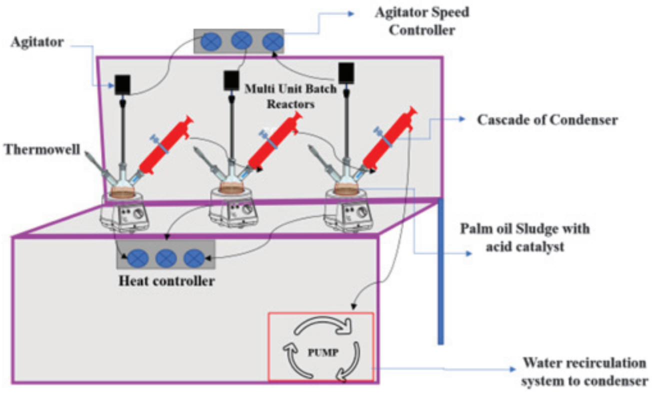

Figure 1: The laboratory set-up used for Biodiesel production

2.4 Statistical Analysis by Box–Behnken (BB) Design used for Esterification process

The study for optimizing the reaction parameters for pretreatment of palm oil sludge was performed using response surface methodology (RSM) using Statistica v7.0 (Statsoft, USA). Box Behnken experimental design with fifteen experimental runs with 3 factors each at 3 levels were conducted. The effect of three independent process variables methanol to waste POS molar ratio (x_1 ranging from 3.5:1 to 9.5:1), catalyst loading (x_2 ranging from 2% to 6 % wt of HCl/ wt of POS), and reaction time (x_3 ranging from 30 min to 120 min) on removal of % FFA (dependent variable) was studied using 3 centre points. The range of the variables were selected based on the initial studies conducted in lab. The levels and range of the variables selected are, mentioned in Table 1.

Table 1: Levels of Independent variables

Independent variable	Levels		
	-1	0	+1
Methanol : POS (mol ratio)	3.5:1	7.5:1	9.5:1
Methanol (mol)	0.46	1	1.27
Catalyst/POS (% wt/wt)	2	4	5
Time (Min)	30	90	120

Table 2 represents the Box Behnken Design matrix for the esterification process along with experimental and predicted values for % free fatty acid reduction. The ANNOVA was given

Table 2: Box Behnken Design matrix for the Biodiesel production from POS using HCl catalyst

	Three factor BBD, 1 block, 15 runs			% FFA Removal	
	Methanol (mol)	Catalyst/POS (%wt/wt)	Time (min)	Observed	Predicted
1	0.46	2	60	19.15	25.4378
2	1.27	2	60	29.69	38.8728
3	0.46	5	60	51.27	46.6786
4	1.27	5	60	87.71	76.8308
5	0.46	3	30	12.259	10.7023
6	1.27	3	30	25.570	25.0012
7	0.46	3	90	43.259	43.1193
8	1.27	3	90	64.570	66.8352
9	1.0	2	30	30.030	23.7117
10	1.0	5	30	18.36	26.8038
11	1.0	2	90	52.030	42.8777
12	1.0	5	90	97.53	99.9800
13	1.0	3	60	66.350	66.3500
14	1.0	3	60	66.350	66.3500
15	1.0	3	60	66.350	66.3500

Table 3: Characteristics of POS waste in comparison with the standard palm oil

Parameters	POS Waste	Standard palm oil
Colour	Reddish brown	Straw colour
FFA (%)	18.96% ±1.2	0.36
Moisture content (%)	1.9 ± 0.2	0.2
Iodine Value	65.04 ± 1.4	5.8
Saponification Value (mg of KOH/g oil)	243.06 ± 1.9	160.32
Acid number (mg of KOH/mg oil)	17.95 ± 1.5	< 1
Peroxide value (ml mole /kg)	1.32 ± 0.5	4.38
Specific Gravity	0.8 ± 0.02	0.8

in Table 3. The effectiveness of the quadratic models was determined from the regression coefficients (R^2=0.94, adj R^2=0.84). The lowest FFA value obtained at reaction time (90 Min), methanol concentration 7.45:1 at 5% HCl.

2.5 Transesterification Process

The transesterification process is carried out using the pre-treated palm oil sludge waste from the esterification process to yield crude biodiesel. This step was conducted in batch mode at 60°C reaction temperature, methanol to POS waste molar ratio 7.5:1, agitator speed 400 rpm, and reaction duration 60 min. However, the NaOH concertation was optimized in the range of 0.2 to 1.5%wt of NaOH/wt of POS by considering 100g of ester for each trial. In this step crude biodiesel was obtained.

2.6 Separation and Purification of Biodiesel

The crude biodiesel was repetitively washed with distilled water at 70ºC, and finally allowed to settle down. This process was continued for about 4 to 5 times until water used for washing purpose is clear and free from any debris[3]. Later the biodiesel was maintained at 70ºC using hotplate. Finally the biodiesel was analysed for the properties fuel as per IS: 1448.

3.0 Results and Discussion

3.1 POS waste characteristics

The POS waste collected for the present study has a bad odour which is due to the oxidation of oil present in the sludge sample and the exposure time.[17] The characteristics of POS waste and standard palm oil are tabulated in Table 3, which illustrates that the samples are non-edible, and therefore it can be used for the biodiesel production. Several authors suggested the calculation of molecular weight based

Table 4: Free Fatty Acid percentage (%FFA) of POS waste sample utilised for the present study

	Compound name	Chemical Formula	FFA (%)	Type of Fatty Acid
1.	Dodecanoic acid (Lauric acid)	$C_{13}H_{26}O_2$	1.72	Saturated
2.	Palmitic acid (Hexadecanoic acid)	$C_{17}H_{34}O_2$	43.05	Saturated
3.	Tetradecanoic acid (Myristic acid)	$C_{15}H_{30}O_2$	2.29	Saturated
4.	Octadecanoic acid (Steric Acid)	$C_{19}H_{38}O_2$	4.92	Saturated
5.	Oleic acid	$C_{19}H_{36}O_2$	46.84	Unsaturated
6.	Hexadecenoic acid (Palmitoleic acid)	$C_{17}H_{32}O_2$	0.67	Unsaturated
5.	Eicosenoic acid	$C_{21}H_{40}O_2$	0.51	Unsaturated

on saponification value and acid value of POS waste based on which the molecular weight of POS was calculated as 747.6 by using following equation[15,18].

$$\text{Molecular weight} = \frac{168300}{SV-AV} = \frac{168300}{243.06-17.95} = 747.6$$

The FFA profile of the SPO waste obtained by Chromatographic analysis. Table 4 indicates that POS samples are non-edible and contain more amount of unsaturated acid than saturated fatty acids. The POS waste samples collected for the present work contain fatty acids like Oleic and Palmitic acid which are essentially required for the production of biodiesel[7]. The Oleic and Palmitic acids have higher concentration in sludge palm oil waste and are good for the biodiesel production[8]. The POS used for the present study has more percentage of saturated FFA than unsaturated FFA i.e. oleic acid is 46.84% and palmitic acid is 43.05% (Table 4).

3.2 Reaction Parameters Optimization for Esterification Process

In order to convert FFA content in POS waste to FAME, esterification process was opted using HCl catalyst. The FFA content of the waste POS is found to be 18.96%, which is not suitable for direct biodiesel production via transesterification reaction, since this reaction is not possible to conduct if the % FFA in the feed is greater than 3%[20]. Therefore, the FFA limits was set to 1% as maximum for all esterification step for the better biodiesel yield during transesterification step. Hence the optimization of esterification reaction was performed in order to bring the FFA level to less than 1% by varying HCl concentration varying from 2 to 6% wt./wt, methanol to POS waste molar ratio, 7.5:1 and reaction time from 30 to 120 min at 60°C temperature, stirrer speed of 400 rpm stirrer speed.

3.3 Effect of Molar Ratio of Methanol to SPO Waste on FFA Removal

Different molar ratios of alcohol (methanol) to POS varying from 3.5:1 to 9.5:1 was used for the present study and

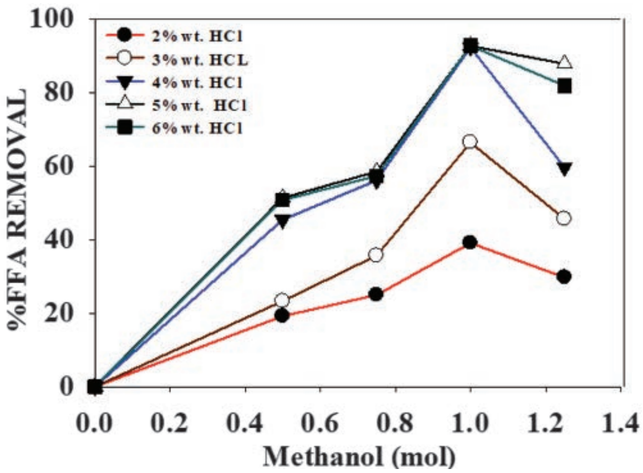

Figure 2: Effect of Methanol to SPO waste molar ratio for varying HCl concentrations at a constant temperature of 60°C and stirrer speed of 400 rpm for 90min.

effect of the same on FFA removal is presented in Figure 2. The surge in methanol to POS waste molar ratio had positive effect on the esterification process up to 7.5:1 molar ratio as the reaction equilibrium is reached. With further increase in molar ratio the FFA removal from POS is reduced. This could be due to extreme dilution of the reaction contents which has reduced the frequency of collision between the reacting molecules[4]. And also at high methanol concentration, the glycerol separation becomes practically more difficult due to the formation of an emulsion of glycerol and FAME which results reduced biodiesel yield.[3]

3.4 Effect of HCl catalyst dosage on FFA removal

Figure 2 also shows the effect of various catalyst dosages varying from 2 to 6% wt./wt on the decrease in the %FFA content in POS waste samples. At low catalyst dosages such as from 2% to 4% wt./wt. of HCl, the FFA removal was significantly low indicating inadequate amount of catalyst availability while converting triacylglycerols to methyl ester.

The HCl reduces the FFA content from 18.96% to 1.38% at 5% wt./wt. of catalyst which is slightly higher than the selected limits 1% FFA which could affect the biodiesel yield. At 6% catalyst the FFA reduction is not significant.[9] Hence the effect of time on FFA removal is studied.

3.5 Effect of Esterification Reaction Time on FFA Removal

The reaction time is a significant parameter for esterification step as prolonged heating can reverse the reaction. In the present work, the reaction time for esterification reaction was varied from 30 to120 min (Figure 3). It was found that the % FFA removal surged with surge in reaction duration up to 90 min with 97.53% FFA removal. With further enhancement of reaction duration the FFA removal was observed to be reduced as it favoured backward reaction[11]. The choice of proper reaction duration is essential for energy conservation and cost of pre-treatment process, hence the 90min reaction time was selected for present study[12].

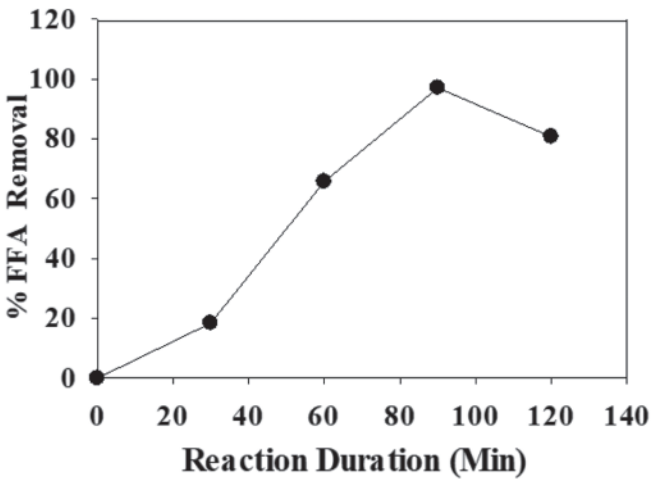

Figure 3: Effect of reaction duration on the FFA reduction in methanol to POS waste ratio of 7.5:1 for HCl catalyst concentration of 5% wt./wt.at a constant temperature of 6°C and stirrer speed of 400 rpm.

3.6 Optimized Esterification Reaction Condition

The optimum reaction conditions obtained for the reduction of FFA by esterification step using HCl catalyst were catalyst concentration 5% (wt./wt.), methanol to POS waste molar ratio 7.5:1 and reaction duration of 90 min at a temperature of 60˚C. The effective FFA of POS waste feedstock reduced from 18.96% to 0.57%. Using the above conditions, 91.6% ester yield was obtained.

3.7 Box Behnken Analysis

The process variables (Methanol to POS molar ratio, concentration of HCl and esterification process duration) and % FFA removal from POS was found to be in agreement with the second order polynomial regression equation. It was found from ANOVA Table 5 that a quadratic model is suitable to analyse the experimental data. The acceptability and accuracy of the formulated model were further explained by observing value of R^2=0.945 and adjusted R^2=0.848, which specify that the model is substantial to explains 84.8% of the variation in the experimental data with 95% level of significance. This confirm that the model is reliable and flexible[14].

The quadratic term $x_1^2, x_{2,}^2\ x_{3,}^2$ indicates the negative effect of the increase in the process variables.

$$Y = -107.296 + 143.483x_1 - 88.024x_1^2 + 13.529x_2 - 4.163x_2^2 + 1.333x_3 - 0.015x_3^2 + 6.88x_1x_2 + 0.194x_1x_3 + 0.325x_2x_3$$

The Response Surface plots are shown in Figure 4a, 4b, 4c. The surface plots were made between methanol to palm oil sludge ratio (x_1) and HCl (x_2) with FFA removal. Increase in both methanol/POS molar ratio and HCl concentration shows increase in the FFA removal up to 92.62%. Experimental observations revealed that with further increase in methanol concentration from 1 to 1.27 (9.5:1) the FFA reduction.

Table 5: Analysis of variance table (ANOVA) for the quadratic model

	SS	df	MS	F	p
Methanol (gmol) x_1	1882.493	2	941.246	9.12848	0.021431
Catalyst/POS (g/g) x_2	1717.292	2	858.646	8.32740	0.025618
Time (Min) x3	4672.629	2	2336.314	22.65825	0.003113
1*2	77.629	1	77.629	0.75287	0.425245
1*3	23.337	1	23.337	0.22633	0.654320
2*3	903.273	1	903.273	8.76020	0.031528
Error	515.555	5	103.111		
Total SS	9506.482	14			

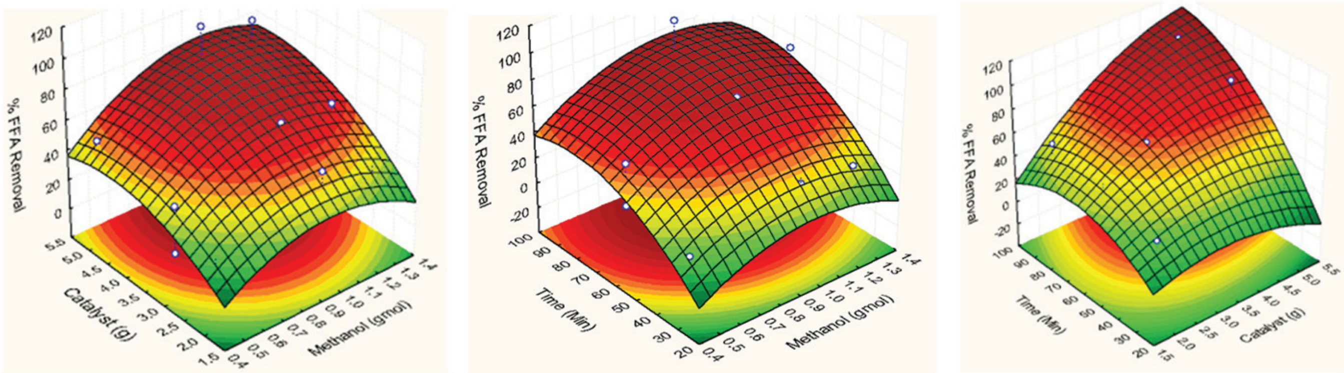

Figure 4: Three-dimensional Response surface plots for the (a) Effect of methanol/SPO molar ratio. (b) Effect of Reaction Time on Methanol molar ratio (c) Effect of reaction time on HCl catalyst concentration.

Increase in both methanol/POS molar ratio and reaction duration have positive influence on FFA removal. Increase in HCl concentration and reaction duration initially free fatty acid removal was increased and further increase in both shows negative influence on free fatty acid removal.

The optimal methanol concentration was 7.5:1, HCl concentration 5% and reaction duration 90 min yields final FFA removal to 97.53%. Table 6 shows the optimised process parameter fort the maximum removal of FFA from waste SPO.

3.8 Alkaline Catalysed Transesterification for Crude Biodiesel Production

In the second phase of reaction for biodiesel production, the esterified POS waste was considered for the transesterification process. During this reaction not only the viscosity of oil is reduced but also converts the triglycerides into ester.[2] The transesterification reaction was carried out with varying NaOH base catalyst concentration varying from 0.2 to 1.5% wt./wt. in the present work, 60°C temperature, stirrer speed of 400 rpm and 60 min of the reaction duration. The traces of FFA left was neutralized by using alkaline catalyst during present step. The maximum biodiesel yield obtained in this step was 94.66% at 0.25% wt./wt. of NaOH catalyst (Figure 5).

Table 6: Optimized process parameters for FFA removal from POS using HCl catalyst

Parameter	Optimum value
% FFA removal	92.62
Methanol to POS molar ratio	7.5:1
Catalyst	5% wt./wt.
Duration	90 min

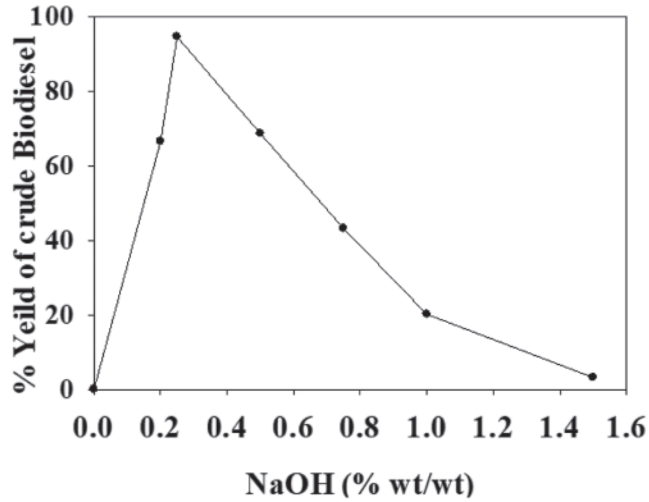

Figure 5: Effect of NaOH catalyst loading on yield of crude biodiesel at a constant temperature of 60°C and stirrer speed of 400 rpm for a reaction duration of 60min.

3.9 Separation and Purification

After the completion of the transesterification step, the mixture was kept in the separating funnel to settle down for about 24 hours followed by repeated washing and drying at 70°C till the crude biodiesel is free from suspensions and impurities. Further the biodiesel was maintained at 70°C with continuous stirring so settle the debris. The similar process for the purification of crude biodiesel obtained from palm oil was performed after transesterification process by other researchers[3].

3.10 Biodiesel Characteristics

The properties of biodiesel differ with the source used for its preparation. The fatty acid compositions of raw materials determines the properties of the biodiesel produced. Table 7

Table 7: The Fuel properties for the SPO waste biodiesel compared with Standard Biodiesel and Standard Petroleum Diesel

Fuel properties	Test Protocol	POS waste Biodiesel	Biodiesel Standard as per (ASTM D6751)	Fuel properties of Petroleum Diesel as per (ASTM D6751)	ASTM Standards
Density at 15°C	IS: 1448 (P 32)	0.858	870 – 900	820	ASTM D445
Cloud point (°C)	IS: 1448 (P 6)	-14	-3 to 12	-28 to -7	ASTM D287
Calorific value (MJ/kg)	IS: 1448 (P 6)	40.98	37 to 42.5	43.5	ASTM D613
Viscosity (40°C)	IS: 1448 (P 25)	10.4	1.9 – 6.0	2.54	ASTM D97
Pour point (C)	IS: 1448 (P 10)	10	-15 to 10	-15	ASTM D613
Flash point (°C)	IS: 1448 (P 66)	164	130	54	ASTM D2500

shows the properties of SPO waste-based biodiesel analysed as per IS 1448 standards are comparable to ASTM D6751 petroleum diesel standards and ASTM D6751 biodiesel standards. The fuel properties of biodiesel show the effectiveness of the proposed processing of waste SPO waste using esterification and transesterification reactions for the biodiesel production

3.0 Conclusions

The FFA content from the POS selected was reduced up to 97.53% using optimised condition of 7.5:1 methanol to SPO molar ratio 5% wt/wt. of HCl, 90 min during esterification step for further alkaline catalysed transesterification process. Else it would have been practically not possible to conduct the direct transesterification process as suggested by many authors. The esters yield was observed to be 91.6% using which the 94.66% of biodiesel yield was obtained by using 0.25% wt/wt NaOH catalysed transesterification. The SPO waste biofuel produced in the current study meets ASTM D6751 standards of biodiesel fuel. The response surface methodology (RSM) through Box- Behnken Design (BBD) was utilised to study the effects of the process parameters on FFA removal. The ANOVA showed that the results obtained are acceptable. A decent agreement was found between the experimental and intended values. This indicates the fitness of the regression analysis as a tool towards the optimization of production parameters. R^2 = 0.94 which signifies that the developed model fits well.

4.0 Acknowledgment

The authors would like to acknowledge the organization of Sir MVIT (Sir M Visvesvaraya Institute of Technology, Bengaluru and MSRIT (M S Ramaiah Institute of Technology), Bengaluru for their continuous support.

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