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Yield Optimisation for Biodiesel Production from Locally Available Waste Cooking Oil (WCO) using Taguchi Technique and Its Characterisation

Prasanta Kumar Choudhury[1*], Dilip Kr. Bora[2], Uddipta Das[3], Syed Fakhruz Zafri Zaman[4],

[1] Associate Professor, Assam Engineering College, Guwahati, Assam, India*
[2]Principal, Dhemaji Engineering College, Dhemaji, Assam, India
[3] Senior Design Engineer, Cummins India Limited, Pune, Maharashtra, India
[4] Assam Engineering College, Guwahati, Assam, India

Abstract:- The majority of energy demand is met by traditional energy sources such as coal, petroleum, and natural gas (NG). Diesel and petrol engines play an important role in the economy as well as in the daily lives. However, these fuels have a finite supply that is concentrated in only few places throughout the world. With the growing consumption, these resources are rapidly becoming extinct. But the global need for energy continues to rise. Due to this limitation, renewable energy sources have become increasingly appealing. Alternative fuels are the most practical option to achieve this expanding need. They will not only fulfill the increasing demand but also reduce carbon footprint. In this regard biodiesel has proved itself as a very potent fuel so far its sustainability and nature friendly behavior is concerned. Being a mixture of mono-alkyl esters of long-chain fatty acid and popularly known as Fatty Acid Methyl Esters (FAME), biodiesel is synthesised from renewable lipid feedstocks such as vegetable oil or animal fats. It is usually blended with mineral diesel in different percentages. By using biodiesel, we can lower the emission of harmful gases which causes various environmental problems. Waste cooking oil (WCO) being very easily accessible in abundance at low cost can be put in to use for producing FAME i.e., biodiesel. WCO has been found to create lots of problems such as clogging drainage system because of its non-biodegradable nature and also creating health threatening issues due to its repeated consumption. So instead of spilling or repeated use it can be put in to process for producing necessary biodiesel which is pollution free and will also lead to the economy of the energy sector. Here WCO was collected from a college canteen and biodiesel was synthesised from it through transesterification. The physico-chemical properties of the obtained biodiesel with its characterisation study conformed to the ASTM standard. For yield (%) optimisation of biodiesel, Taguchi's Orthogonal Array (L_9) based design strategy was made considering Methanol to Oil Molar Ratio, Catalyst amount (%w/w), Reaction time (min) and Reaction temperature (^{0}C) as controlling factors taken each at three different levels i.e., low, medium and high. The obtained optimal setting for yield from Average Performance and Signal-to-noise ratio (S/N) graph was validated through the regression model generated using MINITAB-21 software. The concerned optimal setting for yield (%) of biodiesel production was found to be at methanol to oil ratio (6:1), catalyst amount (1% KOH concentration), reaction time (90min) and reaction temperature (55˚C). This setting for maximum yield was also validated through the prediction formula. From the Analysis of Variance (ANOVA) carried out with the yield response data, all the factors were found to be significant. Although there was observed the relative significance amongst the factors. Catalyst amount was found to be most significant followed by Reaction temperature, Methanol to Oil molar ratio and at last the Reaction time.

Keywords*: Waste Cooking Oil (WCO), Fatty Acid Methyl Esters (FAME), Taguchi's Orthogonal Array, Signal-to-noise ratio (S/N), ANOVA.*

1. Introduction

The global stockpile of fossil fuel is limited and it is coming to an end soon. Moreover its exponential rise of pollution has made the world to delve in to the field of alternative sources of energy along with meeting the energy demand of the ever-increasing population. In India, the need to search for alternatives is very critical as it mostly depends upon foreign countries for the energy demand. Besides wind, solar, nuclear energy, etc. it has biodiesel as a very potent fuel that can be produced at a very minimal cost. It is a clean-burning fuel that releases significantly lower levels of harmful pollutants such as sulphur oxides, particulate matter and carbon monoxide compared to traditional diesel. Biodiesel also reduces greenhouse gas emissions, primarily carbon dioxide (CO_2), when considering the full life cycle of its production, usage and eventual combustion. Biodiesel is considered a carbon-neutral fuel because the CO_2 released during combustion is roughly equivalent to the CO_2 absorbed by the plants used to produce the feedstock [7]. This closed-loop carbon cycle makes biodiesel a more sustainable option compared to fossil fuels. For example, the net CO_2 emission of biodiesel is zero. Because the sources of biodiesel are predominantly plant-based oils, so the CO_2 is first absorbed by the plants in producing the oil for biofuel generation and the same amount of CO_2 is released after combustion in engines. So, biodiesel when used as a blend or pure form does not contribute to global warming. In terms of heat release, biodiesel has higher heat release (39-41 MJ/kg) than coal (32-37 MJ/kg) but lower than gasoline (46 MJ/kg), petro diesel (43 MJ/kg), or petroleum (42 MJ/kg) [1].

Research in biofuel sector had started way back in 1930 where first generation feedstocks were used. But from the year 2000 the trend has shifted more on producing biodiesel from waste products; mostly Waste Cooking Oil (WCO). WCO refers to edible oil which has formerly been used for frying in households, restaurants and hotels, and no longer be used for similar purpose. A thorough and comprehensive assessment of waste cooking oil-based biodiesel manufacturing research is becoming increasingly important. The research done from the period 2000 to 2020 has been divided into 3 stages: the starting stage (2000–2007), the investigation stage (2008–2015), and the steady development stage (2016–2020). During the starting stage research work were very few in number, but the steady development stage showed almost 11 times the growth compared to starting stage. This might be attributed in part to the international push to meet the 17 United Nations Sustainable Development Goals (SDGs) by 2030, which was first proposed in 2015[23]. However this has proved to be a boon in disguise as the number of research work in this sector has increased.

Most countries have found that disposing of Waste cooking oil (WCO) has become a difficulty due to the vast volume of WCO created each year. WCO cannot be dumped into drains or sewers since it will cause obstructions, odour and vermin problems, as well as polluting waterways, causing animal concerns. If it is placed in a municipal solid waste landfill or a municipal sewage treatment facility, it is likewise forbidden and will cause difficulties [24]. Using them for producing biodiesel opens up quite a number of prospects.

Some of the feedstocks for biodiesel production are rapeseed oil, soybean oil, sunflower oil, canola oil, palm oil, animal tallow, poultry oil, cooking oil etc. Waste cooking oil being the most easily available and also being the cost-effective source.

2. Materials and Method

In this work Waste Cooking Oil (WCO) was used as the concerned feedstock for the production of biodiesel through transesterification. A local college canteen provided the necessary WCO produced daily from refined oil used for papad frying. Using filter paper the oil was filtered for solid impurities. After collection of the oil, its different requisite physico-chemical properties were determined based on ASTM methods as shown in the Table 1. A batch stirred reactor was used for carrying out experimental reactions through transesterification. The reactant alcohol here used was Methanol whereas KOH was applied as the alkali catalyst because of its ability to catalyze at low temperature and also having high yield rate and economy.

Table 1: Determination of ASTM based properties of WCO [2, 9]

Properties	Units	ASTM Test method	Obtained values of WCO
Density at 15^0C	kg/m^3	D1298	912.78
Kinematic viscosity @ 40^0C	cSt	D445	32.45
Saponification number	$mgKOH\text{-}g^{-1}$	D5558	14.025
Iodine Value	g Iodine/g of sample	D5554	31.876
FFA content	%	D974	0.561

2.1 Design Strategy:

For biodiesel production by the transesterification process the yield of biodiesel is affected by the factors like alcohol to oil molar ratio, catalyst concentration, reaction temperature, reaction time, stirring speed, etc. So far the maximum yield is concerned; it has been experienced from literature survey that the contribution of all these factors is noticeable. The factors are varied in an ascending order like low, medium and high. Here, in this work four controlling factors, such as, Methanol to oil molar ratio, catalyst amount (%w/w), reaction time (min) and reaction temperature (^{0}C) have been selected with three levels corresponding to each factor as shown in Table 2. These factors are also called process parameters. Based on this, Taguchi's L_9 orthogonal array is designed as shown in Table 3. The transesterification reaction is done for these 9 treatment conditions.

Table 2: Control factors with their levels for yield

Designation	Control factors	Levels		
		Level 1	Level 2	Level 3
A	Methanol to oil molar ratio	4:1	6:1	9:1
B	Catalyst amount (%w/w)	0.5	1	1.5
C	Reaction time (min)	60	75	90
D	Reaction temperature (℃)	50	55	60

Table 3: Taguchi's L_9 orthogonal array

Treatment Condition (TC)	Control factors and levels			
	A	B	C	D
1	1	1	1	1
2	1	2	2	2
3	1	3	3	3
4	2	1	2	3
5	2	2	3	1
6	2	3	1	2
7	3	1	3	2
8	3	2	1	3
9	3	3	2	1

2.2 Data Collection and Analysis:

2.2.1 Experimental runs and data collection:

The transesterification reactions were carried out according to the orthogonal array L_9 and the respective percentage of yields were tabulated as shown in the Table 4. Three replications were done against each treatment condition.

Table 4: Observed yield for each treatment condition

TC	Control factors and levels				Yield (%)			Mean Yield (%)
	A	B	C	D	Rep1	Rep2	Rep3	
1	4:1	0.5	60	50	71.5	73.2	71.6	72.1
2	4:1	1	75	55	92.7	92.8	93.5	93.0
3	4:1	1.5	90	60	89.6	90.1	91.2	90.3
4	6:1	0.5	75	60	85.5	85.8	86.7	86.0
5	6:1	1	90	50	88.3	89.4	87.5	88.4
6	6;1	1.5	60	55	94.8	93.9	96.3	95.0
7	9:1	0.5	90	55	84.2	83.1	85.6	84.3
8	9:1	1	60	60	91.5	90.0	92.7	91.4
9	9:1	1.5	75	50	82.8	83.0	83.2	83.0

2.2.2 Data analysis:

After obtaining all the nine number of yields the response table for the means for each factors at all the levels has been formed as shown in Table 5. From this table the average performance graph has been plotted as shown in the Fig 1. Here the optimal setting was obtained at $A_2B_2C_3D_2$ i.e., i.e., medium level (6:1) for methanol to oil molar ratio, medium level (1.0% w/w) for catalyst amount, high level (90min) for reaction time and medium level (55^0C) for reaction temperature.

Table 5: Response table for means

Levels	Control Factors			
	A	B	C	D
	Methanol to Oil Molar Ratio	Catalyst amount (%w/w)	Reaction time (min)	Reaction temperature (℃)
1	85.13	80.80	86.17	81.17
2	***89.80***	***90.93***	87.33	***90.77***
3	86.23	89.43	***87.67***	89.23
Delta	4.67	10.13	1.50	9.60
Rank	3	1	4	2

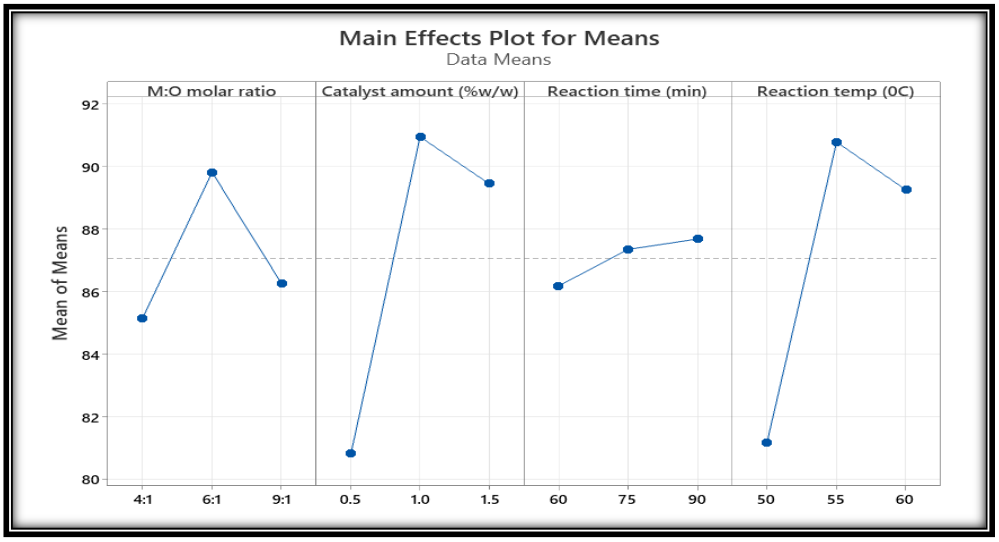


Fig 1: Average Performance Graph

For validation of the results of above obtained optimal setting the average signal to noise (S/N) ratio graph was plotted as shown in Fig 2 using the Table 6 and Table 7. Here also the same optimal setting i.e., $A_2B_2C_3D_2$ was obtained.

Table 6: S/N ratio for each treatment condition

TC	Control factors and levels				Yield (%)			S/N Ratio
	A	B	C	D	Rep1	Rep2	Rep3	
1	1	1	1	1	71.5	73.2	71.6	37.16
2	1	2	2	2	92.7	92.8	93.5	39.37
3	1	3	3	3	89.6	90.1	91.2	39.11
4	2	1	2	3	85.5	85.8	86.7	38.69
5	2	2	3	1	88.3	89.4	87.5	38.93
6	2	3	1	2	94.8	93.9	96.3	39.55
7	3	1	3	2	84.2	83.1	85.6	38.52
8	3	2	1	3	91.5	90.0	92.7	39.22
9	3	3	2	1	82.8	83.0	83.2	38.38

Table 7: Response table for mean Signal to Noise (S/N) ratios

Levels	Control Factors			
	A	B	C	D
	Methanol to Oil Molar Ratio	Catalyst amount (%w/w)	Reaction time (min)	Reaction temperature (℃)
1	38.55	38.12	38.64	38.16
2	***39.06***	***39.17***	38.81	***39.15***
3	38.70	39.02	***38.85***	39.01
Delta	0.51	1.05	0.21	0.99
Rank	3	1	4	2

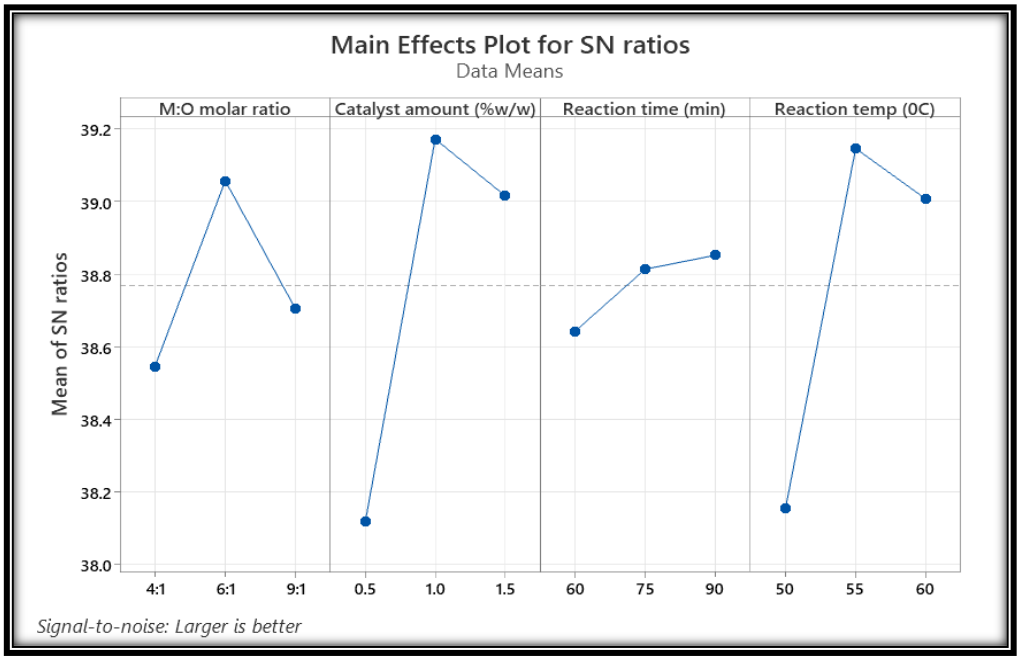


Fig 2: Average Signal to noise (S/N) ratio Graph

For further validation of the obtained optimal setting of the yield process parameters, a regression analysis was carried out. Here a concerned regression model for yield was generated as shown below in Eq (i) using the response data with the help of Minitab-21 statistical software at 95% confidence level.

YIELD (%) = 87.056- 1.922 M:O MOLAR RATIO_4:1+ 2.744 M: O MOLAR RATIO_6:1- 0.822 M:O MOLAR RATIO_9:1-6.256 CATALYST AMOUNT (%W/W)_0.5+ 3.878 CATALYST AMOUNT (%W/W)_1.0 + 2.378 CATALYST AMOUNT (%W/W)_1.5 - 0.889 REACTION TIME (min)_ 60 + 0.278 REACTION TIME (min)_ 75 + 0.611 REACTION TIME (min)_ 90 – 5.889 REACTION TEMP (^{0}C)_50 + 3.711 REACTION TEMP (^{0}C)_55 + 2.178 REACTION TEMP (^{0}C)_60

Eq (i)

Table 8: Regression model summary

S	R-sq	R-sq (adj)	R-sq (pred)
0.941630	98.61%	98.00%	96.88%

As seen from the Table 8 of model summary, R^2 value was found to be 98.61% and it corresponds to a comparatively good fitting. A comparison of regression model fits with experimental values of yield was made as shown in the Table 9 and a corresponding comparative graph was drawn as shown in Fig 3.

Table 9: Comparison of experimental and regression model based values of Yield

TC No.	Experimental Yield Value (%)	Regression Model based Yield Value (%)
1	72.1	72.1
2	93.0	93.001
3	90.3	90.841
4	86.0	86.0
5	88.4	88.4
6	95.0	95.0
7	84.3	84.3
8	91.4	91.4
9	83.0	83.001

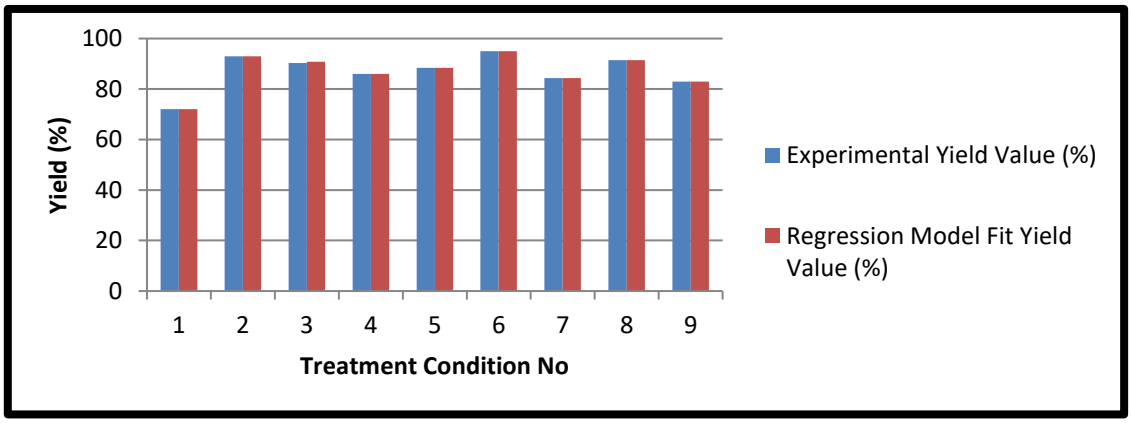


Fig 3: Comparative graph of experimental and regression model based values of Yield

The yield value at the obtained optimal setting was calculated using the model equation for validation. It was found that the yield obtained from the regression model for the concerned optimal setting (i.e., 98.61%) was

highest amongst all the nine treatment conditions. Moreover a confirmation run was again carried out at the obtained optimal setting. Its yield value (97%) was found very near to the model given value (98.61%) as shown in the Table 10.

Table 10: Optimal yield (%) from regression model and confirmation run

Yield (%) at Optimal Setting		
Optimal Setting	From Regression model	From Confirmation Run
$A_2B_2C_3D_2$	98.61%	97%

The theoretical maximum value of response under optimum condition can be predicted by using the following Eqn (ii) –

$$Y_{max} = 10^{(\frac{S_o}{20})} \quad \text{Eq (ii)}$$

Where, Y_{max} is the theoretical maximum response value and S_o is the corresponding S/N ratio under optimum condition.

S_o is calculated using additive model Eq (iii) as given below –

$$S_o = S_m + \{(S_A - S_m) + (S_B - S_m) + (S_C - S_m) + (S_D - Sm)\} \quad \text{Eq (iii)}$$

Where, S_m is the mean S/N ratio and S_A, S_B, S_C, S_D are the level mean S/N ratio at the optimal level of each parameter. [51, 52]

Here $S_o = 38.77 + \{(39.06 - 38.77) + (39.17 - 38.77) + (38.85 - 38.77) + (39.15 - 38.77)\}$

$S_o = 39.92$

Now $Y_{max} = 10^{(\frac{39.92}{20})} = 99.08$

As seen here, the predicted theoretical percentage yield value corresponding to the optimal setting i.e., 99.08% was found to be the highest amongst all the obtained mean yield values of Table 4. This result also conforms to the optimum yield value and setting of factors as obtained from regression analysis.

To analyse the significance of the controlling factors over yield Analysis of Variance (ANOVA) was done at 95% confidence level as shown in the Table 11.

Table 11: Analysis of Variance (ANOVA) table for Yield

Source		DF	Adj SS	Adj MS	F value	Tabulated F value	Significant/ Insignificant
A	Methanol to Oil Molar Ratio	2	107.13	53.563	60.41	$F_{0.05,2,18}$=3.55	Significant
B	Catalyst amount (%w/w)	2	538.41	269.203	303.61		Significant
C	Reaction time (min)	2	11.17	5.583	6.30		Significant
D	**Reaction temperature (℃)**	2	478.75	239.373	269.97		Significant
Error		18	15.96	0.887			
Total		26	1151.41				

As shown in the above Table 11 of ANOVA, all the factors were found to be significant. Although there was observed the relative significance amongst the factors. Catalyst amount was found to be most significant

followed by Reaction temperature, Methanol to Oil molar ratio and at last the Reaction time. The same order of significance was also reflected in the rank row of Table 4 and Table 5.

After finding out the optimal yield setting, the WCO biodiesel was synthesised accordingly and its different properties were compared with ASTM standard and tabulated as shown in Table12. Here it was observed that the properties of the derived biodiesel well conformed to the standard values and it behaved nearly as that of the petro-diesel.

Table 12: ASTM based properties of biodiesel derived from WCO [2, 9]

Properties	Units	Biodiesel		Obtained values of WCO biodiesel
		Test method	Limits	
		ASTM D6751		
Density at 15^0C	kg/m^3	D941	860 - 900	895
Kinematic viscosity @ 40^0C	cSt	D445	1.9 - 6	4.35
Calorific value	MJ/kg	D240	35-41	39.72
Flash point	^{0}C	D93	>130	168.4
Fire point	^{0}C	D6751	176	178.8
Poor point	^{0}C	D97	-4 to -1	-1
Cloud point	^{0}C	D2500	-3 to 15	3
Cetane number	-	D613	>47	51

2.2.3 Characterisation study of produced WCO biodiesel:

After the production of WCO biodiesel at its optimal setting its following characterisation studies were carried out.

(i) Nuclear Magnetic Resonance Spectroscopy (^{1}HNMR)Analysis :

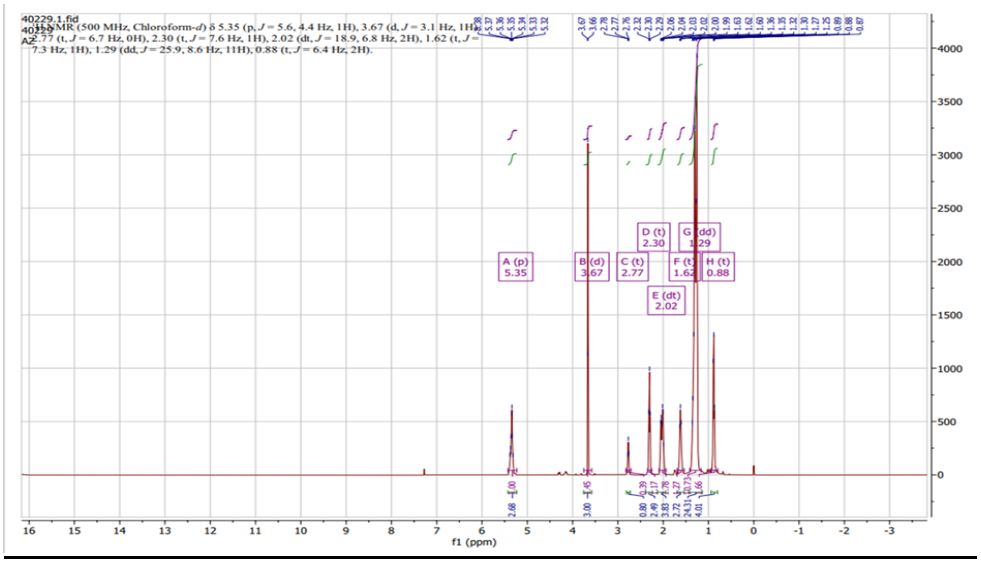


Fig 4: ^{1}H NMR spectrum of FAME

The ^{1}H NMR spectrum of the synthesised FAME is presented in Fig 4 and its corresponding peak characteristics have been summarised in the Table13. The peaks at δ = 5.38-5.32 ppm represent the presence of olefinic protons in FAME. A strong doublet peak at δ = 3.67 ppm is due to the -CH_3 group present in methyl ester. A triplet in the range δ = 2.78-2.76 ppm is assigned to the presence of α-methylene group attached to two double bonds. Presence of α-methylene group to ester is confirmed by a triplet at δ = 2.32-2.29 ppm. The appeared peaks at δ = 2.06-1.99 ppm for the protons in the olefinic (-CH=CH) group. The peaks for β-methylene proton are appeared at δ = 1.63- 1.60 ppm. The peaks in the range δ =1.36 - 1.25 ppm represent the protons of all the internal CH_2 groups present in the FAME backbone, whereas the triplet at δ=0.89- 0.87 ppm correspond to the protons of terminal methyl group.

Table 13: Peak characteristics of the synthesised FAME from ^{1}H NMR analysis:

Chemical Shift Value (δ, ppm)	Functional Group	Assigned proton(s)
5.38-5.32	-CH=CH-	Olefinic protons
3.67-3.66	-$COOCH_3$	Methyl ester
2.78-2.76	=CH-CH_2-CH=	α-methylene group in between two double bonds
2.32-2.29	-CH_2COOR	α-methylene group attached to ester
2.06-1.99	=CH-CH_2-	α-methylene group attached to one double bond
1.63-1.60	-CH_2CH_2-COOH	β-methylene proton
1.36-1.25	-CH_2-	CH_2 present in FAME backbone
0.89-0.87	CH_3-C	Terminal methyl group

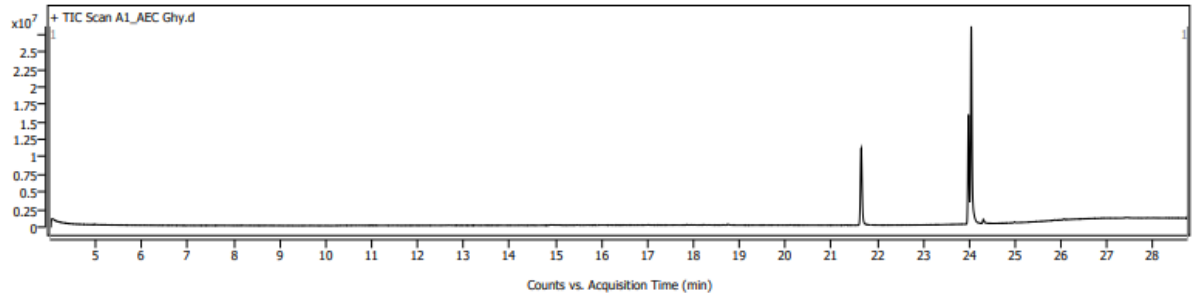
(ii) Gas chromatography-mass spectrometry (GC-MS) analysis:

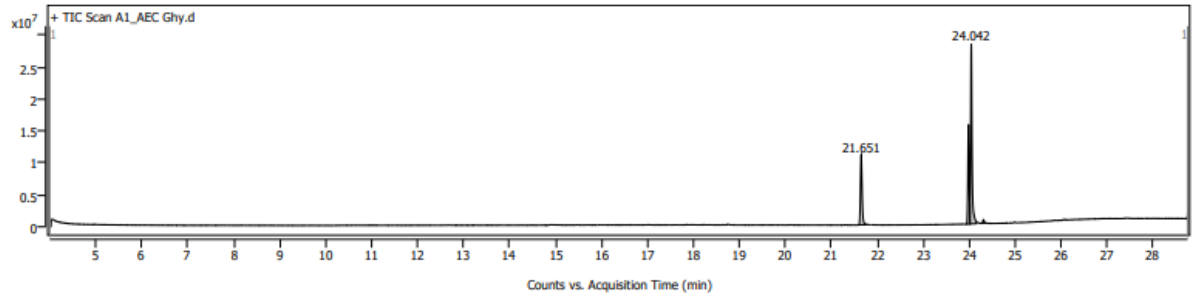
GC-MS analysis was executed to find out the different components present in the synthesised FAME. The results are presented in the gas chromatogram (Fig 5(a), (b) & (c)). The four components of biodiesel are obtained at retention times (min) of 21.651, 23.981, 24.042 and 24.307 show the base peaks at m/z 74.00, 67.07, 55.10 and 44.02 respectively. The synthesised biodiesel has a higher content of 6-Octadecenoic acid, methyl ester (50.71 %), 9, 12- Octadecadienoic acid (Z, Z)-methyl ester (24.47 %), Hexadecanoic acid, methyl acid (23.82 %) and Methyl stearate (1.00 %). The biodiesel consists of 24.82 % saturated FAMEs and 75.18 % unsaturated FAMEs. The components of FAMEs are from C17 and C19. Table 14 shows the details of the peaks obtained in GC-MS analysis of the synthesised biodiesel.

Sample Information

Name	A1_AEC Ghy	**Data File Path**	D:\MassHunter\GCMS\1\data\EXTERNAL SAMPLES\AEC Ghy\A1_AEC Ghy.D
Sample ID		**Acq. Time (Local)**	5/19/2022 10:47:03 AM (UTC+05:30)
Instrument	GCMS	**Method Path (Acq)**	D:\MassHunter\GCMS\1\methods\General_260_28.75.m
MS Type	QQQ	**Version (Acq SW)**	MassHunter GC/MS Acquisition 10.0.384.1 14-Feb-2019 Copyright © 1989-2018 Agilent Technologies, Inc.
Inj. Vol. (ul)	0.3		
Operator	Saikat		

Sample Chromatograms



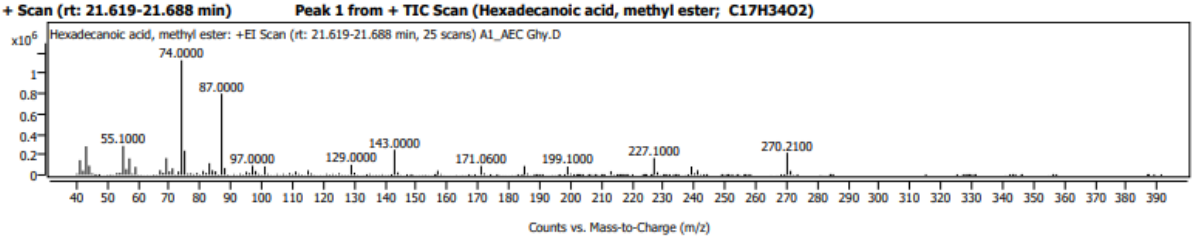


Chromatogram Peaks

Peak	RT	Area Sum %
1	21.651	23.82
2	23.981	24.47
3	24.042	50.71
4	24.307	1.00

Sample Spectra

+ Scan (rt: 21.619-21.688 min) **Peak 1 from + TIC Scan (Hexadecanoic acid, methyl ester; C17H34O2)**



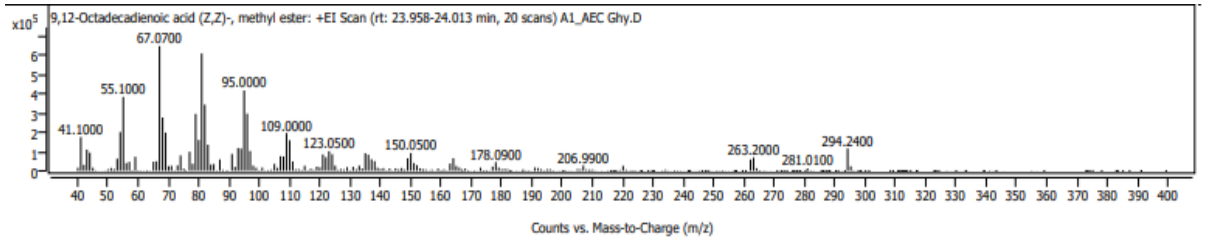
Spectrum Identification Table

Best	ID Source	Name	Formula	Species	m/z	Diff (ppm)	CAS	Score	Score (Lib)	Score (DB)	Score (MFG)	Lib/DB
Yes	LibSearch	Hexadecanoic acid, methyl ester	C17H34O2				112-39-0	93.31	93.31			W11N17main.L
No	LibSearch	Hexadecanoic acid, methyl ester	C17H34O2				112-39-0	92.71	92.71			W11N17main.L
No	LibSearch	Hexadecanoic acid, methyl ester	C17H34O2				112-39-0	92.37	92.37			W11N17main.L

Best	Name	Formula	m/z (prec.)	CAS	RT (DB)	RT Diff	Score	Score (Lib)	Score (Fwd)	Score (Rev)	Lib/DB
Yes	Hexadecanoic acid, methyl ester	C17H34O2		112-39-0	31.300		93.31	93.31			W11N17main.L

+ Scan (rt: 23.958-24.013 min) **Peak 2 from + TIC Scan (9,12-Octadecadienoic acid (Z,Z)-, methyl ester; C19H34O2)**

Fig 5(a): GC-MS analysis of FAME

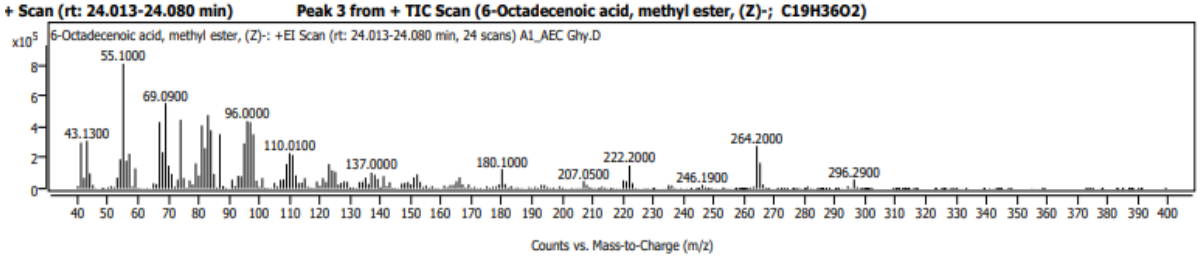


Spectrum Identification Table

Best	ID Source	Name	Formula	Species	m/z	Diff (ppm)	CAS	Score	Score (Lib)	Score (DB)	Score (MFG)	Lib/DB
Yes	LibSearch	9,12-Octadecadienoic acid (Z,Z)-, methyl ester	C19H34O2				112-63-0	94.94	94.94			W11N17main.L
No	LibSearch	9,11-Octadecadienoic acid, methyl ester, (E,E)-	C19H34O2				13038-47-6	93.61	93.61			W11N17main.L
No	LibSearch	9,12-Octadecadienoic acid (Z,Z)-, methyl ester	C19H34O2				112-63-0	93.00	93.00			W11N17main.L

Best	Name	Formula	m/z (prec.)	CAS	RT (DB)	RT Diff	Score	Score (Lib)	Score (Fwd)	Score (Rev)	Lib/DB
Yes	9,12-Octadecadienoic acid (Z,Z)-, methyl ester	C19H34O2		112-63-0	34.883		94.94	94.94			W11N17main.L

+ Scan (rt: 24.013-24.080 min) Peak 3 from + TIC Scan (6-Octadecenoic acid, methyl ester, (Z)-; C19H36O2)

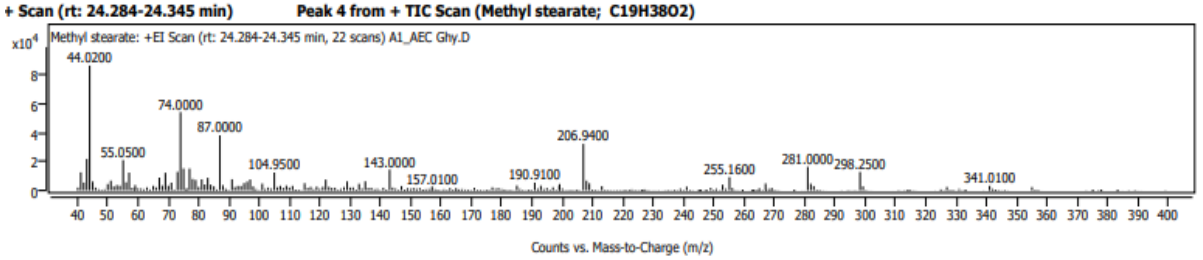


Spectrum Identification Table

Best	ID Source	Name	Formula	Species	m/z	Diff (ppm)	CAS	Score	Score (Lib)	Score (DB)	Score (MFG)	Lib/DB
Yes	LibSearch	6-Octadecenoic acid, methyl ester, (Z)-	C19H36O2				2777-58-4	93.62	93.62			W11N17main.L
No	LibSearch	9-Octadecenoic acid (Z)-, methyl ester	C19H36O2				2462-84-2	93.50	93.50			W11N17main.L
No	LibSearch	9-Octadecenoic acid, methyl ester, (E)-	C19H36O2				1937-62-8	91.87	91.87			W11N17main.L

Best	Name	Formula	m/z (prec.)	CAS	RT (DB)	RT Diff	Score	Score (Lib)	Score (Fwd)	Score (Rev)	Lib/DB
Yes	6-Octadecenoic acid, methyl ester, (Z)-	C19H36O2		2777-58-4	34.750		93.62	93.62			W11N17main.L

+ Scan (rt: 24.284-24.345 min) Peak 4 from + TIC Scan (Methyl stearate; C19H38O2)



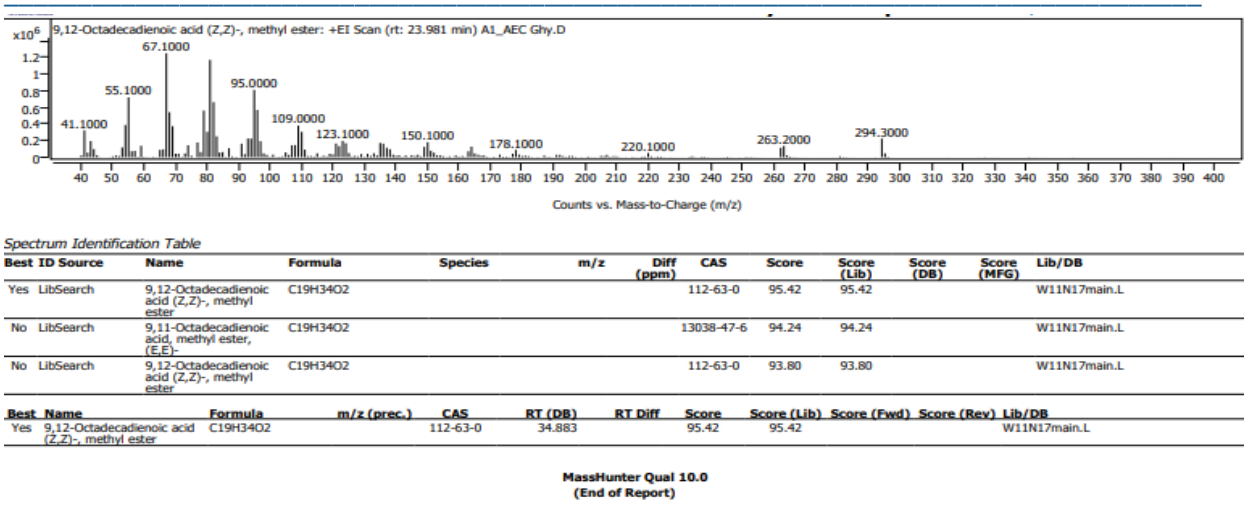
Spectrum Identification Table

Best	ID Source	Name	Formula	Species	m/z	Diff (ppm)	CAS	Score	Score (Lib)	Score (DB)	Score (MFG)	Lib/DB
Yes	LibSearch	Methyl stearate	C19H38O2				112-61-8	62.14	62.14			W11N17main.L
No	LibSearch	Heptadecanoic acid, 16-methyl-, methyl ester	C19H38O2				5129-61-3	61.97	61.97			W11N17main.L
No	LibSearch	Methyl stearate	C19H38O2				112-61-8	61.31	61.31			W11N17main.L

Best	Name	Formula	m/z (prec.)	CAS	RT (DB)	RT Diff	Score	Score (Lib)	Score (Fwd)	Score (Rev)	Lib/DB
Yes	Methyl stearate	C19H38O2		112-61-8	34.617		62.14	62.14			W11N17main.L

+ Scan (rt: 23.981 min) 9,12-Octadecadienoic acid (Z,Z)-, methyl ester; C19H34O2

Fig 5 (b): GC-MS analysis of FAME



Spectrum Identification Table

Best	ID Source	Name	Formula	Species	m/z	Diff (ppm)	CAS	Score	Score (Lib)	Score (DB)	Score (MFG)	Lib/DB
Yes	LibSearch	9,12-Octadecadienoic acid (Z,Z)-, methyl ester	C19H34O2				112-63-0	95.42	95.42			W11N17main.L
No	LibSearch	9,11-Octadecadienoic acid, methyl ester, (E,E)-	C19H34O2				13038-47-6	94.24	94.24			W11N17main.L
No	LibSearch	9,12-Octadecadienoic acid (Z,Z)-, methyl ester	C19H34O2				112-63-0	93.80	93.80			W11N17main.L

Best	Name	Formula	m/z (prec.)	CAS	RT (DB)	RT Diff	Score	Score (Lib)	Score (Fwd)	Score (Rev)	Lib/DB
Yes	9,12-Octadecadienoic acid (Z,Z)-, methyl ester	C19H34O2		112-63-0	34.883		95.42	95.42			W11N17main.L

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Fig 5(c): GC-MS analysis of FAME

Table 14: GC-MS analysis of the synthesised biodiesel

Peak	Retention Time (RT in min)	Area (%)	Name of the FAME	Chemical formula
1	21.651	23.82	Hexadecanoic acid, methyl ester	$C_{17}H_{34}O_2$
2	23.981	24.47	9,12-Octadecadienoic acid (Z,Z)-, methyl ester	$C_{19}H_{34}O_2$
3	24.042	50.71	6-Octadecenoic acid, methyl ester	$C_{19}H_{36}O_2$
4	24.307	1.00	Methyl stearate	$C_{19}H_{38}O_2$

(i) Fourier Transform Infrared (FTIR) Spectroscopy analysis:

The FTIR spectrum of the synthesised biodiesel from waste cooking oil is depicted in Fig 6.

The different absorption bands in the spectrum are indicative of the presence of C–H, C=O, C=C, C–O functional groups in the FAMEs. As shown in the Table 15 the two sharp peaks at ~ 2923.26 cm^{-1} and 2853.68 cm^{-1} are due to C – H stretching vibration present in the methylene group of FAMEs. A strong peak at ~ 1741.82 cm^{-1} is due to the presence of the carbonyl (C = O) group of methyl esters. The peaks at ~ 1462.30–1435.80 cm^{-1} represent the C = C bond linked to ester. The peak at ~ 1168.83 cm^{-1} confirms the presence of alkoxy (C–O) group in the compound. Aliphatic (C–H) bending vibration is observed at 723.04 cm^{-1}.

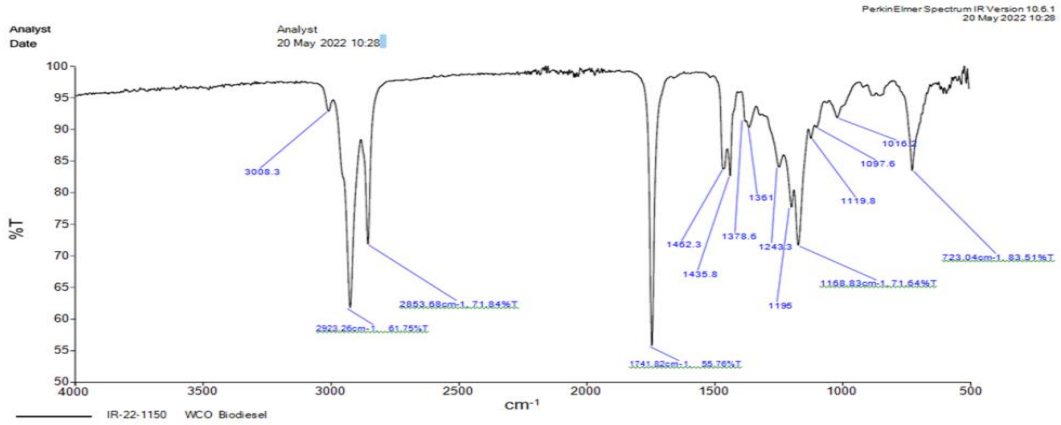

Fig 6: FTIR spectrum of FAME

Table 15: Peak characteristics obtained from FTIR analysis

Wave Number (cm^{-1})	Functional Groups
2923.26, 2853.68	C – H (stretching)
1741.82	C = O
1462.30, 1435.80	C = C
1168.83	C–O
723.04	C – H (bending)

3. Results and Discussions

In the present work after synthesising the biodiesel from WCO and carrying out its yield process optimisation along with characterisation study the following observations have been revealed:

(i) The properties of the derived WCO biodiesel were found to lie well within the ASTM standard limits.

(ii) The optimal yield setting was obtained at levels 2,2,3 and 2 i.e., i.e., medium level (6:1) for methanol to oil molar ratio, medium level (1.0% w/w) for catalyst amount, high level (90min) for reaction time and medium level (55^0C) for reaction temperature.

(iii) The optimal value of molar ratio is found to be 6:1. This means medium level of molar ratio is suitable for getting optimum yield. Stoichiometrically 3:1 alcohol to oil molar ratio is needed for the transesterification reaction. However, an increased alcohol to oil molar ratio is preferred for better yield of biodiesel because there may be loss of alcohol due to evaporation. Increasing the molar ratio increases the yield up to a certain level. Further increase in the molar ratio does not increase the yield, rather biodiesel yield is found to be declined after the optimal value. This decrease may be due to the presence of excess amount of methanol which hinders the separation of methyl ester and glycerol by increasing glycerol solubility.

(iv) The optimal value of the catalyst concentration is found to be 1% (w/w). The medium value of catalyst is found to be optimum as insufficient amount of catalyst leads to the incomplete conversion of triglycerides into fatty acid esters. Also, addition of excess amount of alkali catalyst reacts with triglycerides to form more soap which decreases the yield.

(v) The optimal value of reaction time is found to be 90 min. In the beginning the reaction is slow and the rate increases with time. The yield of biodiesel increases with increasing the reaction time. However, if too much time is allowed for the reaction, the yield may decrease due to the reversible nature of the transesterification reaction as well as soap formation.

(vi) The optimal value of reaction temperature is found to be 55℃. Increasing the reaction temperature increases the rate of reaction. Thus, the yield of biodiesel increases with reaction temperature up to a certain value. However, after 55℃ the yield of biodiesel is found to be declined. This may be because of the fact that evaporation of alcohol increases at high temperature. Also, the saponification reaction of triglycerides increases with temperature which decreases the biodiesel yield.

(vii) In ANOVA, all the factors were found to be significant. Still the relative significance was observed amongst the factors. Catalyst amount happened to be the most significant followed by Reaction temperature, Methanol to Oil molar ratio and at last the Reaction time. The rank row of Table 4.3 and Table 4.5 also depicted the same order.

(viii) The different characterisation studies such as ^{1}HNMR analysis, GC-MS analysis and FTIR analysis of the derived WCO biodiesel were also carried out to extract its physical and chemical specifications. That helped to know its compatibility to use in blended mode for engine.

(ix) In the future study of this work more other factors such as stirring speed, different types of catalyst etc. can be introduced for yield study

4. Conclusion

WCO has been experienced as an easily abundant source for biodiesel generation at nearly no cost. The work here paved the way for using the non-biodegradable and toxic WCO that is being generated daily from the canteen for the production of biodiesel. The biodiesel produced from this unwanted WCO which can be used in the blended mode with petro-diesel for running the diesel generator set which is being used for the power backup of the canteen itself. So this experimental work done here will finally help in the engine compatibility testing for using the produced biodiesel in the blended mode with petro-diesel so far its performance and emission is concerned. The application of different statistical tools and techniques in the present work helped in ensuring and validating the common optimal setting of the yield process control factors. Converting the waste to useful energy in this way will not only add to economy but it will also help in sustaining the green environment and enhancing the longevity of both the people and the society in coming days.

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