HOMOGENEOUS CATALYZED METHANOLYSIS OF MUSTARD SEED OIL FOR BIODIESEL PRODUCTION USING SODIUM HYDROXIDE AS CATALYST

***Arohkesi, A. I.[1], Umeuzuegbu, J. C.[2], Ndive, J. N.[3], Ezeugo, J. O.[4], Dzarma, G. W.[5]**

[1,2,3,4]Department of Chemical Engineering, Chukwuemeka Odumegwu Ojukwu University, Uli, Anambra State, Nigeria.

[5]Department of Chemical Engineering, Michael Okpala University of Agriculture Umudike.

*Corresponding Author: ifeanyianthony116@yahoo.com

ABSTRACT

Rapid consumption of fossil fuels coupled with rising environmental deterioration caused by high CO_2 emissions has increased the search for clean and renewable energy sources. Vegetable oils are a main possible alternative to fossil fuel. This present work focuses on biodiesel production from mustard seed oil and evaluation of its fuel properties. Mustard seed oil was extracted using a soxhlet extractor, with n-hexane as solvent. The biodiesel was synthesized via sodium hydroxide (NaOH) catalysed transesterification. Standard ASTM methods were employed to analyze the physiochemical properties of the oil (MSO). The functional groups and fatty acid profile of the oil were determined using Fourier Transform Infra-Red Spectroscopy and Gas Chromatography Mass Spectroscopy (GC-MS) respectively. The effects of process variables, methanol/oil molar ratio, catalyst concentration, reaction time, reaction temperature and agitation speed were investigated. The fuel properties of the mustard seed oil FAME (MSO FAME) produced were also determined based on ASTM standards. The physiochemical properties of the oil were: saponification value 147.70 mgKOH/g, peroxide value 13.80 mEq/kg, kinematic viscosity 30.00 mm^2/s, iodine value 94.40 gI_2/100 g, flash point 98.00 °C, fire point 182.00 °C, refractive index 1.42, cloud point 6.00 °C, pour point 1.50 °C, specific gravity 0.95, moisture content 2.99 %, acid value 0.46 mgKOH/g, free fatty acid 0.23 %. The optimized process parameters for obtaining the highest biodiesel yield of 82 %, were methanol/oil ratio of 6:1, catalyst concentration 1.0 %, temperature 60 °C, reaction time 60 min and agitation speed 350 rpm. The fuel properties of the biodiesel were: density 880 kg/m^3, kinematic viscosity 3.00 mm^2/s, cetane number 58, flash point 210 °C, cloud point 9 °C, moisture content 0.03 %, acid value 0.40 mgKOH/g, calorific value 37.21 MJ/kg, iodine value 46.4 gI_2/100 g, pour point 3 °C, free fatty acid 0.2 %, and refractive index 1.455. The significant reduction in viscosity and acid value, and the ASTM-compliant fuel properties, show that mustard seed oil biodiesel meets ASTM biodiesel standards and is a suitable alternative to diesel fuel.

Keywords: Mustard seed oil, Biodiesel, Characterization, Fuel properties, Transesterification, Optimization, FTIR.

1.0 INTRODUCTION

The rapid increase in the world population and more industrialized countries has suddenly increased the global energy demand (Bitire *et al*., 2021; Ndasi *et al*., 2018). The current demand for energy is insatiable, the crisis surrounding the cost and environmental effects of fossil fuels both in the present and nearest future has brought up the need to look for alternative source of energy (Jamo *et al*., 2023). The world is dependent heavily on coal, petroleum and natural gas for energy and as feedstock for chemicals. These sources are commonly termed as fossil or non-renewable resources (Griffiths *et al*., 2021). Fossil resources are extracted from the Earth's crust, processed and burnt as fuel or converted to chemicals. Burning fossil fuels cause environmental concerns such as greenhouse gases (GHG) emission, the major substance responsible for climate change. Other harmful substances released during fossil fuel production and utilization includes sulphur oxides (SOX), nitrogen oxides (NOX) and methane (Loganathan and Kannan, 2022).

However, the world economy depends on energy generation. Hence, the consequences of inadequate energy could be severe. These have prompted world leaders, organizations, industries and educational institutions to look for alternative energy sources that are sustainable, with less negative environmental impact. Energy production from biomass such as oil crops and waste materials has a great advantage over fossil fuels (Im-orb *et al*., 2021). The energy producing substances derived from biomass are referred to as biofuel. biofuels comprise of biodiesel, bio-ethanol, biogas, etc. The sources of biodiesel determine the environmental, economic and social impacts of such biodiesel. Biodiesel is becoming alternative renewable energy because of its environmentally eco-friend and non-toxicity (Anwar *et al*., 2019). It is a renewable and biodegradable fuel with high lubricity and high cetane number. However, biodiesel has its shortcomings like, having low calorific value, higher nitrous oxide emission, high density and viscosity, and poor cold-flow properties (Romano and Sorichetti, 2011)

Considering Nigeria as a case study, biodiesel (liquid biofuel from vegetable oils or animal fats) seems to be of promising alternative to fossil fuels. This is because the crops required for biodiesel production are readily available and are cultivated in large quantity, under favourable climatic conditions. Mostly, biodiesel can be produced using edible and non-edible sources; however, owing to the consumable source, which is used as food (Abomohra *et al*., 2020), a new boulevard of producing biodiesel through non-edible sources as possible feedstock is an alternative for renewable energy production (Anwar *et al*., 2019).

Biodiesel technology involves simple procedures that can be practiced by even rural dwellers (making biodiesel easily available). A proper selection of feedstock for biodiesel production is important for viable alternative fuel to Petro-diesel. Mostly, biodiesel can be produced using edible and non-edible sources. Generally, edible vegetable oils have been used as main raw materials in biodiesel production. However, the use of edible vegetable oils for biodiesel production has been criticized owing to food security concerns (Tomei and Helliwell 2016). A new avenue of producing biodiesel through non-edible sources as possible feedstock is an alternative for renewable energy production (Anwar *et al*., 2019). Also, the fuel is renewable, sustainable and environmentally friendly. In addition, it does not involve petroleum-diesel engine modification (Avhad *et al*., 2016; Hoseini *et al*., 2018). Most country biodiesel production are from edible feedstock, this is because their oils contain less free fatty acid than non-edible oils and most times do not require esterification or pretreatment before transesterification (Umeuzuegbu *et al*., 2023). Much research efforts are now geared towards identifying and evaluating non-edible seed oils as suitable feedstocks. However, the cost of non-edible oils biodiesel purification is high because of their high free fatty acid content which must be considered before making a good choice of the feedstock. However, high yield and high quality biodiesel can only be achieved through scientific assessment of production processes. Biodiesel can be produced from trans-esterification process which involves chemical reaction between plant oil and methanol (alcohol) in the presence of a catalyst (such as NaOH) to give biodiesel and glycerol. The assessment of biodiesel production includes the use of different feedstocks (edible and non-edible) like; neem seed oil, camelina seed oil, sunflower seed oil, rapeseed seed oil, palm oil, soybean seed oil, jatropher seed oil, sesame seed oil, mustard seed oil, etc. *Brassica nigra* commonly known *as* mustard seed is a member of the Brassica family of plants. It is related to canola, but is more tolerant to drought and heat. It is an important oil seed crop cultivated in many parts of the world with oil content of 29 % to 49 % depending on the specific variety, growing condition and extraction method. Various vegetable-based oils are composed of different chemical compositions, which helps in achieving the targeted yield at the end of the reaction process. Mustard seed oil contains three types of fatty acids: saturated (Cn:0), monounsaturated with one double bond (Cn:1), and polyunsaturated with two or three double bonds (Cn:2,3) (Ding *et al.,* 2007). It should be noted that the majority of biodiesel's important fuel qualities are highly influenced by the fatty acid level of the feedstock (Lang *et al.,* 2001). Hence, fatty acid compositions of feedstocks particularly will initially be investigated prior utilizing it for the effective production of biodiesel. The selection of an appropriate catalyst is also a critical factor; because of the presence of impurities and high free fatty acid in the product (Milano *et al*., 2018; Macawile *et al*., 2020). Most investigators use the distinctive mechanism for the production of biodiesel as a basic homogeneous catalyst such as sodium hydroxide (NaOH) or potassium hydroxide (KOH) (Júnior *et al*., 2020; Moazeni *et al*., 2019). The base catalyst is more effective in a reaction that has free fatty acid less than 1% (Esonye *et al*., 2019; Mamtani *et al*., 2021). In this work, single step homogeneous base catalyst was used for transesterification reaction, because of the low FFA content of the feedstock below 1%. The benefits of using NaOH catalyst for transesterification reaction includes; ability to catalyse reaction at low reaction temperature and pressure, high conversion in shorter time, also, they are economically available.

2.0 MATERIALS AND METHODS

2.1 Materials

Mustard seeds (plate 1), reagents, glass wares, equipment's including; Fourier Transform Infra-Red spectroscopy (FTIR), Gas Chromatography Mass Spectrometer (GC-MS), magnetic hot plate, Soxhlet extractor, viscometer, specific gravity bottle, electrostatic oven etc.

2.2 Experimental Methods

2.2.1 Sample preparation

The mustard seed used for this experiment was purchased from Ochanja market Onitsha Anambra state. The mustard seeds were sorted to remove sands, dirt's and other impurities. 10 kg of the mustard seeds were washed, then sundried for four days in other to eliminate the moisture content and then size-reduced by grinding with mechanical grinder. The sample was then kept ready for extraction.

2.2.2 Extraction of oil from ground mustard seed.

Extraction of mustard seed oil was carried out by Soxhlet extraction method. The solvent used for the extraction was n-hexane. The extraction was done using 500 ml capacity Soxhlet apparatus. 80 g of sample was put into timble and placed in the Soxhlet chamber. n-hexane was used as a solvent and initially it was vaporized by heating by means of a heating mantle. The vapor went upward through the distillation arm and cooled down by the condenser. The hot condensate was added continuously to the seed kept in the thimble filter chamber. The condenser was fixed to ensure that the condensed solvent directly dropped back to the chamber and came in contact with the seed. The chamber was slowly filled with hot solvent to dissolve the oil in the seed. When the Soxhlet chamber was entirely filled with the condensed solvent, it was emptied by the siphon process. In this process, the solvent was again returned to the distillation tank. The thimble filter keeps the seed collected and stops entering the siphon process. This cycle of vaporization and condensed returning to the distillation flask is allowed for several hours to days to obtain the desired compound. After around 4 h, the oil was concentrated in the solvent tank. After completing the extraction process, the solvent was removed from the distillation tank and separated from the oil using a vacuum rotary evaporator at 60 °C.

Then the solvent-free oils were left in an airtight container and subjected to characterization as per the standard testing method to find their suitability for the production of biodiesel (Al-muhtaseb *et al*., 2018). The obtained oil percentage was calculated based on the weight of mustard seed powder, and the recovery was expressed as percentages of the oil yield (Tan *et al*., 2019).

$$\text{Oil yield (\%)} = \frac{mass\ of\ oil\ extracted}{mass\ of\ sample\ used\ in\ feed}\ x\ 100$$

Plate 1: Mustard seed

2.2.3 Characterization of mustard seed oil

The raw mustard seed oil extracted was analyzed in other to determine its physiochemical properties. The properties of the extracted mustard seed oil were ascertained using American Society for Testing Materials, ASTM D6751 method. Analytical equipment's; GC MS (QP2010 plus Shimadzu, Japan) and FTIR (M530 Bulk scientific FTIR) were used to determine the fatty acid profile and the functional groups of the oil respectively.

2.2.4 Effect of process parameters on biodiesel yield

The effects of process parameters on the biodiesel yield from mustard seed oil was investigated using one factor at a time method, where each factor is studied independently while keeping others constant (Hazrat *et al*., 2023). The five factors investigated were, effect of time, effect of temperature, effect of catalyst concentration, effect of stirring speed, effect of methanol/oil ratio.

2.2.5 Production of mustard seed oil fatty acid methyl ester

Among several production processes, transesterification process is the easiest and inexpensive conversion process of biodiesel production. Specified quantity of the oil samples were placed in a 500 ml three-necked round bottomed flask equipped with a reflux condenser, on the middle arm and side arms were a thermometer and sample outlet respectively which served as the reactor. The flask was immersed in an oil bath with a temperature controller and magnetic stirrer. Methanol mixed with catalyst (sodium methoxide) was added in the specified amount established for the reaction and the stirrer turned on at a given speed which was taking to as the zero time of the reaction. The reaction mixture was vigorously stirred and refluxed for the required reaction time. After the reaction period, the reaction product was allowed to stand for 24 hours in the separatory funnel and two distinct layers were formed, the upper biodiesel layer and lower glycerol layer. The lower glycerol layer was tapped off first followed by the upper biodiesel layer. The produced biodiesel usually contains excess alcohol, catalyst, or soap as residues and glycerol as byproduct, they were removed by wet washing. The washed biodiesel was then dried on a laboratory hot plate at 100 °C for 60 mins to remove all traces of moisture remaining in it. The percentage biodiesel yield is given by the expression,

$$\%\ \text{biodiesel yield} = \frac{\text{Volume of biodiesel produced}}{\text{Volume of oil used}}\ x\ \frac{100}{1}$$

Plate 2: Experimental set up for biodiesel production by transesterification

2.2.6 Determination of the fuel properties of mustard seed oil FAME

The fuel properties of the mustard seed oil biodiesel produced were characterized based on ASTM method. The properties characterized for include viscosity, peroxide value, density, saponification value, iodine value, cetane number, acid value, free fatty acid, calorific value, flash point, cloud point, pour point, fire point etc.

2.2.7. Experimental Design and Statistical Analysis

The experimental data were analyzed using Design Expert software v13. The optimization experiments were designed using Response Surface Methodology based on five factors two levels fractional factorial design, resulting to 32 experiments and six centre points per block was used so as to have good prediction and estimation of errors. Reaction temperature, catalyst concentration, methanol/oil molar ratio, reaction time and agitation speed were selected as the independent factors for the optimization. The experimental runs were randomized to minimize the effect of unexpected variability in the observed responses. The response chosen was the methyl ester yields obtained from transesterification of mustard seed oil. The transesterification process parameters were optimized using Response Surface Method (RSM) and the significance of the experimental result was determined from analysis of variance (ANOVA). Analysis of variance ANOVA was performed to determine the statistical significance of the model and model terms at 95 % confidence level $p < 0.05$. Model adequacy was checked using the coefficient of determination R^2, Adjusted R^2, Predicted R^2 and Lack of Fit test, as can be seen in Table 5.

3.0 RESULTS AND DISCUSSION

3.1 Oil content of mustard seed

The percentage of oil extracted from mustard seed using solvent extraction (Soxhlet extractor) gave the oil yield of mustard to be 34.0%. This is in agreement with the findings of (Sharif *et al*., 2017) who reported on the range of oil content of three different varieties of mustard seed as 40.95 %. to 49.51 %. The result clearly indicate that mustard variety can be considered as better source of oil for biodiesel production. This present study value of mustard seed oil content was higher than the reported values of Gadei *et al*., (2012) and Moser *et al*., (2009), who found that oil content ranges from 28 % to 32 %. These variations might be due to biological factors, climate, plant species, soil condition and improper processing techniques.

3.2 Characteristics of mustard seed oil

3.2.1 Physiochemical properties of mustard seed oil

The physiochemical properties of the extracted mustard seed oil are presented in Table 1. The oil yield was 34.00 %, indicating that mustard seed is a good potential feedstock for biodiesel production. The oil exhibited a brownish yellow colour with a density of 880.00 kg/m^3 and a specific gravity of 0.95. The moisture content was 2.99 %, and the refractive index was recorded as1.42. The saponification value of 147.70 mgKOH/g suggests the presence of fatty acids of moderate molecular weight, while the iodine value of 94.40 gl_2/100g indicates a moderate degree of unsaturation. The free fatty acid and acid value were 0.23 % and 0.46 mgKOH/g respectively, which are within acceptable limits for alkali-catalysed transesterification without the need for a pre-esterification step. The kinematic viscosity of the crude oil was high at 30.00mm^2/s, which is much higher than the ASTM limit for biodiesel. This high viscosity is expected to reduce after conversion to FAME. Other properties such as peroxide value, flash point, fire point, cloud point and pour point were 13.80 mEq/kg, 98.00 ^{0}C, 182.00 ^{0}C, 6.00 ^{0}C and 1.50 ^{0}C respectively. The calorific value of 38.00MJ/kg shows that the oil has good energy content comparable to conventional diesel fuel. In general, the result indicate that mustard seed oil possesses suitable physicochemical characteristics for biodiesel production.

3.3.2 Fatty Acid Profile of mustard seed oil (GC –MS)

Fatty acid composition in mustard seed oil is highly variable and depends on cultivar, agro-climatic conditions and geographical locations. The mustard seed used in this study were *Brassica juncea* sourced from Nigeria. The fatty acid profile of mustard seed oil was obtained with the aid of Gas Chromatography Mass Spectroscopy (GC-MS). The fatty acid profile of mustard seed oil is presented in Table 2. Mustard seed oil consist of 18.71% saturated fatty acid namely: palmitic acid, margaric acid and stearic acid, and 66.24% of unsaturated acids namely: oleic acid and linoleic acid. The most dominant polyunsaturated fatty acid of the mustard seed oil is linoleic acid, accounting for 43.44 % of the total fatty acid profile, hence, the oil belongs to Linoleic acid category. The linoleic acid composition of this study is comparable to other Nigerian *Brassica juncea* reports. (Nwokonkwo *et al*., 2014) reported *Brassica juncea* from Ebonyi state, Nigeria with 19.87 % linoleic acid, 28.48 % oleic acid and 23.22 % linolenic acid. (Bello *et al.,* 2019) also reported *Brassica juncea* oil from Nigeria containing 14.20 % linoleic acid and 13.00 % linolenic acid. The variation in erucic acid content is also well documented. While some *Brassica juncea* varieties contain 40-57 % erucic acid, low-elucic acid cultivers have been developed and natural variation exists. However, the fatty acid components of the mustard oil were found to be consistent with the fatty acids present in typical oils used for producing biodiesel.

Table 1: Physiochemical properties of mustard seed oil

Properties	Values	Units
Oil yield	34.00	%
Color	Brownish yellow	
Density	880.00	Kg/m^3
Moisture content	2.99	%
Refractive index	1.42	
Saponification value	147.70	mgKOH/g
Iodine value	94.40	$(gI_2/100g)$
Free fatty acid	0.23	%
Acid value	0.46	mgKOH/g
Kinematic viscosity	30.00	mm^2/s
Peroxide value	13.80	mEq/kg
Specific gravity	0.95	
Flash point	98.00	°C
Fire point	182.00	°C
Cloud point	6.00	°C
Pour point	1.50	°C
Calorific value	38.00	MJ/kg

Table 2: Fatty acid profile of mustard seed oil

Fatty Acid	**Lipid Number**	**Composition (wt. %)**	**Nwokonkwo *et al.*, 2014**	**Bello *et al.*, 2019**
Palmitic acid	C 16.0	11.80	3.78	Not reported
Margaric acid	C 17.0	0.51	Not reported	Not reported
Stearic acid	C 18.0	6.40	23.47	Not reported
Oleic acid	C 18.1	22.80	28.48	Not reported
Linoleic acid	C 18.2	43.44	19.87	14.20
Linolenic acid	C 18:3	ND	23.22	13.00
Erucic acid	C 22:1	ND	Not reported	45.70

Note: ND = Not Detected

3.3.3 Fourier Transform infrared spectra analysis (FTIR) of mustard seed oil

The Fourier transform infrared spectra of mustard seed oil was analyzed using Fourier transform infrared spectroscopy (M530 Buck scientific FTIR). This analysis was done to identify functional groups present in the oil prior to transesterification. From the result, detectable peaks of note were recorded. The key peaks observed include: 893.97 cm^{-1} assigned to =C-H out of plane bending vibration of vinyl/terminal alkene. The peaks around 1313.06 cm^{-1} assigned to $-CH_3$ bending vibration of terminal methyl groups. The wavelength around 1602.81 cm^{-1} assigned to C=C stretching of aromatic rings, and the peak around 1743 cm^{-1} was assigned to C=O ester carbonyl of triglycerides. The bands at 3171 - 3468 cm^{-1} indicate O-H stretching from moisture and free fatty acids. While FTIR analysis of the FAME product was not performed in this study, successful methyl ester formation is supported by, a tenfold reduction in kinematic viscosity from 30 mm^2/s for oil to 3.00 mm^2/s for FAME. Secondly, reduction in acid value from 0.46 to 0.40 mgKOH/g. Thirdly, from

82% biodiesel yield under optimized conditions, and finally from the fuel properties meeting ASTM D6751 limits. Literature reports that transesterification results in characteristic new peaks at approximately 1436 cm^{-1} for $-0CH_3$ bending and 1195 cm^{-1} for C-O stretch of methyl esters, with a shift of C-O from approximately 1158 cm^{-1} to 1170 cm^{-1}. Future work will include FTIR and GC-MS analysis of the FAME to provide direct spectroscopic confirmation.

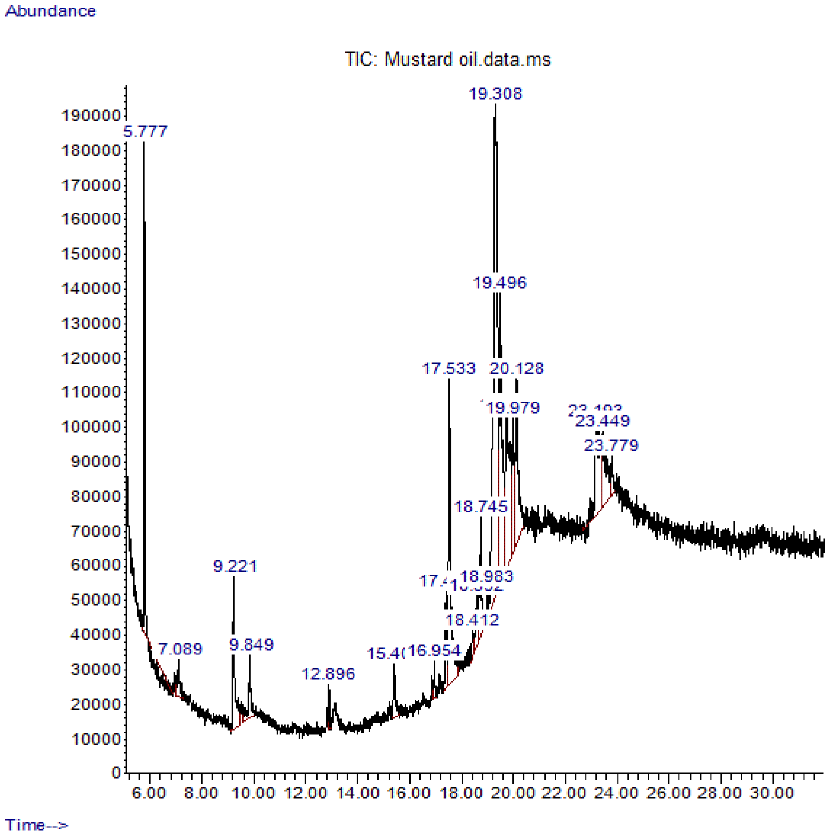

Figure 1: GC-MS plot of mustard seed oil

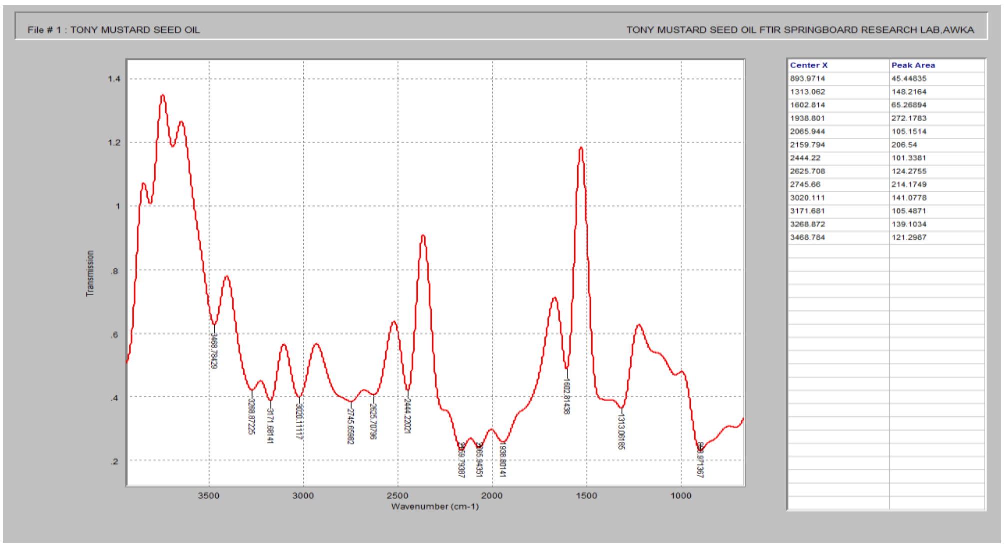

Figure 2: FTIR spectrum of mustard seed oil

3.4. Effects of Process Parameter on Biodiesel Yield.

3.4.1. Effect of methanol/oil molar ratio on biodiesel produced.

One of the most critical parameters influencing biodiesel yield is the methanol/oil molar ratio. Although the needed stoichiometric ratio is 3:1, the transesterification procedure is typically carried out with an additional amount of alcohol to move the equilibrium to the desired product methyl ester side. It has been reported that transesterification is insufficient at methanol/oil ratios less than 5:1 (Hoque *et al*., 2011). The effect of methanol to oil molar ratio on biodiesel yield was investigated, as shown in Fig. 4.3. When all other process parameters were held constant (catalyst concentration, temperature, time and agitation speed), the effect of alcohol/oil molar ratio ranging from 2:1 to 12:1 was examined. The biodiesel yield increased with increase in methanol/oil molar ratio and attend maximum value at 6:1 for mustard seed biodiesel. On exceeding the optimal methanol to oil molar ratio of 6:1, the yield started decreasing. The decrease in yield after attaining the optimum methanol/oil molar ratios could be attributable to excess methanol deactivating the catalyst, resulting in reduction of biodiesel produced (Zhang *et al.,* 2003)

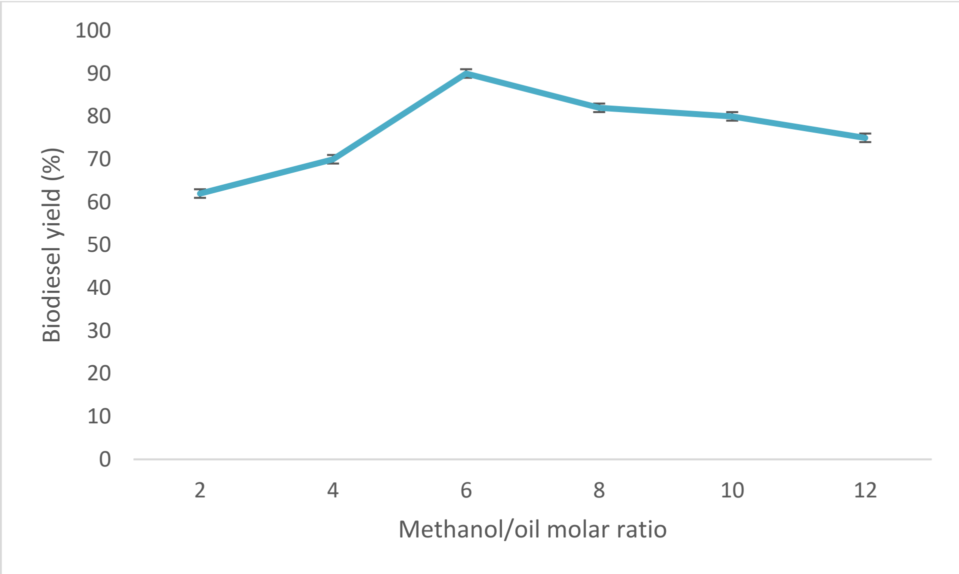

Figure 3: Effect of methanol/oil molar ratio on biodiesel produced

3.4.2. Effect of catalyst concentration on biodiesel yield.

The effect of the catalyst concentration on the yield of biodiesel was investigated from 0.25 % to 1.25 % wt. catalyst concentration, at a step increase of 0.25 %. Catalysts offer different reaction paths for bond breaking in chemical reactions. The activation energy for this alternative pathway is frequently less than that of the conventional pathway. In this study, sodium hydroxide was used as a base catalyst for the transesterification reaction. Figure 4.4 depicts the influence of catalyst concentration on biodiesel yield. The maximum biodiesel yield was found at catalyst concentrations of 1.0 % weight. This maximum yield might be attributed to maximal ester conversion by a sufficient amount of catalyst (Aworanti *et al*., 2019, Lee *et al*., 2015). However, when catalyst concentrations increased further, the biodiesel output decreased significantly due to the creation of fatty acid salts (soap), a process known as saponification. The soap inhibited a clear separation of biodiesel from the glycerine fraction, increasing the viscosity of the biodiesel and reducing the biodiesel production (Maneerung *et al*., 2016, Birla *et al*., 2012).

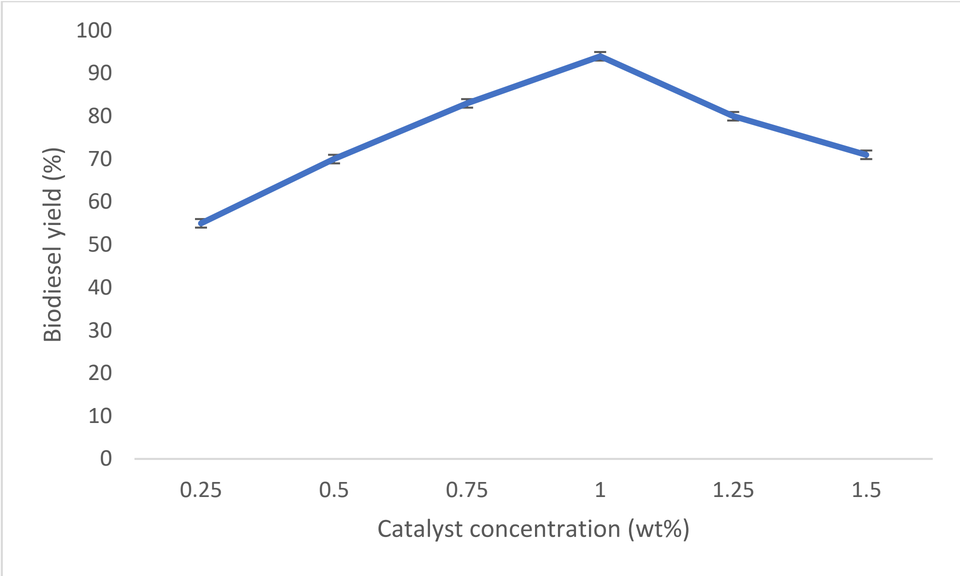

Figure 4: Effect of catalyst concentration on biodiesel yield.

3.4.3. Effect of reaction temperature on biodiesel yield.

Transesterification can occur at a variety of temperatures ranging from room temperature to near to the boiling point of methanol. Higher reaction temperatures on the other hand, accelerate the reaction and shorten the reaction period. The transesterification reaction was carried out at different temperatures (50 ^{o}C, 55 ^{o}C, 60 ^{o}C, 65 ^{o}C, and 70 ^{o}C), while all other parameters remained constant. As shown in Figure 4.5, the FAME yield grew and then declined as the reaction temperature increased, achieving an optimal temperature of 60 ^{o}C. At temperatures below the boiling point of methanol, ester formation was encouraged; but, above the boiling point of methanol, the reverse reaction was encouraged, resulting in a large amount of methanol lost by evaporation and a reduction in biodiesel yield.

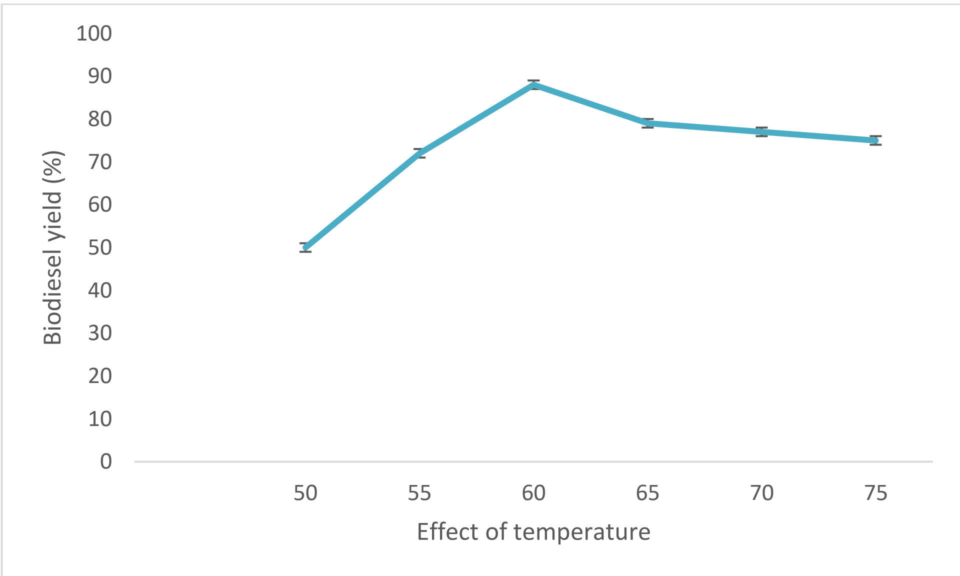

Figure 5: Effect of reaction temperature on biodiesel yield.

3.4.4. Effect of reaction time on biodiesel yield.

The influence of reaction time on biodiesel yield was examined by running the transesterification reaction from 30 to 90 minutes, while keeping other parameters constant. Figure 4.6 depicts the biodiesel yield at various reaction time. The reaction time of 60 minutes was needed for a maximum yield of mustard seed oil FAME. It was also discovered that the yield increased substantially from 15 to 60 minutes, indicating that the bulk of transesterification occurred during the first hour. This could be related to the oil's chemical structure, which contains saturated fatty acids. Since these fatty acids have a larger activation energy, they require a longer heating time to react. The yield decrease after 60 minutes could be attributed to the reversible nature of the transesterification process. Prolonged heating may cause the produced biodiesel to return to its original condition, limiting overall biodiesel yield (Syazwani *et al*., 2017, Wong *et al*., 2015, Aworanti *et al*., 2019).

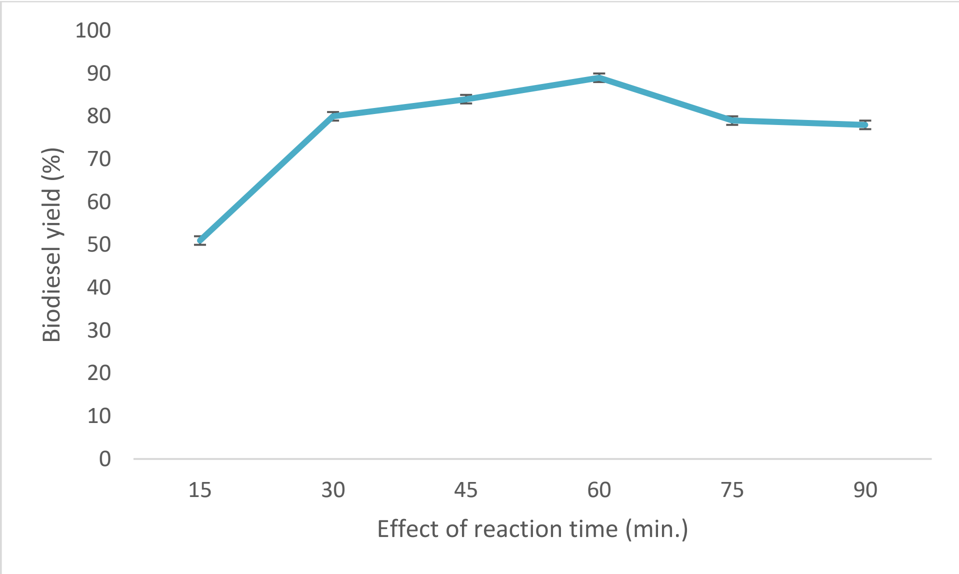

Figure 6: Effect of reaction time on biodiesel yield.

3.4.5. Effect of agitation speed on biodiesel yield.

Mixing is very crucial throughout the transesterification process because it provides homogeneity within the reaction mixture (Dhawane *et al*., 2017., Umeuzuegbu *et al.,* 2023) The agitation speed increases the contact of the reactants during the transesterification process, causing the reaction to start faster (Mohan *et al*., 2016). Figure 4.7 depicts the biodiesel yield at various mixing speeds. The reaction of metanalysis was essentially incomplete at the lowest mixing speed of 150 rpm, exhibiting only a yield that was difficult to separate. The yield decreased as the mixing rate increased up to 350 rpm for mustard seed FAME. When the mixing intensity was increased above the stated level, the backward reaction may be favoured and thus lowering biodiesel formation. The increase in biodiesel production with increasing mixing speed indicates that the turbulence induced by high mixing speed leads to good reactants mixing. Furthermore, rapid mixing reduces the external mass transfer diffusion resistance, boosting the rate of the reaction and hence the methyl ester yield (Ajala *et al*., 2017, Panchal *et al*., 2020).

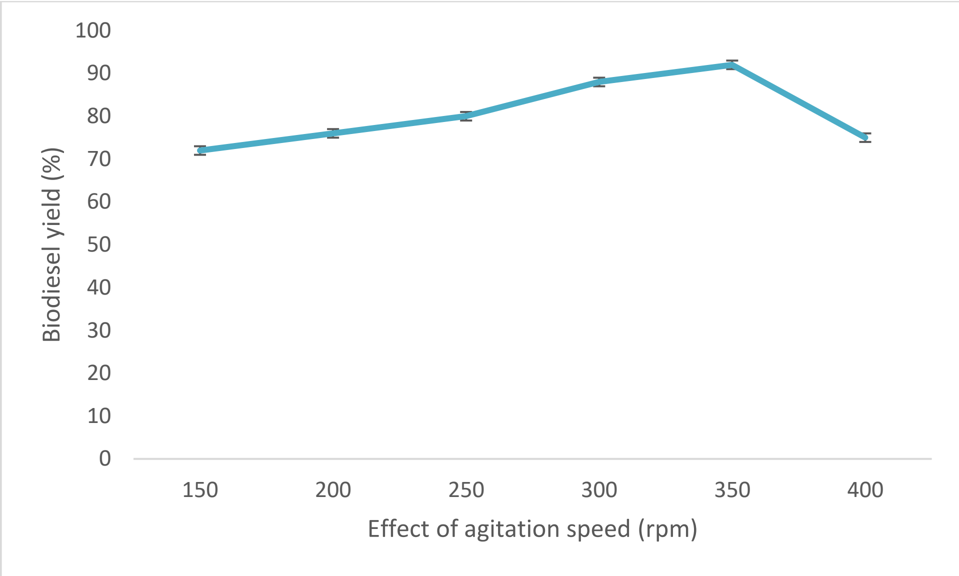

Figure 7: Effect of agitation speed on biodiesel yield.

3.5. Fuel Properties of mustard seed oil FAME Produced.

The fuel properties of the mustard seed oil FAME produced in this study are presented in Table 3 and compared with ASTM D6751 standards and literature values. The density of the biodiesel produced is higher than that of the Petro diesel. This is as a result of the fatty acid composition and molecular weight of the oils (Ezekwe and Ajiwe, 2011). Density plays a crucial role in diesel fuel injection systems and directly affects the fuel performance like the quality of atomization and combustion (Chen *et al*., 2024). The denser the oil the higher the energy content per liter. The value of Density obtained for the biodiesel produced from mustard seed oil is 880 kg/m^3 which is close to the value (873kg/m^3) reported by (Zulfiqar *et al*., 2021). Also, the kinematic viscosity of the produced mustard seed oil biodiesel is higher than that of Petro diesel, this is as a result of the fatty acid composition and molecular weight of the oil (Ezekwe and Ajiwe, 2011). Viscosity obtained for biodiesel produced from mustard seed oil at 40 °C was 3.00 mm^2/s. This value is appropriate as it is within the ASTM D6751 range of 1.90 – 6.00 mm^2/s, as well as high combustibility and non-deposition in the engine due to its lower value as reported by (Nath *et al*., 2019). The reason for transesterification is to reduce density and viscosity of oil in order to avoid the above problems. However, the viscosity of fuel should not be too low as this produces very slight spray which cannot properly get into the combustion chamber, thus forming a fuel rich zone that give rise to formation of sooth. The kinematic viscosity of 3.00mm^2/s represents a significant reduction from the crude oil viscosity of 30.00mm^2/s in Table 1, confirming successful transesterification. The flash point temperature is the lowest temperature at which the fuel will ignite (flash) on application of an ignition source. The flash point of the produced biodiesel was 210 ^{0}C. The biodiesel produced is safe for use and handling as fuels with lower flash points often appear to catch fire at lower temperatures if not properly handled or stored. Pour point is the lowest temperature at which a material (fuel) will continue to flow when undergoing cooling in the absence of stirring, for this study, pour point of 3.00 °C was obtained. This value fell within the range of biodiesel standard of −15 to 10 (ASTM D6751). The value was higher than the −6 °C that was obtained by (Zulfiqar *et al*., 2021). The pour point value implies that the biodiesel produced can be useful as a good fuel during cold temperature. The cloud point refers to the cooling temperature at which the oil components begin to precipitate or crystallize (Cao *et al*., 2022). The cloud point was measured to be 9 °C which also fell within the range for biodiesel standard (−3 to 12) according to ASTM D6751 standard. The value obtained for the cloud point might be a result of the maximum decrease in the degree of unsaturation of the oil. Cetane number is an indicator of the combustion speed of diesel fuel and compression needed for ignition. This is the most pronounced change from vegetable oil to the trans-esterified product. The higher the cetane number, the better the fuel burns within the engine. Fuels with low cetane number show an increase in emission due to incomplete combustion. The value obtained for the mustard seed oil biodiesel is 58 which is within the standard range of ASTM limit and an indication that the produced biodiesel possesses good ignition quality. The acid value is an important indicator of oxidation of the oil. It is the weight (mg) of potassium hydroxide required to neutralize the free acid in 1 g of the oil. In good fuel, the acid value should be very low (< 0.1) and an increase in acid value is an indicator of oxidation of the fuel which may lead to gum and sludge formation beside corrosion of engine. The acid value obtained for mustard seed oil biodiesel was 0.40 mgKOH/g which is within the range of ASTM D6751 limit. The calorific value of 37.21 KJ/kg and iodine value of 46.40 $gI_2/100g$ further show that the fuel has good energy content and oxidative stability. All measured fuel properties of the MSO FAME in this work meet ASTM D6751 specifications and are comparable with values reported in literature, confirming mustard seed oil a suitable alternative to diesel fuel.

Table 3: Fuel properties of FAME produced from mustard oil and the ASTM standards.

Properties	ASTM 6751	This work	Zulfiqar *et al* 2021
Density (kg/m^3)	-	880.00	873.00
Kinematic viscosity (mm^2/s)	1.90 – 6.0	3.00	-
Refractive index	-	1.46	-
Acid value (mgKOH/g)	0.50 max	0.40	-
Free fatty acid (%)	-	0.23	-
Iodine value (g I_2/100g	-	46.40	-
Flash point (°C)	>130.00	210.00	132 ± 1
Calorific value (KJ/Kg)	-	37.21	-
Cloud point (°C)	-3 to 12	9.00	11
Cetane number	47 min	58.00	-
Pour point (°C)	-15 to 10	3.00	-6

3.6. Process Modelling using Response Surface Methodology.

The experimental data were fitted to a quadratic polynomial model using Response Surface Methodology (RSM). The model summary statistics in Table 4, show that the quadratic model was the most suitable with the highest R^2 of 0.9992 Predicted R^2 of 0.9886.

Table 4.: Model summary statistics showing quadratic model as the most suited model.

Source	Std. Dev.	R^2	Adjusted R^2	Predicted R^2	PRESS	
Linear	14.42	0.3649	0.2428	0.0930	7726.05	
2FI	18.07	0.3864	-0.1889	-3.0548	34540.25	
Quadratic	**0.7930**	**0.9992**	**0.9977**	**0.9886**	**97.51**	**Suggested**
Cubic	0.8339	0.9995	0.9975	0.8926	915.20	Aliased

3.7. Analysis of variance (ANOVA) for yield of FAME from mustard seed oil.

The ANOVA results in Table 5, show the model was highly significant with F-value of 676.76 and P < 0.0001. The lack of fit was not significant with p = 5593, indicating the model fits the data well. All five main factors (methanol/oil molar ratio, catalyst concentration, reaction time, reaction temperature and agitation speed) had significant effect on yield.

Table 5: ANOVA for the quadratic model for mustard seed oil FAME.

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	8511.35	20	425.57	676.76	< 0.0001	significant
A-Molar Ratio	661.50	1	661.50	1051.95	< 0.0001	
B-Catalyst Concentration	1290.67	1	1290.67	2052.48	< 0.0001	
C-Temperature	73.50	1	73.50	116.88	< 0.0001	
D-Reaction time	600.00	1	600.00	954.15	< 0.0001	
E-Agitation speed	482.87	1	482.87	767.88	< 0.0001	
AB	4.00	1	4.00	6.36	0.0284	
AC	6.25	1	6.25	9.94	0.0092	
AD	2.25	1	2.25	3.58	0.0852	
AE	12.25	1	12.25	19.48	0.0010	
BC	100.00	1	100.00	159.03	< 0.0001	
BD	4.00	1	4.00	6.36	0.0284	
BE	9.00	1	9.00	14.31	0.0030	
CD	42.25	1	42.25	67.19	< 0.0001	
CE	0.2500	1	0.2500	0.3976	0.5412	
DE	2.25	1	2.25	3.58	0.0852	
A^2	4611.28	1	4611.28	7333.09	< 0.0001	
B^2	820.26	1	820.26	1304.42	< 0.0001	
C^2	8.49	1	8.49	13.50	0.0037	
D^2	208.03	1	208.03	330.82	< 0.0001	
E^2	38.21	1	38.21	60.76	< 0.0001	
Residual	6.92	11	0.6288			
Lack of Fit	3.58	6	0.5973	0.8960	0.5593	not significant
Pure Error	3.33	5	0.6667			
Cor Total	8518.27	31				

3.8. Equation of quadratic polynomial model

The equation was created to demonstrate the empirical relationship between the dependent and independent variables The positive coefficients indicate that the factors have a positive effect on the response (FAME yield), whilst the negative signs suggest that the factors have an opposing effect on the response. The final empirical model in terms of coded factors is given by equation (1).

$$Yield = 76.41 + 5.25A + 7.33B + 1.75C + 5D + 4.49E - 0.5AB + 0.63AC + 0.88AE + 2.5BC + 0.5BD + 0.75BE - 1.63CD + 0.13CE - 12.54A^2 - 5.29B^2 - 0.54C^2 - 2.66D^2 - 1.14E^2 \quad (1)$$

Where:
A = Methanol/oil molar ratio.
B = Catalyst concentration (% wt)
C = Reaction temperature (^{0}C)
D = Reaction time (min)
E = Agitation speed (rpm)
This empirical model can be used to predict mustard seed oil FAME yield within the studied range and thus addresses the process modelling requirement

4.0 CONCLUSION

This study investigated the optimization and characterization of biodiesel production from mustard seed oil. Based on the experimental and statistical analysis, the following conclusions were drawn: The optimum conditions for FAME yield of 82 % were found to be methanol/oil ratio of 6:1, catalyst concentration of 1.0 % w/w NaOH, reaction temperature of 60 °C, reaction time of 60 min and agitation speed of 350 rpm. Response Surface Methodology was successfully used to develop a quadratic empirical model to predict FAME yield. The model was highly significant with R^2 of 0.9992, adjusted R^2 of 0.9977 and F-value of 676.76. This model can be used to predict and optimize biodiesel yield within the study range. The fuel properties of the produced mustard seed oil FAME were within the limits specified by ASTM D6751 standards, indicating its suitability as a diesel fuel substitute. Therefore, the various data obtained from the production of mustard seed oil to mustard seed biodiesel proves mustard seed feedstock/biodiesel suitable alternative to diesel fuel.

5.0 LIMITATIONS AND FUTURE WORK

While this study focused on process optimization and fuel property evaluation of mustard seed oil biodiesel, direct spectroscopic confirmation of methyl ester formation such as FTIR and GC-MS analysis of the mustard seed oil FAME was not performed. Future studies will include FTIR and GC-MS characterization of the biodiesel product alongside glycerin content determination according to ASTM D6584 to provide additional evidence of transesterification and FAME composition

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