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Catalytic Performance of Newly Synthesized Heterocyclic Hydrazone Derivatives for Production of High Yield Neem Biodiesel

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Abstract: Biodiesel, a sustainable and environmentally friendly substitute for diesel, has attracted growing attention in recent years. The reuse of non-edible neem oil as a feedstock for biodiesel production is affordable and naturally safe. This study aimed to understand the understudied benefits of using heterocyclic organic hydrazone derivatives as catalysts for high yield biodiesel production. The catalysts were characterized using techniques such as EIMS, NMR, CHN and FTIR analysis, which revealed the morphological and functional characteristics of the catalyst. The optimum process conditions were found to be catalyst concentration of 50 mg/10 mL, methanol-to-oil molar ratio of 3:1, reaction temperature of 60 °C, and reaction duration of 60 min; these conditions yielded 95% biodiesel. The produced biodiesel was analyzed using FTIR, and different parameters like moisture content, saponification value, density, acid value, iodine value, and FFA value. The use of neem oil and organic based catalysts for biodiesel production is an economical and environmentally sustainable process.

Keywords: Biodiesel, Neem oil, Hydrazone, Energy crisis, Catalysis.

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1. INTRODUCTION

In terms of energy security, modern society faces a number of challenges. As a result of overpopulation, energy demand has increased significantly on earth (1,2). Energy needs around the world are largely met by fossil fuels. Increasing population is causing these natural resources to rapidly deplete because of overconsumption of energy (3). In addition, fossil fuels are non-renewable and their combustion causes a number of environmental problems (4). Globally, 89 million barrels of fossil fuel diesel are consumed each year. In 2007, there were 806 million cars and trucks on the road, which will rise to 1.3 billion by 2030 and 2 billion by 2050 (5).

Currently, researchers are exploring alternative energy sources, and biodiesel (fatty acid methyl ester (FAME)) known as neat-fuel (6) or bio-oil (7) is one of the best options due to its cheapness, non-polluting, environmentally friendly, non-toxic nature, and recyclable properties (8-10). Almost 95% of biodiesel is produced from plant oils extracted from seeds (11). Here is a high demand for edible oils (sunflower, palm, coconut, soya bean, etc.), but non-edible oils (neem, castor, karanja, tobacco, jojoba, rubber seed, etc.) can also be used for biodiesel production (12). Since, neem *(Azadirachta indica)* is natural antiseptic and widely harvested around the globe (13), however, a large amount of neem seeds wasted. It is estimated that neem seeds contain 30-40% oil, with a very high value of free fatty acids (1). Biodiesel production for oils with high FFA (free fatty acid) value have two major steps, 1st step (esterification), to reduce FFA by using an acid catalyst and 2nd step (transesterification), to convert esterified oil into monoester by using alkaline catalyst (14,15).

The production of biodiesel is accelerated by the use of catalysts. In order to accomplish this goal, various catalysts can be used, including homogeneous, heterogeneous, enzyme, and biocatalyst catalysts (16). In homogeneous catalysts, triglycerides are converted into esters when sodium hydroxide or potassium hydroxide react with methanol or ethanol to form alkoxide ions (17). The product is difficult to separate because of its extremely basic nature (16). Apart from these, sodium carbonate and sodium bicarbonate also show effective results (18). Since heterogeneous catalysts can be used both for esterification and transesterification, researchers prefer heterogeneous catalysts (19,20) due to their hydrothermal stability and acid-base nature (21), which include metal salts, metal oxides (14) like MgO (22,23), CdO_2 (24), CaO (10,25,26), Al_2O_3 (27), ZnO, Mn-doped ZnO (28,29), BaO (30), TiO_2 (31), heteropoly acids (32), zeolites (33), ZrO_2-SBA-15 (34), lipases (35), laccases (36), LOBE (37).

Besides these inorganic catalysts, a limited number of organic compounds can also be used to catalyze biodiesel production, including imidazole (38), sulphonic acid derivatives (39), organic amine derivative (40), cellulose derivatives (41,42), graphene-based heterogeneous catalyst (43,44) and MOFs (45-49). Organic-based catalysts can be easily separated or recycled due to their organic nature and exhibit promising results (50).

In recent years, organic compounds have attracted a great deal of attention for the production of biodiesel due to their ease of use, high thermal stability, easy racialization, less CO & CO_2 emissions and high yield (51). The current work aims to synthesize some heterocyclic-organic compounds (hydrazones) and investigate the efficiency of these synthesized catalysts for biodiesel production from neem oil. Hydrazone contain azomethine linkage and gained much importance during the past few decades due to its unique nature, structure and properties (52). The synthesized catalysts were characterized a variety of spectroscopic techniques including EIMS, NMR, FTIR, and CHN, while FTIR was used to confirm and characterize produced biodiesel. Based on the results of this study, more than 75% of the production can be achieved with these synthesized heterocyclic catalysts in a shorter time frame.

2. MATERIAL METHOD

2.1. Feedstock

Neem oil is readily available on the local market, obtained from the neem tree and stored at room temperature for a long time.

2.2. Catalyst Preparation

For the production of neem biodiesel, eight heterocyclic hydrazone derivatives were synthesized. previously, three hydrazone (L2, L21 & L24) were reported (53,54) while five (L12, L19, L20, L22 & L23) were newly synthesized. All furan-2-carbaldehyde derivatives were synthesized by the reaction of substituted anilines and furan-2-carboxyaldehyde via Meerwien Arylation (55). These substituted aldehydes were refluxed with different hydrazides (benzohydrazide, isoniazide, nicotinic acid hydrazide, salicylic acid hydrazide) in ethanol for 3 hours with 2-3 drops of catalyst (HCl). Recrystallization of synthesized yellow colored products was carried out with ethanol and ethyl acetate (3:1). For further use, the desired products were characterized and stored.

2.3. Characterization

Vactor 22 FTIR, Bruker AV 300 & 400 NMR, Thermo Scientific FLASH 2000 CHN analyzer, and MAT 312 mass spectrometer were used to characterize all synthesized hydrazone derivatives. A pre-coated TLC was used to minister the reaction, and spots were visualized in a UVC-11 compact UV lamp at 254 nm and 365 nm.

2.4. Acid Value & Free Fatty Acid Value

Acid value and free fatty acid values of neem oil, esterified oil and biodiesel were calculated via titration method as reported (56,57), the sample was titrated with 0.1 N KOH solution while phenolphthalein was used as indicator until solution become light pink. The acid value and free fatty acid value was calculated by the mentioned formula equation 1&2.

$$\text{FFA}\ (\%) = \frac{A \times N \times 28.2}{W} \quad (1)$$

$$\text{Acid value (mg/g)} = \frac{A \times N \times 56.1}{W} \quad (2)$$

2.5. Reaction Procedure

Free Fatty acid value of neem oil is very high, so, to reduce this FFA value and increase efficiency of biodiesel, two-step process esterification before transesterification was performed (15). This was accomplished by using organic heterocyclic hydrazone derivatives instead of normal acid as catalysts in 1st step and alkali catalyst in 2nd step.

2.6. Esterification of Neem Oil

50 mg of catalyst (hydrazone) and 15 mL methanol were added to 10 mL of neem oil. In a Pyrex container, the mixture was heated for 60 minutes at 40 °C. The resulting mixture was then poured into a funnel and kept undisturbed for 24 hours until two clear layers were formed. Oil layer was separated, washed and stored for further use.

2.7. Transesterification of Esterified Oil

10 mg of KOH in 8 mL of methanol was mixed with 10 mL of pretreated oil for 60 min at 60 °C. The mixture was poured in separating funnel until two layers formed. During this synthesis, the top layer contains biodiesel, the middle layer contains glycerin, and the bottom layer mostly contains unreacted catalysts.

2.8. Washing & Drying of Biodiesel

Hot distil water was added in biodiesel layer and separated. Process was continued for several times until a clear biodiesel layer separated. After washing biodiesel, it may contain traces of water, that are removed by heating it at 100°C. In order to characterize, it was cooled and stored at room temperature.

Percentage yield was calculated by Equation below;

$$Percentage\ yield = \frac{\text{Weight of biodiesel produced}}{\text{Weight of neem oil used}} \times 100 \quad (3)$$

3. RESULTS AND DISCUSSION

3.1. Synthesis of Heterocyclic Hydrazone Catalysts

Substituted aldehydes were prepared according to the reported procedure (Meerwein Arylation). These aldehydes were treated with four different hydrazides to produce hydrazone moieties.

Prior to their use as catalysts for biodiesel production, all yellow-colored synthesized hetero-cyclic compounds were purified, recrystallized and characterized.

3.2. Characterization of Heterocyclic Catalysts

Structure, ketonic nature, purity and bonding of these moieties was confirmed by spectral analysis and elemental analysis. EIMS confirms the structure by molecular ion peak and fragmentation peaks. Important functional groups like N-H, O-H, C=O, N-N, C=N, and C-N show absorption bands at 3200 cm^{-1}, above 3000 cm^{-1}, above 1600 cm^{-1}, ~1030 cm^{-1}, ~1600 and ~1100 cm^{-1} in FTIR. Two singlet peaks appeared in the 11-12 ppm region, confirming the presence of N-H and O-H. A singlet at 8.4 ppm was also a sign of hydrogen directly attached to C=N.

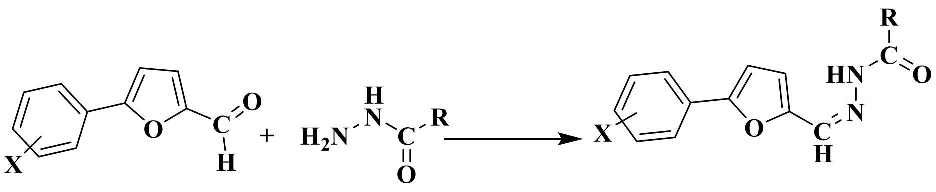

Figure 1: General scheme for synthesis of catalysts.

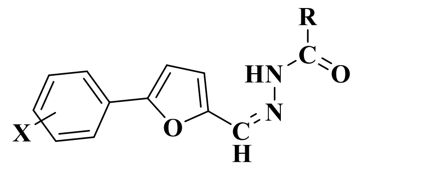

Figure 2: Ketonic structure of synthesized catalysts.

3.3. Production of Biodiesel

These synthesized compounds were used as an efficient acid catalyst for biodiesel formation from neem oil. The N-H group in these compounds enhances their acidic activity. In the same way, the electronic effects of azomethine groups influence the acidic character indirectly. With these hydrazone derivatives, we achieved yields of over 75% within a short period of time.

3.4. Optimization of Reaction Parameters

Several parameters can effect on the yield of biodiesel, including reaction time, reaction temperature, choice of solvent and amount of catalyst.

3.4.1. Reaction Time

Reaction time, an important parameter that effect biodiesel's yield and quality. Daramola reported that an increase in reaction time can lead to an increase in impurities or soap formation (58). The goal is to test the efficiency of the synthesized catalysts during esterification, which produces biodiesel. The yields of all catalysts increase from 20 min to 60 min but decrease when time increases to 80 min, which may be caused by side reactions. As the time increased to 80 min, a thick waxy layer formed that was difficult to separate.

Table 1: Characterization of synthesized hydrazone catalysts.

Heterocyclic catalyst	**EIMS**	**FTIR**	**^{1}H-NMR**	**CHN (found)**
L2	$[M^+]$ 336, $[M^+\text{-}NO]$ 306, $[M^+\text{-}C_6H_4NO_2]$ 214, $[M^+\text{-}C_{11}H_8N_3O_3]$ 106, $[M^+\text{-}C_{12}H_8N_3O_4]$ 78	**N-H** (3219.0), **C=O** (1664.9 $_{Sh}$), **C=N** (1602.7), **C-N** (1147.9)	N-**H** (12.2, $_s$), C-**H**=N (8.44, $_s$)	60.63 **(C)** 3.38 **(H)** 16.37 **(N)**
L12	$[M^+]$ 351, $[M^+\text{-}NO]$ 321, $[M^+\text{-}C_7H_5O_2]$ 231, $[M^+\text{-}C_8H_7N_2O_2]$ 188, $[M^+\text{-}C_{10}H_6NO_3]$ 163, $[M^+\text{-}C_{11}H_7N_2O_3]$ 137, $[M^+\text{-}C_{11}H_8N_3O_3]$ 121	**N-H** (3237.7), **O-H** (3060.3 $_b$), **C=O** (1623.9 $_{Sh}$), **C-N** (1148.4), **N-N** (1034.5)	N-**H** (11.9, $_s$), **O-H** (11.8, $_s$), C**H**=N (8.412, $_s$)	61.55 **(C)** 3.76 **(H)** 11.81 **(N)**
L19	$[M^++2]$ 361, $[M^+]$ 359, $[M^+\text{-}CO]$ 329, $[M^{+2}\text{-}C_2H_2Cl]$ 302, $[M^{+2}\text{-}C_6H_5N_2O]$ 239, $[M^+\text{-}C_6H_5N_2O]$ 237, $[M^+\text{-}C_{11}H_8N_3O_2]$ 145, $[M^+\text{-}C_{11}H_7Cl_2N_2O]$ 106, $[C_5H_4N]^+$ 78	**N-H** (3177.0), **C=O** (1654.4 $_{Sh}$), **C=N** (1564.8), **C-N** (1153.5), **N-N** (1026.8), **C-Cl** (794.3)	N-**H** (12.1, $_s$), C**H**=N (8.39, $_s$)	56.73 **(C)** 3.03 **(H)** 19.56 **(Cl)** 11.49 **(N)**
L20	$[M^++2]$ 376, $[M^+]$ 374, $[M^{+2}\text{-}C_4H_2Cl_2]$ 256, $[M^+\text{-}C_4H_2Cl_2]$ 254, $[M^+\text{-}C_7H_6NO_2]$ 237, $[M^+\text{-}C_7H_5Cl_2]$ 219, $[M^+C_9H_7N_2O_3]$ 182, $[M^+\text{-}C_{11}H_7Cl_2N_2O]$ 121, $[C_6H_5O]^+$ 93	**N-H** (3218.3), **O-H** (3072.2 $_b$), **C=O** (1640.8 $_{Sh}$), **C=N** (1559.9), **C-N** (1169.9), **N-N** (1028.2), **C-Cl** (801.2 Sh)	N-**H** (11.9, $_s$), **O-H** (11.8, $_s$), C**H**=N (8.417, $_s$)	57.48 **(C)** 3.18 **(H)** 18.84 **(Cl)** 7.36 **(N)**
L21	$[M^++2]$ 360, $[M^+]$ 358, $[M^+\text{-}2]$ 356, $[M^+\text{-}C_5H_7]$ 295, $[M^{+2}\text{-}C_7H_5O]$ 255, $[M^{+2}\text{-}C_7H_6NO]$ 240, $[M^{+2}\text{-}C_{10}H_5Cl_2O]$149, $[C_5H_7]^+$ 69	**N-H** (3217.7), **C=O** (1649.5 $_{Sh}$), **C=N** (1150.4), **C-N** (1142.8), **N-N** (1026.7), **C-Cl** (796.6)	N-**H** (12.0, $_s$), C**H**=N (8.44, $_s$)	59.91 **(C)** 3.29 **(H)** 19.79 **(Cl)** 7.82 **(N)**
L22	$[M^++2]$ 361, $[M^+]$ 359, $[M^{+2}\text{-}C_2H_2Cl]$ 302, $[M^+\text{-}C_6H_5N_2O]$ 237, $[M^{+2}\text{-}C_6H_5N_3O]$ 225, $[M^+\text{-}C_8H_5Cl_2O]$ 174, $[M^{+2}\text{-}C_{11}H_8N_3O_2]$ 147, $[M^+\text{-}C_{11}H_7]$ 220, $[Cl_2N_2O_3]^+$ 106, $[C_5H_4N]^+$ 78	**N-H** (3146.2), **C=O** (1667.2 $_{Sh}$), **C=N** (1550.0), **N-N** (1030.6), **C-Cl** (790.6)	N-**H** (12.19, $_s$), C-**H**=N (8.44, $_s$)	56.39 **(C)** 3.02 **(H)** 19.62 **(Cl)** 11.55 **(N)**
L23	$[M^++2]$ 361, $[M^+]$ 359, $[M^+\text{-}Cl]$ 324, $[M^{+2}\text{-}C_2H_2Cl]$ 302, $[M^+\text{-}C_2H_2Cl_2]$ 266, $[M^{+2}\text{-}C_6H_5N_2O]$ 239, $[M^+\text{-}C_6H_5N_2O]$ 237, $[M^+\text{-}C_8H_5Cl_2O]$ 174, $[M^{+2}\text{-}C_{11}H_8N_3O_2]$ 147, $[M^+\text{-}C_{11}H_7Cl_2N_2O]$ 106, $[C_5H_4N]^+$ 78	**N-H** (3192.3), **C=O** (1611.1 $_{Sh}$), **C=N** (1552.3), **C-N** (1150.0), **N-N** (1026.6), **C-Cl** (797.8)	**H**-N) (12.12, $_s$), C-**H**=N (8.43, $_s$)	56.57 **(C)** 3.02 **(H)** 19.69 **(Cl)** 11.56 **(N)**
L24	$[M^++2]$ 376, $[M^+]$ 374 $[M^{+2}\text{-}C_2H_3O]$ 335, $[M^+\text{-}2Cl]$ 305, $[M^+\text{-}C_4H_2Cl_2]$ 254, $[M^+\text{-}C_{12}H_9N_2O_3]$ 145, $[M^+\text{-}C_{11}H_6Cl_2NO]$ 135, $[M^+\text{-}C_{11}H_7Cl_2N_2O]$ 121, $[C_6H_5O]$ 93, $[M^{+2}\text{-}C_{13}H_9Cl_2N_2O_2]$ 85, $[M^+\text{-}C_{14}H_9Cl_2N_2O_2]$ 69	**N-H** (3234.4), **O-H** (3083.4 $_b$), **C=O** (1619.4 $_{Sh}$), **C=N** (1538.0), **C-N** (1140.6), **N-N** (1024.2), (**C-Cl** (790.4)	N-**H** (11.96, $_s$), O-**H** (11.74, $_s$), C**H**=N (8.44, $_s$)	57.81 **(C)** 3.18 **(H)** 18.97 **(Cl)** 7.37 **(N)**

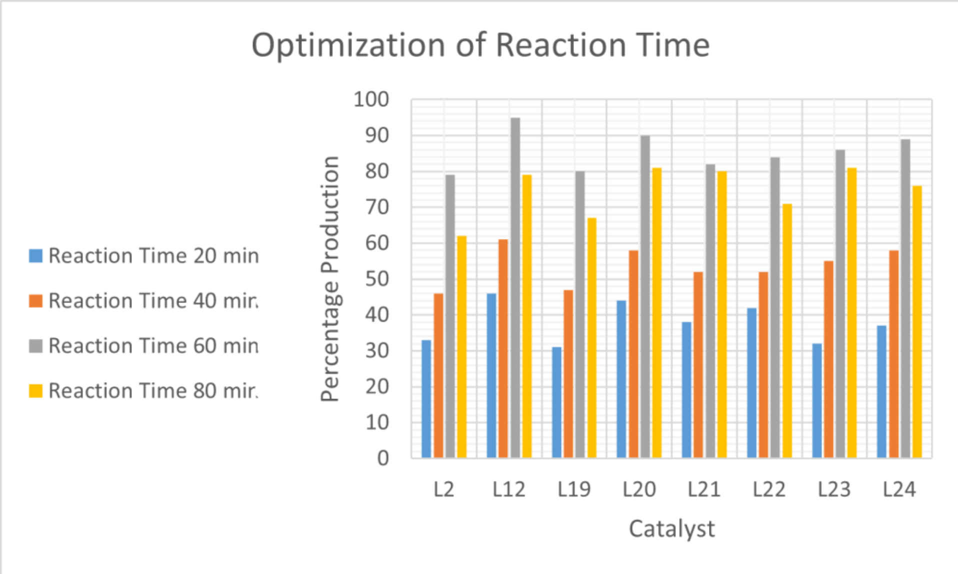

Figure 3: Optimization of reaction time.

3.4.2. Reaction Temperature

No doubt, the reaction temperature is one of the most critical parameters that affects the production and quality of biodiesel. Leung reported, the yield is generally increased as the temperature is increased during the esterification and transesterification process (59), but the quality is usually decreased because of the presence of byproducts during these processes (60). Using the silica-based catalysts, Zuo and coworkers proposed that 60°C is the optimal temperature for esterification (61). During the esterification process, the highest yield (up to 95%) was obtained at 60°C, but this decreased (up to 80%) as the temperature increased to 80°C. Similarly, the same effect was observed in transesterification. The maximum yield was obtained at 60°C and as the temperature increased, the yield decreased due to the formation of soap and by-products as the temperature increased.

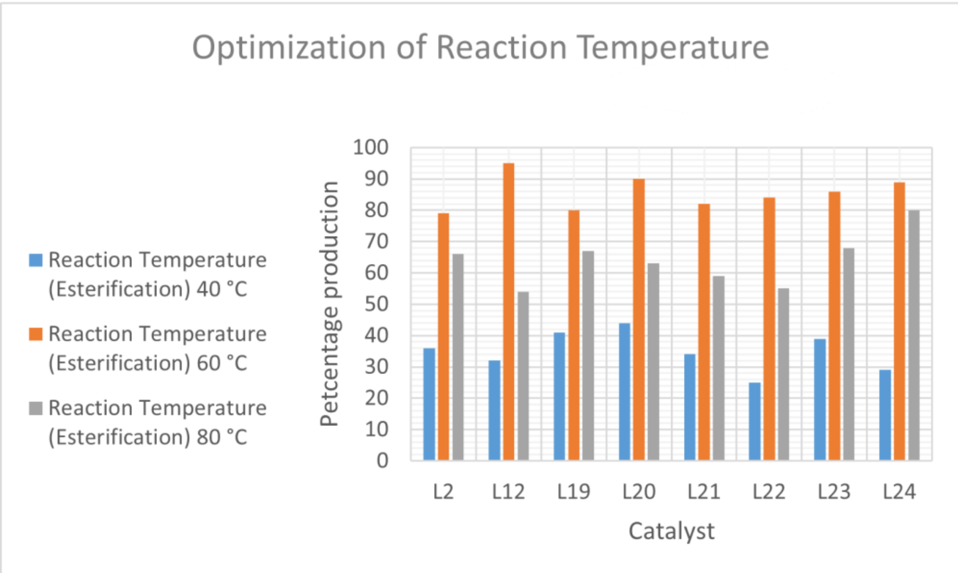

Figure 4: Optimization of reaction temperature during esterification.

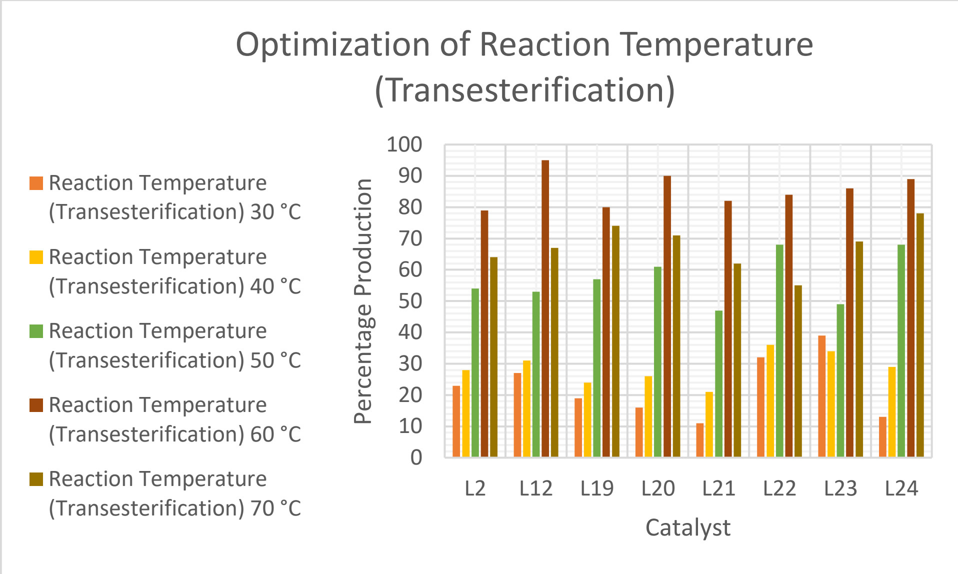

Figure 5: Optimization of reaction temperature for transesterification.

3.4.3. Solvent Type

Additionally, solvent is directly related to biodiesel production. A polar solvent, such as methanol, or an alcohol, can facilitate and solubilize the reactants in order to improve biodiesel yields. It was preferable to use methanol as a solvent instead of ethanol or any other alcohol since it was easy to separate with less soap precipitation (34). There is a larger amount of solvent required for non-edible oils as compared to edible oils, less alcohol amount causes thick material to form, which is more difficult to separate. Ali et.al., reported the molar ratio of oil and methanol should be 1:3 for high production (1). Furthermore, the use of ethanol in non-edible oils can lead to the formation of soap. It has also been reported that heptane, hexane, and toluene have been used as co-solvents to increase the yield of biodiesel. However, this can lead to toxic environmental effects or increase biodiesel toxicity (62).

3.4.4. Catalyst Amount

Biodiesel production is strongly influenced by the amount and type of catalyst used. The basic catalyst can be used for biodiesel production if the free fatty acid content is less than 1-2% (63). However, the free fatty acid content in non-edible oils like neem oil exceeds 20% and the basic catalyst causes soap formation (64). As a result, it is necessary to minimize this FFA value by esterifying with an acid catalyst before transesterification or using a basic catalyst (65). The study used organic derivatives as acid catalysts during esterification, which affected biodiesel production. The optimal amount of acid catalyst for biodiesel production was 50mg, and by increasing or decreasing the amount, the yield also decreased, possibly due to the formation of by-products or side reactions.

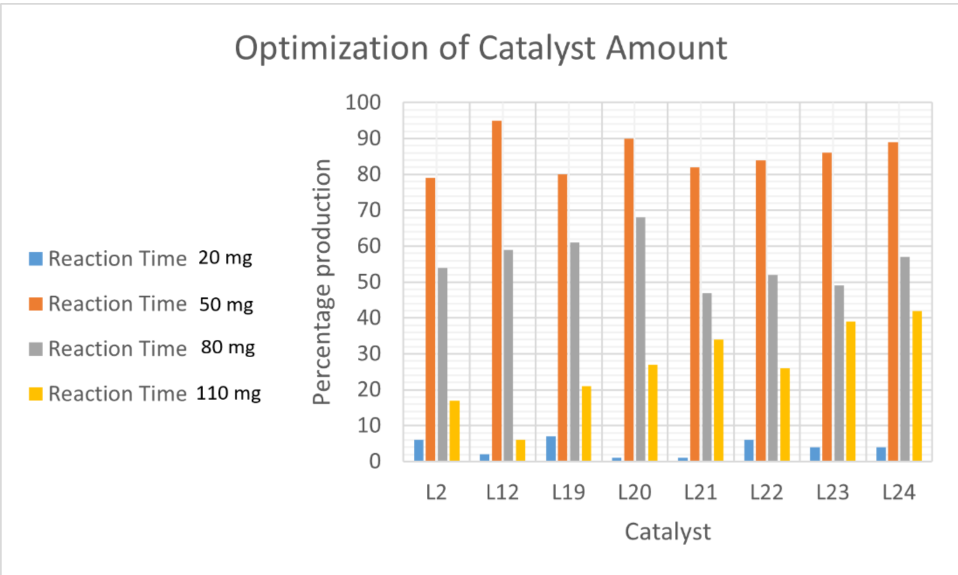

Figure 6: Optimization of catalyst's amount.

Similarly, the biodiesel production is also effected by concentration of basic catalyst (transesterification). The optimum amount calculated experimentally was 10 mg of KOH. According to Aboelazayem and co-workers, the optimum KOH ratio should be 1:3-1:7 for high production yields (66). Strong alkali causes soap formation and decreases the yield of biodiesel (64). To avoid this problem, KOH was preferred as a best activator for transesterification (67) with FAME's yield up-to 99% (68).

3.5. Characterization of Biodiesel

A range of parameters such as moisture content, viscosity, density, pH and color were presented in Table 2.

Table 2: Characterization of biodiesel synthesized from organic heterocyclic catalysts.

Sample	Color	%age Yield	Density g/cm^3	Viscosity mm^2/s	pH	Moisture content (%)
Neem Oil (69,70)	light yellow	-	0.91	31.99	6.10	4.61
Biodiesel (71) (standard)	Yellow-colorless	-	0.83-0.89	1.9-6	5.97-6.76	0.3-6.0
Neem Biodiesel (70,72) (standard)	Golden yellow	-	0.89	4.99-5.21	6.69	>0.5
L2	Bright yellow	79	0.81	5.1	6.52	0.3
L12	Yellow	95	0.86	4.79	6.73	0.13
L19	Light yellow	80	0.87	5.16	6.66	0.27
L20	Yellow	90	0.81	5.41	6.91	0.19
L21	Dull yellow	82	0.86	5.33	6.36	0.14
L22	Light yellow	84	0.86	4.66	6.71	0.22
L23	Light yellow	86	0.83	4.82	6.71	0.19
L24	Golden	89	0.87	4.97	6.55	0.15

As, high moisture content promote microbial growth (9). Moisture content of neem biodiesels was low ranging 0.13-0.3 % that was within the standard limits indicating purity of these biodiesels. The samples ranged in color from yellow to colorless, with little variation in pH between 6.3 and 6.91. According to the results, FFA value of neem oil was very high 24.76 (mg/g), therefore, alone transesterification cause soap formation and affect the quality as well as yield of biodiesel (73). To reduce this FFA, esterification with acid catalysts (organic hydrazone derivatives) was successfully performed and FFA value is less than 1 in all cases indicating it as an excellent diesel fuel. Density of biodiesel is 0.83-0.89 g/cm^3 while for neem biodiesel 0.91 g/cm^3. All the synthesized biodiesel exhibit densities ranges 0.81-0.87g/cm^3 suggest the good quality of these biodiesels. Viscosity of neem oil is very high 31.99 (mm^2/s) and cause smoke while standard biodiesel and neem biodiesel has low viscosity 1.9-6 (mm^2/s) and 4.99-5.21 (mm^2/s) respectively. All the synthesized biodiesel has also low viscosity ranges 4.66-5.33 (mm^2/s) that is better for good combustion and less smoky. Moisture content is also low in all biodiesels indicate the purity.

Basically, acid value is the mg of KOH to neutralize FFA of 1 g oil/fat, higher the acid value less will the quality and quantity of biodiesel (9). Acid value of neem oil is very high due to high FFA (9.163 mg/g) while biodiesels have low acid value (0.161-0.261 mg/g) within the standards. Iodine value indicate the unsaturation of neem oil due to the presence of unsaturated fatty and is very high 73.814 (mg I_2/100 g), while neem biodiesel has 49.49 (mg I_2/100 g), other biodiesels also have low iodine value 51-58 (mg I_2/100 g). Saponification value of neem oil is also very high (199.810 mg/g) indicating its high tendency to form soap when reacted to basic catalyst which reduces to (167-176 mg/g) significantly and presented in Table 3.

Table 1: Acid value, iodine value, FFA and saponification value of biodiesels.

Sample	Acid value (mg/g)	Iodine value (mg I_2/100g)	FFA value	Saponification value (mg/g)
Neem Oil (71,74)	9.163	73.814	24.76	199.810
Biodiesel (71,75) (standard)	≤0.80	8.9	≥2	-
Neem Biodiesel (71,76) (standard)	0.13	49.49	0.7	167.36
L2	0.228	56.31	0.87	171.33
L12	0.161	51.55	0.76	167.37
L19	0.182	53.20	0.82	170.29
L20	0.166	52.11	0.71	167.61
L21	0.171	53.04	0.83	167.67
L22	0.299	57.93	0.81	176.31
L23	0.261	55.63	0.83	170.11
L24	0.223	56.79	0.89	172.74

3.6. FTIR Characterization

In addition to the physical parameters mentioned above, the synthesized biodiesels were characterized using FTIR (Figure 7-14). Broad absorption band of –OH near 3000-3400cm^{-1} is absent indicate these biodiesels are almost free from moisture. Sharp absorption peak near 1743 cm^{-1} are caused by C=O stretch indicating the presence of esters in all samples, while CH stretching results in peaks near 2922 cm^{-1} and 2850 cm^{-1}. Asymmetric and symmetric deformation vibrations of CH are approximated at 1458 cm^{-1} and 1380 cm^{-1}, respectively indicate mono, di or triglyceride glycols in all tested samples. Due to C-O stretching, there are absorption peaks near 1166 cm^{-1}, 1240 cm^{-1}, and 1100 cm^{-1}, while long chain absorption peaks appear at 720 cm^{-1}.

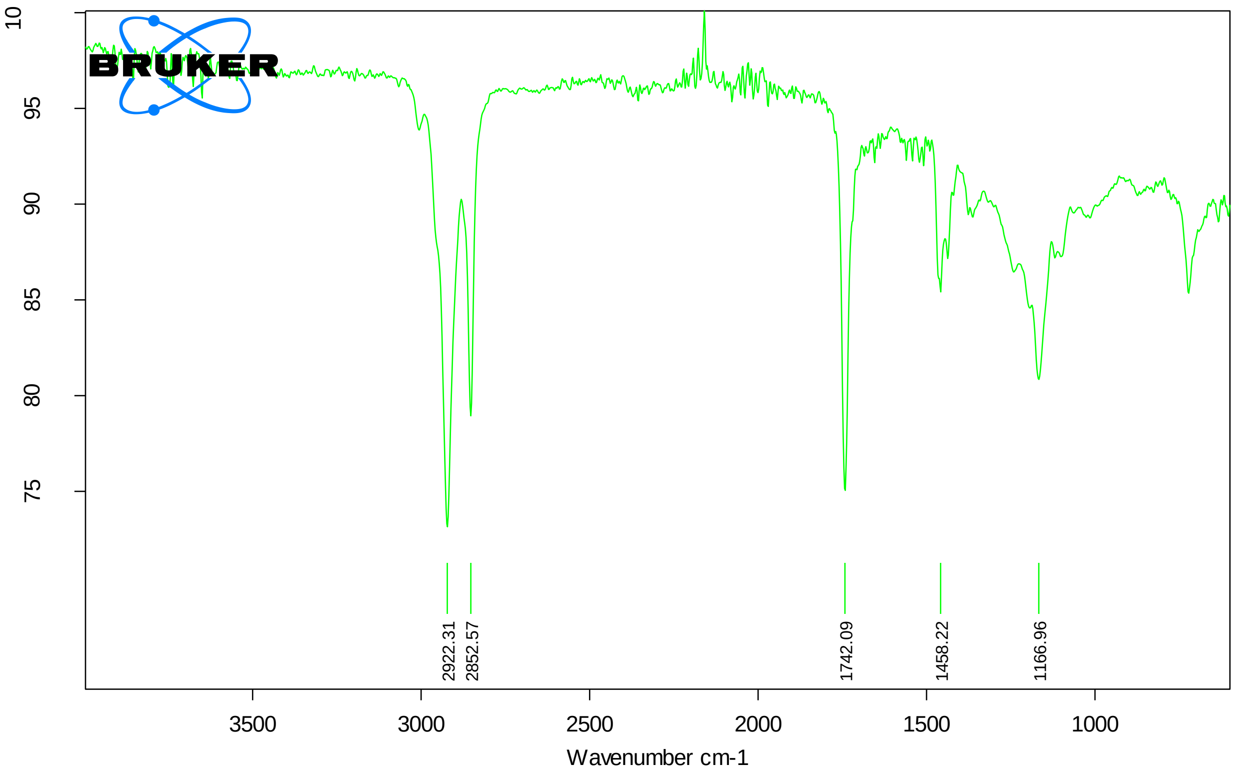

Figure 7: FTIR spectra of biodiesel prepared by L2 as a catalyst.

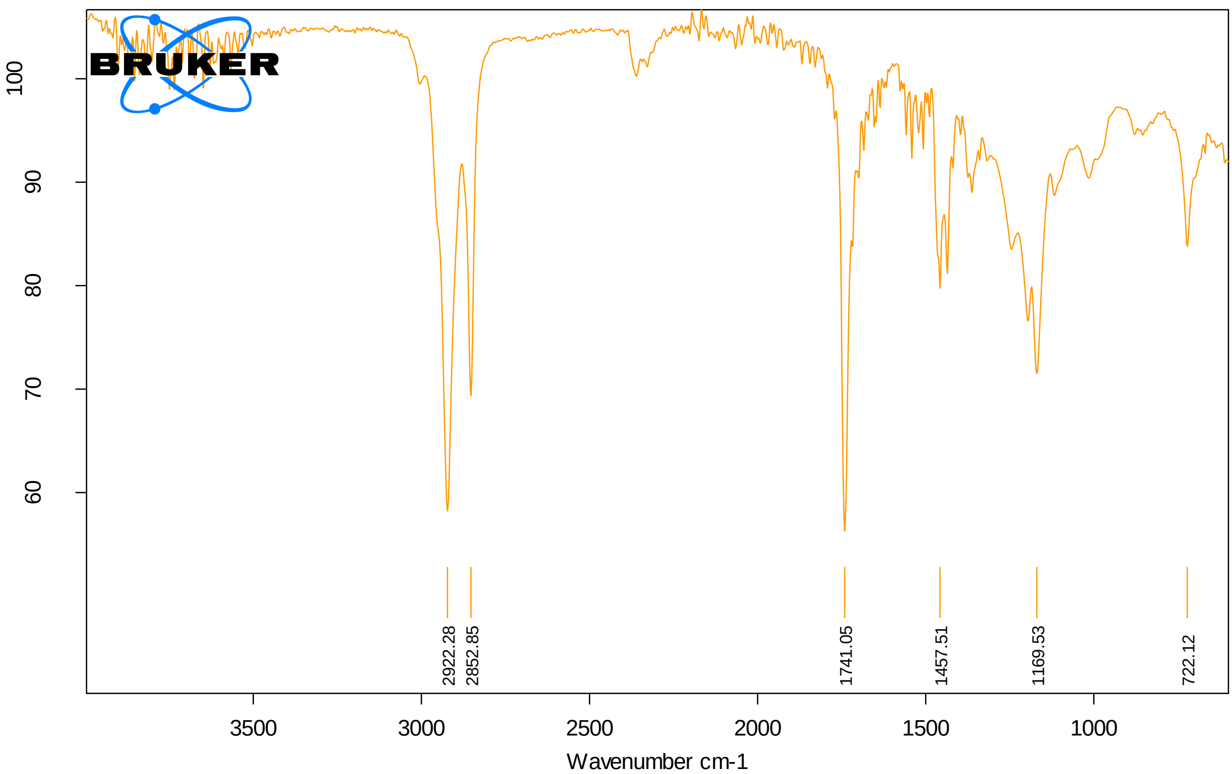

Figure 8: FTIR spectra of biodiesel prepared by L12 as a catalyst.

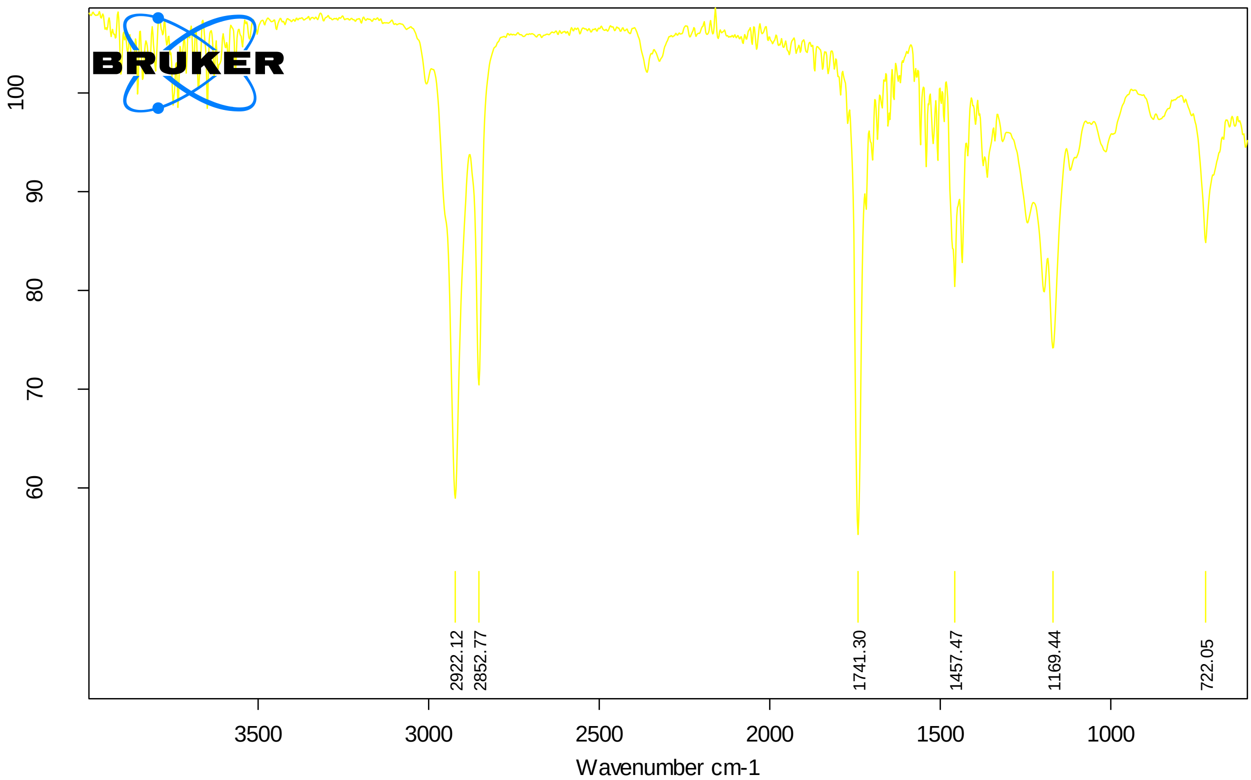

Figure 9: FTIR spectra of biodiesel prepared by L19 as a catalyst.

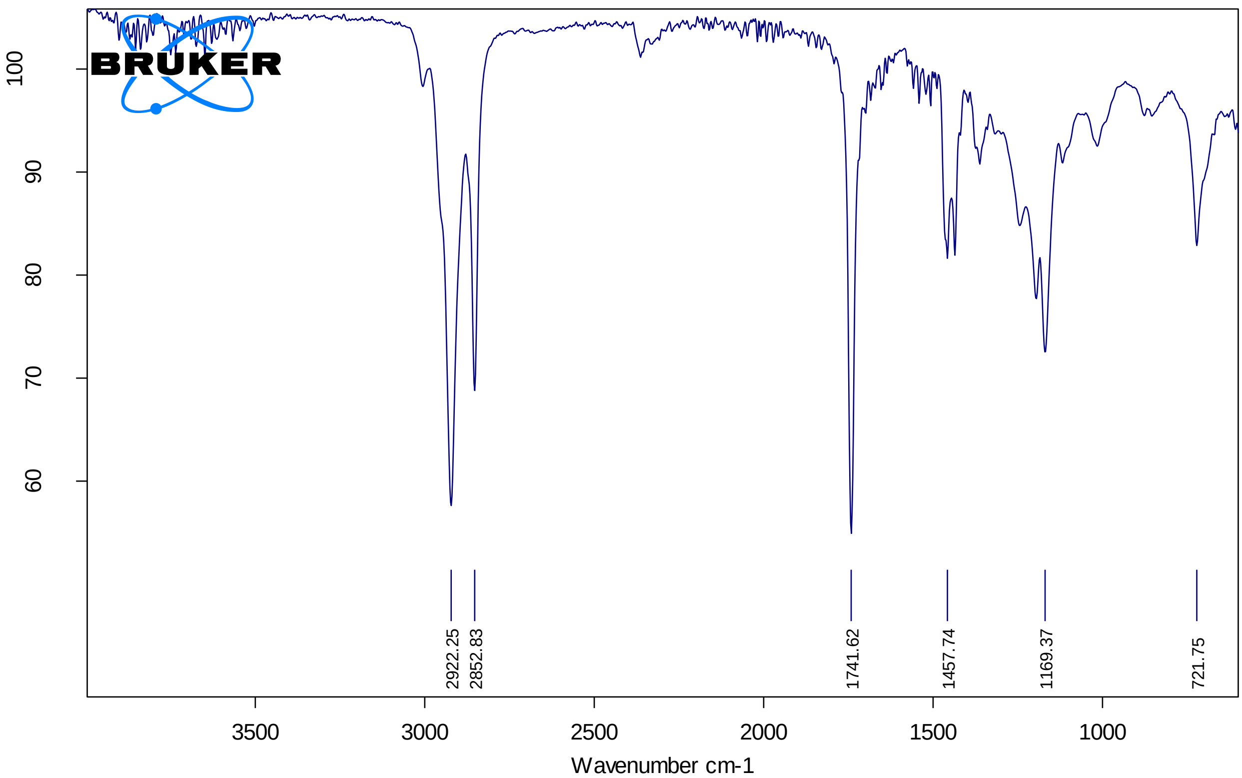

Figure 10: FTIR spectra of biodiesel prepared by L20 as a catalyst.

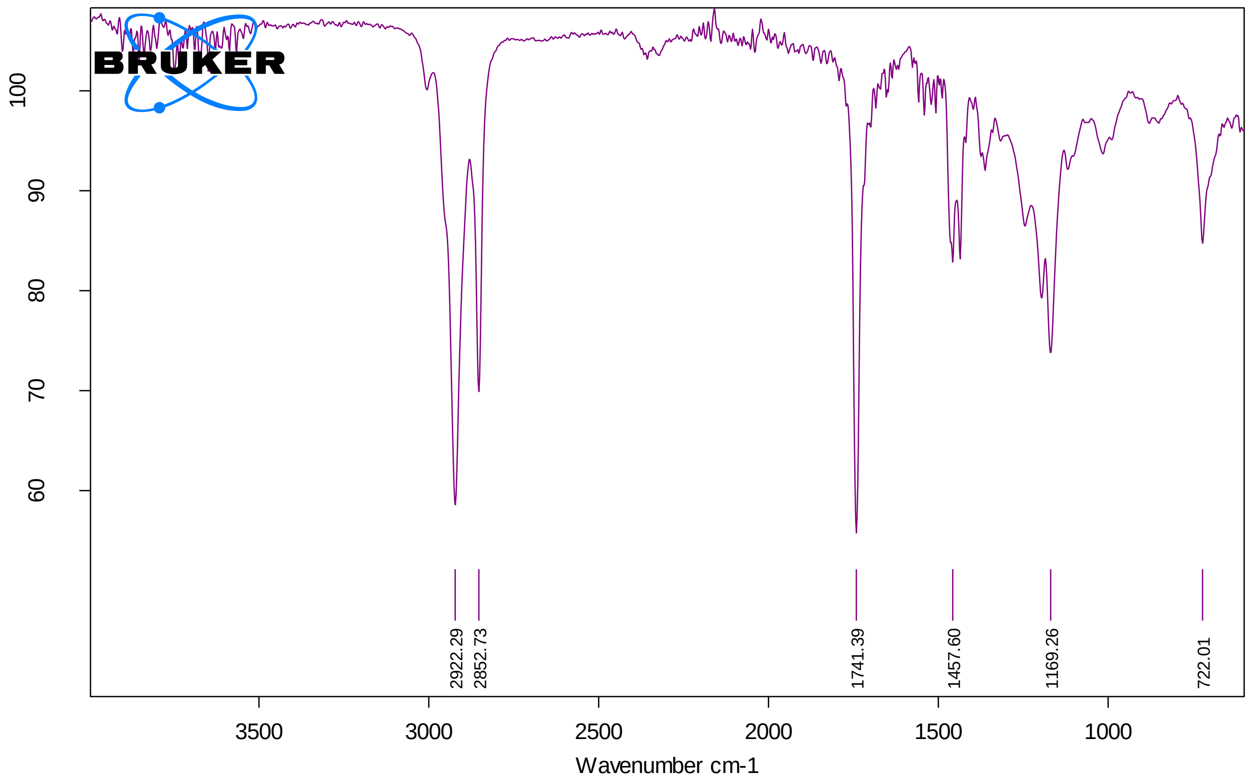

Figure 11: FTIR spectra of biodiesel prepared by L21 as a catalyst.

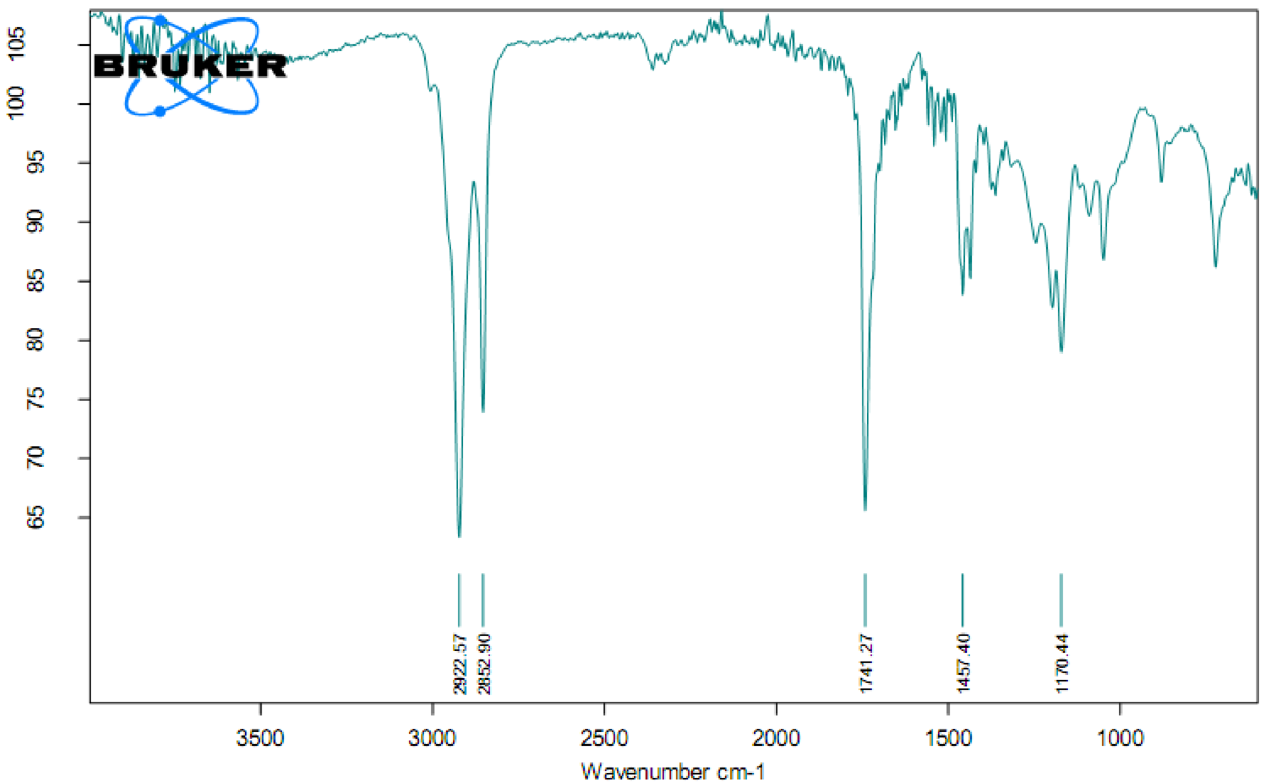

Figure 12: FTIR spectra of biodiesel prepared by L22 as a catalyst.

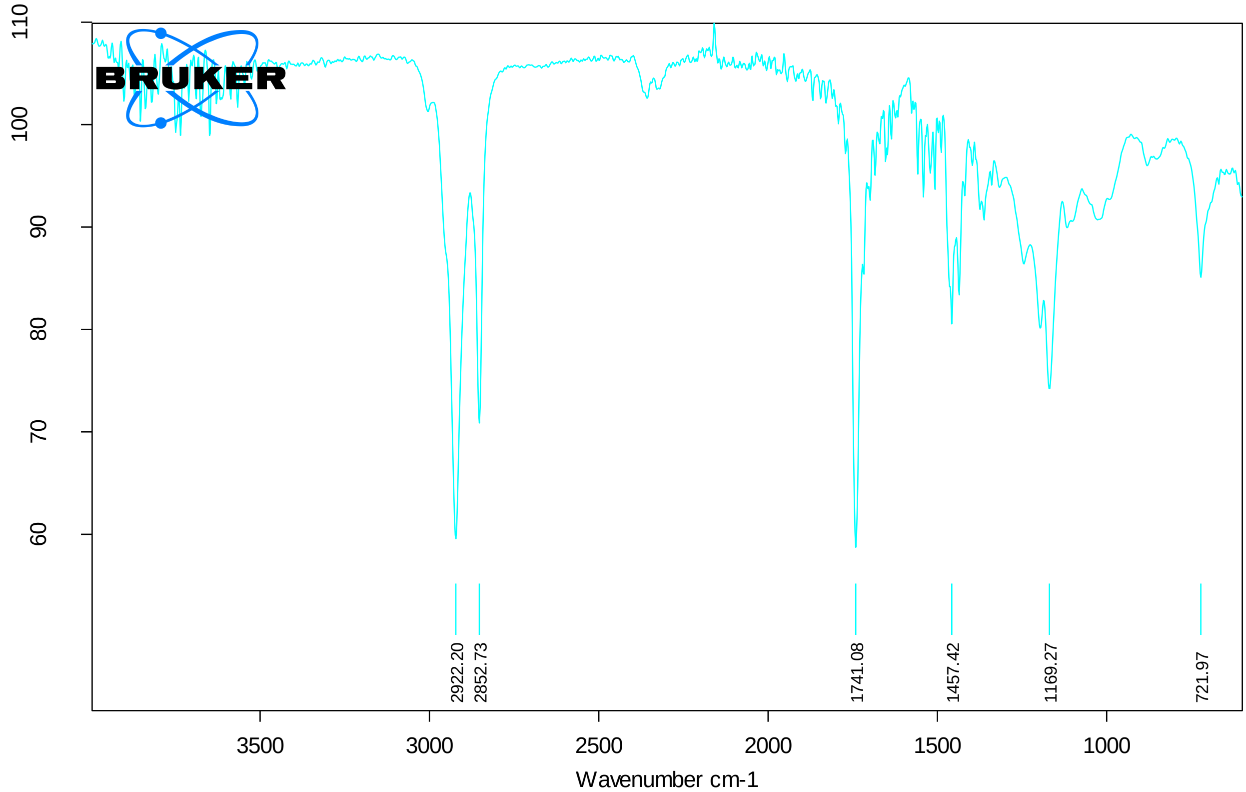

Figure 13: FTIR spectra of biodiesel prepared by L23 as a catalyst.

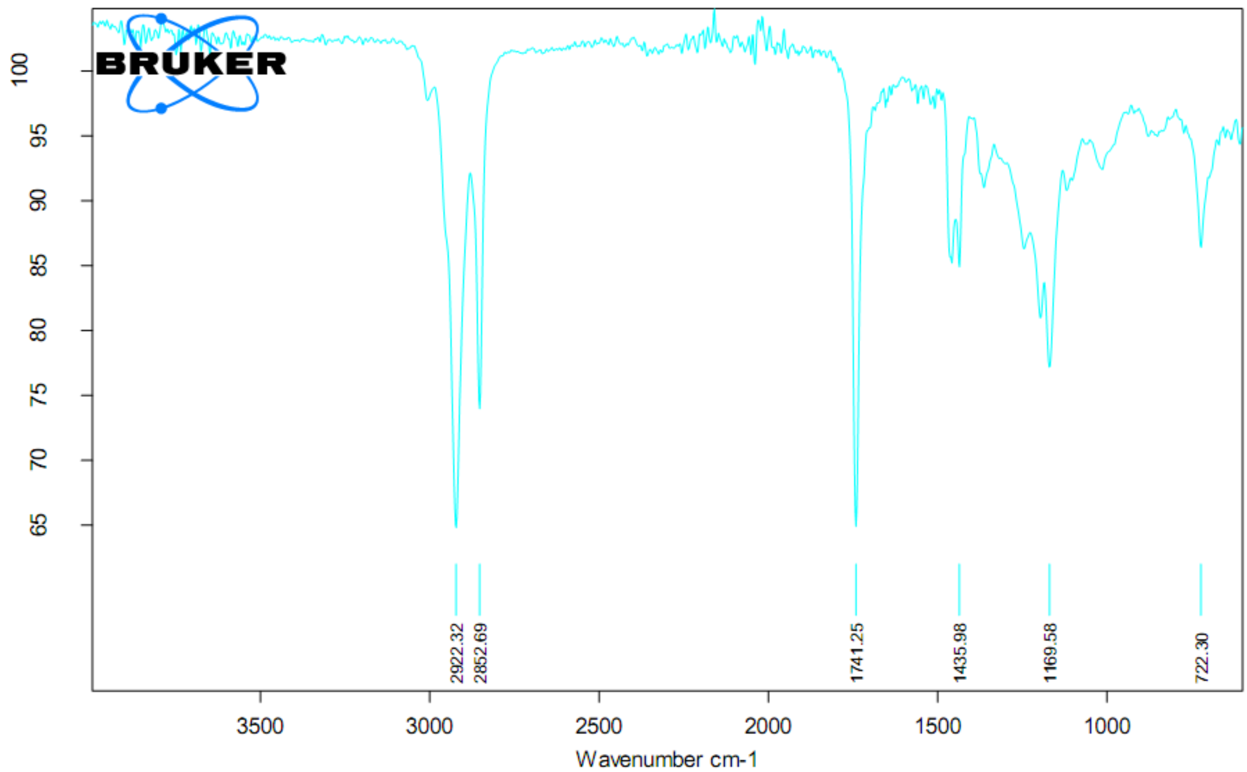

Figure 14: FTIR spectra of biodiesel prepared by L24 as a catalyst.

4. CONFLICTS OF INTEREST

No conflict of interest was declared by the authors.

5. CONCLUSION

Biodiesel is an alternative fuel that contributes to energy stability. A variety of renewable sources can be used to produce biodiesel today, making it an extremely attractive alternative to fossil fuels that is non-toxic, biodegradable, and can be produced from a variety of renewable energy sources. In recent years, the extraction of neem oil from neem seeds has attracted the attention of many scientists based on the ease of cultivation, the lack of impact on food production, and the ability to grow on non-cultivable lands, compared to other biomass sources.

This paper summarizes the use of some newly synthesized organic heterocyclic hydrazone derivatives as catalysts for the production of neem biodiesel instead of previously reported catalysts due to their high yields and ease of optimization. Using ultrasonic irradiation method, we synthesized hydrazone derivatives in less than three minutes and were able to characterized these compounds using EIMS, NMR, FTIR and CHN spectroscopic methods. It was expected that these compounds exist in ketonic form and were highly pure since they showed a significant N-H peak in the 1H-NMR range of 11.9-12.2 ppm and in the FTIR range of 3146-3237 cm^{-1}, which confirmed their purity. Accordingly, the O-H absorption peak was found at 11.8 ppm in 1H-NMR, and the broad band was found to be above 3000 cm^{-1} in FTIR. A sharp peak range of 1600-1700 cm^{-1} was observed by FTIR for the carbonyl group. Elemental analysis and mass spectra confirmed their molecular weights and molecular formula.

As FFA acid value of neem oil is very high 4.2% and before biodiesel formation it should be reduced and esterification performed before transesterification. For this purpose, we use, these derivatives as acid catalysts instead of simple acids. The reaction parameters like reaction temperature, reaction time, solvent and catalyst amount were optimized for better understandings. The optimized time for esterification was 60 min, optimized temperature for esterification as well as for transesterification was 60°C, methanol used as optimized solvent while optimized amount of catalyst was 50 mg. These optimized parameters produced high yield and highly purified biodiesel ranges 79-95%.

These produced biodiesels showed 6-6.91 pH range, density (0.81-0.87 g/cm^3), viscosity (5.41-4.79 mm^2/s) and moisture content less than 0.5. Acid value, FFA, iodine value and saponification value of all these biodiesels were 0.161-0.261(mg/g), 0.71-0.89 (%) 51-58(mgI_2/100g), and 167.37-176.31 (mg/g) very close to the reported standard neem biodiesel. These neem biodiesels were characterized by FTIR spectra, exhibited CH stretching peaks near 2900 cm^{-1} and 2800 cm^{-1} while sharp absorption peak for C=O above 1700 cm^{-1} while –OH absorption band was absent. This conclude that hydrazone derivatives can be used as excellent acid catalysts in esterification for production of highly purified biodiesel from neem oil with a yield up to 95%.

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