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EFFECTS OF WASTE HYBRID FEEDSTOCKS AND HETEROGENEOUS CATALYST ON BIODIESEL SYNTHESIS: WASTE MUTTON-BENNE SEED OIL AND GOAT BONE-PLANTAIN PEDUNCLE APPLICATIONS

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Abstract - This study investigates the effects of using hybrid feedstocks and catalysts on the efficiency and yield of fatty acid methyl ester synthesis. The hybrid feedstocks used were goat fat and Benne seed oil, while the catalysts used were plantain peduncle and goat bone. In this study, the characterization of the blended oil was done and it was compared with other works. The characterization of the blended catalyst was done using Fourier transform infra-red spectroscopy (FTIR) and X-ray diffractometry (XRD) for the raw blended catalyst and the thermally activated blended catalyst at 800ºC. The result indicated that the blended catalyst contains mainly of graphite (pure carbon). The optimal biodiesel yield was 89.20% at catalyst concentration of 1.5%, temperature of 70ºC, reaction time of 180min, and a methanol to oil ratio of 9:1 and it was further characterized and compared with other literature works. This study finally shows that the application of hybrid catalysts, with combine the properties of heterogeneous catalysts and fused feedstock, enhances reaction kinetics, reduce process energy requirements, and improves product purity.
Key words: hybrid feedstocks; heterogeneous catalyst; biodiesel; waste mutton; bene seed oil; goat bone; plantain peduncle

1. Introduction

Globally, there is an urgent and pressing need to move away from fossil fuel sources to sustainable and renewable energy sources due to the inherent benefits in renewable energy sources, while fossil energy sources are characterized by disturbing health and environmentally degrading emissions and by-products (Esonye et al., 2022). Among the renewable energy sources is biodiesel, which can replace petrodiesel. Biodiesel is derived from triglycerides (oil and fats) through many processes with transesterification as the prominent method. The use of agro-waste materials like waste vegetable oils and animal fats (Esonye et al., 2018) and animal shells, bones, scales, etc., and plant wastes and parts such the barks, seed coats, husks etc. (Ezekannagha et al., 2024; Esonye et al., 2023a) has increased the economic feasibility of biodiesel production through the use of cheap raw material sources. Transesterification involves the use of a catalyst: heterogeneous or homogeneous with triglycerides and methanol as reactants and biodiesel and glycerin as products. Quite different from homogeneous catalysts, heterogeneous catalysts are typically solid, resulting in the reaction mixture and the catalyst existing in different phases. The catalyst surface serves as the primary site for the reaction. The utilization of solid catalysts in transesterification offers several green advantages; the catalyst can be reused, minimal wastewater is generated, glycerol separation from the final mixture is easier, and high-purity glycerol is obtained (Wu et al., 2018).

Heterogeneous catalysts possess many advantages compared with homogeneous catalysts, which include simple separation, recyclability, and reusability. They are eco-friendly, less toxic, and exhibit minimal corrosion with reduced energy consumption, offering an efficient and economical pathway for biodiesel production (Roy et al., 2019). Heterogeneous catalysts are categorized into basic and acidic types. Recent advancements have led to the development of heterogeneous catalysts capable of simultaneously promoting esterification and transesterification reactions in a single reaction vessel, or "one-pot" process. These catalysts are particularly useful for biodiesel synthesis from vegetable oils or animal fats with high free fatty acid (FFA) content without the need for additional pretreatment steps to reduce the FFA content (Patel et al., 2020). Recent studies from 2016 to 2024 have shown significant advancements in the field. For instance, novel catalysts have been developed that exhibit higher catalytic efficiency, stability, and easier recovery processes (Gopinath et al., 2017). Research has also focused on improving the sustainability of the catalysts by utilizing waste materials and biopolymers as supports, thereby enhancing the green credentials of biodiesel production (Patel et al.,2020). Additionally, studies have demonstrated that these advanced heterogeneous catalysts can significantly reduce production costs and improve the overall efficiency of biodiesel production processes (Zhang et al., 2020).

Hybrid biocatalysts exhibit improved stability and activity compared to individual components, owing to synergistic interactions between biological and synthetic elements (Wang et al., 2021; Jones et al., 2019). Incorporation of nanomaterials enhances active surface area and facilitates mass transfer, thereby improving reaction kinetics (Wang et al., 2021; Smith et al., 2018). Enzyme immobilization onto suitable supports enhances stability and recyclability, prolonging catalyst lifespan and reducing operational costs. Common support materials include mesoporous silica, magnetic nanoparticles, and hydrogels (Jones et al., 2019; Wang et al., 2021). Hybrid biocatalysts exhibit biocompatibility crucial for biomedical applications such as drug delivery and tissue engineering. Integration of biologically derived components ensures minimal cytotoxicity and immunogenicity, making them suitable for therapeutic use (Smith et al., 2018; Jones et al., 2019). The fusion of hybrid feedstocks and catalysts leads to biodiesel yield (Rothenberg et al., 2016) with improved fuel properties, such as higher cetane number oxidative stability leading to a higher-quality product (Lee et al., 2019). Also, hybrid feedstocks and catalysts contribute to the optimization of cold flow properties in biodiesel, reducing the risk of fuel gelling and improving cold weather performance (Kiss et al., 2016). The fusion of hybrid feedstocks and catalysts results in biodiesel that is more compatible with existing diesel engines and infrastructure (Esonye et al., 2023) and releases low emissions (Xie et al., 2018).

Economically, integration of hybrid feedstocks diversifies the feedstock base, reducing supply chain risks and enhancing overall supply security (Lee et al., 2019). Fusion of hybrid feedstocks and catalysts enables cost optimization through the use of lower-cost or waste materials, leading to potential cost savings in biodiesel production (Chen et al., 2018). Hybrid systems enhance process efficiency, resulting in reduced energy consumption, shorter production times, and lower operational costs (Rothenberg et al., 2016). The use of hybrid feedstocks and catalysts leads to biodiesel with improved quality and performance characteristics, reducing downstream processing costs and enhancing market competitiveness (Ryu et al., 2019). Investment in hybrid feedstock and catalyst technologies can yield long-term cost reductions through improved yield, process optimization, and enhanced sustainability, leading to improved economic viability of biodiesel production (Xie et al., 2018). Although there are a few efforts made in literature on hybrid feedstock applications, there are many feedstocks yet to be fused together to ascertain their satisfaction of the above benefits. The usefulness of waste mutton, benne seed oil, waste goat bone and plantain peduncle in biodiesel production has been extensively reported earlier (Esonye et al., 2023b; Ume et al., 2024). Therefore, this study presents for the first time the effects of waste mutton-benne seed oil and goat bone-plantain peduncle applications on biodiesel synthesis as hybrid feedstocks and catalysts respectively.

2. Materials and Methods

2.1 Materials

Materials used in this work include glass wares and other consumables, analytical grade reagents and electronic equipment. The feedstocks and catalyst were obtained from benniseed, goat fat, goat bone and plantain peduncle (Fig. 1a-1d).

Fig. 1: Feedstocks and catalyst sources: a: Benne seed; b: Goat fat; c: goat bone and d: Plantain peduncle.

2.2 Methods

2.2.1 Benne seed collection and preparation

Raw seeds were bought from retail traders. The seeds were selected to remove impurities and washed in distilled water to remove dust. They were allowed to dry in open air. The dried seeds were milled using electric grinding machine to permit proper oil extraction. The milled sample is stored in air tight container until use for oil extraction.

2.2.2 Oil extraction

The seed oil was carried out using the method applied by Ume et al., (2024) with slight modification. The oil yield was calculated using equation (1).

$$Oil\ yield\ (\%) = \frac{weight\ of\ oil}{Sample\ weight}\ x\ 100 \quad (1)$$

2.2.3 Pre-treatment (acid- esterification) of goat fat

The fat obtained from goat wastes was in solid form. It was transformed into useable oil form by speed blending and esterification. The goat fat was introduced into kitchen blender. It was blended at high speed such that the fat solids were transformed to liquid oil following the methods demonstrated by Ume et al., (2024).

2.2.4 Oil characterization

The obtained oil and fats were characterized to ascertain its physico-chemical properties using AOAC methods (AOAC, 1999).

2.2.5 Synthesis of nano –catalyst from blend of goat bone and plantain pendicle

Nano catalyst synthesis was prepared according to the method of Fatah *et al*., (2016). The goat bone and plantain pendicle were washed and oven dried, grinded using industrial blender and is screened to 100 micrometer particle size. Then, the dried samples (mixed in equal ratio of 1:1) were mixed with hot sulfuric acid and mixed vigorously to ensure that the slurry mixture is in solid state. Further calcination was done in Muffle furnace at 800 ºC while the activation of the catalyst was further perfected by washing it with distilled water before adding KOH solution. Later, the mixture was washed using distilled water, dried and stored airtight in container.

2.3 Transesterification process

Biodiesel was produced by transesterification (reaction of methanol and oil) using the nano catalyst. The reactor consisting of three-neck round bottom flask fitted with a quick-fit condenser was placed on a magnetic hot plate. The set up was held in position using a retort stand with clamp. Water was made to be circulated at the outer jacket of the condenser to ensure the materials were not lost by evaporation. The reaction which was done following the experimental design ensured that for each set of reaction, biodiesel yield was determined. Fifty (50) ml of moisture free oil were introduced into the reactor with a calculated amount of methanol (mol). A known amount of catalyst (weight percent of the sample) was thereafter added, with given temperature (°C), reaction time (minutes) and agitation speed (revolution per minute). Having determined the reaction parameters, equations (2) to (4) were adopted to quantify the reaction constituents according to Edmilson et al., (2014) and Umeagukwu et al., (2024b).

$$Methanol\ (g) = \frac{oil\ weight\ (g) x\ methanol\ ratio\ x\ molecular\ weight\ of\ methanol\ (\frac{g}{mol})}{oil\ ratio\ x\ molecular\ weight\ of\ triglyceride\ (\frac{g}{mol})} \quad (2)$$

$$Oil\ weight\ (g) = (oil\ volume (ml) x\ density\ of\ oil\ (g))/(1ml) \quad (3)$$

$$Catalyst\ (3\%wt) = \frac{oil\ weight\ x\ 3}{100} \quad (4)$$

At the end of each reaction, the product (consisting of methyl ester, methanol, glycerol and catalyst) was transferred into a 500ml separating funnel, and washed using boiling distilled water. During washing, methanol is evaporated off, while the methyl ester (biodiesel) being less dense than water as the supernatant, with water and other impurities settled at the bottom. The water afterwards was run off and the biodiesel collected in a beaker and dried in water bath to remove the excess water.

2.4 Effects of Process Parameters

By keeping all other parameters constant (temperature 50 °C, time 80 min., agitation speed 300 rpm, mole ratio 9:1), the catalysts initially prepared at diverse concentrations (1.0, 1.5, 2.0, 2.5 and 3.0 % weight of oil) were varied one after the other. The process time for the production of biodiesel was varied at different intervals (40, 60, 80, 100, and 120 min.). For each production, other process conditions were kept constant (temperature 50°C, catalyst 2.0 %, speed 300 rpm, mole ratio 9:1, agitation speed 300 rpm). The reaction temperature was varied at 30, 40, 50, 60, and 70°C. While temperature is varied, other process conditions are kept constant as follows; mole ratio 9:1, catalyst 1.5 %, speed 300 rpm, time 3 hrs., agitation speed 300 rpm while methanol to oil molar ratio was varied at 5:1, 7:1, 9:1, 11:1 and 13:1, other process conditions were varied as follows; temperature 50°C, catalyst 2.0%, speed 300 rpm, time 80 min., agitation speed 300 rpm. The effect of agitation speed on biodiesel production was studied at different agitation speed of 100, 200, 300, 400 and 500 rpm. Catalyst concentration, reaction time, reaction temperature and others are varied as follows; mole ratio 9:1, catalyst 2.0 %, speed 300 rpm, time 80 min, temperature 50°C.

2.5 Characterization of Biodiesel

2.5.1 Physico-chemical characterization

Biodiesel is characterized for Kinematic viscosity (Zhu et al., 2006), Aniline point (ASTM 1994), the API, diesel index and Cetane number (Rajarshi *et al.,* (2012).

2.5.2 Fourier transform infrared (FTIR) Spectrometry and X-ray diffraction (XRD)

To ascertain the available functional groups, FTIR spectrometry machine by Empyphrem PAN was used at a resolution of 2 cm^{-1} (Umeagukwu et al., 2024; Mba et al., 2021). Detection of the composition of the samples were done using Powder X-ray Diffractometer with CuKα radiation (λ = 1.54018 Å) (Umeagukwu et al., 2024; Mba et al., 2021).

3. Results and Discussion

3.1 Characterization of blended feedstock in comparison with the single feedstock

Table 1: Characterization of blended feedstock (Goat fat oil + Benniseed oil) in comparison with the single source oil.

S/N	Physiochemical properties	Unit	Goat fat/ Benniseed oil - This study	Goat fat oil (Ume et al., 2024)	Benne seed oil (Kumar et al., 2016)
1	Density	g/mol	0.9347	0.993	0.96
2	Kinematic viscosity	mm^2/s	62.19	70.18	22.63
3	Acid value	mgKOH/kg	5.271	9.28	3.15
4	Free fatty acid	mgKOH/kg	2.636	4.64	1.58
5	Saponification value	mgKOH/kg	217.74	173.29	142.2
6	Peroxide value	meq/kg	2.83	4.86	2.89
7	Molecular weight	g/mol	792.12	1026.16	874.49
8	Ester value	%	97.58	94.64	73.14
9	Moisture content	%	0.216	0.18	0.23
10	Iodine value	$gI_2/100g$	27.42	87.50	86.15
11	Refractive index	@ 25 °C	1.4635	1.4739	1.473

The summary of the physico-chemical properties of oil blend (goat fat oil + benniseed oil) in comparison with those of goat fat oil and benniseed oil are contained in Table 1. The density of the oil blend was 0.9347 g/mol while that of goat fat oil and benniseed oil were 0.993g/mol and 0.96g/mol respectively. Most oils used for biodiesel production have densities in the range of 0.8 to 0.95 g/cm^3 which shows that the density value of 0.9347g/mol is satisfactorily within the range of densities of fats and oils used in synthesis of biodiesel. Hence, biodiesel with optimal density range shows efficient combustion, engine compatibility and reduced emission.

The kinematic viscosity of the oil blend from the Table 1 was 62.19 which is suitable for high yield biodiesel production compared to 70.18 of goat fat oil, but 22.62 mm^2/s kinematic viscosity of benniseed oil is best for biodiesel production compared to that of oil blend and goat fat. High viscosity of oil may cause challenges during biodiesel production process, because it may require high temperature and longer reaction time to achieve adequate conversion of oil. The acid value of the oil blend was at 5.271mgkOH/kg which is moderate and more suitable for biodiesel production compared to that of goat fat oil (9.28 mgkoH/kg). But that of benniseed oil (3.15mgkoH/kg) is at a more convenient rate compared to others. Acid value shows the amount of acid in an oil and high value shows that the oil has high acid content which may pose challenges to the biodiesel product. The saponification value of the oil blend was found to be 217.74mgKOH/kg oil which is an indication that oil blend is a normal triglyceride which is suitable for fatty acid methyl ester (FAME) production. But compared to others, that of benniseed oil (142.2), is more suitable, saponification value shows the molecular weight of the fatty acid present in the oil. The iodine value of 27.42 means that the oil is relatively low in unsaturated fatty acid compared to that of goat fat oil at 87.50 and benniseed oil at 86.15 for biodiesel production. The peroxide value which is an indication of the degree of oxidation that occur shows that the value of the oil blend at 2.83 undergo a minimized oxidation process, which is suitable for an optimized biodiesel product compared to that of goat fat oil 4.86.

An ester value of 97.58% for the oil blend signifies that higher portion of the oil has been converted to biodiesel. A higher ester value indicates a higher degree of conversion. This is considered as a relatively high ester value which denotes that the oil blend is a good feedstock for the production of biodiesel and it's more suitable compared to that of goat fat oil and benniseed oil which were at 94.64% and 73.14% respectively. Excess moisture in the oil can lead to hydrolysis. Therefore, the moisture content of the oil blend from the table makes it more suitable for biodiesel production compared to that of benniseed at 0.23% because it is lesser, but that of goat fat at 0.18% the best compared to others for biodiesel production. The obtained free fatty acid value of 2.636 for the oil blend, signifies a relatively low amount of free fatty acids compared to that of goat fat oil at 4.64, but that of benniseed at 1.58 is the best for biodiesel production compared to others. Low FFA values are generally desirable. High FFA can react with alcohol and catalyst used in transesterification process leading to the formation of soap and undesirable products. The refractive index value of 1.4635 clearly shows that it has a moderately relative refractive index compared to that of goat fat oil and benniseed oil at 1.4739 and 1.473 respectively. Moderate refractive index indicates high quality biodiesel.

3.2 Effect of process conditions

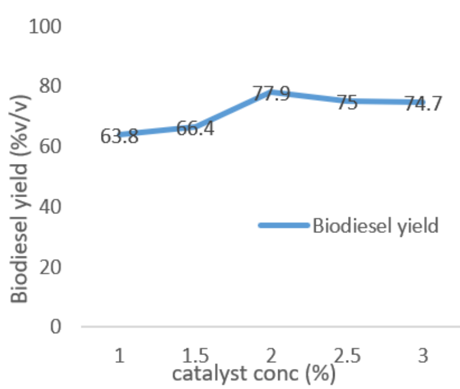

Fig 2: Effect of catalyst concentration on biodiesel yield.

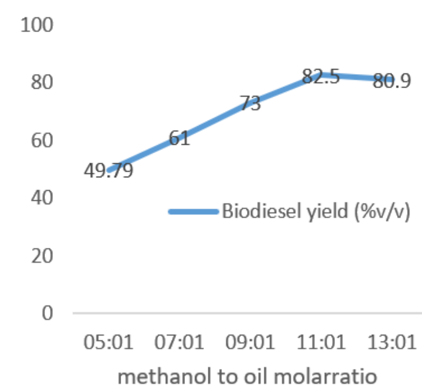

Fig. 3: Effect of methanol to oil ratio on biodiesel yield.

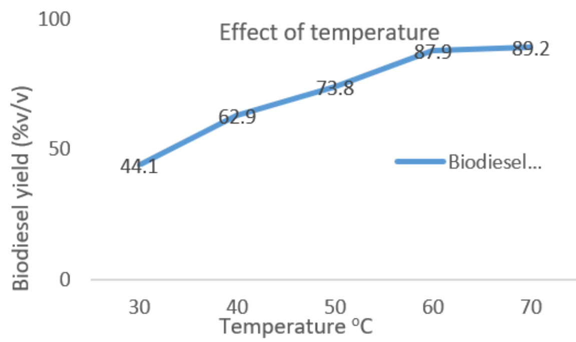

Fig 4: Effect of temperature on biodiesel yield.

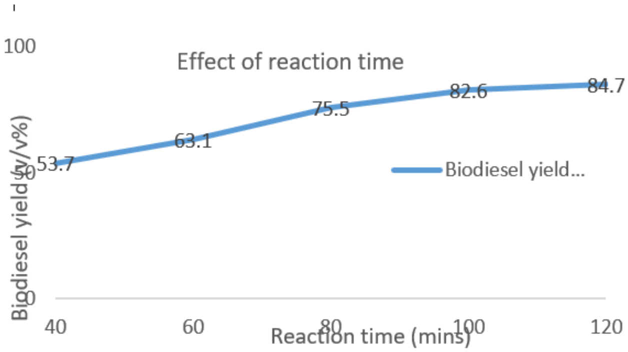

Fig.5: Effect reaction time on biodiesel yield

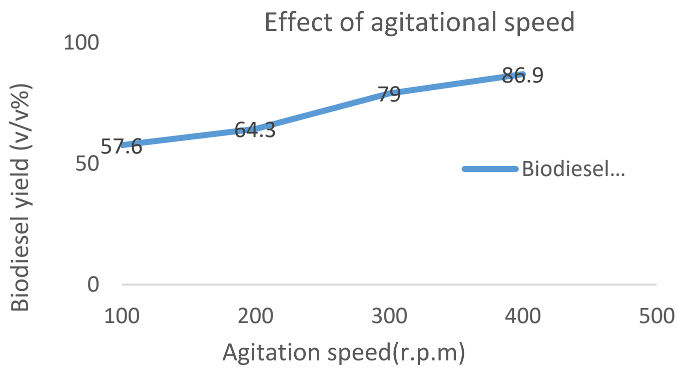

Fig 6: Plot of the effect of agitation speed on biodiesel yield.

3.2.1. Effect of catalyst concentration

Other process parameters were kept constant and the catalyst concentrations were varied. Hence, temperature 50 ºC, time 80 min., agitation speed 300 rpm, mole ratio 9:1 Effect of catalyst loading is one important parameter that can affect the rate, conversion and yield of biodiesel (Fig. 2). Constant parameters are; temperature 50°C, reaction time 80min, agitation speed 300rpm and mole ratio 9:1. At 1.0% catalyst concentration, keeping other parameters mentioned above constant, the biodiesel yield was 63.80v/v%; at 1.5%, it was at 66.40v/v%; at 2.00%, it was at 77.90v/v%; at 2.50%, it was at 75.00v/v%; and at 3.0%, It was at 74.70v/v%. Hence, the biodiesel yield at 2.00% catalyst concentration was the highest (77.90v/v%).

3.2.2 Effect of molar ratio

While other parameters like; temperature of 50°C, catalyst of 2.0 %, time of 80 min, agitation speed of 300 rpm, were kept constant, the mole ratio was varied. Methanol to oil ratio is another parameter that can affect the conversion and yield of biodiesel as well as its rate. From Fig 3., keeping other parameters constant, that is; temperature 50°C, catalyst 2.0%, Time 80min, agitation speed 300rpm. The methanol to oil ratio at 5:1, 7:1, 9:1, 11:1 and 13:1 gave biodiesel yield; 49.7v/v%, 61.00v/v%, 73.0v/v%, 82.50v/v%, 80.90v/v% respectively. Hence, methanol/oil ratio at 11:1 gave the highest biodiesel yield (80.90v/v%).

3.2.3 Effect of temperature

Other process parameters like; mole ratio 9:1, catalyst 1.5 %, time 3 hr, agitation speed 300 rpm, were kept constant and temperature was varied. From Fig 4, the temperature was varied at 30°C, 40°C, 50°C, 60°C and 70°C to give biodiesel yield 44.10v/v%, 62.90v/v%, 73.80v/v%, 87.90v/v% and 89.20v/v% respectively. Keeping other parameters constant at mole ratio 9:1, catalyst 1.5%, speed 300rpm, time 3hrs. From Fig. 4, Temperature at 70°C gave the highest biodiesel yield (89.20%).

3.2.4 Effect of Reaction time

Keeping temperature 50 ºC, catalyst 2.0 %, mole ratio 9:1, agitation speed 300 rpm constant, with time being varied. At constant conditions of parameters; Temperature 50°C, Catalyst 2.0%, Mole ratio 9:1, agitation speed 300rpm. The reaction time at 40, 60, 80, 100 and 120 (hr) gave rise to 53.70, 63.10, 75.50, 82.60, 84.70 (v/v %) respectively. From Fig. 5, reaction time at 120min gave the highest biodiesel yield (84.70v/v%).

3.2.5 Effect of agitation speed

Keeping other parameters like; mole ratio 9:1, catalyst 2.0 %, speed 300 rpm, time 80 min, temperature 50 ^{0}C, constant and varying the agitation speed (Fig. 6). At Varying agitation speed; 100rpm, 200rpm, 300rpm, 400rpm, 500rpm, the biodiesel yield was gotten to be 57.60v/v%, 64.30v/v%, 79.00v/v%, 86.90 v/v%, and 80.40v/v% respectively. Keeping mole ratio constant at 9:1, catalyst at 2.0%, speed at 300rpm, time at 80min, and temperature at 50°C. From Fig. 6, agitation speed at 400rpm gave the highest biodiesel yield (86.90v/v%).

From Table 2A and 2B, the optimal biodiesel yield for blended oil and feedstock was gotten to be 89.20% at catalyst concentration1.5%, Temperature 70, Reaction time 180 and methanol/oil ratio While that of a single source feedstock and catalyst according to (Ume et al; 2024) was 87.4% at catalyst concentration 2.5%, Temperature 800 and time 180 min. This shows that, the blended source produced more biodiesel yield compared with that of the single source

Table 2A: Blended feedstock and hybrid catalyst (This study)

Catalyst concentration %	Temperature °C	Reaction time mins	Methanol/oil molar ratio	Optimal biodiesel yield %
1.5	70	180	9:1	89.20

Table 2B: Single source feedstock and catalyst (Goat fat and goat bone) (Ume et al; 2024)

Catalyst concentration %	Temperature (°C)	Time(min)	Methanol	Optimal biodiesel yield %.
2.5%	800	-	-	87.4%

3.3 Properties of optimal biodiesel yield.

Different properties of the biodiesel produced from oil blend has been listed in Table 3. When the density of the biodiesel is higher, it can enhance the mixing and contact between the reactants, facilitating the reaction and improving the biodiesel yield. From the table, the density of the biodiesel yield from hybrid feedstocks and catalysts was at 0.8660g/cm³ which falls between the range of ASTM, comparing it with that of the single source catalyst and feedstock (goat bone and goat fat oil) from a research work by (Ume et al., 2024) which is 0.8702g/cm³, it's lesser, which shows a better-quality yield biodiesel product. The kinematic viscosity is at 5.8110mm²/s which is in line with the ASTM value, hence a more high-quality biodiesel product compared to that of the single source catalyst and feedstock (6.730). Flash point is the temperature at which a flammable liquid can vaporize and ignite when exposed to an ignition source. The flash point for the hybrid feedstocks and catalysts was at 162°C which is in line with the ASTM value and it's slightly less than that of the single source feedstock and catalyst (164°C) making a high-quality biodiesel yield property. The fire point was at 170°C, for the hybrid feedstocks and catalysts biodiesel yield which is less than that of the single source feedstock and catalyst gotten at 174°C from the already mentioned literature work. The fire point in biodiesel production is crucial as it determines the minimum temperature at which the fuel will continue to burn after ignition, impacting safety, storage, and handling procedures.

The refractive index of the hybrid feedstocks and catalysts biodiesel yield was gotten to be 0.4619. Compared to that of the single source feedstock and catalyst (1.4688), it is lesser, making it a better-quality biodiesel. The refractive index in biodiesel is important as it serves as a rapid, non-destructive, and cost-effective quality control parameter to verify its purity, adulteration, and conformity to international standards, such as ASTM D6751. Low refractive index shows better biodiesel property.

The acid value of the hybrid feedstocks and catalysts biodiesel yield was gotten to be 1.52 which is slightly less than that of the single source feedstock and catalyst biodiesel yield (1.56). This shows that the single source feedstock and catalyst has a better acid value for a better-quality biodiesel yield. Also, the free fatty acid value for the optimal biodiesel yield of the hybrid feedstocks and catalysts was at 0.68, which indicates a lower free fatty acid content compared to that of the single source feedstock and catalyst optimal biodiesel yield (0.78). Hence the single source feedstock and catalyst biodiesel yield shows a better-quality property. The API gravity of the hybrid feedstocks and catalysts optimal biodiesel yield is at 34.12 and it's higher compared to that of the single source (31.11). A higher API gravity indicates a better-quality biodiesel yield with improved engine performance, lower viscosity, and better cold flow property.

The Aniline value of the hybrid feedstocks and catalysts biodiesel yield was determined to be 191.00°C compared to 124.30°C of the single source feedstock and catalyst. The aniline value is a measure of the resistance of biodiesel to corrosion and damage caused by acidic compounds. It is an important property that affects the quality and performance of biodiesel. A higher aniline value is desirable in biodiesel, as it indicates better corrosion resistance, stability, and overall fuel quality. Conversely, lower aniline values suggest increased risks of corrosion, degradation, and engine problems. The diesel index and the cetane index value of the optimal biodiesel yield from hybrid feedstocks and catalysts were at 56.41°C and 53.41°C respectively, which are higher compared to that of the single source feedstock and catalyst gotten from literature. 38.67 and 35.67°C respectively (Ume et al., 2024). The diesel index and cetane index are two related but distinct measures used to evaluate the quality and performance of diesel fuels. Diesel index is a calculated value that represents the volatility and combustion characteristics of diesel fuel. It's typically calculated using the fuel's density and aniline point (the temperature at which the fuel becomes cloudy due to precipitation of wax). The diesel index provides an indication of volatility, combustion quality, engine performance. cetane index, also known as the cetane number (cn), measures a diesel fuel's ignition quality and combustion characteristics. A higher cetane number indicates better ignition quality. Hence, cetane Index focuses on ignition quality, while Diesel Index assesses overall combustion quality.

Table 3: The properties of optimal biodiesel yield using hybrid versus single feedstock sources.

S/N	Property	Unit	Hybrid-feedstocks and catalysts (This study)	Goat fat and goat bone. (Ume et al; 2024)	ASTM D 6751
1	Density	g/cm^3	0.8660	0.8702	0.860-0.894
2	Kinematics viscosity	mm^2/s	5.8110	6.7930	1.9-6.0
3	Flash point	ºC	162	164.00	> 120
4	Fire point	ºC	170	174.00	-
5	Refractive index	-	0.4619	1.4688	-
6	Acid value	mgKOH/kg	1.52	1.56	-
7	Free fatty acid	MgKOH/kg	0.68	0.78	≤ 0.5
8	API gravity	-	34.12	31.11	-
9	Aniline value	ºC	191.00	124.30	-
10	Diesel index	-	56.41	38.67	-
11	Cetane index	-	53.41	35.67	-

3.4 Characterization of catalyst

3.4.1 FTIR for combined catalyst (Goat bone and plantain peduncle)

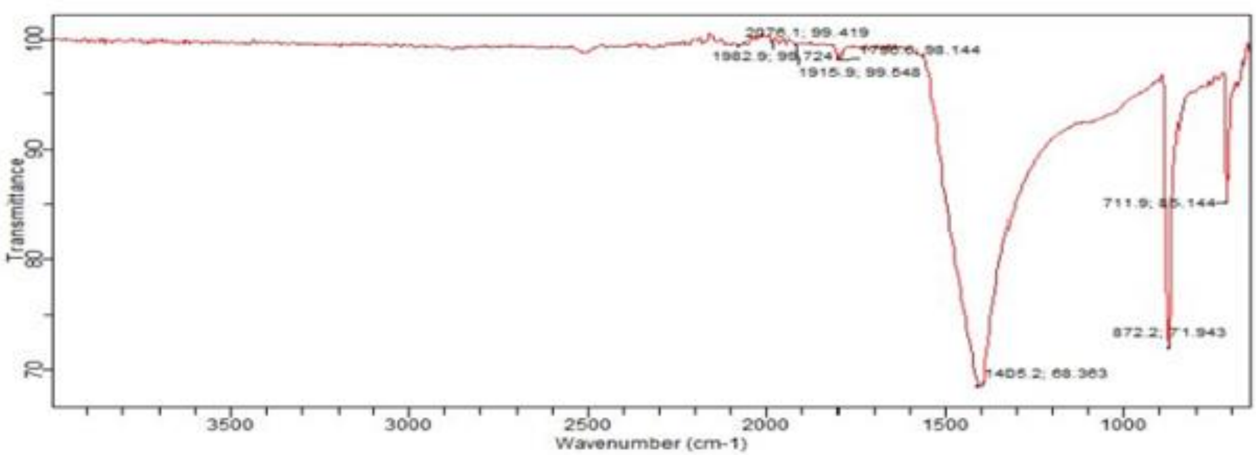

Fig 7: FTIR for combined catalyst (Goat bone and plantain peduncle).

Fourier transform infra-red (FTIR) spectrometer analysis of the goat bone and plantain peduncle blend catalyst (Fig.7) reveals a complex material with functional groups. The peak at 872.2 cm^{-1} can be attributed to O—C—O stretching peak of carbonate. The occurrence of band at 1408.2 is attributed to metal oxides of Ca—O, K—O and the silicate ion, siloxane or silicone group (Si—O—Si) respectively. New peaks at 1982.9 and 2076.1 cm^{-1} are attributed to N=C=S stretching isothiocyanate

3.4.2 FTIR of goat bone

Fourier transform infra-red (FTIR) spectroscope of the activated waste goat bone (Fig. 8) was done to ascertain the available functional groups and type of vibration. The peak at 3511.2 cm^{-1} is attributed to internally bonded —OH group. The occurrences of bands at 1407.1 cm^{-1} and 1012.0 cm^{-1} are attributed to metal oxides of Ca—O, K—O and the silicate ion, siloxane or silicone group (Si—O—Si) respectively, while the peak at 870.3 cm^{-1} is attributed to O—C—O stretching peak of carbonate (Ume et al., 2024). The twin of the − CH_3 and − CH_2 anti-symmetric stretching vibration at 2855.1 cm^{-1} were detected. The FTIR spectrum of the combined catalyst shows an increment in O-C-O stretching peak of carbonate (872.2 cm^{-1}) compared to that of goat bone (870.3 cm^{-1}) in Fig 8. The increased O-C-O stretching peak in the combined catalyst indicates enhanced carbonate substitution in hydroxyapatite, potentially improving acidity, thermal stability and surface area for biodiesel production. The occurrence of band for the combined catalyst at 1408.2 cm^{-1} shows an increment in the oxides Ca-O, K-O, and silicon ion, siloxane or silicon group (Si-O-Si) compared to that of the goat bone at 1407.1 cm^{-1} which shows that the combined catalyst (goat bone and plantain peduncle) exhibits enhanced Ca-O, K-O, and silicate/siloxane (Si-O-Si) species at 1408.2 cm^{-1} indicating increased alkalinity and surface reactivity compared to goat bone alone. This modification is expected to improve the catalyst transesterification efficiency, stability and tolerance to impurities, ultimately enhancing the biodiesel production yield and quality. (Jiang et al; 2019).

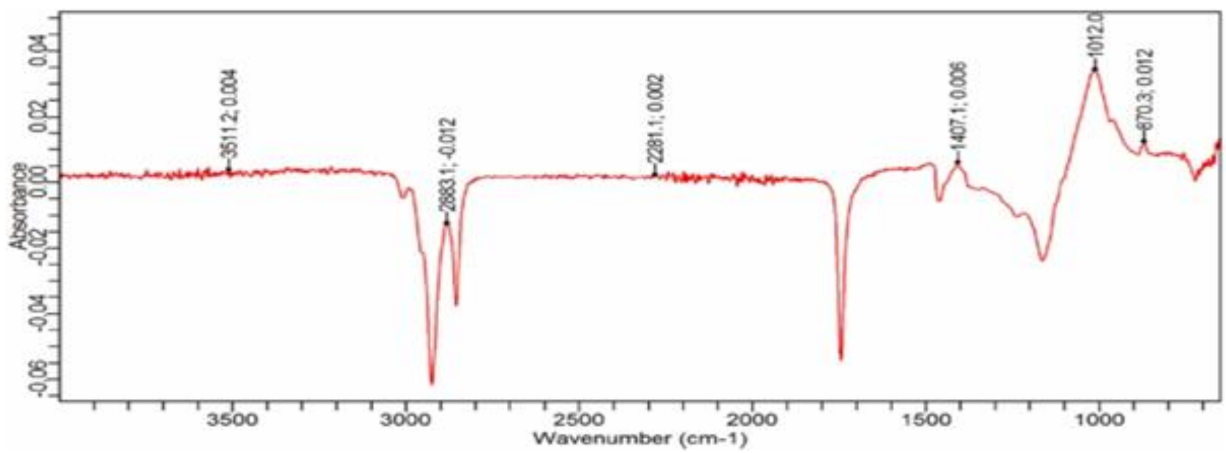

Fig. 8: FTIR of goat bone (Ume et al; 2024)

3.4.3 FTIR of the hybrid oil

The FTIR spectra of blended oil (goat fat oil and benniseed oil) is presented in Fig. 9. The different assignment of the FTIR spectra of the blended oil (goat fat oil and benniseed oil) presented mostly alkanes having 1379.1 cm^{-1} at a sharp peak value of 1379.1 cm^{-1} with C-H bond as well as the peak value of 913.2 cm^{-1} of aromatic functional group. The aliphatic amino composition was discovered with C-N bond at 1237.5 cm^{-1}. More so, there were stretching vibrations observed between 2922.2 cm^{-1} and 2855.1 cm^{-1} of alkane constituent. The lower band value of 1744.4 cm^{-1} exhibits a double stretching uniqueness made up of esters.

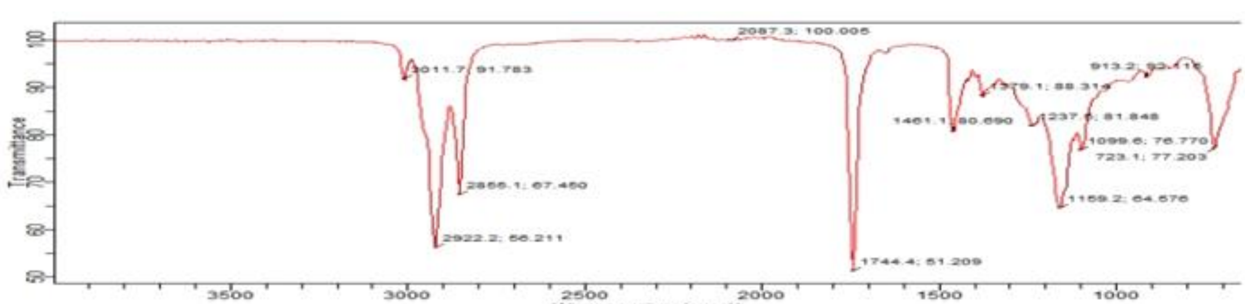

Fig. 9: FTIR for combined oil.

3.4.4 FTIR for goat fat oil

The FTIR spectra of goat fat by Ume *et al.,* (2024) is shown in Fig. 9. Various assignments of the FTIR spectra of the goat fat contains alkanes having 1375.4 cm^{-1} at a sharp peak value of 1375.4 cm^{-1} with C-H bond, as well as the peak value of 879.7 cm^{-1} of aromatic functional group. The presence of alkanes at 1379.1 cm^{-1} in the blended oil indicates a higher saturation level compared to goat fat oil (1375.4 cm^{-1}), suggesting that the blended oil has improved oxidative stability and potentially longer shelf life (Srivastava et al; 2018). This increased saturation level may also contribute to better cold flow properties in the blended oil. The blended oil exhibits a peak of 913.2 cm^{-1}, indicating a higher presence of aromatic functional groups compared to goat fat oil (879.7 cm^{-1}), suggesting that the blended oil has increased unsaturation levels and potentially improved lubricity (Esonye et al., 2023). This higher unsaturation level may also contribute to lower oxidative stability and potentially reduced life. The blended oil exhibits a peak of 1237.5 cm^{-1}, indicating a stronger C-N bond in aliphatic amino composition compared to goat fat oil (1233.7 cm^{-1}), suggesting enhanced nitrogen-containing compound presence and potentially improved fuel stability (Esonye et al., 2023b). This shift may also indicate altered protein-like structures, influencing biodiesel's storage and handling properties.

The blended oil-catalyst system (goat fat oil + benniseed oil and plantain peduncle + goat bone) as seen in Fig.10 and individual goat bone and goat fat system as seen in Fig. 11 both exhibit a peak at 3008.0 cm^{-1}, indicating the presence of internally bonded C-H stretching of aromatic functional groups. However, the identical peak position suggests similar aromaticity and potentially comparable reactivity for optimal biodiesel yield (Srivastava et al., 2018). Both exhibits' peaks between 2855.1 cm^{-1} to 2922.2 cm^{-1}, indicating the presence of C=H stretching vibrations in aromatic and aliphatic functional groups. This overlap suggests similar hydrocarbon chain lengths and branching. Potentially influencing biodiesel cold flow properties. The blended oil-catalyst system (goat fat oil + benniseed oil and plantain peduncle + goat bone) as seen in Fig.12 exhibits a lower energy level at 1337.1 cm^{-1}, indicating reduced C-H bending vibrations in alkanes, compared to the goat fat system (1375.4 cm^{-1}). This shift suggests a decrease in alkane branching and potentially improved biodiesel's oxidative stability and cold flow properties (Srivastava et al., 2018).

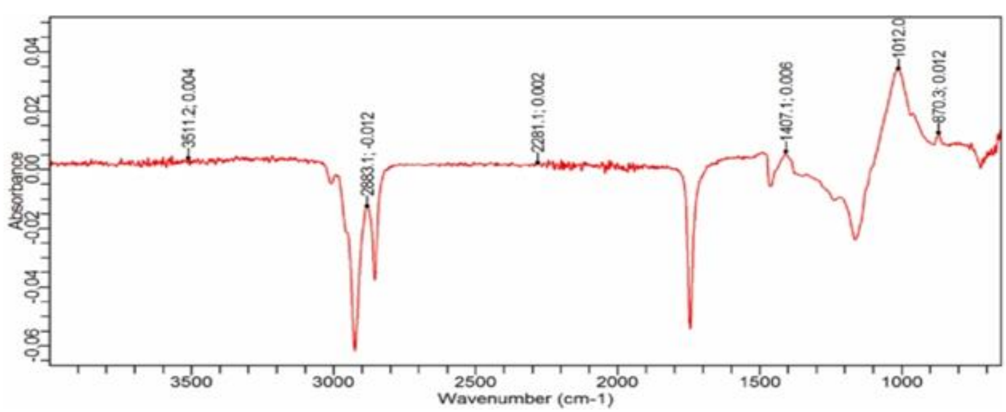

Fig.10: FTIR for goat fat oil (Ume et al., 2024)

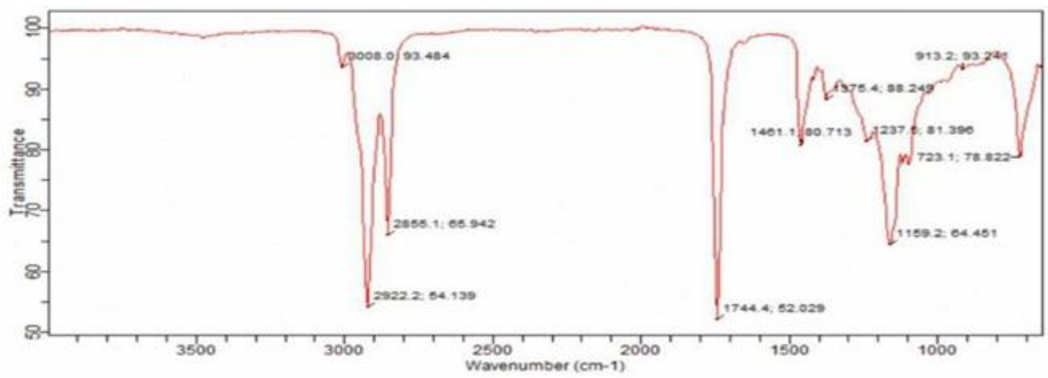

Fig.11: FTIR for optimal biodiesel yield for goat fat oil and goat bone (Ume et al; 2024).

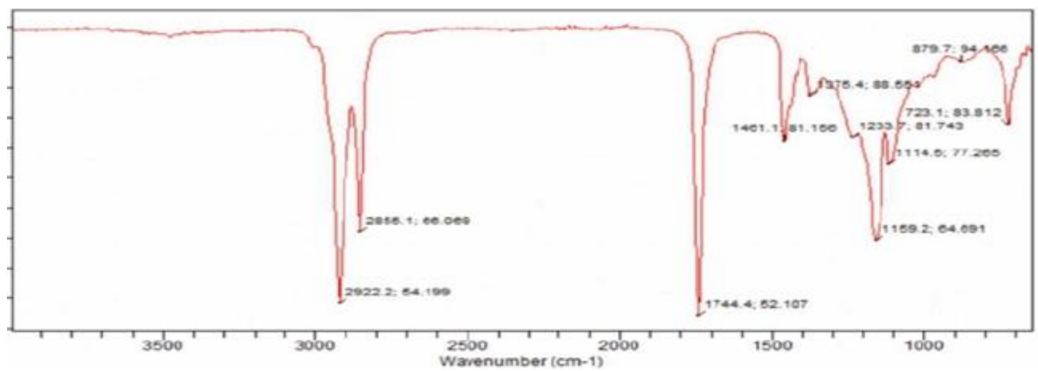

Fig. 12: FTIR of optimal biodiesel yield (blended catalyst and oil) -This study

4.4.5 XRD for combined catalyst

X-ray diffraction analysis indicates the angle of diffraction or pattern of atoms arrangement in their crystals. Fig. 13 shows the X-ray diffractograms of raw and thermally activated catalyst blend with the broad peak at 2. The diffraction peak shows that graphite (pure carbon) is the most prevalent in the sample with occurrence rate of 44%, showing that it is a major component of carbon. From Fig. 13, there is slight presence of other components found in the activated catalyst blend which includes; Urea (33%), graphite (44%), marialite (5%), sylvine (11%), freibergite (6.8%), and silicon (6.2%). Comparing this with a literature work (Ume et al., 2024) shown in Figs. 16 and 17 which has its diffraction peak at 2 shows that apatite is the most prevalent in the sample with an occurrence rate of 34% signifying that it is a major component of calcium. The catalyst blend's dominance of graphite (44%) over apatite (34%) indicates enhanced thermal stability, potentially improving biodiesel yield and selectivity (Kumar et al; 2016). However, the presence of apatite suggests maintained acid base properties and surface reactivity, contributing to efficient transesterification reactions.

After the blended catalyst was activated at 800ºC it is shown in Fig. 14 that graphite was frequent in the activated sample because it is a major mineral component, and apatite was frequent for that of goat bone. Hence, graphite will produce peaks that are unique to its crystal lattice, have good catalytic activity, and stability in transesterification process. From Fig.13, there was a massive peak from the ground state of 0º to massive intense peak between 22º and 24º which drops from 40º to 70º which corresponds to the crystal planes. Compared with that of the literature work as shown in Fig.15, which has a massive peak from the ground state of 0º to massive intense peak between 32º and 33º which drops from 52º to 70º range of values which corresponds to the crystal plane. The combined catalyst exhibits a prominent peak between 22º to 24º, indicating a strong crystalline plane, likely attributed to graphite's (002) plane (Kumar et al; 2017). This peaks intensity and position suggest enhanced thermal stability and conductivity. Goat bone catalyst shows a distinct peak between 32º to 33º, corresponding to apatite's (211) or (300) plane, indicating a well crystallized hydroxyapapite structure (JCPDS 09-0432).

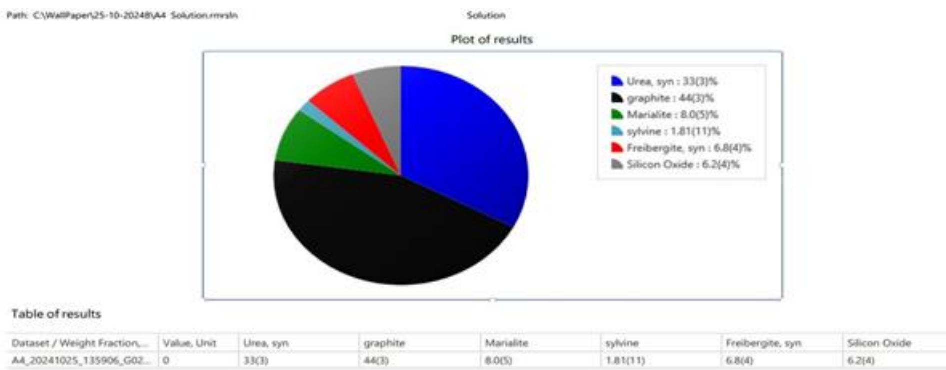

Fig. 13: Phase data view of raw combined catalyst (Goat bone and plantain peduncle) using XRD.

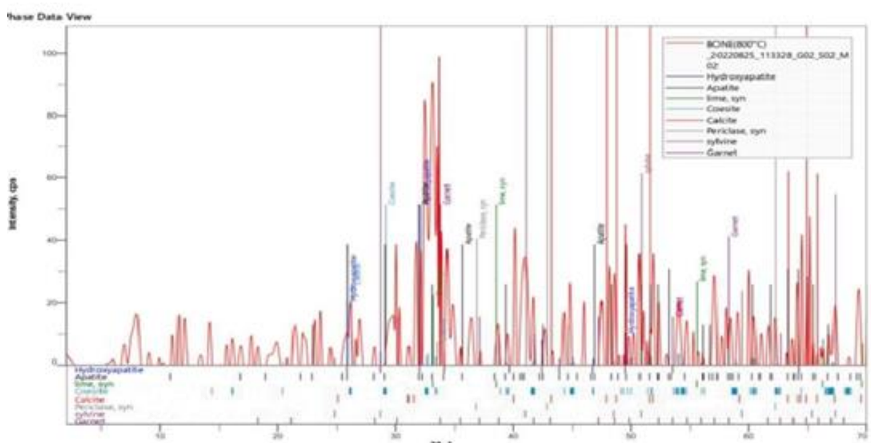

Fig. 14: Extended phase view of catalyst blend using XRD

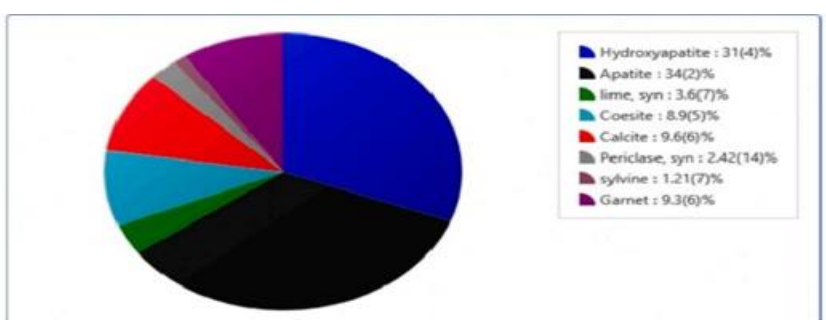

Fig. 15: Phase view of raw goat bone using XRD (Ume et al; 2024).

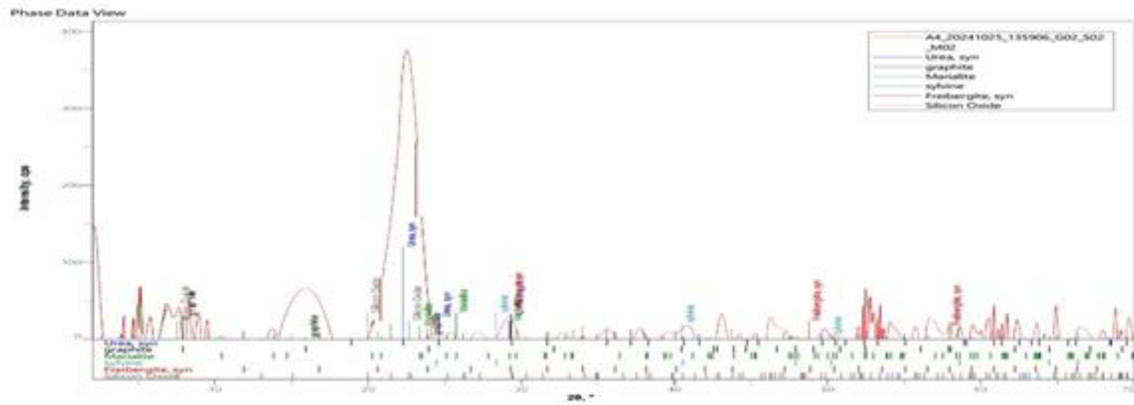

Fig. 16: Phase view of raw goat bone using XRD (Ume et al., 2024).

4. Conclusion

The synthesis of fatty acid alkyl esters (biodiesel) using hybrid feedstocks and catalysts presented several notable effects on both the quality of biodiesel and its yield, according to this work. In terms of quality, the hybrid feedstocks produced biodiesel with improved properties, such as better cold flow performance, oxidative stability, and cetane number. Goat fat oil and benniseed oil each have unique fatty acid profiles, goat fat oil, being animal-based, was composed of higher saturated fatty acids, which contributed to better oxidative stability and higher cetane number, improving combustion quality. Benniseed oil, on the other hand, was rich in unsaturated fatty acids, which showed improved cold flow properties and lower fatty acid content. Combining these two oils created a balance, enhancing both yield and biodiesel quality by leveraging the strengths of each and maximizing their full potentials at once. From this study, the optimal biodiesel yield was 89.20% at catalyst concentration of 1.5%, temperature of 70ºC, reaction time of 180mins and methanol to oil ratio of 9:1. Blending high-cost oil (Benniseed oil) with cheaper waste oil or non-edible oil (goat fat oil), lowed the overall feedstock cost. Additionally, hybrid catalysts can be reused and they have longer lifespans, therefore, it reduced catalyst replacement costs.

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