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Research Article

The Extraction and Synthesis of Biodiesel from Algae Oil

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Abstract
The extraction of oil from algae with ethanol using Soxhlet extraction apparatus was done and a substantial amount of oil obtained. The production of biodiesel was demonstrated by transesterification reaction process considering parameters such as reaction temperature, reaction time, methanol-to-oil molar ratio and catalyst concentration. At the end of the research the algae oil yielded biodiesel up to 90% at a temperature of 65^{0}C, under a period of 110 minutes reaction time, molar ratio of 3:1 and a catalyst concentration of 1.25wt %. The characterization results show density, specific gravity, pour point, flash point, cloud point, kinematic viscosity, cetane number and free fatty acid to be0.863 Kg/m^3, 0.868126, 278.90K, 440.00K, 284.00K, 5.49m^2/s, 49.50 and 0.51% agreeing with the ASTM D6757 standard of 0.84-90Kg/m^3, 0.88, 258-289K, 373-443K, 270-285K, 1.50-6.0m^2/s and 48-60, 0.50% in that order. Two of these properties - iodine value and acid value with 91.24gl$_2$/100 and 0.60mKOH/g slightly do not come in consonant with ASTM D6757 having 120.0gl$_2$/100 and 0.50mKOH/g respectively. In the overall, algae oil is a good potential renewable feedstock for the production of biodiesel.

KEY WORDS: *Algae, Biodiesel, Transesterification, Methanol, Characterization, ASTM Standard*

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Introduction
Algae are simple plants that can range from the microscopic to large seaweeds, giant more than one hundred feet in length. Microalgae include both cyan bacterial, (similar to bacterial and formally called blue-green algae) as well as green algae, brown and red algae. There are more varieties of microalgae (Liu et al., 2006b).

Algae can be grown using waste water unsuitable for cultivating agricultural crops. When using waste water such as municipal, animal and even some industrial runoff, they can help in its treatment and purification, while benefiting from using the nutrient present. Most microalgae grow through photosynthesis by converting sunlight, carbon (IV) oxide and a few nutrient including nitrogen and phosphorus into material known as biomass (Romano and Sorichetti, 2011).

High oil prices and advances in biotech over the past decade have refuelled the algae biofuel race. Among the fastest growing plant about 50% of their weight is oil which contains no sulphur and non-toxic high biodegradable (Radich, 2006).

All algae are eukaryotic (cell having nuclear materials of deoxyribonucleic acid (DNA) organised within a discrete membrane) organisms bounded by organelle known as nucleus. Algae have chloroplast that contain chlorophyll given them a bright green colour as well as the accessory pigment (Abdulkareem *et al*., 2011).

Energy is undoubtedly the greatest driving force behind global science/technology and has been behind the earliest inventions. It is also an undeniable fact that the use of energy for transportation was a changing point for the progress of humanity and a major step for science. Despite the fact that the entire economy of most nations is based on transportation fuels, little therefore, has being into developing fuel from renewable sources that are able to be converted into transportable energy. The majority of energy needed about 88% is for transportation derived from fossil (Liu et al., 2006b). In view of the finite availability and environmental concern of fossil fuel, biodiesel is one of the promising fuel alternatives. Its production was incubated as a result of research suggesting the gradual extortion of fossil fuel (Asha *et al*., 2009). This alarming discovery has been the need for alternative form of fuel to substitute fossil petroleum. This increasing need could be fulfilled by changing the dominant idea of using the feedstock just to produce energy and adopt an attitude of producing the raw material and improving the renewable character of the feedstock. In this case, what could be extracted from biomass is algae oil, cooking oil, animal fat. Henry Ford, in 1908 manufactured a car which could move with bio-fuels derived from corn. The model could use only ethanol or a mixture of ethanol and petrol (Al-Zuhair, 2007)

Biodiesel is an organic, non-toxic and biodegradable fuel made from everyday renewable resource; feedstock and animal fat. Biodiesel cut down the emission of carbon dioxide, in fact according to Patle *et al*. (2014) it is the only available alternative fuel that has higher buoyancy than crude oil. Additionally, biodiesel is an effective solvent to oil due to ethylester component with low carbon monoxide emission. Carbon dioxide produced can be recycled by photosynthesis, a fact that favours the decreasing of greenhouse effect. It has been estimated that the overall life cycle emissions of Carbon dioxide from 100% biodiesel are 78.45% less than those of petroleum diesel (Fragkou, 2014). If this is applied to city buses and coaches, 100% biodiesel reduces the life cycle consumption of petroleum diesel by 95% helping cities to lessen their air pollution by trafficking, possibly due to the high load injection to the engine which could be overcome by controlling the injection time in accordance to the combustion of the engine. Furthermore, other parameters that biodiesel holds over petroleum diesel are its high flash point -150°C which makes it less volatile thus safer in transportation. It also has lubricating properties causing less grinding in engines (American Chemical Society, 2012).

Biodiesel has undoubtedly proven to be a viable renewable alternative fuel to petro-diesel that can be used effectively to power the current diesel vehicles either when used singly (B100) or blended (B50, B20, B5) with regular petro-diesel. Biodiesel provides the benefit of a renewable resource product as well as a zero-sulphur-emission fuel (Helwani *et al*., 2009).

Biodiesel is a renewable source of energy that can help reduce greenhouse gas emissions and minimize the "carbon footprint" of agriculture. It contributes less to global warming because the carbon in the fuel can
be removed from the air by the plant feedstock. (Liu *et al.*, 2006a).

Numerous types of oils from renewable feedstock such as soybean, canola, sunflower, safflower, groundnut, peanut, jatropha and cashew nut oil are used ranging from cooking, culinary to industrial uses. Oils such as castor oil are used industrially for the production of candles, perfumes, paints and so on. (Mushrush *et al*, 2001).

In this research project, algae as the feedstock for the production of biodiesel was chosen due to the availability of algae in water ways, ponds, stagnant water, river bank and also it simple, fast multiplication and non-edible.

Esterification

Esterification is a term used to describe the chemical formation of an ester. An ester is an organic chemical compound derived from an inorganic acid or organic acid in which one or more hydroxy1 (OH) group is replaced by an alky1group (U. S Dept. of Energy, 2006). Esters are generally derived from a carboxylic acid and an alcohol. Esters contains carbony1 centre which gives rise to 120° C-C-O and O-C angles. Their flexibility and low polarity is manifested in their physical properties; they tend to be less rigid (low melting point) and more volatile (Vincent *et al*., 2004).

Transesterification

Nowadays, there are four known methods to reduce the high viscosity of algal oils to enable them be used in conventional compression ignition engines. These methods include, blending with diesel, pyrolysis, emulsification and transesterification. The pyrolysis and the emulsification, however, produce heavy carbon deposits, incomplete combustion, an increase of lubricating oil viscosity and undesirable side products such as alkanes, alkenes, alkadienes, aromatic compounds and carboxylic acids. Regarding the direct use of algal oils as fuel for combustion engine, this requires the engines to be modified (Demirbas, 2005). Therefore, the most common way to produce biodiesel is by transesterification of triglycerides of refined/edible types of oils using alcohol in the presence of an acid or a basic catalyst (Dalai and Kulkarni, 2006). The alcohol used for trans-esterification is usually methanol or ethanol. Producing Biodiesel is a bulk process; the general scheme of the transesterification reaction is where R is a mixture of various fatty acid chains (Hamamci *et al*, 2011) Transesterification is the process of exchanging the organic group R″ of an ester with the organic group R′ of an alcohol. These reactions often catalyzed by the addition of an acid or base. The reaction can also be accomplished with the help of enzymes (biocatalysts) particularly lipases (Aghan, 2005).

Transesterification= alcohol + ester- different alcohol + different ester

Aim

The aim of this work is to:

(i) Extract oil from algae plant by soxhlet extraction

(ii) Synthesize biodiesel from algae oil using transesterification process in a homogeneous catalytic reaction taking into account the reaction time, reaction temperature, methanol-to- algae oil ratio and catalyst concentration for optimal yield.

(iii) Look for alternative renewal sources of energy because the fossil fuel is speedily depleting.

(iv) Characterize the biodiesel produce from algae oil and compare with fossil diesel considering the kinematic viscosity, density, pour point, flash point, cloud point, iodine value, saponification value and octane number using ASTM standard.

Research Methodology

A sample of green microalgae (*Chlorella vulgaris*) was collected around river banks at Heipang village in Barkin-Ladi Local Government Area of Plateau state, Nigeria, using a spatula. It was sun dried; ground and filtered to reduce impurities and give greater surface area of contact with the alcohol.

The extraction was done in the Chemistry laboratory of the department of Science Laboratory Technology (SLT), Plateau State Polytechnic, Barkin-Ladi. A sample of 200g of algae powder was sealed in a filter paper and dropped into the thimble place inside the 250ml round bottom flask where 0.1M ethanol was added to it. The apparatus was attached to a soxhlet extractor mounted with a condenser on an isomantle. The side arm was lagged with glass wool. The ethanol was heated at 68^{o}C using the isomantle, vapour formed, moved through the apparatus, come in contact with the condenser where it condenses then dropped into the thimble containing the powdered algae wrapped in a filter paper. The condensate then extracted the oil out of the algae, once the level of the mixture of the oil and the solvent reaches the siphon it refluxes into the reservoir and a fresh cycle begins. The process continued until no oil was observed to have been extracted. The same process was repeated until after the desired amount of sample was used. A volume of about 800ml of oil was extracted from 1000g of the ground algae powder.

Transesterification of the Algae Oil by Homogeneous Catalysis

A volume of 50ml of algae oil was measured using an electric measuring balance, poured into a 250ml conical flask, 0.5% by weight sodium hydroxide was dissolved into methanol of ratio 3:1 ethanol-to-algae oil and heated to a temperature of 45^{0}C in a water bath for 60 minutes. The product was transferred into a separating funnel for 24 hours to separate. After settling, the bottom layer which was glycerol plus probably soap was allowed out. While the upper layer, the biodiesel was also allowed out, measured and recorded. The yield was calculated using the formulae below.

$$\text{Yield (wt \%)} = \frac{\text{methyl ester (g)}}{\text{feed(algae oil) (g)}} \times 100$$

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The procedure was repeated by changing the temperature (45, 55, 65, 75 and 85ºC) and keeping all other parameters (reaction time, ratio of methanol-to-algae oil and volume of catalyst) constant.

The temperature at which the highest yield was obtained was kept as the constant temperature and the reaction time was investigated by altering the time (70, 80, 90, 100, 110 minutes) and maintaining the rest of the parameters constant.

This procedure was repeated for the ratio of methanol-to-algae oil (4:1, 5:1, 6:1, 7:1 and 8:1) and volume of catalyst (0.75, 1.00, 1.25, 1.50 and 1.75wt%) considering the same style.

Washing of Biodisiel Produced

The biodiesel produced was 0.66L and was washed using a separating funnel with warm water of about 45ºC to remove any remaining methanol, glycerine, catalyst, soap and other impurities. The water was periodically removed from the vessel until the wash water was clear.

Drying of Biodiesel Produced

The biodiesel was dried by heating it in a beaker to a temperature of 110°C for 10 minutes. The volume of the dried biodiesel measured 0.64L.

Characterization

The characterization was done in the department of Water, Aqua-culture and Fisheries, School of Agriculture and Agricultural Technology, Federal University of Technology, Minna, Niger State.

Determination of Specific Gravity

This procedure was used to measure the specific gravity of the biodiesels. A clean dry empty 50ml density bottle was weighed and the mass recorded as Mx. It was then filled up with distilled water and subsequently with the samples. The mass of the bottle and water was taken and recorded as My and that of biodiesel as Mz, respectively hence, the specific gravity was evaluated and recorded.

Determination of Cloud Point

The cloud point is the lowest temperature at which the biodiesel begins to solidify to prevent it from flowing freely (El-Sabagh, 2009). It was determined at a temperature of which the liquid biodiesel began to cloud from the separation of wax on cooling.

Determination of Pour Point

The sample was homogenized and poured into a test jar to a mark level. The jar was closed tightly with the cork carrying the high thermometer that was placed 3mm below the surface of the oil. The disc was placed on the bottom of the jacket and the ring gasket was placed round the jar at 25mm from the bottom. The test jar was then placed on the jacket the oil was allowed to cool without disturbance to avoid error. The test jar from the jacket was removed carefully and stiffed to ascertain whether there was movement of oil. The procedure continued in this manner until a point was reached at which the oil in the jar showed no movement when the test jar was held in a horizontal position for 5minutes.

Determination of Viscosity

A viscometer was inserted into a water bath with a set temperature and left for 30 minutes. The sample was added to the viscometer and allowed to remain in the bath as long as it reached the test thermometer. The sample was allowed to flow freely and the time required for the meniscus to pass from the first to the second timing mark was taken using a stopwatch. The procedure was repeated a number of times and the average value taken which was then multiplied with the viscometer calibration to give the kinematic viscosity.

Acid Number Determination

A sample of 2g of the biodiesel was measured and poured in a beaker. A neutral solvent (a mixture of petroleum ether and ethanol) was prepared and 50ml of it was taken and poured into the beaker containing the sample. The mixture was stirred for 30 minutes, up to 0.56g was measured and placed in a separate beaker and 0.1M KOH was prepared, 3 drops of phenolphthalein indicator was added to the sample and was titrated against 0.1M KOH till the colour change observed turned pink and persisted for 15 minutes.

The relationship between acid value and percentage free fatty acid was established as follows

$$\text{Acid Value} = [(V-B) \times N \times 56.1]/W$$

$$\text{Percentage free fatty acid} = [(CY \times N)/W] \times 2.8.2$$

Where: W = weight of sample in gram
V = titration value for sample in ml
B = titration value for blank in ml
N = Normality of potassium hydroxide KOH

Determination of Cetane Number

Cetane Number is a measure of the fuel's ignition delay. Higher cetane numbers indicate shorter times between the injection of the fuel and its ignition. Higher numbers have been associated with reduced engine roughness and with lower starting temperatures for engines (Hossain and Boyce, 2009).

Results

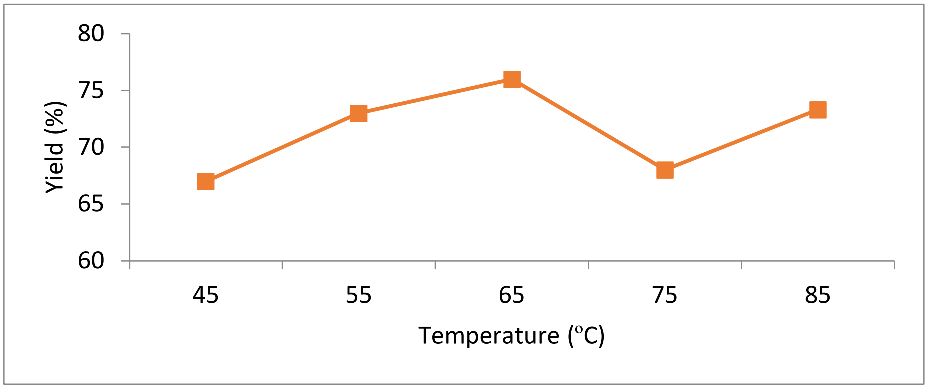

Figure 1.0: Effect of Temperature

The Influence of Reaction Temperature

The temperature ranges from 45, 55, 65, 75, and 85°C and the yield was 67.0, 73.0, 76.0, 68.3 and 73% respectively. The yield increased from 67, to 76%, decreased from 76 to 68% and then increased again to 74%. The temperature of 65°C gave the highest yield of 76%.

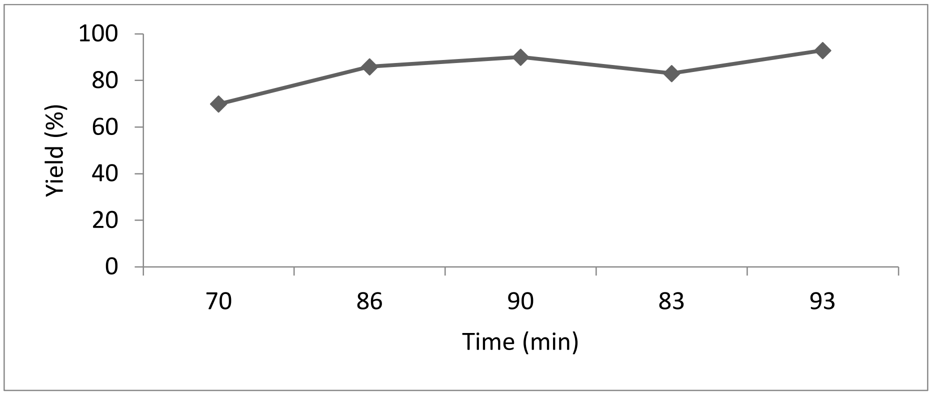

Figure 2.0: Effect of Time

The Influence of Reaction Time

Reaction time from 70, 80, 90,100, and 110 minutes yielded 70.0, 86.0, 90.0, 83.0, and 93.0%. The Yield increased from 70, to 90% and decreased to 82% then again increased to 92 % the highest yield of biodiesel was at 93.0% at 110 minutes.

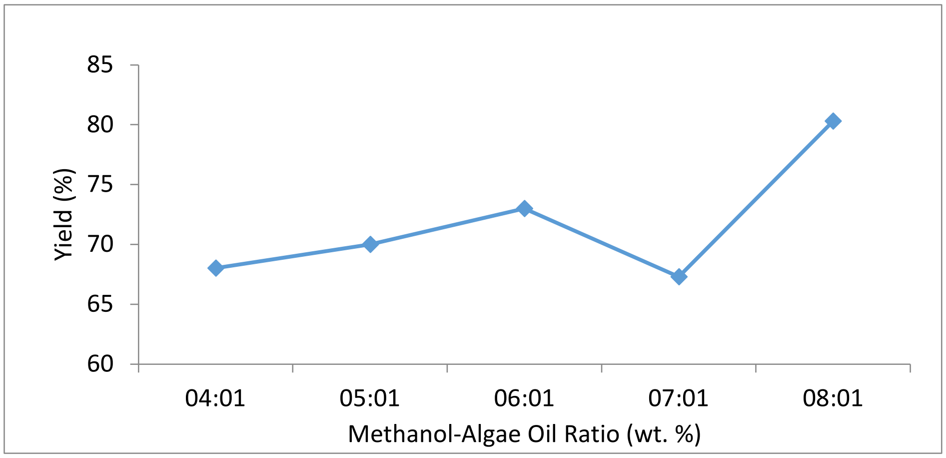

Figure 3.0: Effect of Methanol to Algae Oil Ratio

The Effect of Ratio of Methanol to Oil

The effect of methanol-to-algae oil ratio yielded 68.0, 70.0, 73.0, 67.3, and 80.3% of biodiesel with corresponding ratios of 4:1, 5:1, 6:1, 7:1, and 8:1 in that order. Yield increased from 68 to 78% and decreased to 67% and finally increased to 80 %. The highest yield of biodiesel was 80.3% at 8:1 methanol-to-oil ratio.

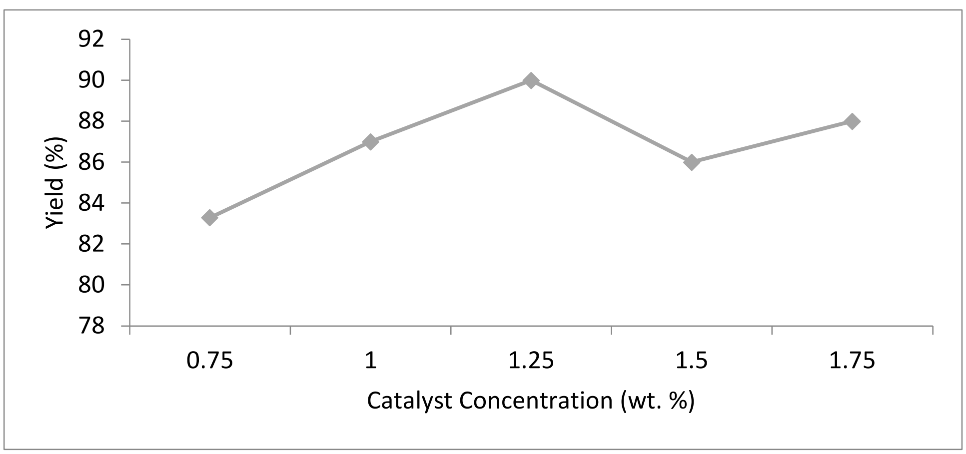

Figure 4.0: Effects of Catalyst Concentration

Effect of Concentration of Catalyst

Catalyst concentration at 0.75, 1.00, 1.25, 1.50, and 1.75wt% yielded 83.30, 87.00, 90.00, 86.00, and 88.00% of biodiesel respectively. The highest yield of biodiesel was at 90% with catalyst concentration of 1.25wt %.

The Result of Characterization of Biodiesel

Table 1.0: Results of Characterization of Biodiesel

S/N	PARAMETERS	UNIT	DETERMINED	STANDARD (Eavera *et al*., 2011)
1	Density (15°C)	Kg/m^3	0.863	0.84-90
2	Specific Gravity	-	0.868126	0.88
3	Pour Point	K	278.90	258-289
4	Flash point	K	440.00	373-443
5	Cloud point	K	284.00	270-285
6	Iodine Value	$gl_2/100$	91.24	120
7	Acid Value	mKOH/g	0.60	0.50
8	Saponification Value	mg/gKOH	238.18	
9	Kinematic viscosity (40°C)	m^2/s	5.49	1.50-6.00
10	Cetane Number	-	49.50	48-60
11	Free Fatty Acid (FFA)	%	0.51	0.50

In comparison, the determined results of parameters such as density at 15℃ gave 0.863kg/m which fall within the range of the standard value and the specific gravity having 0.868126 falls just slightly below the standard value.

The pour point, which is the lower temperature at which the biodiesel begins to solidify to prevent it from flowing freely, is a very important factor. This falls within the standard value. Flash point was determined to be 440.00K likewise is within the conventional range.

Cloud point at 284.00K also agrees with the standard range. Iodine value is short of the standard value while acid value of 0.60mKOH/g falls above the standard value. The kinematic viscosity at a temperature of 40 ^{0}C, measured 5.49m^2/s meeting up to the standard value. The cetane number is within the boundary of the standard cetane number value.

Conclusion

The research work conducted on the extraction of oil from algae plant gives a considerable amount of oil making it a potential source of oil for biodiesel production. The synthesis of biodiesel from algae oil gave a high yield (90%) considering the four most important parameters (reaction temperature, reaction time, methanol-to-oil ratio and concentration of catalyst) that governs optimal yield of biodiesel. The results from the characterization compared to ASTM standard revealed density, specific gravity, pour point, flash point, cloud point, kinematic viscosity, cetane number and free fatty acid agree with those of the conventional standard. Therefore, biodiesel converted from algae oil is a potential source of energy which needs more little care in its production to give an excellent ignition engine fuel.

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