

Performance Evaluation of a Solar Photo-Voltaic Pilot Biodiesel Plant

By

T O K Audu*, Matahula Winner, and Akinsola O. Akinbanjo

Abstract

A method for producing Bio-diesel (fatty acid alkyl ester), from vegetable oils of non-edible seeds or used cooking oil with a homogeneous catalyst, preferably an alkali, dissolved in a primary alcohol to form a liquid-liquid mixture, is herewith presented. The liquid-liquid mixture is pumped through a static mixer, for preliminary agitation and reaction into the main stirred-tank reactor where the triglycerides are converted / transesterified into fatty acid alkyl ester, the Bio-diesel. The method also provides for further turbulent agitation in a centrifugal contactor separator to ensure maximum conversion of the reactants to products and facilitate the separation of the bio-diesel from the by-product glycerol. The transesterification is conducted at atmospheric pressure and a temperature slightly below the boiling point of the primary alcohol which is recovered from the products through flash evaporation. A Solar Photo-Voltaic Assisted Bio-diesel Plant, designed for sequential modular operation, with a high potential for replication as a model for dissemination and transfer of Bio-diesel production technology in Nigeria, has been developed, constructed, and tested. The Performance Characteristics of the Pilot Plant, with special reference to the Static Mixer and Centrifugal Contactor Separator incorporated in the design show that a reasonable Bio-diesel yield of 86.8% to 96% can be achieved in 4 to 5 minutes after the reaction.

Introduction

Biodiesel is a fatty acid alcohol ester. It is a renewable fuel produced from vegetable oil feed stock from any oil-bearing seeds. It is an alternative oxygenated fuel for petroleum- diesel engines which can be blended with fossil diesel in any ratio wholly or partly. The presence of the chemically-bound oxygen results in more complete combustion, and reduces carbon monoxide emissions. In addition, biodiesel is non-toxic; hence it is useful in transportation applications in very sensitive environments, like marine ecosystems and mining enclosures. Biodiesel is biodegradable. It therefore has environmental & health benefits. However important disadvantages of biodiesel include high feedstock cost, increased emission of NO_x, inferior storage and oxidative stability, low volumetric energy content and low-temperature operability¹.

The major raw materials for producing biodiesel are vegetable / animal oil, primary alcohols, catalysts such as sodium hydroxide (NaOH) or potassium hydroxide (KOH), or sulphuric acid (H₂SO₄), or hydrochloric acid (HCl), amongst others.

Authors are in the Department of Chemical Engineering, University of Benin, Benin City, Nigeria

*Corresponding author: auduttokka@yahoo.com

¹ Marachetti, J.M., Errazu, A.F., (2008): Comparison of different heterogeneous catalyst and different alcohols for the esterification reaction of oleic acid, Fuel **87** 3447-3480.

Different methods of biodiesel production include either or a combination of: creating micro-emulsions of the vegetable or animal oil with short chain alcohols², pyrolysis (thermal decomposition of the oil, catalytic cracking)³, super critical technology, and transesterification (with or without ultra-sonication and micro-wave)⁴. Some of these methods, depending on the source of oil and the pyrolytic method adopted produce alkanes, alkenes, carboxylic acids, aromatic compounds, esters, carbon dioxide, carbon monoxide, water, and hydrogen in varying proportions. Such methods lead to loss of oxygen from the triglyceride molecules, thus making fuels obtained less environmentally-friendly than their petroleum-derived counterparts with regard to oxygen content. Also, additional separation steps are required for the removal of the solid ash and carbon residues formed during the process. Supercritical technology, though promising for future large-scale biodiesel production, suffers from its high operating conditions and the attendant high capital cost of equipment.

Of all these alternatives, trans-esterification, (alcoholysis) of oil (triglycerides) with methanol in the presence of a catalyst which gives biodiesel (fatty acid methyl esters, FAME) and glycerol (by-product), seems to be the best choice. The physical characteristics of fatty acid esters (biodiesel) are very close to those of petroleum-diesel fuel, and the process is relatively simple. Moreover, the alkyl esters of fatty acids can be burned directly in unmodified diesel engines, with very low deposit formation.

Although the emerging technologies of ultra-sonication and microwave trans-esterification offer good promise, they are, at present, not cost effective. Synthesis may be done in a single-step or two-step transesterification or both. Single step involves the use of a base catalyst at a temperature of 48.2 to 65° C, and alcohol to oil mol ratio of 6:1, 7:1, 10:1; or an acid catalyst at 70° C, and up to 50:1 alcohol to oil mol ratio.

The Two-Step method has acid-base at 60° C, 7:1, 10:1, 15:1 alcohol to oil mol ratio; co-solvent and acid-base at 60° C, 4:1 alcohol to oil mol ratio and base-base at 70% of alcohol, then 30% as for base only⁵. The method used for the transesterification depends on the level of free fatty acid FFA in the oil.

² Hymore, F. K., and Audu, T. O. K., (2002): 'Kinetics of the Alcoholysis of Rubber Seed Oil', *NJERD*, Vol. 1, No. 1, pp 8-15.

³ Ozemoya, P.O., Audu, T.O.K., & Hymore, F.K., (2000): 'Production of white oils from the residue of a Nigerian refinery,' *Energy & Fuels*, 14 (6), pp 1293 – 1295.

⁴ Ma F, Hanna M A, (1999): Biodiesel production: A Review. *Bioresource Tech* 70 (1) 1-15; Colucci, J. A.; Borrero, E.E.; Alape, F., (2005): Biodiesel from an alkaline transesterification reaction of soya bean oil using ultrasonic mixing. *J. Am. Oil Chem.: Soc.*, 82 (7), 525-530; Lidstrom P, Tierney J, Wathey B, Westman J (2001): Microwave assisted organic synthesis: A review. *Tetrahedron* 57 (45) 9225-9283.

⁵ Issariyakul T, Kulkarni M G, Dalai A K, Bakhshi, N N, (2007): Production of biodiesel from waste fryer grease using mixed methanol/ethanol system. *Fuel Proc Tech* 88 (5) 429-436; Encinar J.M., Susan F.; Gonzalez J.F.; Rodriguez- Reinares A., (2007): Ethanolysis of used frying oils: Biodiesel preparation and characterization: *Fuel PNC. Tech.*, 88 (5) 513-522; Refaat A. A.; (2010): Different techniques for the production of biodiesel from waste vegetable oil. *Int. J. Environ. Sci. Tech.*, 7 (1), 183 – 213

The produced bio-diesel is separated from the glycerol by gravity and refined by having water sprayed as a mist over its surface⁶. Wash water is drained off from the bottom of the tank. Samples of the purified fuel are then withdrawn for characterization, according to ASTM D6751 or EN14214.

Continuous production plants can achieve higher biodiesel throughputs. They are less costly to operate per unit of biodiesel produced. However, batch plants are less expensive to construct and can be more easily adapted to changing feed-stocks and reaction conditions. Therefore, for economic reasons, batch reactors are favoured for the production of Bio-diesel.

Even though biodiesel is still more expensive than petroleum-derived diesel because of higher feedstock and processing costs, countries like Brazil, United States of America, Germany, Austria, Italy, Australia and Malaysia, are already using bio-diesel or its blend with petroleum-diesel. With more countries expected to join the league of Bio-diesel producers and users soonest, Nigeria cannot afford to be left behind.

Design Considerations

There was the need to build a compact demonstration plant; an energy-efficient batch prototype, operated in a sequential modular way, with non-edible seed oil as its major feedstock, but with the possibility to use waste cooking oil, to create awareness at the polytechnic and local government levels. One of the reactants, a primary alcohol, is immiscible in the oil feedstock. Therefore, the method must provide for thorough mixing of the reactants by enlargement of the boundary layer by turbulent flow through a Static Mixer, SM⁷, and Centrifugal Contactor Separator, CCS. The high turbulence is produced by mechanical shear forces as the mixture of the reactants flows through the SM to the Transesterification Reactor, TR, with the attendant reduction in the drop size and increase in the number of drops. Often, owing to limitations that are attributable to heat and mass transfer resistances and inadequate mixing in the TR, the effective concentrations of reactants in the boundary layer are reduced resulting in slow rates, poor selectivity and the need for extensive downstream separation processing. Thus, by the inclusion of the Centrifugal Contactor Separator, the process intensification matches the mixing and heat and mass transport rates to the reaction rate, thus improving selectivity and yield. The rotating cylinder in the CCS is perforated to further create turbulence within the annulus to enhance separation of the phases – Bio-diesel and Glycerol.

A Flash Still (separator) is provided to receive the product from the CCS; then pumped through a nozzle where the pressure is reduced. Thus the liquid and vapour produced by the reduction in pressure have sufficient time to attain equilibrium. The vapour, essentially the primary alcohol, is removed from the top of the Flash Still while the liquid is discharged by gravity from the bottom

⁶ Atadashi, I. M., Aroua, M. K. and Abdul-Aziz, A. (2011): Biodiesel separation and purification: A Review. *Renew. Energ.* **36**: 437-443.

⁷ M. Al-Atabi, 2011 cited in Mazubert, Alex and Poux, Martine and Aubin, Joelle (2013): Intensified processes for FAME production from waste cooking oil: a technological review. *Chemical Engineering Journal*, vol. 233 pp. 201-223. ISSN 1385-8947

into a product settling tank. There is provision for recycling the liquid contents of the Flash Still to the CCS and thence to the main reactor upstream of the CCS to ensure maximum conversion.

Solar energy is used to power the direct current fuel pumps and controllers while electrical power from the grid is used for the heaters and the motor that drives the Centrifugal Contactor Separator.

MATERIALS AND METHODS

Materials

Oils from seeds of *Jatropha curcas*, *Hura crepitans*, *Hevea brasiliensis*, *Luffa cylindrica*, *Chrysophyllum albidum*, and *Ricinus communis* were sourced from Edo and Delta States of Nigeria. Waste cooking oil was got from Eateries in Benin City. Analar grade Methanol CH_3OH , Potassium hydroxide, KOH, Sodium hydroxide NaOH, phenolphthalein, Ethanol $\text{C}_2\text{H}_5\text{OH}$, and Benzene C_6H_6 were supplied by local scientific chemicals distributors in Benin City. The Solar Photo-Voltaic-assisted Biodiesel Pilot Plant designed by the Petroleum Technology Development Fund Chair in Renewable Energy, University of Benin, was used for the experiments, Plate 1. The Plant consists of: a tank for non-edible seed oil feedstock; a tank for alkali dissolved in a primary alcohol; a heated well-stirred tank for preheating the oil feedstock; a heated well-stirred tank for preheating the alkali-primary alcohol solution; a heated well-mixed Transesterification Reactor (Main Reactor); a Static Mixer (Plate 2) connected to the confluence of the discharges from the preheated oil feedstock and alkali- alcohol solution tanks and the inlet to the Transesterification Reactor (Main Reactor); a Centrifugal Contactor Separator (Plate 3) for the final conversion of reactants to products as already stated; a Flash Still (Plate 4) for the primary alcohol recovery; Solar Panels connected via a Charge Controller to the Solar Batteries, and, a Control Panel (Plate 5).

The transesterification reaction commences in the Static Mixer, continues in the Main Reactor and finishes in the Centrifugal Contactor Separator. The primary alcohol is recovered from the Flash Still as the top product. The Bio-diesel and Glycerol are recovered as the bottom product of the Flash Still. The Plant is energy efficient because of its sequential modular operation and the use of Solar Energy to partially power the Controllers and the Direct Current Fuel Pumps.

Other items of equipment used for characterizing the feedstock, and produced Bio-diesel, included the following: Brookfield Low-Cost Digital Viscometer (230V) plus accessories; Koehler Manual Flash Point Tester-Pensky-Martens closed-cup flash tester; and, I—Spec Q Hand-held Bio-diesel Paradigm Sensor. **Plates 1-5**



Plate 1: The Bio-diesel Pilot Plant



Static Mixer

Plate 2: The Vertically-positioned Static Mixer

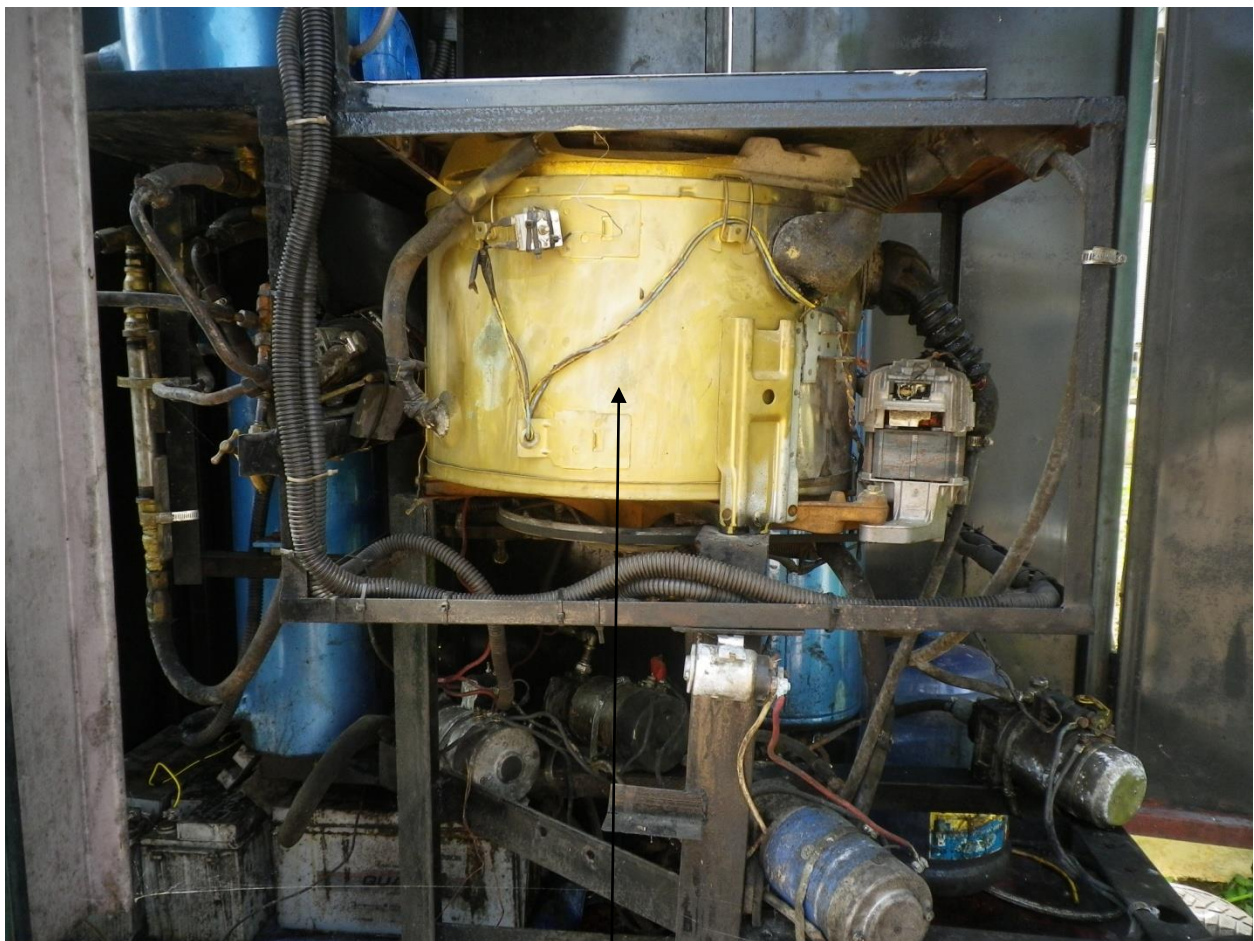


Plate 3: The Centrifugal Contactor Separator



Plate 4: Flash Still to the right-hand side of Centrifugal Contactor Separator



Plate 5: Control Panel

Methods

The Process Flow Diagram of the Pilot Plant used for the experiment is shown in Figure 1. Feed is pumped by a Direct Current pump (P1) to two separate 15.0 litre-feed tanks through valves V1 and V2. The discharge from the two tanks is fed to the inlet of the Static Mixer via another DC pump P2. A sampling port, valve V3, is provided near the inlet of the Static Mixer. The discharge from the Static Mixer is fed directly by gravity into the Main transesterification reactor Tank. This tank is equipped with a motorized stirrer and a temperature-controlled heater. With the aid of pump P3, the mixture of products in the Main Reactor Tank is pumped to a Centrifugal Contactor Separator which has a perforated cylinder rotating at a speed of 120rpm. Product is discharged from the bottom of the Centrifugal Contactor Separator via pump P4 to feed the 20-litre Flash Still Tank provided with a pressure gauge and a pressure-relief valve. Pump P5 is provided for recycling the final product from the Flash Still to the Centrifugal Contactor Separator as the case may be. A sampling port, valve V4, is also provided between pump P4 and the Flash Still. Valve V5 is used to discharge the mixture of the finished product into a settling tank where the biodiesel is separated from the glycerol. The products which settled by differences in densities are therefore withdrawn by opening valve V6.

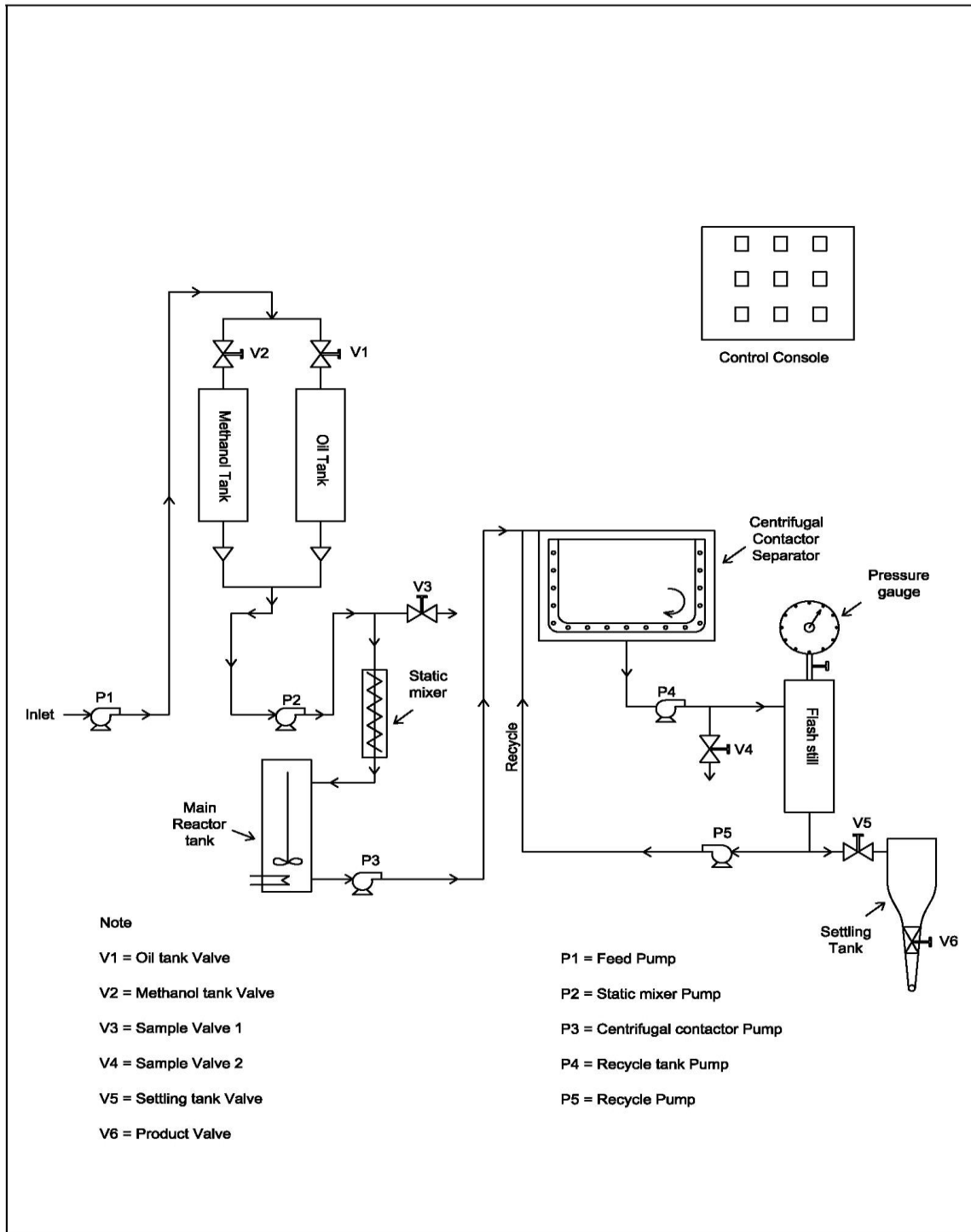


Figure 1: Process flow diagram of the Solar PV assisted Biodiesel Pilot Plant (Petroleum Technology Development Fund Chair in Renewable Energy)

Effect of Static Mixer and Centrifugal Contactor Separator on Trans-esterification

6284.60g (7liter) of *jatropha curcas* oil with 0.18% FFA and 837.95g methanol at a ratio of 6:1 to oil with 1.0 wt% NaOH dissolved in the methanol. The reactants were pumped into the oil and methanol tanks at a flow rate of 70 ml/s. The temperature of the oil tank was maintained at 65°C. Thereafter the two feed streams were mixed and pumped through the Static Mixer to the Main Reactor. Meanwhile samples of product exiting the Static Mixer were collected to determine the extent of the reaction in the Static Mixer. The mixture in the Main Reactor was kept at a constant transesterification reaction temperature of 65°C, with stirring, for 15minutes before being pumped to the Centrifugal Contactor Separator whose perforated cylinder was rotating at a speed of 120rpm for further reaction. Samples of the products exiting the Centrifugal Contactor Separator were taken for analyses, while the bulk of the products were flashed in the Flash Still to expel any un-reacted methanol. To ensure maximum conversion of the reactants to products the bottom product from the Flash Still was recycled to the inlet of the Centrifugal Contactor Separator before discharging to the storage tank where the Glycerol was separated from the desired product Bio-diesel. This process was conducted five times with different recycle times of 2minutes, 4minutes, 6minutes, 8minutes and 10minutes. The produced biodiesel and glycerol separating at different recycle times were noted with the respective yields. The procedure was repeated using the different types of seed oil and waste cooking oil.

Characterization of the Feedstock Oils and Biodiesel Produced

The feedstock oils and Biodiesel produced were characterized using standard methods.

Results and Discussion

The physicochemical properties of the Oils and the Biodiesel produced are presented in Tables 1 and 2 respectively.

Some of the results obtained from the Pilot Plant show that the flash point range of 139⁰C to 205⁰C, is above the minimum specification of 130⁰C. So also are the kinematic viscosities. A comparison of these results with those of diesel fuel shows that the Biodiesel has relatively closer fuel properties to diesel fuel than those of the straight vegetable oils, which is an indication that transesterification improves the fuel properties of the oils.

Table 1: Physico-chemical Properties of the Seed Oils and Waste Cooking Oil

Analysis	Jatropha Seed oil	Rubber Seed Oil	<i>Luffa cylindrica</i> Seed Oil	<i>Chrysophyllum albidum</i> Seed Oil	Castor Seed Oil	Waste Cooking Oil
Specific Gravity (SG) @ 15°C	0.919	0.932	0.896	0.916	0.899	0.999
Kinematic Viscosity@40°C	22.35 mm ² /s	17.85	1.045@29°C	1.077	9.62@28°C	87.1
Flash Point (Closed cup)	254 °C	186	220	200		
Cetane Number	53.23	42.54	64.47	67	58.25	
Cloud point	°C	-12	-15	-15	-19	
Pour Point	15 °C	-18	-17	-17.5	-22	
Acid Value (AV)	3.079 mgKOH/g	22.80	3.72	2.87	3.66	18.6
Free Fatty Acid (FFA)	1.4%mass	11.50	2.18	1.79	1.83	9.5
Iodine Value (IV)	103.63 mg Iodine/g	136.89	82.56	33.18	84.3	53.8
Saponification Value (SV)	182.33 mgKOH/g	208	148.5	193.77	176.5	248.12

Table 2: Physico-chemical Properties of the Corresponding Biodiesel Compared with Diesel Fuel

Analysis	Jatropha Seed oil Biodiesel	Rubber Seed Oil Biodiesel	<i>Luffa cylindrica</i> Seed Oil Biodiesel	<i>Chrysophyllum albidum</i> Seed Oil Biodiesel	Castor Seed Oil Biodiesel	Diesel Fuel ASTM D 975, Biodiesel ASTM D6751*
Specific Gravity (SG) @ 15°C		0.897	0.899			0.87 – 0.9, 0.875-0.9*
Kinematic Viscosity@40°C	10.75 mm ² /s	4.254	3.94	1.064	7.79	1.9 – 4.1, 1.9 - 6.0*
Flash Point (Closed cup)	204.6 °C	145	190	139	201	60 – 80, 130min*
Cetane Number		57				40, 47min*
Cloud point	12 °C	4		18	-7	-35 to 5
Pour Point	15, 7.8 °C	-8		11	-45	-35 to – 15, -5 to 10*
Acid Value (AV)	mgKOH/g	0.72				--, 0.80max*

Effect of flow rate through the Static Mixer on Bio-diesel yield

Results obtained from the Pilot plant are also presented here with the temperature, methanol-to-oil molar ratio and catalyst concentration held constant at 65°C, 6:1 and 1% wt of oil respectively, as shown in Table 3

Table 3: Percentage yield of Biodiesel

Batch Run	Fixed Parameters			Variable	Yield of Biodiesel (weight %)
	Methanol-to-oil Ratio	Temperature (°C)	Catalyst Concentration (weight %)	Flow Rate (cm ³ /s)	
1	6	65	1.0	312.5	85.05
2	6	65	1.0	292.7	87.06
3	6	65	1.0	280.3	87.83
4	6	65	1.0	264.2	93.01
5	6	65	1.0	252.4	93.02

Observations show that the yield of Biodiesel varied significantly with change in flow rate of reactants in the Static Mixer. Results also showed that as the flow rate in the Static Mixer decreased from 312.5 cm³/s to 264.2 cm³/s the Biodiesel yield increased from 85.05 % to 93.01 %. A further decrease in the flow rate to 252.4 cm³/s, did not affect the Biodiesel yield considerably, Figure 2. This trend shows that as the flow rate is further reduced, the biodiesel yield begins to drop due to reduced turbulence of flow in the Static Mixer thereby reducing mass transfer and chemical reaction between the reacting components.

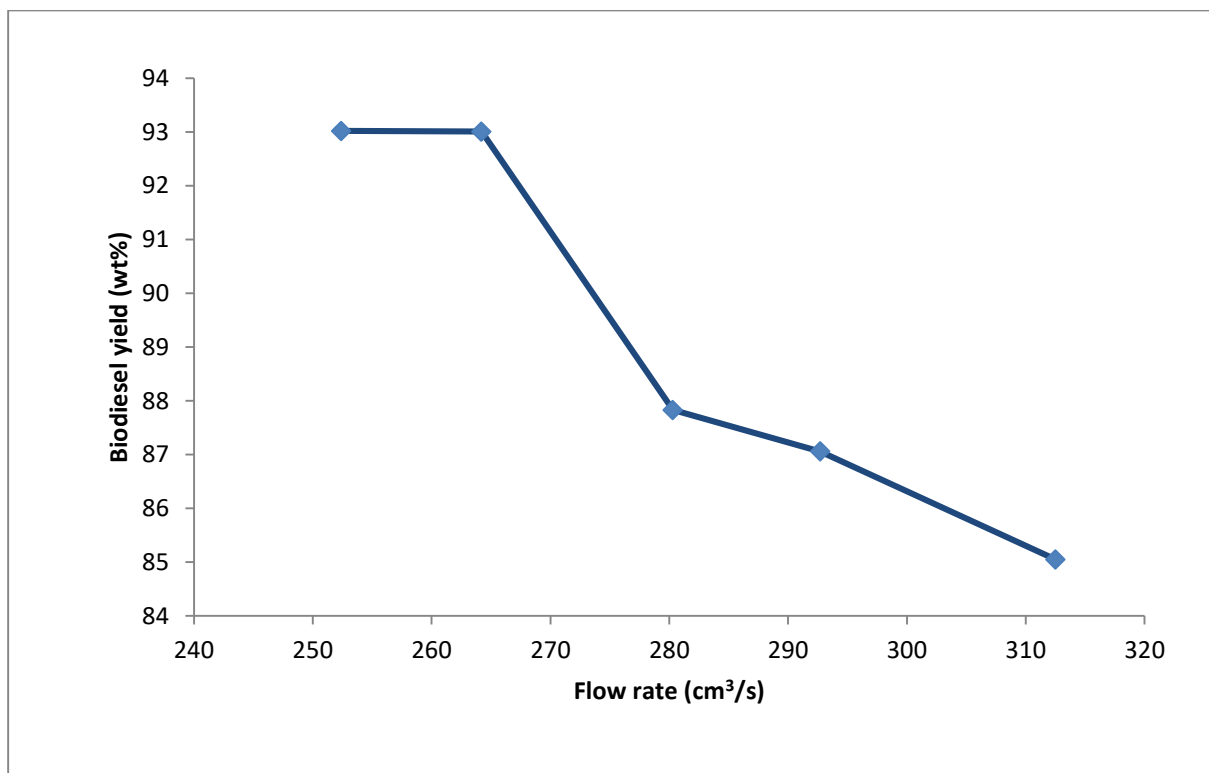


Figure 2: A plot of Yield (wt %) versus Flow rate (cm³/s)

Relationship between Flow Rate and Residence time of Reactants

Residence time, also called removal time, is the average amount of time spent in a control volume by the particles of a fluid. Flow Rate, residence time and dilution time affect reactor dynamics. The higher the Flow Rate the smaller the residence time of reactants in the Static Mixer as can be seen in Figure 3.

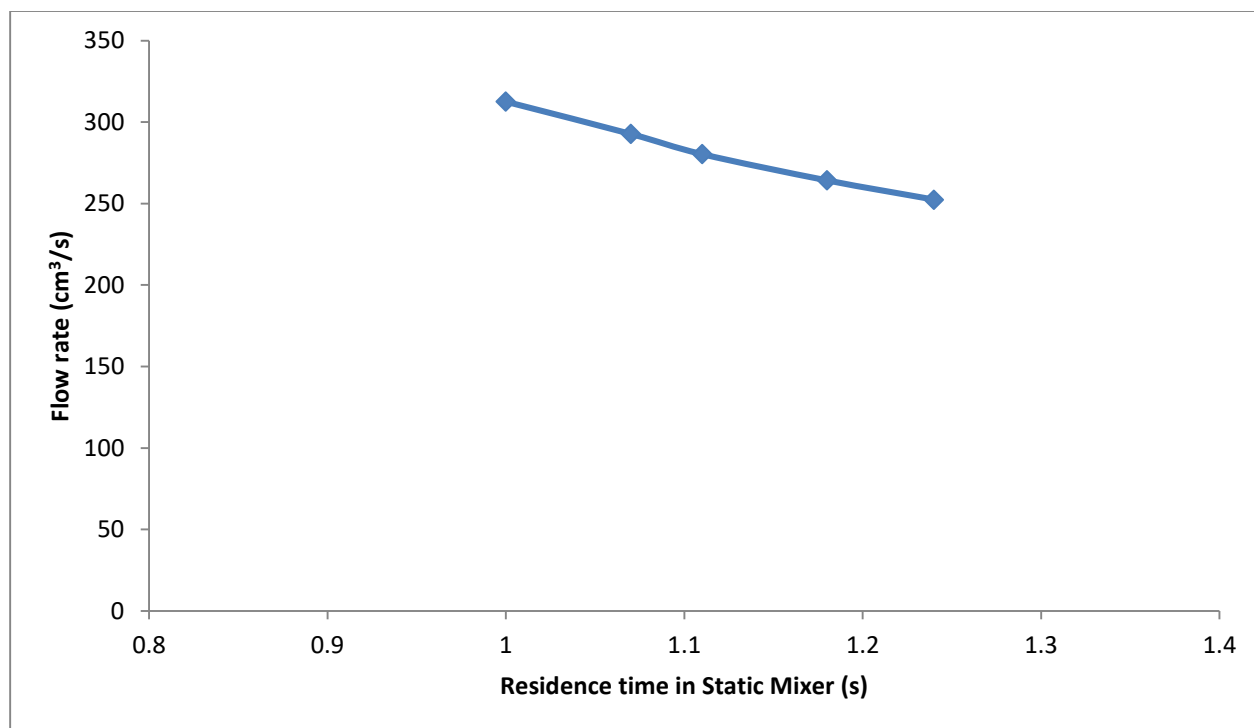


Figure 3: Relationship between flow rate and residence time of reactants in the mixer

The results have shown that the yield of Biodiesel is very sensitive to variation in flow rate of reactants in the Static Mixer.

Effect of the Centrifugal-Contactor-Separator on the Settling Time of the Product Mixture

Figure 4 shows the effect of spinning of the rotating cylinder of the Centrifugal-Contactor-Separator on the separation and settling of the produced biodiesel.

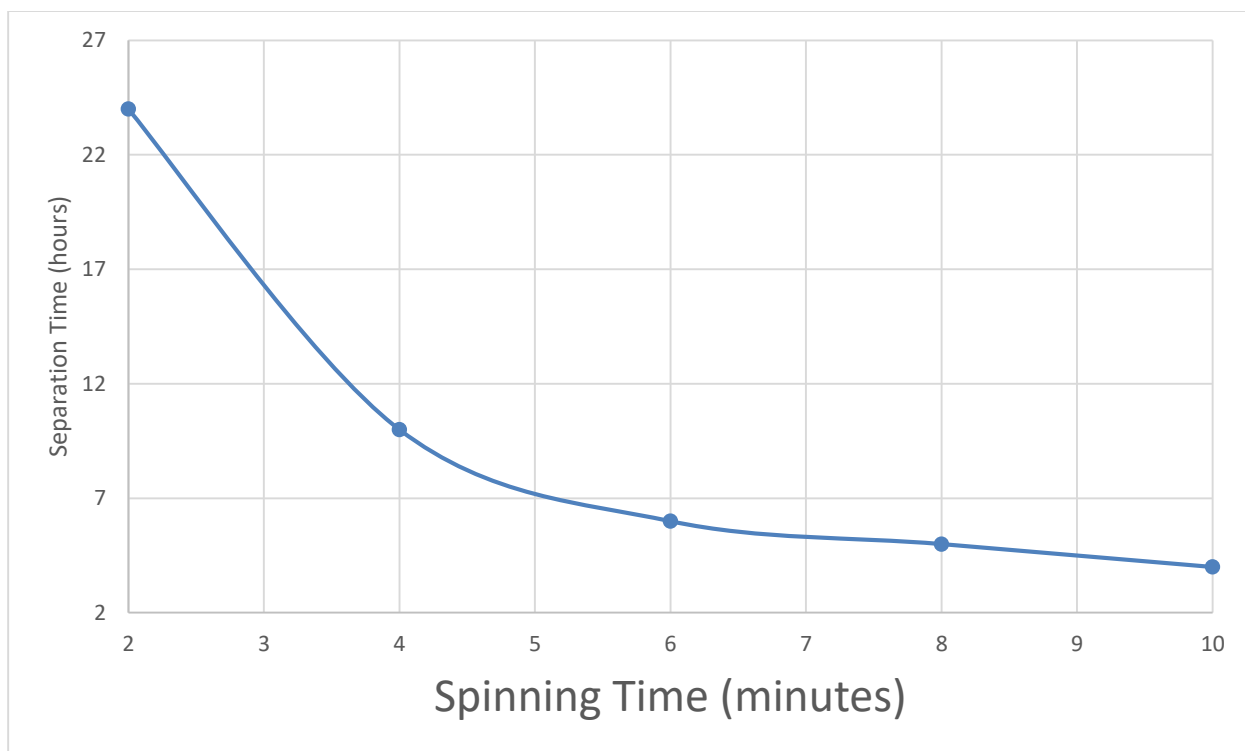


Figure 4: Product Separation Time versus Spinning Time

It was observed that the longer the product was allowed to spin the smaller the settling time. Thus 4 hours were needed for a complete separation of the product into two phases of Biodiesel and glycerol after a spinning time of 10 minutes, perhaps due to coagulation of glycerol components of the product during the spinning and thereby effecting an immediate separation from the less dense Biodiesel. The glycerol easily coagulated leaving a clear Biodiesel to settle on top.

The spinning of the rotating cylinder of the Centrifugal Contactor Separator and a simultaneous recycling of the product from the Flash Still also had a significant effect on the Biodiesel yield. Figure 5 shows the yield with respect to the spinning and recycle duration. It can be observed that longer duration of spin which had an advantage in Figure 5 of a quicker settling and separation also had a disadvantage on the overall Biodiesel yield. The optimum condition from the graph shows that spinning for about 5 minutes gives the highest Biodiesel yield 86.8% when compared to a much longer spinning of 10 minutes and above which resulted in reduced yield of less than 80%. The reduction in yield with longer spinning duration may be attributed to the Biodiesel fraction of the product dissolving in the glycerol thereby forming a stable emulsion.

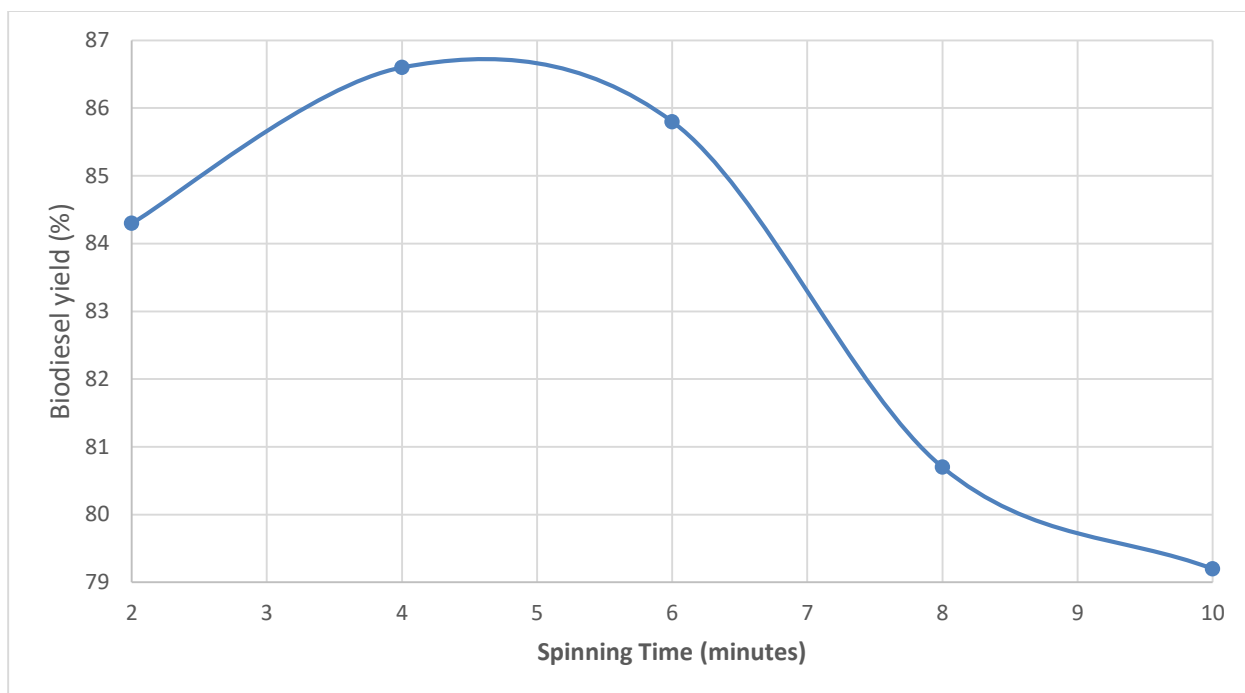


Figure 5: Biodiesel yield with respect to spinning duration

Conclusion

A technology for the production of Bio-diesel from Non-Edible Seed Oils and Waste Cooking Oil, has been developed; equipment constructed and tested successfully. The inclusion of a Static Mixer for preliminary agitation of the reactants and their reaction and a Centrifugal-Contactor-Separator in the design provide for project intensification. Thus the conversion of the triglycerides to fatty acid alkyl ester known as Bio-diesel is facilitated. The Biodiesel produced meets the ASTM D6751 and EN14214 specifications to a large extent.