PROCESSING OF TRIGLYCERIDES TO DIESEL RANGE HYDROCARBON FUELS: EASILY PRACTICABLE SMALL SCALE APPROACH

by

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ABSTRACT

Lipid fraction of biomass has been identified as carbon neutral substitution to fuels from fossil sources in the transportation sector. Although, the diesel engine, invented by Rudolph Diesel over a century ago first ran on peanut oil, the current combustion engines are designed to run on hydrocarbon fuels derived from petroleum. Therefore, a substitute for diesel fuel from renewable source will need to have identical or closely similar properties. The most popular of the existing technology for processing vegetable or animal oils is based on the conversion of the triglycerides constituents to fatty acids methyl esters (FAME). FAME technology does not produce diesel fuel with identical properties as petro-diesel. Other alternative processing routes are dilution of the vegetable oils, emulsification, pyrolysis and hydrotreating. These routes are discussed in this paper. Appropriate technologies for small scale production of diesel range hydrocarbon fuel from vegetable oil without the need for co-reactants such methanol or hydrogen as part of the feedstock is emphased. Also alternative catalyst systems in place of the expensive precious metal supported catalysts are suggested.

Keywords: Biofuels, triglycerides, emulsified fuels, pyrolysis, hydrotreating, deoxygenation.

INTRODUCTION

The role of energy in the socio-economic and political development of a nation cannot be overemphasized. The energy consumption per head of a country is a measure of the standard of living of its citizen.[1] Primary energy sources are classified into renewable (solar, wind, hydro, geothermal, and biomass) and non-renewable (majorly fossil fuels which include: petroleum, coal, bitumen and natural gas) sources. Presently fossil fuels and their products are the chief commercial sources of energy globally. Conversely, the exploration of fossil fuels is not only faced with the challenge of diminishing reserves but also the various activities involved in

exploration and processing of these non-renewable energy sources are associated with environmental pollutions and global warming. Another driving force for alternative to fuels from fossils is strive for energy security as some of recent local, national and international socio-economic and political unrest are traceable to concerns about fossil economy. These challenges informed the global advocacy for environment friendly and sustainable energy sources.[2]

Diversification of energy sources, agricultural activities and having a higher percentage of energy needs being locally produced are goals that can be satisfied by biofuels. The term biofuel refers to liquid or gaseous fuels for the transport sector that are predominantly produced from biomass. Biomass is any organic matter that can be used as an energy source. Biomass (all plants and living organisms) can be converted into liquid and gaseous fuels through thermochemical and biological routes.[3]
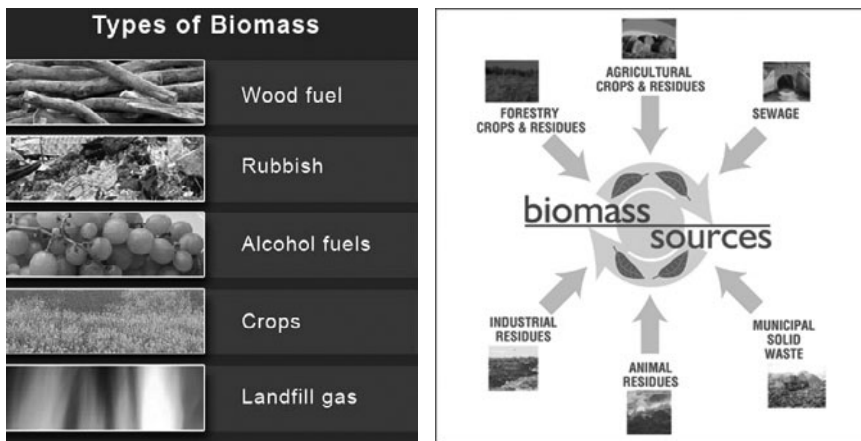

Figure 1. Examples of biomass.

Biofuels are nonpolluting, locally available, accessible, sustainable, and reliable fuel which are obtained from renewable sources. The fractions of biomass that have been used and are still enjoying renewed attention as feedstock for production of liquid biofuels are from agricultural sources, like: lipids, simple sugars and polysaccharides sources.
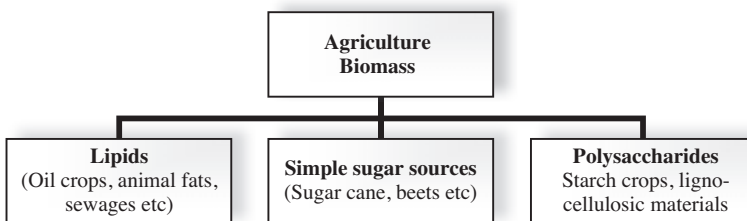

Figure 2. Classification of agriculture biomass.

In this regard, economic conversion of biomass to biofuels are being promoted as a unique environmental strategy and are considered a safe and clean liquid fuel alternative to fossil fuels. It also has the potentials of being a tool of economy empowerment for the citizens of a nation that will exploit these advantages.

VEGETABLE OILS AS TRANSPORTATION FUEL

The transportation sector of the society has been identified as second to the industrial sector in the total global energy consumption but it accounts for more than 95% energy consumption from petroleum sources. The transportation sector requires fuels that burn cleanly; that have high energy density and stability for efficient storage at ambient conditions. These criteria are best fulfilled by liquid hydrocarbons derived from petroleum. Thus, an attractive renewable option for production of transportation fuels would be to utilize a resource such as biomass to generate liquid fuels that are similar to those being used today derived from crude oil. Although, the diesel engine, invented by Rudolph Diesel over a century ago first ran on peanut oil, however, with the advent of petroleum and its appropriate fractions, being cheaper, petroleum became the alternative to vegetable oils for use in engines. However, during the energy crisis periods (1970s), vegetable oils and alcohol were widely used and in recent times there has been renewed global attention on vegetable oils and their derivatives for use as engine fuel. Vegetable oils are composed of mainly triglycerides, which are glycerol molecules esterified with three fatty acids. [4]
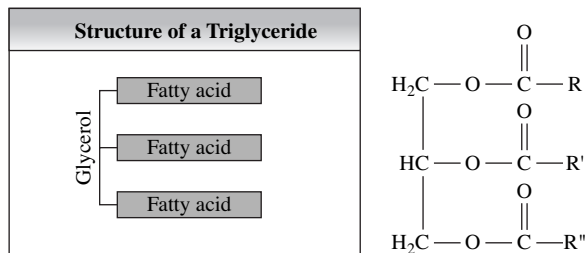

Figure 3. Structure of a triglyceride molecule which is a glycerol molecule esterified with three fatty acids, of which R, R′ and R″ may all be the same, two the same or all different.[5]

The fatty acid composition of vegetable oils are known to depend on the plant species, soil conditions, moisture content in the seeds, and the oil extraction method. The fatty acid composition determines its fuel properties, such as oxidation stability, cetane number, and specific gravity, and its distillation characteristics. Vegetable oils that are rich in unsaturated fatty acids are more prone to oxidation and the formation of sludge on storage for longer period of time. Also direct or straight use of vegetable oils as alternative engine fuels suffer from the problem high viscosities ranging from 10 to 20 times higher than petroleum diesel fuel. Thus, compression ignition engines that runs on vegetable oils are susceptible to many problems because they are designed to run on petroleum diesel fuels. Some of the problems include: coking and trumpet formation on the injectors, to such an extent that fuel atomization does not occur properly or even prevented as a result of plugged orifices; carbon deposits; oil ring sticking; thickening, or lubricating problems due to gelling of the lubricating oil as a result of contamination by vegetable oils.[6]

Diesel fuels from crude oil are made-up of hydrocarbon with C_{10}–C_{15} carbon chains. They are usually mixtures of aromatic, napthalenic and linear hydrocarbons. The fuel quality and cetane number is a function of the proportion of the hydrocarbon classes in the fuel. In general, the cetane number decreases with increasing aromatic content in the fuel. While it is technologically demanding and much economically undesirable to redesign compression ignition engines to run on vegetable oils, it is both economically and technologically more feasible to process vegetable oils to hydrocarbon fuels having identical or similar properties with petroleum diesel.

(a)   (b)   (c)
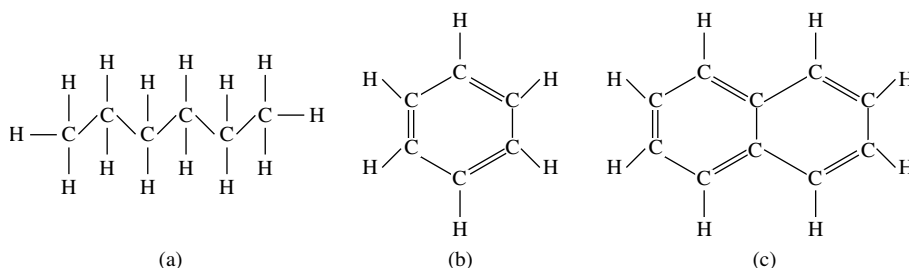
Figure 4. Examples of the constituent hydrocarbons in petroleum diesel.

Thus, the conversion of vegetable oil to fuel of identical properties to those of petroleum diesel will entail the following:

- Cleavage of the triglyceride into its component fatty acid or linear hydrophobic components.
- Elimination of the polar interactions between them by deoxygenation of the fatty acids or triglycerides to linear hydrocarbons.
- Elimination of the reactive groups (unsaturation) to enhance the fuel storage life.

The ultimate goal is to achieve the above listed objectives in one or two step process units at a lower cost as much as possible.
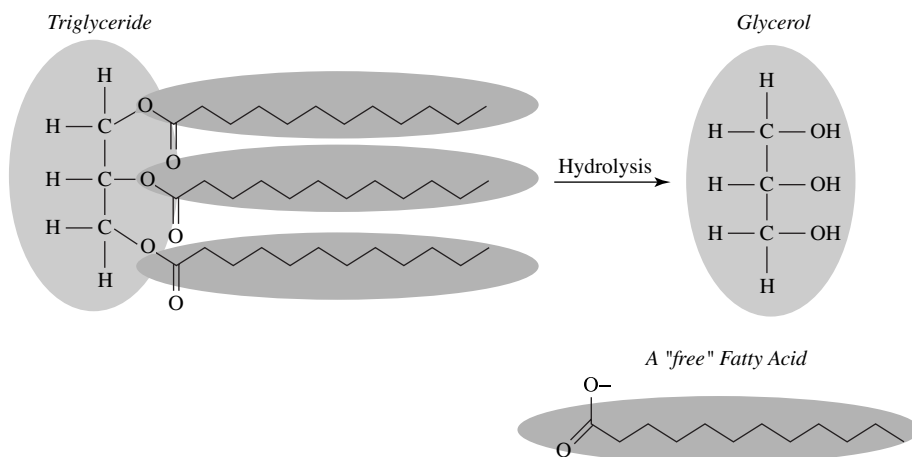

Figure 5. Cleavage of the triglyceride into its component fatty acid or linear hydrophobic components.
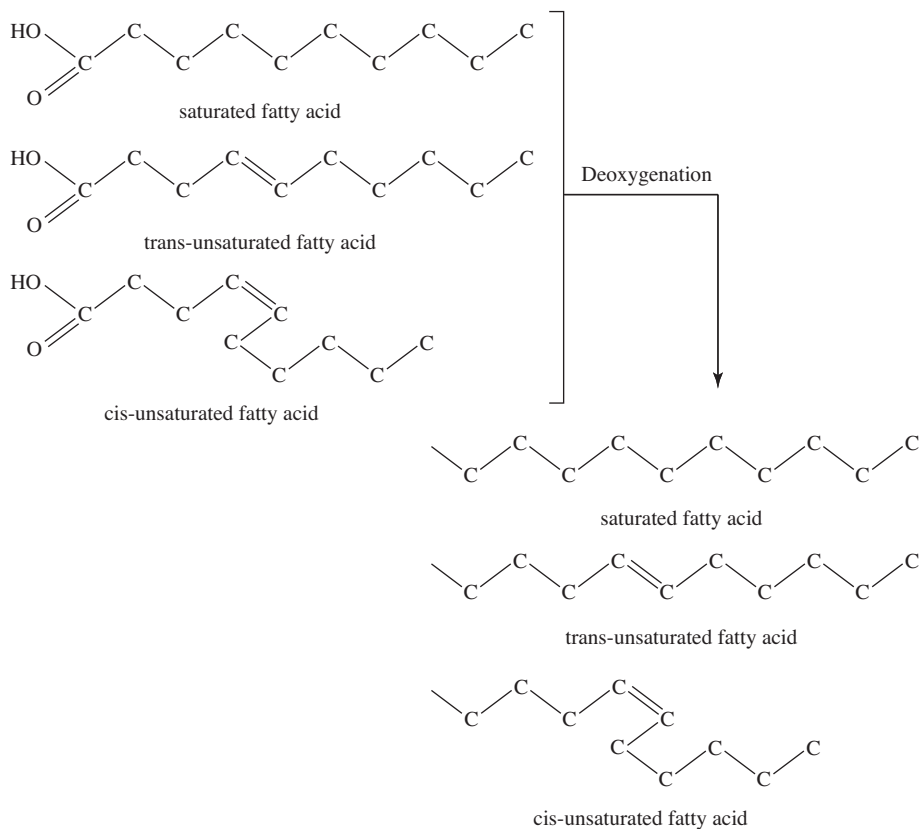
Figure 6. Examples of fatty acids and their deoxygenation to linear hydrocarbons.

Figure 7. Linear alkyl fragment of triglycerides after elimination the reactive group (unsaturation) to enhance the fuel shelf-life.

PROCESSING OF TRIGLYCERIDES

One of the challenges of the straight use of vegetable oils as fuel in diesel engine is their high viscosity. Reduction of the viscosity of a vegetable oil will improve its atomization and combustion characteristics. The various methods commonly

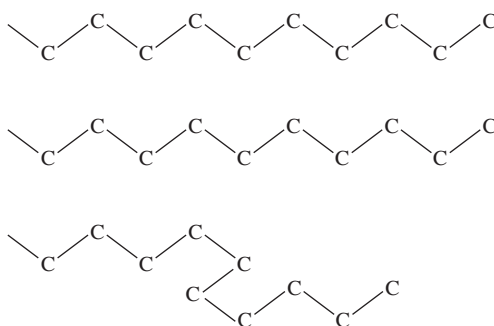employed for reducing the viscosity of oil can be classified into three approaches, which include dilution, partial cleavage and re-building of the triglyceride structure to conform to that of petroleum diesel hydrocarbons and complete cleavage and re-building of the triglyceride structure to form fuels of desired properties.
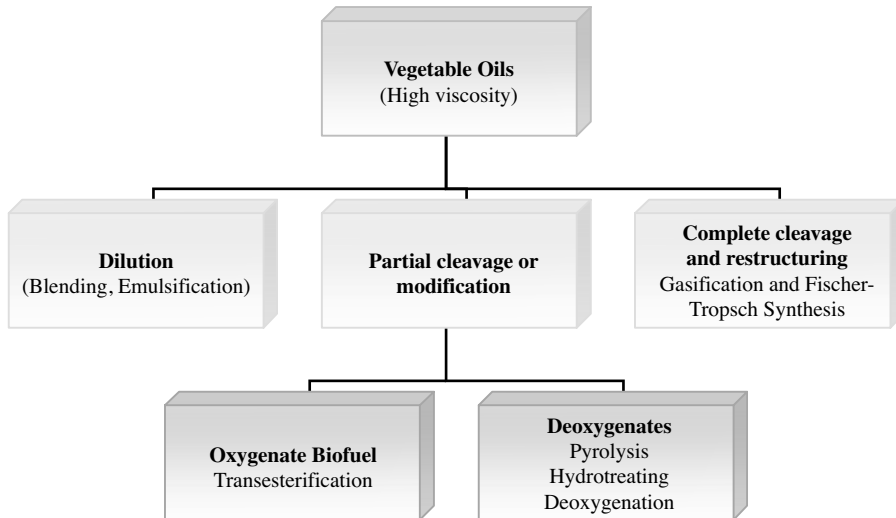

Figure 8. Classification of Process routes for converting vegetable oils to biofuels.

Dilution

Blending

This involves direct mixing of a vegetable oil with conventional diesel fuel or other less viscous liquid hydrocarbon fuels to form blends that have been termed *hybrid fuels*. Reports on this approach indicate that such hybrid fuels can be used successfully on short-term performance tests in nearly any percentage as a replacement for diesel fuel. Blends above 20 percent on long-term performance tests usually result in engine damage or maintenance problems.[7–9]

Emulsification

Emulsified fuels are not new. They are produced by forming a homogeneous phase called emulsion, from petroleum based products or oils derived from plants and water with the aid of an emulsifier. The water and the hydrocarbon phase are mutually insoluble and can be converted into optically transparent and thermodynamically stable dispersion phase by an appropriate emulsifier system. The colloidal dispersion is such that the dispersed-phase particles is less than one-fourth the wavelength of the visible light and is referred to as microemulsion. Currently there are two kinds of emulsification techniques, conventional emulsification by surfactant and three phase emulsification process by soft nano-particles. Although, the latter technique is more advanced than the former, it is not as widespread as the surfactant based technique. Examples of surfactants used include soaps, dimyristicphosphateglycerol sodium salt, sorbitan sesquiolate (SPAN 83), non-ionic surfactants etc. [10]

Emulsified diesel fuels have been used to run diesel engine vehicles. City buses, metro buses and fleets in countries such as United Kingdom, Italy, France and USA are currently using emulsified diesel fuel. Emulsified diesels are reported to have enhanced combustion efficiency with reduction in harmful emission without any hardware replacement and modifications. This is attributed to micro-explosion of water molecules during the ignition of the emulsified fuel in the combustion chamber. This leads to formation of nano size fuel or oil particles which have greater surface area, thus, supporting cleaner combustion. Other advantages of emulsified fuels include reduction in cost of fuel, enhanced self-life, distribution and dispensing with the existing vehicle fueling facilities.[10]

From the foregoing, it is clear that vegetable oils can be processed to low viscosity emulsified fuels that could be used to replace conventional diesel. However, studies in this area are in its infancy. But the few reported works indicate that water alone as the dispersed phase is not sufficient to produce emulsified vegetable oil fuel. However emulsified vegetable oil fuels had been produced when an alcohol (between $C_1 - C_4$) was added. For example, the reported optimum formulation of emulsified fuel from animal fat with methanol and ethanol are shown in table 1. [11–14]

Table 1. Formulations of emulsified fuels from animal fat 11–12

Components	% by volume	Components	% by volume
Animal fat	68	Animal fat	50.0
Methanol	15	Ethanol	36.4
Water	15	Water	10.0
Surfactant	2	Span 83	3.6
Kerihuel et al., (2005)		Kerihuel et al., (2006)	

Emulsified vegetable oil fuel processing is an easily adaptable technology for small scale or rural settlement production of biofuel. However, this needs to be complemented with an efficient ethanol production process. It has the potential of economic empowerment because of the ready market for fuel. It is a potent tool for poverty alleviation.

Partial Cleavage of the Triglyceride Structure

Here, the lipophilic fatty chains are cleaved from the glyceride back bone of the triglyceride structure. This involves selective C-O and C-C scissions at the carbonyl carbons in the triglyceride structure. The C-O scission give oxygenated fatty chain biofuel while the C-C scission will give deoxygenated fatty chain biofuels.

Oxygenate Biofuel

Transesterification

Here, the C-O cleavage is achieved with the aid of hydrolysis regent as co-reactant in the presence of catalysts to liberate the hydrophobic fatty chain as condensation product with the hydrolysing reagent. The reaction route that is exploited in this case

transesterification. It is the most popular of the existing technology for conversion of vegetable oil to diesel fuel. It is centered on the formation of fatty acid methyl ester, FAME (*biodiesel*), of the oils through alcoholysis of the lipids with simple alcohols such methanol, ethanol, propanol in the presence of catalysts. The transesterification involves the C-O scission of the triglyceride at the carbonyl carbon with the use of hydrolysing agents (e.g methanol) in the presence of catalysts cleaves the triglycerides into the fatty acid components as methyl esters (FAME)[see figure 9]. Several efforts had been made to improve the process and develop efficient catalysts for optimum yield in the biodiesel production operations. FAME has many desirable qualities such as high cetane, lower exhaust emissions, very low sulfur content. As a result of the low sulphur content, there is a reduction in the amount of SOx produced during combustion.
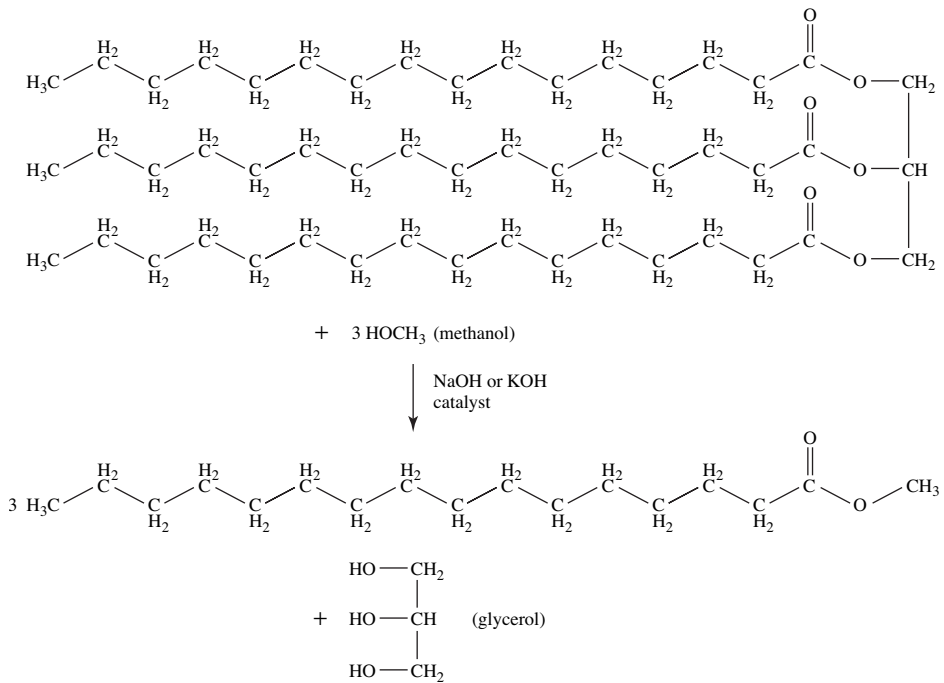
Figure 9. Transesterification involves the C-O scission of the triglyceride at the carbonyl carbon with methanol.

Although transesterification bring about appreciable reduction of the viscosity of vegetable oil, the viscosities of most biodiesels are still significantly higher than that of petro-diesel. Moreover, the oxygen and the reactive unsaturation units of the structure are still in the FAME and issues associated with these structural features that are identified in the direct vegetable oil usage are yet to be completely eliminated. Hence, FAME technology does not produce diesel fuel that is identical to conventional petroleum diesel. A different processing route to convert vegetable oils into a high

quality diesel fuel or diesel blend stock that is fully compatible with petroleum-derived diesel fuel is desired.[6]

Deoxygenated Biofuel
The aim of this route is the selective C-C scission of the carbonyl carbon and adjacent alpha-carbon to it in a triglyceride molecule. It is a direct route to the hydrocarbon chains of the fatty components of the triglycerides. Hence, it is most ideal and also the shortest route at arriving at biofuel that will have identical properties with those of conventional diesel fuels. However, the route suffers from issues relating to process selectivity and economics. The processes commonly employed for obtaining deoxygenated biofuels from triglycerides include thermal and catalytic pyrolysis, but recently hydrotreating and deoxygenation are receiving increasing research attention.

Pyrolysis
This method involves heating the vegetable oil to sufficient temperatures where its viscosity is lowered to near specification range. The oxygen is removed as CO_2, CO or H_2O. The approach is associated with poor selectivity due to uncontrollable side reactions such as cracking or polymerisation of the hydrocarbons. This practical difficulty adversely affects the process economy. However, the use of acid catalysts lowers the reaction temperature and improves the product selectivity. Cracking (or pyrolysis) is used to break down larger petroleum hydrocarbon molecules into smaller more desirable hydrocarbons in the presence of a catalyst and in the absence of oxygen. Catalytic cracking of higher petroleum fractions is an established operation in the petroleum refining (with a well known chemistry). However, studies on the mechanisms of the catalytic cracking of lipids have not received much attention.[15–18]

In a recent study on the elucidation of the reaction pathways for catalytically cracking of unsaturated lipids using triolein as a model triglyceride, Benson[19] reported that that the cracking of unsaturated lipids begins at the double bond. He added that on a heterogeneous catalyst protonation occurs on the outside surface of the catalyst and not within the pores due to molecular size inhibitions. The protonated charge migrates along the fatty acid moiety and β-scission results in the cracking of the fatty acid moiety. The resulting charged species are small enough to readily enter the catalyst pores where additional chemical reaction occurs. Cyclization steps result in the formation of aromatic compounds (chiefly propenylbenzene and phenylbutene). The propenylbenzene and phenylbutene are reaction intermediates that undergo series of methyl shifts, hydride shifts, and isomerizations to form additional mono-aromatic compounds. Oxygen removal as CO_2 is dominantly via decarboxylation while oxygen removal as CO is also likely via decarbonylation. The report also indicated that crystalline catalysts give more gasoline range products with high aromatic components while amorphous catalysts give more diesel range with high dienes content. Catalytic cracking of unsaturated acylglycerides on Faujasite indicated a shift in the product formation when compared to H-ZSM-5. Cracking with Faujasite is reported to yield fewer light hydrocarbon gases and more aromatics. This was attributed to the difference in the pore sizes and acidities of the catalysts. However, catalytic cracking of unsaturated acylglycerides on silica-alumina catalyst favours the formation of

$C_6 - C_9$ dienes. Silica-alumina catalyst also gives significant amounts of ethane and fewer amounts of aromatic formation as compared to the H-ZSM-5 catalyst. Lowering of reaction temperatures from 400 to 350 °C resulted in a decrease in conversions for both Faujasite and silica-alumina catalysts. The lower temperature reactions did yield higher amounts of propenylbenzene. This is perhaps due to lower conversions and also further evidence that propenylbenzene is a reaction intermediate.[19]

As mentioned above, the conversion and product distribution of triglycerides is a function of the catalyst type (crystallinity, pore size & acidity) and reaction temperature. It can be argued that since the cracking reaction begins at the double bond site, then the product distribution of using the same catalyst type and at the same reaction conditions, the product distribution of different unsaturated triglyceride oils will be similar but the conversion will be a function of their properties (degree of unsaturation which can be quantified by their iodine value). This might explain the reported similarities in the product distribution and differences in oil conversions obtained in the catalytic conversion of canola oil to fuels and catalytic conversion of palm oil to hydrocarbons.[20–30] Although, deoxygenation or conversion of triglyceride oils can be achieved through catalytic cracking of the oil, the process is associated with low atom economy due to formation of undesired hydrocarbon gases coupled with poor yield of diesel range product.

Hydrotreating
Another alternative method of converting triglyceride oils into diesel fuel is through hydrotreating process. The hydrotreating process requires hydrogen gas to selectively eliminate the linkage oxygen as water and carbon dioxide. The resulting products are the respective hydrocarbons of the fatty acids of the oil. The diesel fuel produced via this process is called green diesel. The adoption of this approach for the processing of vegetable oils is receiving increasing research attention in recent times because it is a well established existing technology in the oil and gas industry. In hydrotreating, removal of oxygen is accomplished through hydrodeoxygenation (HDO) and other direct mechanisms such as hydrodecarbonylation (HDCN) and hydrodecarboxylation (HDCX) and hydrogenation (HYD). The catalysts employed here are conventional hydrotreating catalysts, such as supported sulphided Co-Mo or Ni-Mo catalysts. Rapeseed oil was reported hydroprocessed at various temperatures (260–340 °C) under a pressure of 7 MPa in a laboratory flow reactor. Three Ni–Mo/alumina hydrorefining catalysts were used. The report indicated that the main components of the organic liquid product (OLP) were identified as C_{17} and C_{18} n-alkanes and i-alkanes. At a low reaction temperature, OLP contained also free fatty acids and triglycerides. At reaction temperatures higher than 310 °C, OLP contained only hydrocarbons of the same nature as hydrocarbons present in diesel fuel.[31] In addition, it was commented that hydrotreating plant oils can give a product with high cetane values called "SuperCetane". It can not only be used directly as a diesel fuel, but has such superior properties to fossil fuel derived diesel fuels such that it can also be mixed with the latter as a diesel fuel cetane enhancer.[32]

The adoption of the hydrotreating technology for the processing of vegetable oils to diesel fuel had been accorded the following merits: a diesel fuel with superior properties to oxygenated biodiesel, ultra-low sulfur content, green diesel also has a high cetane rating and is similar to GTL and CTL diesel; and the cold flow properties of the diesel can be controlled by paraffin isomerization. These properties make green diesel a premium blending component. It is a good replacement for cetane enhancing additives. Green diesels were found to have positively higher net energy balances than petroleum diesel and biodiesel. Production of green diesel from palm oil was estimated as feasible at a crude oil price of $52 bbl and soybean oil at $67 bbl. It can be employed to process low quality vegetable oils (oils that have high free fatty acid content).[6] However, the technology is only practicable at present in the petroleum refinery where hydrogen gas and the attendant high pressure facilities needed for the process are readily available. On the contrary, for small scale processing plants, the facilities to handle hydrogen gas are often absent and the technical and the capital requirement for addition of hydrogen gas unit may adversely affect the economic feasibility of the process. A selective deoxygention of a triglyceride to its hydrocarbon components in the absence of hydrogen will require a less complex or sophisticated process unit that is practicable on a small scale. This will be suitable for rural areas to boost employment and economic empowerment of the rural populace.

Decarboxylation/Decarbonylation

Selective deoxygenation of triglycerides in the absence of hydrogen is a current challenge in the field of heterogeneous catalysis in the quest for sustainable technology for the production of green diesel. This method is economically attractive since it does not require additional inputs such as methanol, hydrogen gas as in the case of transesterification and hyrotreating process respectively. The catalytic activities requirement in a potential catalysts are: high C-O scission activity, i.e deoxygenation, and low C-C activity, i.e mild cracking activity to enhance high selectivity to C_8–C_{16} range. Mild aromatization activity may be desired for isomerisation of vegetable oils that have high iodine value to obtain fuel that are suitable for Jet engines. The conventional catalysts that meet the above requirements are the expensive precious metal on inert supports e.g Pt/C, Pd/C, Ir/C, etc.[33–34] Again, this poses the challenge of economic viability of adopting this process for small scale operations. But less expensive alternative catalysts that have similar performance as the precious metals will enhance the economic feasibility of the process. Reported investigations in this regard and deductions from other studies in the literature revealed good prospects.

Tonga and co-worker [35] carried out investigations on Ni as a lower cost alternative to Pt and Pd. Their study aimed at developing a catalyst for the direct conversion of triglycerides to diesel fuel/jet fuel (diesel fuel: mainly linear paraffins, C_{10}–C_{15} and jet fuel (mainly linear paraffins, C_8–C_{16}) with the following targets as requirements in the prospective catalyst as alternative to precious metals: high selectivity to hydrocarbons boiling in the C_8–C_{16} range, hence mild activity for C-C cracking required; high activity for triglyceride deoxygenation, i.e., C-O scission; and low cost of the catalyst. Ni is known to have high activity for C-O bond scission but with a disadvantage of

high C-C cracking activity which may give rise to mainly light hydrocarbons (i.e, < C_8). The result showed that Ni catalysts also demonstrated acceptable potential for triglyceride deoxygenation. It has C-O activity similar to that of Pd and Pt catalysts but with slightly higher cracking activity than Pd and Pt catalysts. For the best Ni catalysts, selectivity to C_8–C_{17} HCs is similar to Pd and Pt catalysts. For all catalysts, the degree of C-C cracking was heavily influenced by the degree of unsaturation of the fatty acid chains. In some runs catalyst coking was observed. It has been suggested that the catalyst deactivation may have direct link to phosphorus and sulphur content of the oil.[36]

In the same vein, other non-precious metal based catalysts which exhibit similar catalytic activity as Pt or have surface activity resemblance to Pt that have been used in the place of Pt were found to be valuable alternative for Pt in some reactions.[37] Relevant examples of such reactions and catalysts include aqueous-phase reforming of oxygenated hydrocarbons over Sn-modified Ni catalysts [38–41] and nickel promoted tungsten carbide used for direct catalytic conversion of cellulose into ethylene glycol.[40] These catalysts could also exhibit the same ability as alternative to Pt-based catalyst for decarboxylation of triglycerides in the absence of hydrogen. Although, the study of metallic nitride and carbide catalysts for hydrotreating operation in the oil and gas industry has been driven by the increasing restrictions on sulphur content in the catalysts that are being applied in the processing of today's fuels, however, it was noted that carbides of Groups IV-VI B metals show catalytic performances similar to those of platinum-group metals in a variety of reactions involving hydrogen. Tungsten and molybdenum carbides show strong performances in the catalytic decomposition of hydrazine, comparable with those of expensive iridium catalysts. Thus, it can be suggested that nickel promoted metal carbides and nitrides are equally potential candidates for decarboxylation of triglycerides in the absence of hydrogen.

Based on a large amount of experimental investigation with model carboxylic acid compounds, Aihua et al, [41] identified four types of effective decarboxylation catalysts. They are alkaline earth metal oxide, transition metal (oxidative metal) oxides, strong acidic zeolite and supported precious metal catalysts. The representative catalysts for these four types include MgO, Ag_2O/Cu_2O, HZSM-5 zeolite and Pt/Al_2O_3. All these catalysts show excellent catalytic decarboxylation activities at relative low temperature between 200-300 °C. The decarboxylation mechanism was investigated through theoretical calculation and product/ intermediate analyses. The study showed that MgO catalyze the decarboxylation reaction through a ketonization mechanism with two moles of carboxylic acid which gave rise to the formation of one mole of CO_2. A free radical mechanism was suggested for the decarboxylation process involving Ag_2O and Cu_2O. The redox properties of Cu_2O and Ag_2O may have link with their observed decarboxylation properties since they are known to be oxidative catalysts. On the other hand, the high activity of the zeolite towards decarboxylation is probably caused by the C-C cracking catalysed by the strong acidic sites on the zeolite. While the reforming activities of supported precious metal may account for the decarboxylation process which may also be accompanied by hydrocracking at high temperature or in the presence of acidic supports. It was also reported that higher acid conversions were obtained from MgO when small amounts of Ni and Cu were loaded with MgO with the maximum conversion exceeding > 90%. This suggests a synergism that occurs

between metals and MgO, which may possibly involve the enhanced cleavage of C-O bonding due to the presence of Cu or Ni.[41]

Table 2. Four catalysts types for effective decarboxylation [41]

Catalyst Type	Representative Catalyst	Major Reactions and Products
Alkaline earth metal oxide	MgO	$2RCOOH \rightarrow RCOR + CO_2$
Oxidative metal oxides	Ag_2O, Cu_2O	$4RCOOH \rightarrow 2RH + 2CO_2 + H_2 + R\text{-}R$
Acidic zeolite	HZSM-5	$RCOOH \rightarrow RH + CO_2$
Supported precious metal	Pt/Al_2O_3	$RCOOH \rightarrow RH + CO_2$

Reaction temperature: 200–300 ^{o}C

Although, Aihua et al. reported that the above representative catalysts were effective for the decarboxylation of the model acid (Naphthenic Acids), there are not many studies focussed on exploring their effectiveness for decarboxylation of triglycerides. The report of Avelino et al.[41] revealed that MgO displayed good catalytic activity for ketonic decarboxylation of lauric acid in a tubular, fixed bed continuous reactor. The introduction of a second catalytic bed of Pt/MgO in the presence of H_2 gave 58 % tricosane selectivity. But when the Pt was deposited on γ-Al_2O_3 (a very mild acidic support), a total yield of $C_{10} – C_{23}$ n-alkane of about 90 % was obtained. The possibility of decarboxylation of fatty acids and their methyl esters in the absence of hydrogen was demonstrated by Murzin and co-worker. Pd/C catalyst was used and the result obtained showed that the catalyst is active for the decarboxylation reaction.[34]

Within the limits of available evidence there is yet a report on the used of oxidative metal oxides (Ag_2O, Cu_2O) used for decarboxylation of triglycerides, despite their potentials as an inexpensive alternative catalyst system for decarboxylation of triglycerides in the absence of hydrogen. Also a large number of other example catalysts under these catalyst types have potential of being a low cost substitute to the well known expensive ones for decarboxylation of triglycerides in the absence of hydrogen. The table 3 gives a list of expected potential catalysts for selective deoxygenation of triglycerides to diesel range hydrocarbon fuel in the absence of hydrogen.

Table 3. Potential catalysts for deoxygenation of triglycerides in the absence of hydrogen to diesel range hydrocarbon fuel

Catalyst Type	Potential Catalyst
Alkaline earth metal oxide	CeO_2,
Redox catalyst	Ceria-zirconia mixed metal oxide ($Ce_{(1-x)}Zr_xO_2$
Oxidative metal oxides	MnO, SnO, Tl_2O, In_2O, Ga_2O, TiO,
Acidic zeolite	Substituted zeolite catalyst with the general formula W/X-[Y]ZSM-5.
	Where W= dehydrogenation metal or metal oxides
	(Pt, Pd, Zn, Co, Ga, Fe, Mo, etc)
	X= basic metal ions/species (Na^+, K^+, Li^+, NH_4^+, Cu^+, Ag^+ etc)
	Y= trivalent cations as substitute for Al^{3+} (Fe^{3+}, Ga^{3+}, Co^{3+}, Cr^{3+}, Mo^{3+}, Sc^{3+}, Y^{3+}, La^{3+} ,W^{3+} etc)
	The Si in the Zeolite framework can also be replaced with Ge, Ti, Zr, Ce
Supported precious metal	Raney Ni-Sn, Mo_2O_3/SiO_2-Al_2O_3, W_2O_3/SiO_2-Al_2O_3, carbides and nitrides of (Mo, Co, Ni, W, T, V)
others	Ca–montmorillonite, (excess water at 250 ^{o}C)

Complete Clearage and Re-Structuring
Gasification and Fischer Tropsch Synthesis
Here, the whole C-C and C-H bonds in the vegetable oil (triglyceride and other content of the oil) are cleaved via gasification to produce synthesis gas (mainly CO and H_2). The synthesis gas can then be made to undergo Fischer-Tropsch synthesis to selectively produce methanol, higher alcohols or hydrocarbons (synthetic crude oil). The syncrude will then be separated and processed into desired hydrocarbon fractions in the same manner as conventional petroleum crude oil.[43]
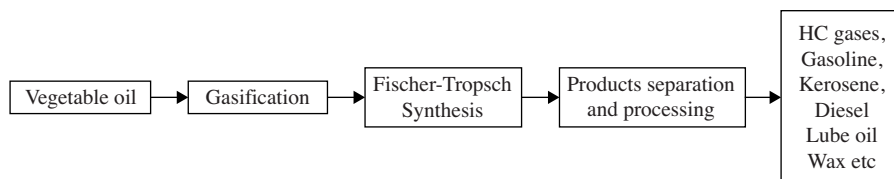
Scheme 1. Fischer -Tropsch Synthesis using syngas feed from vegetable oil.

The C : H ratio in vegetable oil is higher than that of carbohydrate biomass feedstock and it is such that vegetable oil feedstock can generate syngas feed with H_2/CO (1.5-2.0) that is similar to what is obtainable from natural gas when appropriate gasification technology is employed. Such syngas feeds are suitable for high wax selectivity especially on Co-based catalysts. Also, nitrogen and sulphur content of vegetable oils are usually lower than that of the carbohydrate biomass feedstocks.[44] Therefore, the syngas feed from vegetable oil can be use directly in the Fischer-Tropsch synthesis. However, this approach of upgrading vegetable oil to hydrocarbon fuels involves several unit operations and processes each of which require highly skilled manpower. It is labour and capital intensive. Hence it is not suitable for small scale or distributed processing units. While the technical feasibility of a large scale operation is highly probable, the economic viability is still a determinant factor.

CONCLUSION
The conversion of vegetable oil to biofuels is currently one of the strategies for obtaining transportation fuel from renewable sources. The strategy is considered part of the effort at reducing CO_2 emission and cob global warming. The elemental composition of vegetable oils (mainly composed triglycerides) portrays them as suitable substitute for petroleum diesel. However, physico-chemical properties especially viscosity renders most of them unsuitable to be use directly in the combustion ignition engine. Several methods have been devised to reduce the viscosity of vegetable oil, they include: blending with Emulsification, pyrolysis, transesterification, hydrotreating, deoxygenation and gasification and Fischer-Tropsch synthesis. Hydrotreating and Gasification & Fischer-Tropsch synthesis are considered unsuitable for small scale or distributed processing operations. Small scale operations methods are envisaged to serve as a potent tool of economic empowerment and poverty alleviation in rural communities. In addition to efficient conversion of vegetable oils (triglycerides) and biomass in general to acceptable boifuels, it will be crucial to create

a similar comprehensive network of process chains of oleo-chemicals & bio-chemicals as petrochemicals in the crude oil industry. However, the dynamics of this process are largely dictated by the market prices and political decisions rather than by purely chemical reasoning. [44]

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