Fatty acid chain length optimization for biodiesel production using different chemical and biochemical approaches – A comprehensive review

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Abstract

Biodiesel is oxygenated diesel fuel and a potential alternative made from animal fats and vegetable oils by conversion of triglycerides into esters via conventional transesterification either with or without the use of catalyst. Extensive utilization of biodiesel comes with several advantages over petroleum based diesel owing to renewable nature, superior flash point, potentially high biodegradability, lower toxicity, inherent lubricity and negligible sulfur contents. Nevertheless, several technical reasons including higher cost, poor low temperature flow properties, variable chemical composition and complete engine clogging make its excessive usage quite questionable and less popular in comparison with petroleum based diesel. Therefore, the present review was designed to overcome these shortcomings thereby taking a step forward towards sustainable developments by compiling various chemical and biochemical approaches such as fatty acids chain length reduction including direct blending and micro-emulsion, utilization of various antioxidants, ultrasound methods, microwave technologies and fatty acids chain extension constituting culturing, extraction, engineered β-oxidation, ω-oxidation along with double bond induction, fractionation with crystallization, thermolytic breakdown, catalytic cracking, oxidative cleavage, hydrolytic reactions and double bond removal through direct polymerization and formation of biobased epoxy resins. Various oxidative approaches include oxidation of double bonds, autoxidation of fats and addition of transition metal catalyst during simple oxidation. Some assisted transesterification techniques include ultrasound assisted transesterification and microwave assisted transesterification. Similarly, kink production is also an appropriate method to optimize the carbon chain length for production of high quality fatty acid methyl esters.

Key words: Fatty Acids, Biodiesel, Chain Length Optimization, Oxidation, Fractionation, Polymerization, Transesterification, Direct Blending

1. Introduction

In chemistry, particularly in biochemistry, a fatty acid is a carboxylic acid with a long aliphatic chain, which is either saturated or unsaturated. Mostly, the fatty acids from carbon 4 to 28 have an unbranched chain of an even number of carbon atoms of fatty acids [1]. Fatty acids are usually derived from triglycerides or phospholipids. Fatty acids yield large quantities of ATP, when metabolized because they are important dietary sources of fuel for animals. Either glucose or fatty acids can be used for this purpose by many types of cells. Blood–brain barrier (BBB) cannot be crossed by long-chain fatty acids so they cannot be used as fuel by the cells of central nervous system however, free short-chain fatty acids and medium-chain fatty acids can cross the BBB [2], in addition to glucose and ketone bodies. Biodiesel can be chemically defined as a fuel composed of mono-alkyl esters of long chain fatty acids derived from renewable sources, such as vegetable oils and animal fats [3].

Feedstocks for biodiesel production are several vegetable oils varieties such as canola, palm, palm kernel, sunflower and coconut oil. Biodiesel production from these feedstocks is cost-inefficient as the high price of combustible vegetable oils causes big economic losses as compared to fossil based diesel fuel which is the main concerned disadvantage. Due to the low price of non-edible seed oils such as Jatropha or waste cooking oils, these are preferred for biodiesel production [4]. New generation biodiesel intends to derive raw material from algae and other renewable feedstocks which will provide sustainability to the whole biodiesel production process needed to adequately justify the biodiesel industry [5]. The finished biodiesel

must be analyzed for commercial fuel used by using sophisticated analytical equipment to ensure it meets the international standards. A few specifications have been set but the ASTM D 6751 and EN 14214 standards are the most commonly used standards [6].

Biodiesel can potentially be prepared from different varieties of feedstock such as non-edible vegetable oils (e.g. Jatropha oil or Pongamia oil, etc.), edible vegetable oils (e.g. canola oil, sunflower oil etc.), waste cooking oils and animal fats. Price and availability of material are one of the most important factors that determine different types of feedstocks used for biodiesel production from one region of the world to another [7]. Despite the current growth, due to the industry's inability to secure cheap feedstock, the sustainability of the biodiesel industries may be limited. In Canada, most of the current and forecasted biodiesel production comes from canola similarly, others depend on edible vegetable oils as feedstocks in biodiesel producing countries such as US and Europe. This trend also implies the need for a large supply of vegetable oils, which if they are drawn from neat edible oil sources, may lead to food security and ethical issues. Such situation, regarding diversion of food crops to biofuel production, has engendered heated arguments worldwide [8].

Some of these feedstocks include tallow, lard, chicken fat and leather industry solid wastes, etc. AFWs are abundant in some regions resulting in lower feedstock cost. The added advantages of using waste animal fats as feedstock for biodiesel production has reducing environmental damage by creating fuel with lower or equal NOx emission as vegetable oil biodiesel [9]. Biodiesel from AFW feedstocks also has an important quality parameter for diesel fuels of high cetane number. [8]. The AFWs comprise of a high ratio of saturated fatty acids, which are the reason behind high cetane number (460) as compared to most vegetable oils. A higher cetane number is known to lower NOx by lowering temperatures during the critical early part of the combustion process [10]. Similarly, for better oxidative stability in biodiesel, the saturated fatty acids of AFWs contribute significantly. When biodiesel is synthesized by alkaline-catalyzed transesterification, the presence of high content in free fatty acid (FFA) in AFWs has been seen as a challenge [8].

2. Types of Fatty Acids

Fatty acids that have carbon to carbon double bonds are known as "unsaturated fatty acids" while those without double bonds are known as "saturated fatty acids". They differ in length as well. Fatty acid chains differ by length and often categorized as short to very long chain fatty acids. Short-chain fatty acids (SCFA) are fatty acids with aliphatic tails of five or fewer carbons (e.g. butyric acid) [11]. Medium-chain fatty acids (MCFA) are fatty acids with aliphatic tails of 6 to 12 [12] carbons, which can form medium-chain triglycerides. Long-chain fatty acids (LCFA) are fatty acids with aliphatic tails of 13 to 21 carbons [13].

Very long chain fatty acids (VLCFA) are fatty acids with aliphatic tails of 22 or more carbons [14]. If there are one or more double bonds in between carbon atoms, they are known as "unsaturated fatty acids". Pairs of carbon atoms connected by double bonds can be saturated by adding hydrogen atoms to them, converting the double bonds to single bonds. Therefore, the double bonds are called unsaturated. Three-dimensional representations of several fatty acids and their structure formulas are shown.
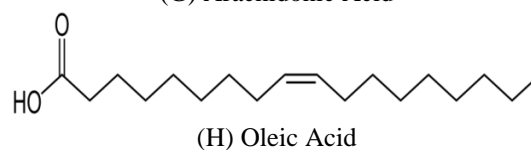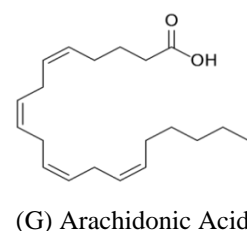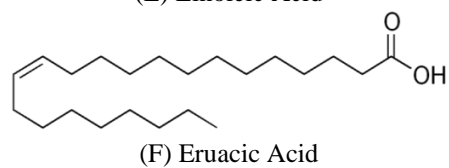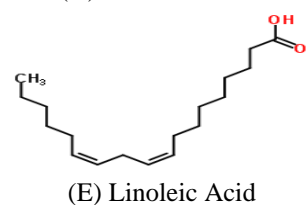
$CH_3(CH_2)_{17}CH_2$—$COOH$

(A) Arachidic Acid

$CH_3(CH_2)_{15}CH_2$—$COOH$

(B) Stearic Acid

$CH_3(CH_2)_{13}CH_2$—$COOH$

(C) Palmitic Acid

$CH_2(CH_2)_5CH_2$—$COOH$ ... CH_3

(D) Linolenic Acid

(E) Linoleic Acid

(F) Eruacic Acid
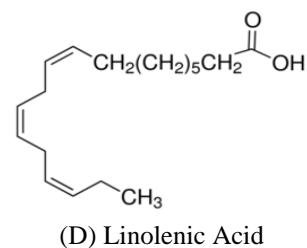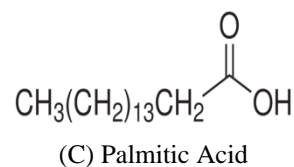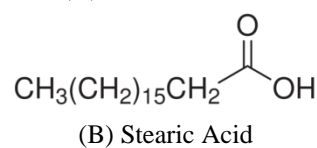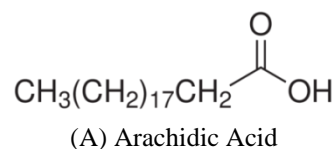
(G) Arachidonic Acid

(H) Oleic Acid

Fig.1 Chemical structure: (A) arachidic acid (B) stearic acid (C) palmitic acid (D) linolenic acid (E) linoleic acid (F) euracic acid (G) arachidonic acid (H) steric acid

In the chain, two carbon atoms that are bound next to either side of the double bond can occur in a cis- or trans-configuration. Two hydrogen atoms adjacent to the double bond stick out on the same side of the chain called "cis-configuration". In case of the cis isomer, the rigidity of double bond freezes its conformation and causes chain to bend and restricts the conformational freedom of fatty acid. It has less flexibility when the more double bonds have cis-configuration in chain. When a chain has many cis bonds, it becomes quite curved in its most accessible conformations. For example, oleic acid has a "kink" in it, with one double bond, whereas linoleic acid has a more pronounced bend with two double bonds. The α-linolenic acid favors a hooked shape with three double bonds. The effect of restricted environments, such as cis bonds limit the ability of fatty acids to be closely packed, when fatty acids are part of a phospholipid in a lipid bilayer or triglycerides in lipid droplets and therefore can affect the melting temperature of the membrane or of the fat.
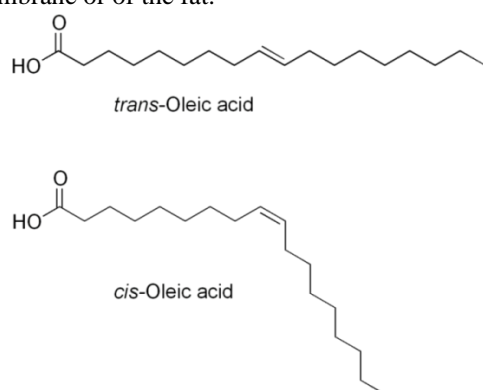

Fig. 2 Comparison of the trans isomer elaidic acid (top) and the cis isomer oleic acid (bottom)

The adjacent two hydrogen atoms lie on opposite sides of the chain by contrast that is called as "trans-configuration". As a result, trans-configuration does not bend the chain too much and their shape is similar as straight saturated fatty acids. In most naturally occurring unsaturated fatty acids, each double bond has three n carbon atoms after it, for some n, and all are cis bonds. In the trans-configuration (trans-fats), most fatty acids are not found in nature and are the result of human processing (e.g., hydrogenation). The differences in geometry play an important role in biological processes and in the construction of biological structures (such as cell membranes), between various types of unsaturated fatty acids, as well as between saturated and unsaturated fatty acids. There is no double bond in saturated fatty acids. Thus, saturated fatty acids are saturated with hydrogen (since on each carbon double bonds reduce the number of hydrogens). Because saturated fatty acids have only single bonds, each carbon atom has 2 hydrogen atoms within the chain (except for the omega carbon at the end that has 3 hydrogens) as shown in Table 2.

3. Composition of Biodiesel

Biodiesel [16] is a liquid biofuel obtained by chemical processes from vegetable oils or animal fats and an alcohol that can be used in diesel engines, alone or blended with diesel oil. ASTM International (originally known as the American Society for Testing and Materials) defines biodiesel as a mixture of long-chain monoalkylic esters from fatty acids obtained by renewable resources, to be used in diesel engines. Blends with diesel fuel are indicated as "Bx", where "x" is the percentage of biodiesel in the blend. For instance, "B5" indicates a blend with 5% biodiesel and 95% diesel fuel; in consequence, B100 indicates pure biodiesel [17]. Vegetable oils, animal fats and short chain alcohols are the raw materials for biodiesel production. The oils most commonly used for worldwide biodiesel production are rapeseed (mainly in the European Union countries), soybean (Argentina and the United States of America), palm (Asian and Central American countries) and sunflower, although other oils are also used, including peanut, linseed, safflower, used vegetable oils and also animal fats. Most frequently used alcohol is methanol although ethanol can also be used. Since cost is the main concern in biodiesel production and trading (mainly due to oil prices), with good results the use of non-edible vegetable oils has been studied for several years. Relatively lower cost of biodiesel is another undeniable advantage of non-edible oils for biodiesel production which lies in the fact that no foodstuffs are spent to produce fuel [18].

These and other reasons using non-edible oils such as castor oil, tung, cotton, jojoba and jatropha, have led to medium- and large-scale biodiesel production trials in several countries. Animal fats are highly acidic grease from cattle, pork, poultry and fish that can be used also as an interesting option, especially in countries with plenty of livestock resources, although it is necessary to carry out preliminary treatment since they are solid. Due to very high oil yield, microalgae appear to be a very important alternative for future biodiesel production. However, it must be taken into account that only some species are useful for biofuel production. Although the properties of oils and fats used as raw materials may differ, the properties of biodiesel must be the same, complying with the requirements set by international standards. Edible vegetable oils such as canola and soybean oil in the USA, palm oil in Malaysia, rapeseed oil in Europe have been used for biodiesel production and found to be a good diesel substitutes. Non-edible vegetable oils, such as *Pongamia pinnata* (Karanja or Honge), *Jatropha curcas* (Jatropha or Ratanjyote) and *Madhuca iondica* (Mahua) have also been found to be suitable for biodiesel production [19].

For the production of biodiesel, major edible oils such as the coconut (copra), corn (maize), cottonseed, canola (a variety of rapeseed), olive, peanut (groundnut), safflower, sesame, soybean and sunflower are extensively used. Nut oils such as obtained from almond, cashew, hazelnut, macadamia, pecan, pistachio and walnut are also some most probable options. Other edible oils include amaranth, apricot, argan, artichoke, avocado, babassu, bay

laurel, beech nut, ben, borneo tallow nut, carob pod (algaroba), cohune, coriander seed, false flax, grape seed, hemp, kapok seed, lallemantia, lemon seed, macauba fruit (*Acrocomia sclerocarpa*), meadow foam seed, mustard, okra seed (hibiscus seed), perilla seed, pequi, (*Caryocar brasiliensis* seed), pine nut, poppy seed, prune kernel, quinoa, ramtil (*Guizotia abyssinica* seed or Niger pea), rice bran, tallow, tea (camellia), thistle (*Silybum marianum* seed), and wheat germ. Non-edible oils from algae, babassu tree, copaiba, honge, jatropha or rattanjyote, jojoba, karanja or honge, mahua, milk bush, nagchampa, neem, petroleum nut, rubber seed tree, silk-cotton tree and tall [20].

For the process modeling and simulation tools, there are various thermodynamic and physical properties of feed oils which are very important. For the characterization of biodiesel, thermo-physical properties of biodiesel are used and they are also required for the combustion modeling. Physical properties of biodiesel and their values or range are given below in Table 3.

The critical properties, for the process modeling and simulation studies which can be carried out for various types of feed oils, are vapor pressure and heat of vaporization of feed oils that are of great important [22]. These include critical temperature (Tc), critical pressure (Pc) and critical volume (Vc.). Because of the decomposition of oils at a higher temperature, there is a dearth of thermodynamic properties for various feed oil as the experimental data is not available. This gives rise to the growing importance of accurate prediction models for these properties. Many models have already been reported, but a systematic study is not done to evaluate the models for the predictions of various thermodynamic properties. The measure of resistance to flow of a liquid due to internal friction of one part of a fluid moving over another is known as "viscosity". It affects the behavior of fuel injection that is why it is a critical property. In general, higher viscosity leads to poorer fuel atomization. High viscosity can cause larger droplet sizes, poorer vaporization, narrower injection spray angle and greater in-cylinder penetration of the fuel spray. This can lead to overall poorer combustion, higher emissions and increased oil dilution. The viscosity of Biodiesel is typically higher than that of petroleum diesel often by two factors [17].

Within the combustion chamber, the air–fuel ratio and energy content are influenced by fuel density. In general, biodiesel fuels densities are slightly higher than those of petroleum diesel and this thing increases the blend's density by increasing the level of biodiesel blends. FAME density is strongly affected by the degree of unsaturation as high density indicates higher unsaturation. It has been reported that chain length also affects the biodiesel density, with higher chain length leading to lower fuel density [23]. Cetane number (CN) is a measure of a fuel's auto ignition quality characteristics. Since biodiesel is largely composed of long-chain hydrocarbon groups (with virtually no branching or aromatic structures) it typically has a higher CN than petroleum diesel. The CN of pure FAME molecules increases with chain length, but this effect is masked when considering complex mixtures of FAME fuels. On the other hand, the CN of FAME fuels clearly varies with an average degree of unsaturation. The literature also reports that decreasing CN leads to an increasing degree of unsaturation [24].

Two important parameters for low-temperature applications of fuel are cloud point (CP) and pour point (PP). Cloud point is defined as the temperature below which wax in diesel or bio-wax in biodiesels forms a cloudy appearance. The presence of solidified waxes thickens the oil and clogs fuel filters and injectors in engines. The temperature at which the amount of wax out of solution is sufficient to gel the fuel is called "pour point". Biodiesel has a higher CP and PP compared to conventional diesel. Cold filter plugging point (CFPP) is the lowest temperature, expressed in 1°C, at which a given volume of diesel type of fuel still passes through a standardized filtration device in a specified time when cooled under certain conditions. In cold temperature countries, it is a very important process as a high CFPP will clog up vehicle engines more easily [25]. Flash point is inversely related to fuel volatility. The biofuel specifications for flash point are meant to guard against contamination by highly volatile impurities – principally excess methanol remaining after product stripping processes [17]. Vegetable oil's methyl esters are much lower than those of vegetable oils. For vegetable oil methyl esters or biodiesels, viscosity increases from 3.59-4.63 mm^2/s with an increase in density ranging from 860 to 885 kg/m^3 and these increasing patterns are highly regular. In vegetable oil methyl esters there is high regression between the density and viscosity values. Irregular relationships between viscosity and flash point for vegetable oil methyl esters have also been observed [21]. Biodiesel has lower mass energy values than petroleum diesel due to its higher oxygen contents. The mass fraction of oxygen decreases as the fatty acid carbon chain increases (for a constant unsaturation level), so the heating value also increases [23].

Some of the advantages of using biodiesel as a replacement for diesel fuel are: [10] (i) it is a renewable fuel source that can be obtained from vegetable oils or animal fats (ii) in comparison with diesel fuel, biodiesel is known to have low toxicity (iii) it minimizes the environmental consequence of biofuel spills because it degrades more rapidly than diesel fuel (iv) carbon monoxide, particulate matter, polycyclic aromatic hydrocarbons and aldehydes causes lower emissions of environmental pollutants (v) due to reduced emissions of carcinogenic substances, it significantly lowers the health risk (vi) no sulfur dioxide (SO$_2$) emissions in case of biodiesel (vii) higher flash point of about 100°C (viii) both fuels may be mixed during the fuel supply to vehicles, may be blended with diesel fuel at any proportion (ix) it acts as a lubricant and known to have

excellent fuel properties (x) without modifications, it is the only alternative fuel that can be used in a conventional diesel engine and (xi) as a raw material, cooking oils and fat residues from meat processing may also be used.

There are certain disadvantages of using biodiesel as a replacement for diesel fuel that must be taken into consideration: (i) due to the lower calorific value of biodiesel, it is slightly higher in fuel consumption (ii) it is slightly higher in nitrous oxide (NOx) emissions than diesel fuel (iii) they may be inconvenient in cold climates because they are known to have higher freezing point than diesel fuel (iv) it ensures long-term storage (more than six months) of biodiesel that is usually not recommended because it is less stable than petroleum diesel (v) in case of replacement, teflon component is recommended as it may degrade plastic and natural rubber gaskets and hoses when used in pure form and (vi) they can cause problems in the valves and injection systems when it dissolves the deposits of sediments and other contaminants from diesel fuel in storage tanks and fuel lines, which then are flushed away by the biofuel into the engine. In consequence, the cleaning of tanks prior to filling with biodiesel is recommended. It must be noted that these disadvantages are significantly reduced when biodiesel is used in blends with diesel fuel.

4. Fatty Acids Chain Reduction

Fatty acids obtained by animal's fats, WAF have long chains which can't be used as fuel so there are different methods which can be used for fatty acids chain reduction:

4.1 Direct Blending

In direct blending (dilution), crude straight vegetable oil (SVO) is mixed with diesel in certain proportion but problems like higher viscosity, higher acid value, higher free fatty acid contents and larger gum formation are faced making its use in engine fuel quite difficult [26]. To reduce the latter's viscosity, blends of animal fats with petro diesel has commonly and preferably been used. Diesel engines have been reported to use the resulting animal fats blends efficiently. The absence of technical modifications and the ease of implementation are the major advantages of the blending. It results in a significant improvement in physical properties when blending of animal fats with alcohols [27].

Over the course of one year storage period, storage stability of poultry fat and diesel fuel mixtures in terms of specific gravity and viscosity were studied and slight changes in viscosity and a specific gravity of the biofuels blends were assessed [28]. In a comprehensive review of the direct use of vegetable oil and animal fat as an alternative fuel in internal combustion engines, Mon dal et al., [29] reported that the effects of the high viscosity of animal fats and their blends as a major cause of poor atomization and difficulty in handling by conventional fuel injection system of compression ignition engines. Micro-emulsifications permit greater atomization of fuel, improved brake thermal

efficiency, and decrease smoke, particulate and nitric oxide emissions due to micro-explosion [8].

4.2 Micro-Emulsion

To form emulsions, micro-emulsions involves mixing of oils with suitable emulsifying agents such as alcohol mainly methanol, ethanol, propanol or butanol. Formation of deposits of carbon in engine and incomplete combustion is the main demerit associated with the use of micro-emulsion engine fuels [26]. The addition of amphiphiles micro emulsification is a process used to formulate hybrid diesel fuels by solubilization of vegetable oil/alcohol mixtures through it. To increase solubility, viscosity is decreased by diluting the oil through addition of alcohols such as methanol (CH_3OH) or ethanol (CH_3CH_2OH) that have limited solubility in nonpolar animal fats and vegetable oils; therefore, amphiphilic compounds such as phospholipids, sorbitan sesquiolate (Span83), n-butanol, 2-octanol, carboxylate surfactants and various other chemical compounds are added for this purpose. An equilibrium dispersion of optically isotropic fluid micro structures with an average diameter less than one quarter the wavelength of visible light that' spontaneously form upon the addition of amphiphiles to a mixture of otherwise nearly immiscible liquids is known as a "micro emulsion" [30]. They are thermodynamically stable as micro emulsions do not require agitation in order to remain in a single-phase and these appear as a translucent solution at constant temperature and pressure [31].

A number of researches are still continuing to ensure the preparation and stabilization of animal fat-water emulsions. However, now-a-days, many researchers are investigating the use of animal fats as compression-ignition (CI) engine fuel by making a stable emulsion with water and methanol. Kerihuel et al., [8] used Span83 (sorbitan sesquiolate) and span80 (sorbitan monooleate) as surfactants. They concluded that animal fats can be transformed into stable biofuel emulsions with improved physical and chemical properties and can be used as a viable fuel in diesel engines. Kerihuel et al., [8] studied the effects of formulations and other influential parameters on the CH_3CH_2OH animal fat emulsions as a diesel engine fuel based on stability, structure, viscosity, fat content and economic aspects. The stobe 36.4% CH_3CH_2OH, 3.6% of SPAN83, 10% of water and 50% animal fat by volume are the determined optimum emulsions condition. Diesel engine test was performed by some Indian scientists and workers on CH_3CH_2OH-animal fat emulsions based fuels and reported an improvement in the heat release pattern during the premixed combustion phase with animal fat emulsion vs. neat animal fat. At high power outputs, they found the fuel emulsion to show a drastic reduction in smoke, nitric oxide, hydrocarbon and carbon monoxide emissions as compared to neat fat and neat diesel.

4.3 Antioxidant

Oxidation cannot be entirely prevented but can be significantly slowed down by the use of antioxidants which are chemicals that inhibit the oxidation process. Two types of antioxidants are generally known: chain breakers and hydro peroxide decomposers [32]. Literature related to hydro peroxide decomposers is very scarce. Phenolic and amine-types are the two most common types of chain breaking antioxidants. To the phenolic type of antioxidants, almost all the work related to the stability of fatty oil and ester applications is limited. The mechanism of all chain breaking antioxidants is shown below in equation 1.

$$\textbf{ROO}^{\bullet} + \textbf{AH} \rightarrow \textbf{ROOH} + \textbf{A}^{\bullet}$$

$$\textbf{A}^{\bullet} \rightarrow \textbf{stable product}$$
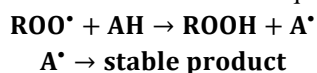
Equation 1 Mechanism of all chain breaking antioxidants The antioxidant contains highly labile hydrogen that is more easily abstracted by a peroxy radical than fatty oil or ester hydrogen, as can be seen. Further resistant to chain oxidation process is the resulting antioxidant free radical that is even stable to further react to form a stable molecule. Thus the chain breaking antioxidants interrupt the oxidation chain reaction. Both with and without the antioxidant, the effectiveness of antioxidant is generally measured by stressing a fatty oil or ester molecule. In fatty oils and esters, antioxidants can come from two sources: natural antioxidants (tocopherols) and synthetic antioxidants. Several studies are available showing the effect of antioxidants on the FAME stability [33]. Tocopherol is a phenolic compound that exists in four isomers (α, β, γ, δ), all of which occur naturally in vegetable oils [34]. Tocopherols may be retained, partially lost or completely lost, depending on the fatty oil processing conditions [35].

Similarly, distillation can remove any tocopherols that were originally present in the vegetable oil feed in post transesterification processing of biodiesel. Natural antioxidants usually are found in unrefined vegetable oils to have improved oxidative stability compared to refined oils but do not meet other fuel specifications [36]. In order to investigate their antioxidant behavior, natural antioxidants have also been deliberately added to biodiesel. On the behavior of FAME used as biodiesel, numerous papers are available on the effect of natural and synthetic antioxidants on stability of oils and fats and little work is available on the effect of antioxidants so far. To fulfil the requirements of current biodiesel specification, Mittelbach and Schober [37] studied the influence of a number of natural and synthetic antioxidants on the oxidation stability of FAME from different feedstocks and reported the significant influence of type and amount of antioxidants on un-distilled and distilled biodiesel samples. Various scientists [38] have reported the effects of various amounts of tocopherol extracted from maize flour [0.01%, 0.02%, 0.05%, 0.1% and 0.2% (w/v)] on the oxidation of neat biodiesel (100% biodiesel). In this study, the oxidation stability of biodiesel based on high oleic acid sunflower oil during the storage and distribution was studied using different percentages of maize flour [0.01%,

0.02%, 0.05%, 0.1%, and 0.2% (w/v)] contaminated by mycotoxins (useless for human consumption) as natural antioxidants. Recently some scientists found that antioxidant effect increased with concentration up to an optimal level however beyond this limit, the increase in antioxidant effect with its concentration was found to be relatively small. Frohlich and Schober studied the influence of tocopherols on the oxidation stability of methyl esters and found that the deactivation rates of tocopherols increased with unsaturation of the particular methyl ester and found the order of decreasing the effectiveness of natural antioxidants in ME as SME>RRME>RVOME>TME. While α-tocopherol was found to be relatively weak but both β-tocopherols and γ-tocopherols increased induction times significantly and may be added to methyl esters as natural antioxidants. Ito et al. [33] have optimized tocopherol concentration in soybean oil deodorized distillate using response surface methodology.

4.4 Ultrasound Method

Ultrasound is the process of propagating an oscillating sound pressure wave with a frequency greater than the upper limit of the human hearing range. Ultrasound frequencies range in between 20 kHz and l0MHz, with associated acoustic wavelengths in liquids of roughly 100–0.15 mm. The chemical processing enhances both mass transfer and chemical reactions leading to shorter reaction times and usage of cheaper reagents. Acoustic cavitation which is the most important element of ultra-sonication is the formation, growth and implosive collapse of bubbles in a liquid irradiated with sound or ultrasound. Liquid causes expansion waves and compression waves through the propagation of sound which forms an aerosol of solvent, solute vapor and previously dissolved gases. This phenomenon causes bubbles to grow and recompress due to the high mass transfer rates arising from the formation of a micro emulsion through ultrasonic cavitation. The application of this method to the transesterification of different vegetable oils has been widely investigated and reported. This technique has been proven to enhance reaction rates. Its implementation has been shown to overcome the inherent issues of slow batch reaction rates and time-consuming phase separation of conventional transesterification processes [8].

4.5 Microwave Method

The microwave radiation region is located between infrared radiation and radio-waves in the electromagnetic spectrum. Microwaves have wavelengths of 1mm to 1 m, corresponding to the frequencies in between 0.3 and 300 GHz [39]. Telecommunication and microwave radar equipment are occupied by the band frequencies in this region. The household and industrial microwave ovens operate at a fixed frequency of 2.45 GHz. In order to avoid the interference with these systems [40], organic synthesis [41] where chemical reactions are accelerated because of selective absorption of microwave energy by polar molecules were preferably employed. Several nonpolar

molecules being inert to microwave were intentionally prohibited as the dielectric loss are including in microwave irradiation has been employed in different applications [42]. The high purity of products, improved yields and greater energy efficiency are other benefits of microwave-assisted chemical syntheses. The application of this method in the process of transesterification of biodiesel from vegetable oils has also been well investigated [43].

5. Fatty Acids Chain Extension

There are some fatty acids which have very small chain lengths because of which they are also not used as biodiesel. So, there are different methods in which small chain fatty acids combine for chain length extension in order to produce superior quality biodiesel.

5.1 Culturing

As far as culturing is concerned, it is usually conducted under suitable sets of conditions in order to promote the production of second medium chain fatty acid subset from various algal strains. The present invention provides methods for producing algal medium chain length fatty acids or hydrocarbons constituting: (a) culturing *Trichodesmiumerythraeum* under suitable sets of conditions to promote production of medium chain fatty acids comprising of C_{10} chain length fatty acids and (b) culturing of *Crypthecodinium* sp. under some appropriate conditions to promote production of medium chain length fatty acids comprising of C_{12} chain length fatty acids. Present activity provides thorough understanding about compositions comprising two or more isolated algal strains selected from the group consisting of *Pinguiococcus pyrenoi-dosus*, *Aphanocapsa* sp., *Biddulphia aurita*, *Crypthecodinium* sp., *Emiliania huxleyi*, *Nitzschia alba*, *Prynnesium parvum*, *Skeletonema costatum* and *Trichodesmium erythraeum*, wherein the two or more algal strains make up at least 90% of the algae present in the composition [44].

5.2 Extraction

Extraction of oil from algal strains is known to contain a detectable level of combination of medium chain fatty acids constituting C_{10}, C_{12} and C_{14} fatty acids or hydrocarbons. Furthermore, extracted oil comprises of C_{14} and C_{16} chain length fatty acids from the cultured *Pinguiococcus pyrenoi-dosus*. The medium chain length combination comprises carbon chain length C_{14} and one or more of carbon chain length C_{10} and C_{12} fatty acids or hydrocarbons [44].

5.3 Engineered β-oxidation

The β-oxidation pathway (Figure 3) is the major route for fatty acid catabolism and is near ubiquitous in living organisms. The pathway is composed of the following iterative steps [45]: (i) activation of fatty acid to fatty acyl-CoA by acyl-CoA ligase/synthetase (ii) conversion of fatty acyl-CoA to 2-enoyl-CoA by acyl-CoA oxidase or acyl-CoA dehydrogenase (iii) hydration of enoyl-CoA to 3-hydroxyacyl-CoA by enoyl-CoA hydratase (iv) reduction of 3-hydroxyacyl-CoA to 3-oxoacyl- CoA and (v) thiolysis of

3-oxoacyl-CoA to acetyl-CoA and fatty acyl-CoA shortened by two carbons. The β-oxidation pathway can shorten the carbon chain, modify the β-carbon and supply acetyl-CoA, which is a common building block for cell growth and the synthesis of many products. Thus, engineering β-oxidation provides the possibility for the conversion of fatty acid feedstock to numerous products.

A variety of commercially important chemical constituents such as alcohols, methyl-esters or amides [46] has been β-oxidized in order to shorten the long chain fatty acid feedstocks into more useful medium chain carboxylic acids [47]. A strain of *Saccharomyces cerevisiae* was engineered for the replacement of its endogenous acyl-CoA oxidase POX1 with *Yarrowia lipolytica* long chain preferring acyl-CoA oxidase POX2. With additional overexpression of carnitine O-octanoyltransferase, which exports medium chain acyl-CoA from the peroxisome to prevent accumulation, titers of C_8-C_{12} fatty acids increased by 3.3-fold compared to the wild type [48]. Engineered β-oxidation was also utilized in the conversion of fatty acids to aliphatic methyl ketones such as flavoring in dairy products, diesel fuel blending agents and pharmacological syntheses which are applications in the industry [49].

The intracellularly synthesized glucose is the major source of microbial production of C_{11}-C_{15} methyl ketones from fatty acid that has been achieved in *Escherichia coli* by the deletion of thiolase FadA, expression of heterologous acyl-CoA oxidase Mlut-11700, overexpression of native enoyl-CoA hydratase/3-hydroxyacyl-CoA dehydrogenase FadB and overexpression of thioesterase FadM [50]. Furthermore, optimizations to fatty acid supply from glucose and to the expression of β-oxidation enzymatic components, along with the removal of acetate synthesis, improved the titer of methyl ketones up to 3.4 g/L using engineered *Escherichia coli* [51]. The 3-hydroxyacids are important building blocks for the synthesis of valuable compounds such as antibiotics [52] and poly-hydroxy-alkanoates (PHA), a class of biodegradable polymers [53] and they are another example of products generated through the engineered β-oxidation of fatty acids. The common strategy for the production of PHAs involves the deletions of host thiolases and 3-hydroxyacyl-CoA dehydrogenase(s). This accumulates 3-hydroxyacyl-CoAs, which are polymerized into PHAs by PHA synthase. Additionally, a thioesterase was overexpressed for hydrolysis of 3-hydroxyacyl-CoA, non-polymerized medium-chain-length 3-hydroxyalkanoic acids which are potentially valuable in pharmaceutical industry [54].

5.4 ω-Oxidation

ω-Oxidation can act upon both alkanes and long-chain fatty acids and generate both dicarboxylic acids and ω-hydroxy fatty acids which are versatile raw materials for oleo chemical industry [55]. The ω-oxidation consists of three key steps which successively oxidize the methyl ends of alkanes or fatty acids to ω-hydroxy acids and ω-fatty

acids which are carried out by cytochrome P450 alkane/fatty acid monooxygenase, alcohol oxidase or aldehyde dehydrogenase. Production of ω-hydroxy fatty acids has been achieved through a range of fatty acid feedstocks by using *Candida tropicalis* engineered to have blocked β-oxidation and the additional deletion of endogenous di-acid production genes consisting of six cytochrome P450s, four fatty alcohol oxidases and six alcohol dehydrogenases [56].

When selected P450 monooxygenases were restored, a total of 174 g/L of 14-hydroxy-tetra-decanoic acid was obtained from 200 g/L of methyl tetradecanoate. Recently, *Escherichia coli* strains was engineered to express heterologous v-oxidation enzymes, blocked β-oxidation, and improve fatty acid uptake by deleting regulator FadR and expressing transporter AlkL. This led to the production of C_{12} and C_{14} dicarboxylic acids from corresponding fatty acids as well as mixed C_{10}-C_{16} diacids from coconut oil hydrolysate, a mixture of C_8-C_{18} fatty acids [57]. Clomburg et al. engineered an *Escherichia coli* strain to have an r-BOX cycle comprised of BktB, FadB and EgTer along with thioesterase YdiI for cycle termination. This, along with alkane monooxygenase AlkBGT for ω-oxidation, yielded more than 0.8 g/L of C_6-C_{10} ω-hydroxy acids from glycerol [58].

Production of nearly 0.5 g/L of C_6-C_{10} diacids was observed, when overexpression of alcohol dehydrogenase ChnD and aldehyde dehydrogenase ChnE was added for further ω-oxidation. In another study, Bowen *et al.* reported the production of C_{12} and C_{14} dicarboxylic acids and ω-hydroxy acids with controlled lengths from glucose in *Escherichia coli* [59]. The preferentially release C_{12} and C_{14} fatty acids from the endogenous FAB pathway, respectively, along with cytochrome P450 (CYP153A) from *Marinobacter aquaeolei* for ω-oxidation was achieved through overexpression of thioesterasesUcFatB2 and TesA.

6. Fatty acids Double Bond Induction

There are following methods which induce double bond in fatty acids that indirectly increase the cold flow properties of biodiesel.

6.1 Low Temperature

Several approaches have been proposed to improve the low temperature properties of biodiesel including: blending with petroleum diesel, use of additives and chemical or physical modification of either the oil feedstock or the biodiesel product. Blending with petroleum diesel is only effective at low biodiesel proportions (up to 30 vol%) with cloud points to around -10°C [60]. Clearly, blends with petroleum diesel do not change the chemical nature and therefore properties of biodiesel and will not facilitate their use at higher concentrations. Since the aim must be to maximize biodiesel utilisation, petroleum blends with biodiesel will not be discussed further in this review. The use of additives can be further classified into traditional petroleum diesel additives and emerging new technologies developed specifically for biodiesel.

6.1.1 Blend Oil

Mixing oils with different fatty acid profiles is the easiest way to enhance biodiesel cold flow properties considering that cold flow properties and viscosity depend mainly on fatty acid profile or oil. So by mixing oils high in saturated fatty acids with oils high in unsaturated fatty acids (especially mono-unsaturated), shorter fatty acids can be possibly obtained to produce biodiesel with better cold flow properties without investing change in the process. Due to the improper removal of saturated fatty acids, these blends also contain high contents of unsaturated fatty acids that appear to be a major drawback. To obtain biodiesel with the best properties, mixing of an equivalent content to 1.26 double bonds by fatty acid molecule having 17 carbons in fatty acid structure is the most appropriate blend [61]. They have lower stability and higher cost of raw material [62]. Dunn [63] concluded that a biodiesel mixture with content of saturated fatty acid methyl esters up to 20% has poor cold flow properties. The ideal composition of the oil used as raw material for biodiesel production to satisfy both cold flow properties and oxidative stability is in between 60 and 80% of monounsaturated and 10–20% of saturated fatty acids [64].

In some recent studies, it has been found that biodiesel can work best at temperatures near 0°C when palm biodiesel is blended with 20% soybean or rapeseed oil [65]. So, the best condition for a palm-soy-rapeseed biodiesels blend was 20:60:20 that can attain a CFPP of −6°C and I.S.O. of 6.56 h [66]. Mixtures of palm biodiesel with methyl oleate showed improved cold flow properties but oleate showed higher percentage among all fatty acid contents [67]. In the work of Zuleta et al [68], it was showed that biodiesel blends that contain palm biodiesel content up to 25% do not exhibit good cold flow properties. In palm oil, biodiesel contents were found to be lower than 50% but different mixtures of palm biodiesel with biodiesel prepared from field pennycress and meadow foam seeds caused decrease in the values of cloud point and pour point [69]. Mixtures of palm and rubber seed biodiesels in a ratio 1:1 can enhance cold flow properties due to having relatively higher contents of unsaturated fatty acid up to 65% [70]. In the work of Sharma [71], classification of 32 microalgal oils and 43 edible and nonedible vegetable oils was carried out according to their cloud point, pour point and oxidation stability index, whereby it can be used as an important tool to evaluate future biodiesel blends that would meet international biodiesel specifications.

6.1.2 Fractionating by Crystallization

By taking into account the fact that oils higher in saturated fatty acids show bad cold flow properties due to lower contents of unsaturated fatty acids via cold fractionation (winterization) [72] or detergents fractionation [73]. The winterization temperature can be calculated from the initial concentration of saturated fatty acid methyl esters [74]. Three consecutive winterization processes at 0.2°C

decreased waste cooking oil biodiesel cloud point from 14.5 to 9°C and its pour point from 13.7 to 7.5°C with 12.6%wt of losses [75]. Cold fractionation process is carried out on palm biodiesel that led to a cloud point of −9°C with raw material losses of 57.7% [76] and detergent fractionation process led to a CFPP of about −16°C using polyglycerol ester like surfactant in a concentration of 0.02% [73].

The use of non-ionic surfactants as additives such as Span 40 and Span 60 (0.5–2.0 %wt), during winterization processes over methyl palmitate-methyl oleate and methyl stereate-methyl oleate blends decreased saturated methyl ester contents and improved cloud point of these blends in between 3 to 9 K [77]. In another work, it was found to be possible to cause decrease in 3°C in beef tallow with 60% of losses [78], as well as an improved cloud point and pour point up to 5.5°C and 6.2°C respectively for waste cooking biodiesel with 12.6% of approximate losses [75]. Besides decreased oxidation stability, unsaturated fatty acids are known to have pronounced effects on cold flow properties of biodiesel that lowers by the introduction of unsaturation [79]. Both cold flow properties and oxidative stability of solvent fractionation can be used to obtain oils with a specific composition that have adequate sustainability [80] but it is quite uneconomical to produce biodiesel at commercial scale [64]. By taking into account the fact that these processes involve high losses of materials, high energy and large time consumption especially with oils high in saturated fatty acids, this material was treated and converted into an easily oxidizable product that is not competitive due to high costs of raw material for biodiesel production [81].

6.2 Thermolytic Reaction

A thermolytic reaction occurs in the absence of oxygen at high temperature. A series of alkanes, alkenes, lower fatty acids, symmetric ketones, oxopropyl esters, carbon monoxide and carbon dioxide are produced by saturated fatty acids. Basically, diametric compounds including dehydrodimers, saturated dimers and polycyclic compounds are formed from unsaturated fatty acids. In addition, dimers and trimers may also be formed when unsaturated fatty acids react with other unsaturated fatty acids through Diels–Alder reaction [82].

6.3 Oxidative Reaction

Oxidative reaction occurs when oxygen in air dissolved in the oil or fat and reacts mainly with unsaturated acyglycerols (AG) resulting in the formation of various oxidation products. The main reactions involved in oxidation are also summarized [83]. RH represents triacylglycerol undergoing oxidation in one of its unsaturated fatty acyl groups. Initially, radicals-alkyl radicals (R˙) are formed. Eventually alkylperoxyl radicals (ROO˙) are produced by the addition of oxygen. Finally, due to the decomposition of hydroperoxides (ROOH) which produce various saturated and unsaturated aldehydes, ketones, hydrocarbons, lactones, alcohols, acids and esters, alkoxyl radicals (RO˙) are formed. Most of these compounds will remain within the oil or fat, e.g. dimeric and polymeric acid, dimeric AG and polyglycerols as products of the radical reactions and increase the viscosity of cooking oil. Others might be further decomposed through alkoxyradicals to volatile polar compounds, e.g. hydroxyl- and epoxy acids that escape from the oil [84].

6.4 Hydrolytic Reaction

The hydrolysis of triglycerides occurs when steam produced during the preparation of food. Part of the water quickly evaporates, but a certain part dissolved in the oil or fat and induces its cleavage to give higher fatty acids, glycerol, monoglycerides and diglycerides at varied concentrations [82].

7. Double Bond Removal

Some vegetable oils and WAF have a double bond which can remove by following methods:

7.1 Direct Polymerization of Carbon to Carbon Double Bond (C=C)

Vegetable oils contain internal C=C double bonds capable of being polymerized. These double bonds can be polymerized through a free radical or a cationic mechanism [85]. Due to the presence of chain-transfer processes to many allylic positions in the molecule, the free-radical polymerization of triglyceride double bonds has received little attention; however, vegetable oils such as linseed and Tung oils have been classically exploited as drying oils and used in paints and coatings. Cationic polymerization of the C=C double bonds has been widely studied by the Larock's group [86]. They reported the preparation of thermosetting polymers ranging from rubbers to hard plastics by the cationic copolymerization of a variety of oils with petroleum-based co-monomers such as styrene, di-vinyl-benzene and dicyclopentadiene in the presence of boron trifluoride diethyl etherate as the initiator. In an attempt to find out some new applications and uses of triglycerides, they investigated the synthesis of new organic/inorganic hybrid materials via hydrosilylation reaction [87]. Although hydrosilylation of olefins has been widely studied, in the last decade only a few studies on fatty acid esters and oils have been reported [88]. They all involved adding a mono-functional silane compound to the double bond and introducing a certain silicon reagent to the ester or the oil. The reaction known as hydrosilylation proceeds when, they undergo addition across the carbon-carbon multiple bonds, after activation of certain hydrosilanes. This reaction usually requires a catalyst, the most commonly used of which are the transition metal complexes [Co (I), Rh (I), Pd (0) or Pt (0)]. It is well known that the reactivity of terminal C=C is higher than that of internal ones. Terminal C=C-containing fatty acid derivatives are available from unsaturated fatty acids by methathesis with ethylene or by pyrolysis. The pyrolysis of ricinoleic acid leads to 10-undecenoic acid. Some researchers investigated the hydrosilylation reaction of terminal unsaturated fatty acid methyl esters with several poly-functional hydrosilylating agents: 1,4-bis(di-methyl-

silyl)benzene (DMSB), tetrakis (di-methyl-silyloxy) silane (TKDS) and 2,4,6,8-tetra-methyl-cyclo-tetra-siloxane (TMCTS) catalyzed by H2PtCl6 in 2-propanol solution (Speier's catalyst) and Pt(0)-divinyl-tetra-methyl-disiloxane complex (Karstedt catalyst). This group of investigators developed hybrid organic-inorganic materials from 10-undencenoyl triglyceride (UDTG) and methyl 3,4,5-tris(10-undecenoyloxy)benzoate (UDBM), a new aromatic fatty acid derivative compound. Elastomeric materials with good thermal stabilities were obtained in all cases. The resulting cured hybrid networks showed good transparency according to good miscibility of organic and inorganic components.

7.2 Bio-Based Epoxy Resins

Renewable materials for industrial applications require slight modifications for which epoxidation is one of the most important functionalization reaction involving C=C double bonds. The epoxidized vegetable oil proves to be an inexpensive alternative. In recent years, extensive work has been done to develop polymers from epoxidized triglycerides or fatty acids [89]. The polymerization of epoxidized vegetable oils has been investigated using either diamine hardeners [90] or thermal latent cationic catalysts [66] to produce bio-based epoxy resins with promising properties. Polymers reinforced with well-defined nano-sized inorganic clusters have attracted much attention and great interest because of their versatility; among these systems polyhedral oligomeric silsesquioxane (POSS) compounds, which possess a unique cage-like structure and nanoscale dimensions, are of particular interest. POSS compounds are 1–3 nm in diameter and their inorganic cage framework is made up of a fixed proportion of silicon and oxygen: (e.g. SiO 1:5)$_n$, where "n" can be 8, 10 or 12. The formation of covalent bonds results in a variety of polymers/POSS nanocomposites having different polymerizable POSS macromers that have been employed to copolymerize with organic monomers [91]. Epoxy resins/POSS nano-composites are the most studied nano-composites that are known to have various mono- or poly-epoxide POSS monomers in order to modify epoxy networks [92]. The properties of polymers include high temperature resistance and mechanical strength along with significant reductions in flammability, evolution of heat and viscosity during processing and incorporation of POSS derivatives into polymeric materials that can lead to substantial improvements in properties.

We have described first example of preparation of biobased POSS-nanocomposites from plant oil derivatives [93]. In this study, organic monomers and inorganic nanoparticles, epoxidized linseed oil (ELO) and 3-glycidylpropylheptaisobutyl-T8-polyhedral oligomeric silsesquioxane (G-POSS) were respectively used. The bio nanocomposites were synthesized by curing the ELO and the designated amount of G-POSS, using 1 wt% of N-benzylpyrazinium hexafluoroantimoniate (BPH) as a thermally latent cationic catalyst on the basis of published

results. All the cured nanocomposites were homogenized and made transparent, implying that no phase separation had occurred. Most of the resulting POSS-containing networks displayed slightly enhanced glass transition temperatures. The storage modules of the networks at the glassy and the rubbery splateau were observed to be somewhat higher than that of POSS-free network. These results can be ascribed to the nanoscale reinforcement effect of POSS cages on the cross-linked matrix.

7.3 Oxidation

Oxidation of unsaturated fatty acids and vegetable oils has recently been reviewed with special emphasis on epoxidation, bishydroxylation and double-bond cleavage [94]. However, for lipids major focus is on autoxidation, photo-oxidation, epoxidation and oxidative cleavage [95].

7.3.1 Double-Bond Oxidation

Double bonds can be oxidized by electron transference and by chemical oxidants. The conjugated diene (14) was converted by anodic oxidation into diacetate (15) which was then transformed into (E,E,E)-triene (16) [96]. Interestingly, (16) and its corresponding isomer are isomers of α-eleostearic acid (9a), which occurs in Chinese tung oil and is used as a component for water resistant varnishes. The ruthenium-catalyzed oxidative cleavage of unsaturated fatty acids gave excellent yield thereby avoiding CCl$_4$ as co-solvent, with 2.2% RuCl$_3$ and 4.1 equivalents NaIO$_4$ in water/MeCN (1:1) under sonication [97]. About 95% NaIO$_4$ can be saved by using the same reagents but re-oxidizing formed iodate back to per iodate in an indirect electrochemical oxidation [98]. Osmium (VIII)-catalyzed double-bond cleavage of (1b) with dioxygen and aldehyde afforded 50–70% of the cleaved products. The oxidant in this case seems to be a per acid formed in situ [99]. Moreover, (1a) was cleaved to 30–35% azelaic acid (nonanedioic acid) with molecular oxygen in supercritical CO$_2$ over micro-porous molecular sieves (MCM-41) that contained chromium, cobalt or manganese [100].
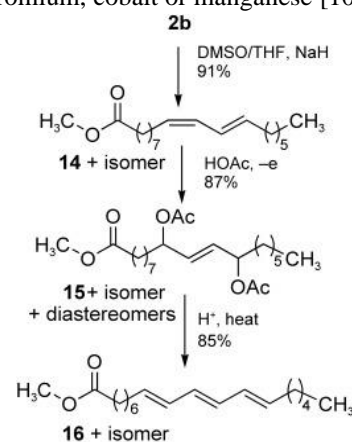

Fig.7 Anodic oxidation of diene (14) to diacetate (15) and conversion of (15) to triene (16)

7.3.2 Autoxidation

Oxidation stability of triglyceride-based vegetable oils is primarily limited by the degree of unsaturated double

bonds. Unsaturated carbon–carbon bonds function as active sites for many reactions including oxidation [101]. A majority of triglyceride-based vegetable oils contain unsaturated fatty acids and are susceptible to oxidation. More will be the number of double bonds higher will be the susceptibility of oil towards oxidation due to increased unsaturation thereby decreasing the number of double bonds [101]. The mechanism for the autoxidation of vegetable oils is well studied and the classical representation of the oil autoxidation mechanism is shown in the table below [101].

Classical representation of the oil autoxidation mechanism

Initiation	$RH \rightarrow R^\bullet + H^\bullet$
Propagation	$R^\bullet + O_2 \rightarrow ROO^\bullet$
	$ROO^\bullet + RH \rightarrow ROOH + R^\bullet$
Branching	$ROOH \rightarrow RO^\bullet + {}^\bullet OH$
	$RO^\bullet + RH + O_2 \rightarrow ROOH + ROO^\bullet$
	${}^\bullet OH + RH + O_2 \rightarrow H_2O + ROO^\bullet$
Termination	$ROO^\bullet + ROO^\bullet \rightarrow ROOH + O_2$
	$ROO^\bullet + R^\bullet \rightarrow ROOH$
	$R^\bullet + R^\bullet \rightarrow R - R$
Peroxide decomposition	$ROOH \rightarrow$ Various lower molecular weight compounds
Polymerization	$ROOH \rightarrow$ Various higher molecular weight compounds

Oxidation of vegetable oil is initiated by the formation of free radicals. Free radicals can easily be formed from the removal of a hydrogen atom from the methylene group next to a double bond. Free radicals rapidly react with oxygen to form a peroxy radical. The peroxy radical can then attack another lipid molecule to remove a hydrogen atom to form a hydroperoxide and another free radical, propagating the oxidation process.

The rate-limiting step of vegetable oil autoxidation is the abstraction of a hydrogen atom by the peroxyl radical to generate a hydroperoxide. The rate constant for the rate-limiting step depends primarily on the strength of carbon-hydrogen bond being broken. Those oils containing double bonds are more susceptible to autoxidation thus the strength of a carbon-hydrogen bond next to a carbon-carbon double bond is lowered and the hydrogen can be removed easily. As the number of double bonds increases, there become more sites susceptible to the abstraction of a hydrogen atom and the autoxidation process can occur at a faster rate. Vegetable oils containing a high percentage of monounsaturated fatty acids will typically autoxidize only at higher temperatures, whereas those oils containing polyunsaturated fatty acids such as linoleic and linolenic acid that readily autoxidize at room temperature.

Hydroperoxides, once formed, can break down to produce more free radicals. This branching step leads to the proliferation of radicals that can go back and aid in the propagation of more hydroperoxides. Not all free radicals, however, some will propagate the oxidation process; some may react with and terminate each other. Hydroperoxides continue to build up in the oil via the propagation and branching steps. At some point, the collection of hydroperoxides no longer remain stable and decompose into a myriad of volatile and non-volatile secondary oxidation compounds. Leading to deposits, they can also be involved in polymerization reactions. The vegetable oil autoxidation mechanism presented here is a simplification of a complex series of reactions. Some experimental factors such as ultraviolet radiations, temperature, pressure and oxygen availability are known to have significant influences, or even by the presence of other compounds such as antioxidants, chelating agents and metals, this process is made further complicated by variations in environmental conditions. Metals, for example, act as a catalyst for the oxidation of vegetable oils speeding up degradation and the production of free radicals. Iron and tin are particularly effective catalysts of the oxidation process, whereas copper and lead have very little impact. Ultraviolet rays decompose hydroperoxides in the process of photo-oxidation [101].

7.4 Transition-Metal-Catalyzed Additions

The application of transition-metal-catalyzed reactions to the C=C double bonds of unsaturated fatty compounds has made important advancements in this field [102]. The synthesis of ω-functionalized fatty acids using commonly available fatty compounds with internal C=C double bonds as substrate was described to proceed via isomerization of the double bond along with fatty acid chain and exclusive trapping of the ω-double bond very interestingly. Thus, isomerizing hydro-formylation of (1b) and (2b) was performed in the presence of a rhodium catalyst to give the ω-aldehyde (28) in yields of only 26% and 34%, respectively [103]. Unfortunately, hydrogenation of the double bonds was the dominating pathway. In contrast, ά,ω-diacid esters were obtained by methoxycarbonylation catalyzed by Pd complexes with selectivity of greater than 95% [104]. Full conversion of (1b) as well as (2b) and (3b) gave dimethyl nonadecanedioate (29) under mild reaction conditions. A mixture of unsaturated fatty acids (1a), (2a) and (3a), commonly occurring in native plant oils, gives one single product. Interestingly, these compounds were already shown to be of high value for the synthesis of industrially relevant semi-crystalline polyesters from renewable resources more importantly [104].

The selective hydroboration of (1b) with pinacol borane at the terminal carbon atom was catalyzed by Ir to give the product (30) giving 45% yield by using a similar concept [105]. Hydro-formylation of (1b) and some native oils using homogeneous rhodium catalysts was applied for the synthesis of novel bio-based polyols [106]. Homogeneous rhodium complexes were also used for the hydro-amino methylation of alkenes [107]. The reaction was applied to (1a) and (1c) using various primary and secondary amines and resulted in amino functionalized branched fatty acid derivatives, such as (31). These compounds are useful intermediates for the preparation of surfactants and can be obtained in a simple one-pot reaction

[108]. Last but not least, a new method for the preparation of fat-derived linear polyesters that show good thermoplastic properties was developed using 10-undecenol (13c). Thus, (13c) and CO were copolymerized in the presence of tetra-carbonyl-cobalt as catalyst to give poly(12-hydroxydodecanoate) [109].
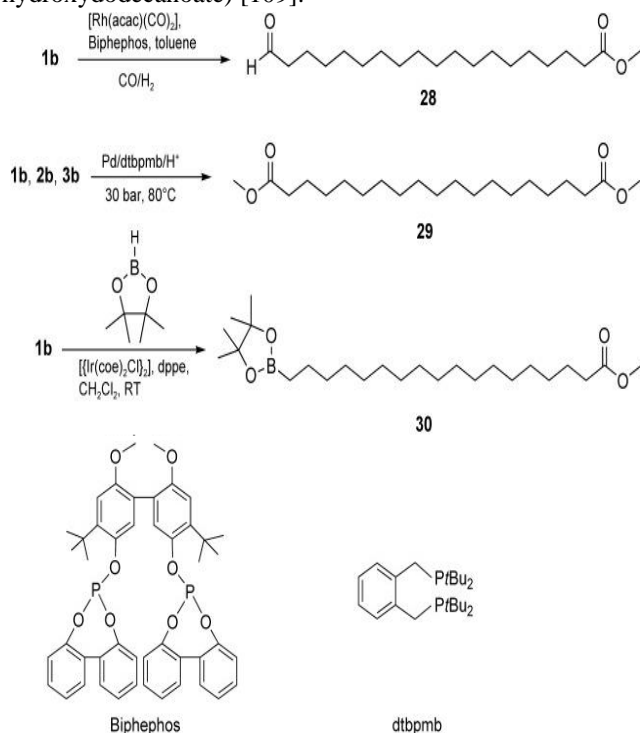

Fig.8 Hydro-formylation, methoxycarbonylation and hydroboration of methyl oleate (1b) by isomerization of internal and trapping of the terminal C=C double bond to give ω-functionalized fatty acid esters (28) [103], (29) [104] and (30) [105]. The synthesis of 29 is also possible using (2b) or (3b) as starting material

7.5 Assisted Transesterification Techniques

The aim of assisted transesterification technique is to reduce the reaction or operation time while achieving the highest possible yield. Assisted transesterification technique employs minimum level of slowly reacting reagent (such as low catalyst concentration sand lower alcohol to fat ratio), a part from benefits in terms of reaction time, thus reducing the overall cost of production. Two types of assisted transesterification techniques are commonly used in biodiesel production from vegetable oil, sand and animal fats. These include ultra-sound assisted technique and microwave assisted technique.

7.5.1 Ultrasound Assisted Technique

The ultrasound is the process of propagating an oscillating sound pressure wave with a frequency greater than the upper limit of the human hearing range. Ultrasound frequencies range between 20kHz and 10MHz with associated acoustic wavelengths in liquids of roughly100–0.15mm. Both mass transfer and chemical reactions lead to shorter reaction times and cheaper reagents utilization during application of ultrasound in chemical processing. The most important element of ultra-sonication is the formation,

growth and implosive collapse of bubbles in a liquid irradiated with sound or ultrasound in acoustic cavitation. The propagation of sound through the liquid causes expansion waves and compression waves which forms an aerosol of solvent, solute vapor and previously dissolved gases.

This phenomenon causes bubbles to grow and recompress due to high mass transfer rates arising from the formation of micro-emulsion through ultrasonic cavitation [8]. Few reports of ultrasound-assisted transesterification technique of AFWs appear in the literature compared to vegetable oils. Comparing conventional methods and ultrasound assisted transesterification of beef tallow to produce biodiesel, Teixeira *et al* [8] showed that the ultra-sonication process led to similar yields of alkyl esters as the conventional procedure with a significant decrease in reaction time. They concluded that methanolysis of triglycerides using ultrasonic irradiation was an efficient, time saving and economical method of producing biodiesel fuel but the effects of reaction parameters and ultrasound conditions were not reported properly.

7.5.2 Microwave Assisted Technique

Microwave radiations are found located in between infrared and radiowave region of electromagnetic spectrum. Microwaves have wavelengths ranging from 1mm-1m corresponding to the frequencies in between 0.3 and 300 GHz. The band frequencies in this region are occupied by telecommunication and microwave radar equipment. The household and industrial microwave ovens operate at a fixed frequency of 2.45 GHz, in order to avoid interference with these systems [110]. These studies have reported the feasibilities of using microwave assisted technique for the production of biodiesel from different varieties of vegetable oils but have only paid limited attention towards the use of AFWs as feedstocks. However, DaRós *et al*. [111] have reported the optimal conditions for the microwave assisted enzymatic synthesis of biodiesel from beef tallow. They noted the optimum conditions for conversion of beef tallow's actual fatty acids to ethanol molar ratio of 1:6, a temperature of 50°C and a reaction time of 8h. This represented a six-fold increase in the rate of the process carried out under conventional system of heating. They limit destructive effects to enzymes and delivered higher biodiesel production as compared to the conventional heating thereby concluding that microwave assisted process promises to be highly energy efficient and cost effective process.

7.6 Catalytic Cracking

It involves the catalytic transformation of non-edible oils or animal fats in the absence of air or oxygen to liquid products having fuel properties similar to diesel fuel. The pyrolyzed material includes considerable amounts of sulphur, moisture and sediments along with sufferable clinker and carbon residues [112]. A renewable source of raw material such as palm oil has been cracked at

atmospheric pressure, a reaction temperature of 450°C and a weight hourly space velocity of 2.5 h⁻¹ in order to produce biofuel in a fixed-bed micro-reactor. The reaction was carried out over micro-porous HZSM-5 zeolite, mesoporous MCM-41 and composite micro-mesoporous zeolite as catalysts in order to study the influence of catalyst pore size and acidity over biofuel production. The products obtained were gas, organic liquid product, water and coke. The organic liquid product was composed of hydrocarbons corresponding to gasoline, kerosene, and diesel boiling point range. The maximum conversion of palm oil up to 99 wt% and gasoline yield of 48 wt% was obtained with composite micro-mesoporous zeolite [112].

8. Kink Production

Lutton stated that if the fatty acids of a TAG differ in length by more than four carbons, it forms a triple chain-length structure. Triple chain-length packing is also observed in TAG containing a cis-unsaturated fatty acid because this causes a kink in the structure. Cis-unsaturated fatty acids do not mix in one layer with saturated fatty acids and triple chain-length crystals are formed. It should be noted that trans-unsaturated fatty acids incorporate into a crystal structure in the same way as the saturated fatty acids [113]. Oleic acid differs from stearic acid by containing one double bond. The presence of a double bond in oleic acid introduces a kink in the molecule. The interaction of the bent molecule with the membrane affects its equilibrium by hindering the diffusion of nutrients and metabolites through the membrane [114].

The effect observed with stearic acid larger than the presence of one double bond in oleic acid had an inhibitory effect. Linoleic acid has two double bonds; hence there are two kinks in the molecule. Subsequently, there is a more pronounced interaction with the cell membrane and the diffusion processes are massively hindered. The effect can also be completely inhibitory to the diffusion as observed here due to the presence of two kinks in the linoleic acid [115]. Stearic acid is a saturated fatty acid with an 18-carbon chain which is present in fermentation medium; it aligns with the fatty acid tails of the membrane. Oleic acid consists only of one double bond and it causes a kink in the molecule which hampers the diffusion of nutrient factors and metabolites through the membrane. Linoleic acid is a compound with a high degree of unsaturation which has two kinks that cause the inhibition of nutrient factors and thereby limit the synthesis of some products. The unsaturated fatty acids with two or more double bonds which are present in crude glycerol have a strong influence on the diffusion of the substrate all along the membrane [116].

Table 1 Chemical structures of different fatty acids

Examples of Unsaturated Fatty Acids				
Common Name	Chemical Structure	Δ^x	C:D	n−x
Myristoleic acid	$CH_3(CH_2)_3CH=CH(CH_2)_7COOH$	cis-Δ^9	14:1	n−5
Palmitoleic acid	$CH_3(CH_2)_5CH=CH(CH_2)_7COOH$	cis-Δ^9	16:1	n−7
Sapienic acid	$CH_3(CH_2)_7CH=CH(CH_2)_7COOH$	cis-Δ^6	16:1	n−10
Oleic acid	$CH_3(CH_2)_8CH=CH(CH_2)_4COOH$	cis-Δ^9	18:1	n−9
Elaidic acid	$CH_3(CH_2)_7CH=CH(CH_2)_7COOH$	trans-Δ^9	18:1	n−9
Vaccenic acid	$CH_3(CH_2)_5CH=CH(CH_2)_9COOH$	trans-Δ^{11}	18:1	n−7
Linoleic acid	$CH_3(CH_2)_4CH=CHCH_2CH=CH(CH_2)_7COOH$	cis,cis-Δ^9 and Δ^{12}	18:2	n−6
Linoelaidic acid	$CH_3(CH_2)_4CH=CHCH_2CH=CH(CH_2)_7COOH$	trans,trans-Δ^9 and Δ^{12}	18:2	n−6
α-Linolenic acid	$CH_3CH_2CH=CHCH_2CH=CHCH_2CH=CH(CH_2)_7COOH$	cis,cis,cis-Δ^9,Δ^{12} and Δ^{15}	18:3	n−3
Arachidonic acid	$CH_3(CH_2)_4CH=CHCH_2CH=CHCH_2CH=CHCH_2CH=CH(CH_2)_3COOH^{NIST}$	cis,cis,cis,cis-$\Delta^5\Delta^8,\Delta^{11}$ and Δ^{14}	20:4	n−6
Eicosapentaenoic acid	$CH_3CH_2CH=CHCH_2CH=CHCH_2CH=CHCH_2CH=CHCH_2CH=CH(CH_2)_3COOH$	cis,cis,cis,cis,cis-$\Delta^5,\Delta^8,\Delta^{11},\Delta^{14}$ and Δ^{17}	20:5	n−3
Erucic acid	$CH_3(CH_2)_7CH=CH(CH_2)_{11}COOH$	cis-Δ^{13}	22:1	n−9
Docosahexaenoic acid	$CH_3CH_2CH=CHCH_2CH=CHCH_2CH=CHCH_2CH=CHCH_2CH=CHCH_2CH=CH(CH_2)_2COOH$	cis,cis,cis,cis,cis,cis-$\Delta^4,\Delta^7,\Delta^{10},\Delta^{13},\Delta^{16}$ and Δ^{19}	22:6	n−3

Table 2 Saturated fatty acids

Common Name	Chemical Structure	C:D [15]
Caprylic acid	$CH_3(CH_2)_6COOH$	8:0
Capric acid	$CH_3(CH_2)_8COOH$	10:0
Lauric acid	$CH_3(CH_2)_{10}COOH$	12:0
Myristic acid	$CH_3(CH_2)_{12}COOH$	14:0
Palmitic acid	$CH_3(CH_2)_{14}COOH$	16:0
Stearic acid	$CH_3(CH_2)_{16}COOH$	18:0

Arachidic acid	$CH_3(CH_2)_{18}COOH$	20:0
Behenic acid	$CH_3(CH_2)_{20}COOH$	22:0
Lignoceric acid	$CH_3(CH_2)_{22}COOH$	24:0
Cerotic acid	$CH_3(CH_2)_{24}COOH$	26:0

Table 3 Physical properties of biodiesel [21]

| Common Name	Biodiesel
Common Chemical Name	Fatty Acid Methyl Ester (FAME)
Chemical Formula Range	C_{14}–C_{24} Methyl Esters
Kinematic Viscosity Range (mm²/s, at 313 K)	3.3–5.2
Density Range (kg/m³, at 288 K)	860–894
Boiling Point Range (K)	>475
Flash Point Range (K)	420–450
Distillation Range (K)	470–600
Vapor Pressure (mm Hg, at 295 K)	<5
Solubility in Water	Insoluble in Water
Physical Appearance	Light to Dark Yellow, Clear Liquid
Odor	Light Musty/Soapy Odour
Biodegradability	More Biodegradable than Petroleum Diesel
Reactivity	Stable but Avoid Strong Oxidizing Agents
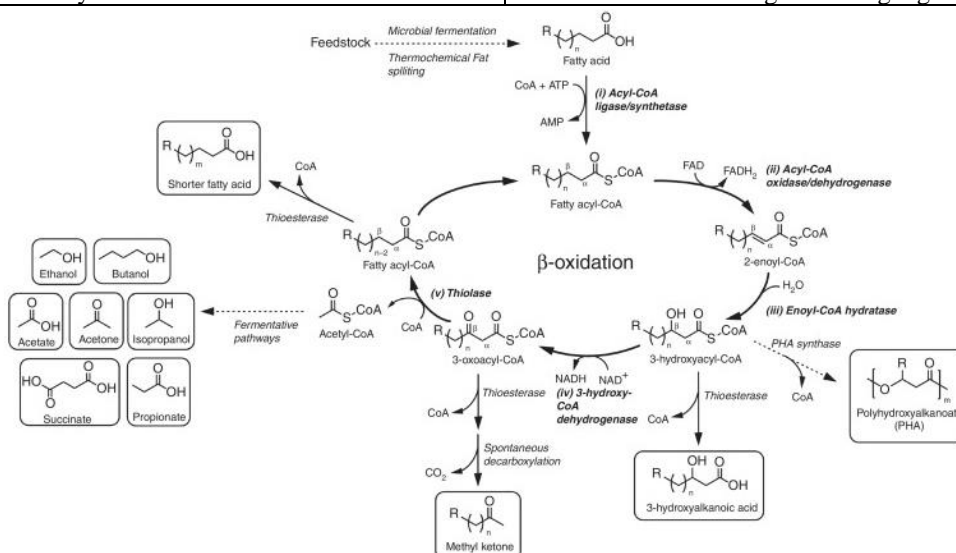
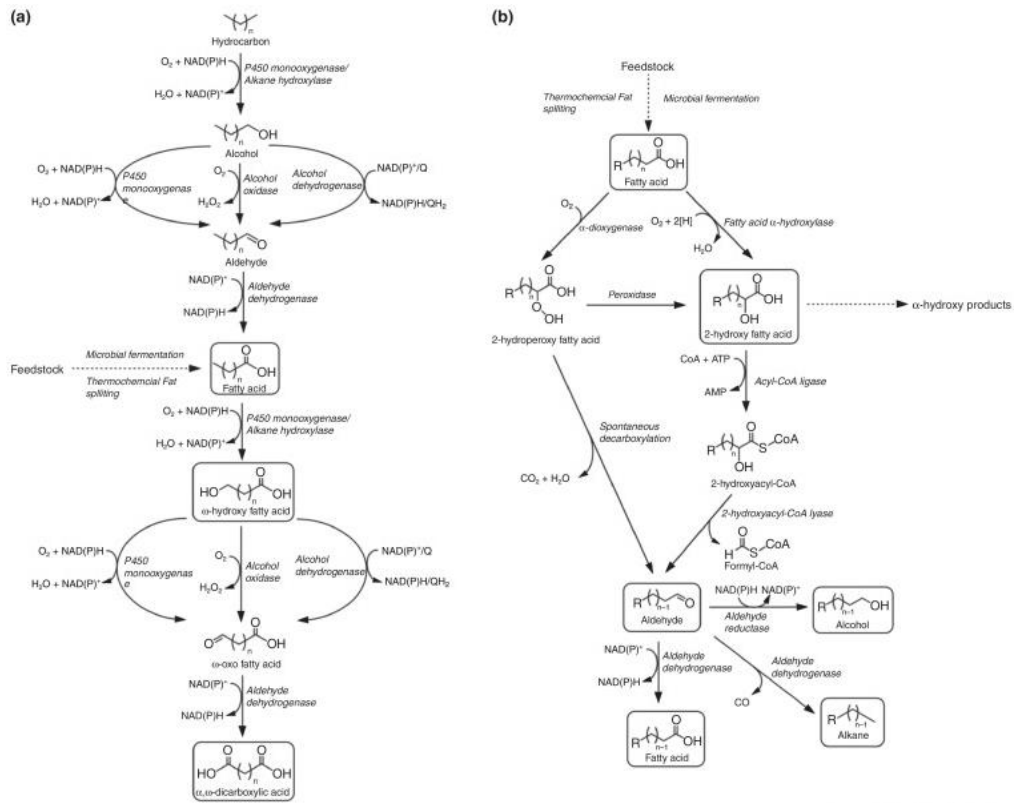Fig.3 Biochemical production from fatty acids via β-oxidation pathway

Fig.4 Biochemical production via (a) ω-oxidation pathway, a minor fatty acid metabolism route found in yeast and plants capable of utilizing both alkanes and long-chain fatty acids as sole carbon source and (b) α-oxidation pathway, an important route for the degradation of 3-methyl-branched fatty acids that shortens fatty acids by one carbon. Solid and dashed line arrows indicate single and multiple reactions, respectively. Boxed products are those whose synthesis has been demonstrated from ω- and α-oxidation pathways.
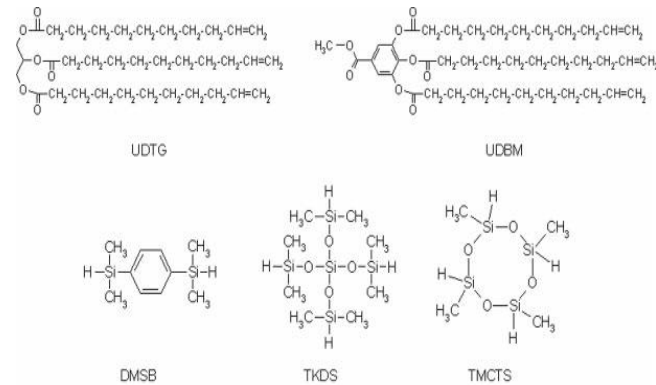

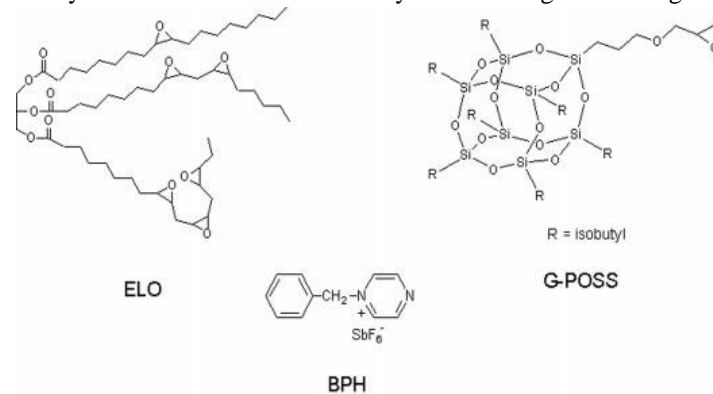Fig.5 Terminal unsaturated fatty acid derivatives used in the synthesis of organic – inorganic hybrid materials

Fig.6 Epoxidized linseed oil (ELO), polyhedral oligomeric silsesquioxane (G-Poss) and catalyst (BPH) used in the synthesis of bio nanocomposites

9. Future Perspective

Biodiesel is completely biodegradable, potentially renewable, environmentally benign, highly energy-efficient and a substitute of conventional fuel which can fulfil the needs of energy security without sacrificing engine's operational performance thereby providing a feasible solution to twin crisis of extensive environmental degradation and rapid fossil fuel depletion. Individual characteristic of fatty esters that forms biodiesel usually determines the aggregate properties of biodiesel fuel. At the same time, some important properties of different fatty esters are also determined by structural variations of essential fatty acids and alcohol moieties which comprise a fatty ester. Furthermore, a thorough understanding of the relationship between structural variations and physical characteristics in fatty acid esters is of great importance while choosing vegetable oils that can give the desired quality of produced biodiesel. By having accurate knowledge about the effects of molecular structure on physiochemical properties determined, the chemical composition of the oils and alcohol used can both be selected to give the optimal performance. In this review article, the relationship between physical properties and chemical structure of vegetable oil esters is reviewed and engineering fatty acid profiles to optimize biodiesel fuel characteristics is highlighted in order to ensure the production of high-quality biodiesel and sustainable future.

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