

## Review

# Biodegradation of vegetable oils: A review

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**Vegetable oils have traditionally been applied in food uses, but recent trends suggest their economic usefulness as industrial fluids. Increasing crude oil prices and emphasis on the development of renewable, environmentally friendly industrial fluids have brought vegetable oils to a place of prominence. Biodegradability provides an indication of the persistence of any particular substance in the environment and is the yardstick for assessing the eco friendliness of substances. The superior biodegradation of vegetable oils in comparison with mineral based oils has been demonstrated severally, leaving scientists with the lone challenge of finding economic and safe means to improve their working efficiency in terms of their poor oxidative stability and high pour points.**

**Keywords:** Biodegradability, oxidative stability, environment, eco friendliness, renewable.

## INTRODUCTION

The use of fats and oils by man dates back to antiquity. Their chemical composition and specific properties have allowed them to find use as foods, fuels and lubricants. Their sources are numerous, encompassing vegetable, animal, and marine sources. As it is with all matter, their usefulness to man is determined by their chemical nature; and all fats and oils have certain characteristics in common.

Fats and oils are naturally occurring substances which consist predominantly of mixtures of fatty acid esters of the trihydroxy alcohol or glycerol (Nwobi et al., 2006). Different fats and oils come about due to the fact that there are numerous fatty acids of various kinds and these can be combined in an infinite number of ways on the hydroxyl centers of glycerol. Moreover, the physical properties of fats and oils are dependent on the nature of fatty acids involved in the ester. Hence the traditional distinction of fats as solids and oils as liquids arises from the fact that due to the different chemical structures of the different fatty acids combined in the esters, the bonding forces in existence vary in strength resulting in different melting points. These differences are manifested in different chain lengths, the presence or otherwise of unsaturation as well as geometric conformations.

The present emphasis on conservation and environmental friendliness has brought about renewed interest in the use of these "natural oils" for non edible purposes. Their established superiority in terms of biodegradability

(Charley, 1970), when compared with mineral oils, as well as the fact that they are renewable and generally non toxic has focused attention on technologies that would enhance their usefulness as bio fuels and industrial lubricants (Honary, 2004). There are also concerns as to what to expect in case of vegetable oil spills. This is the subject of some researchers (Zhengkai et al., 2001, Li et al., 2005) including the process of remediating such spills (Wincele et al., 2004). This paper examines the extent of work that has been carried out on the biodegradability of vegetable oils.

## VEGETABLE OILS - GENERAL PROPERTIES

Vegetable oils are obtained from oil containing seeds, fruits, or nuts by different pressing methods, solvent extraction or a combination of these (Bennion, 1995). Crude oils obtained are subjected to a number of refining processes, both physical and chemical. These are detailed in various texts and articles (Bennion, 1995; Fennema, 1985).

There are numerous vegetable oils derived from various sources. These include the popular vegetable oils: the foremost oilseed oils - soybean, cottonseed, pea-nuts and sunflower oils; and others such as palm oil, palm kernel oil, coconut oil, castor oil, rapeseed oil and others. They also include the less commonly known oils such as rice bran oil, tiger nut oil, patua oil, koème oil, niger seed oil, piriroma oil and numerous others. Their yields, different compositions and by extension their physical and chemical properties determine their usefulness in various applications aside edible uses.

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Cottonseed oil was developed over a century ago as a byproduct of the cotton industry (Bennion, 1995). Its processing includes the use of hydraulic pressing, screw pressing and solvent extraction (Wolf, 1978). It is classified as a polyunsaturated oil, with palmitic acid consisting 20 – 25%, stearic acid 2 – 7 %, oleic acid 18 – 30% and linoleic acid 40 – 55% (Fennema, 1985). Its primary uses are food related – as salad oil, for frying, for margarine manufacture and for manufacturing shortenings used in cakes and biscuits.

Palm oil, olive oil, cottonseed oil, peanut oil, and sunflower oil amongst others are classed as Oleic – Linoleic acid oils seeing that they contain a relatively high proportion of unsaturated fatty acids, such as the monounsaturated oleic acid and the polyunsaturated linoleic acid (Dunn, 2005), (Gertz et al., 2000). They are characterized by a high ratio of polyunsaturated fatty acids to saturated fatty acids. They thus, have relatively low melting points and are liquid at room temperature. Iodine values, saponification values, specific compositions and melting points in addition to other physical properties have been determined and are widely available in the literature. (Williams, 1966; Oyedeji and Oderinde, 2006).

Other oils fall under various classes such as the erucic acid oils which are like the oleic linoleic acid oils except that their predominant unsaturated fatty acid is erucic acid ( $C_{22}$ ). Rapeseed and mustard seed oil are important oils in this class. Canola oil is a type of rapeseed oil with reduced erucic acid content (Applewhite, 1978). It is a stable oil used in salad dressings, margarine and shortenings. Soybean oil is an important oil with numerous increasing applications in the modern day world. It is classed as a linolenic acid oil since it contains the more highly unsaturated linolenic acid. Other oils include castor oil (a hydroxy-acid oil) which contains glycerides of ricinoleic acid (Erhan et al, 2006). Also worthy of note is that coconut oil, which unlike most vegetable oils is solid at room temperature due to its high proportion of saturated fatty acids (92%) particularly lauric acid. Due to its almost homogenous composition, coconut oil has a fairly sharp melting point, unlike other fats and oils which melt over a range (Bennion, 1995). Oils from several sources are the subject of recent researches. Examples include corn oil (Sanchez, 2008); *camelina sativa* oil (Abramovic and Abram, 2005); Palmarosa oil (Mohanani et al, 2007) and Cineole oil (Rodriguez, 2006).

## INDUSTRIAL USES OF VEGETABLE OILS

The application of vegetable oils and animal fats for industrial purposes and specifically lubrication has been in practice for many years. Inherent disadvantages and the availability of inexpensive options have however brought about low utilization of vegetable oils for industrial lubrication (Honary, 2004). When applied in the science of tribology, vegetable oils fall under the class known as fixed oils (Gunther, 1971). They are so named because

they do not volatilize without decomposing. Prior to recent developments, vegetable and animal oils in tribology have functioned mainly as additives to mineral lubricating oil formulations, although in some cases they are applied exclusively, or in blends.

For instance, tallow (acidless) has been used as an emulsifying agent for steam cylinder oils, while castor, peanut and rapeseed oils have been used in blends with mineral oils to improve lubrication performance. Palm oil has been used in isolation as a fluxing dip in the tin plating of steel, while olive oil has applications as a yarn lubricant (Gunther, 1971).

Reasons for the use of vegetable oils in the science of lubrication abound. Their superior lubricity and emulsifying characteristics increase their desirability as additives to the cheaper but less effective mineral oil based lubricants. Their superior lubricity in industrial and machinery lubrication sometimes even necessitates the addition of friction materials in tractor transmissions in order to reduce clutch slippage (Honary, 2004).

Other advantages that encourage the use of vegetable oils include their relatively low viscosity-temperature variation; that is their high viscosity indices, which are about twice those of mineral oils (Honary, 2004).

Additionally, they have low volatilities as manifested by their high flash points. (Honary, 2004) Significantly, they are environmentally friendly: renewable, non toxic and biodegradable (Howell, 2007). In summary, engine lubricants formulated from vegetable oils have the following advantages deriving from the base stock chemistry:

- i. Higher Lubricity resulting in lower friction losses, and hence more power and better fuel economy.
- ii. Lower volatility resulting in decreased exhaust emissions.
- iii. Higher viscosity indices.
- iv. Higher shear stability.
- v. Higher detergency eliminating the need for detergent additives.
- vi. Higher dispersancy.
- vii. Rapid biodegradation and hence decreased environmental / toxicological hazards. (Erhan and Perez, 2002).

In a comparison of palm oil and mineral based lubricants, palm oil based lubricants were found to be more effective in reducing the hydrocarbon and carbon monoxide emission levels, among other things (Masjuki et al., 1999).

Vegetable oils have also been identified as having a lot of potential as alternative diesel engine fuels (Kayisoglu et al., 2006). This is supported by an interest in a cleaner environment, as well as the increasing cost of mineral deposit based energy (Howell, 2007). Based on availability to meet demand, soybean, peanut and sunflower oils have been identified as the most promising fuel sources (Kayisoglu et al., 2006). When used as a fuel, the term “biodiesel” is applicable.

Biodiesel is defined strictly as “...the mono alkyl ester

(usually methyl ester) of renewable fats and oils...” (Howell, 2007). It consists primarily of long chain fatty acid esters, produced by the transesterification reaction of vegetable oils with short chain alcohols. Distinct advantages of biodiesel include a high flash point of over 100°C, excellent lubricity, a BTU content comparable to that of petro diesel, and virtually no sulfur or aromatic content. Above all, biodiesel is non-toxic and biodegradable (Howell, 2007).

Results from investigating performance of vegetable oils in blends with diesel indicate that blending up to 25% biodiesel (sunflower) with mineral diesel has no adverse effect on performance. (Kayisoglu et al., 2006).

Vegetable oils have also been applied as transformer coolant oils and have been found to conform to all industry standards with performances and cost profiles comparable to the conventional mineral oils applied in transformer cooling (ABB Inc., 2002; McShane, 2002). Transformer oil products have been produced from soybean oils as well as castor oils (Honary, 2004).

The major disadvantage militating against the use of vegetable oils in industrial applications is its oxidative stability. This factor has been most researched (Bahrudin et al., 2008; Nedyalka, 2001) particular as biodiesel (Kapilani et al., 2009). Several proposals on how to tackle this problem have been investigated (Anderson, 2007). Ways of evaluating the oxidative stability of oils have occupied several authors (Tan et al., 2001; International organization for Standards, 1996; Gertz et al., 2000). Several oils have been proposed for industrial uses primarily due to their recognized high oxidative stability compared to other oils (Brimberg and Afaf, 1994). Ghazalia et al. (2006) investigated the effect of light on the stability of palm olein. Others have investigated the stability of these oils when anti oxidants are added (Nedyalka, 2001; Gordon and Lenka, 1995; Schober and Mittelbach, 2004; Ruger et al., 2002).

## BIODEGRADATION AND ITS MEASUREMENT

### Biodegradation

Is the process by which organic substances are broken down by the enzymes produced by living organisms. The term is often used in relation to ecology, waste management and environmental remediation (bioremediation). Organic material can be degraded aerobically, with oxygen or anaerobically, without oxygen. A term related to biodegradation is biomineralisation, in which organic matter is converted into minerals (Diaz, 2008).

By definition, biodegradation is the chemical transformation of a substance caused by organisms or their enzymes. There are two major types of biodegradation – Primary Biodegradation, which refers to the modification of a substance by microorganisms such that a change is caused in some specific measurable property of the substance (US Army Corps of Engineers, 1999). When the term primary biodegradation is used it refers to

minimal transformation that alters the physical characteristics of a compound while leaving the molecule largely intact. Intermediary metabolites produced may however be more toxic than the original substrate (wiserenewables.com, 2006). Thus mineralization is the true aim. When this happens it is referred to as Ultimate or Complete Biodegradation; which is the degradation achieved when a substance is totally utilized by microorganisms resulting in the production of carbon dioxide, methane, water, mineral salts, and new microbial cellular constituents (US Army Corps of Engineers, 1999).

Various methods exist for the testing of biodegradability of substances. Biodegradability is assessed by following certain parameters which are considered to be indicative of the consumption of the test substance by microorganisms, or the production of simple basic compounds which indicate the mineralization of the test substance. Hence there are various biodegradability testing methods which measure the amount of carbon dioxide (or methane, for anaerobic cases) produced during a specified period; there are those which measure the loss of dissolved organic carbon for substances which are water soluble; those that measure the loss of hydrocarbon infrared bands (bioblend, 2008); and there are yet others which measure the uptake of oxygen by the activities of microorganisms (the Biochemical Oxygen Demand, BOD).

However, when the reference is specifically to lubricants, there are 2 major methods of biodegradability testing, and these are outlined in brief below:

1. ASTM test method D 5864 determines lubricant biodegradation. This test determines the rate and extent of aerobic aquatic biodegradation of lubricants when exposed to an inoculum under laboratory conditions. The inoculum may be the activated sewage-sludge from a domestic sewage-treatment plant, or it may be derived from soil or natural surface waters, or any combination of the three sources. The degree of biodegradability is measured by calculating the rate of conversion of the lubricant to CO<sub>2</sub>. A lubricant, hydraulic fluid or grease is classified as readily biodegradable when 60% or more of the test material carbon is converted to CO<sub>2</sub> in 28 days, as determined using this test method.
2. The most established test methods used by the lubricant industry for evaluating the biodegradability of their products are Method CEC-L-33-A-94 developed by the Coordinating European Council (CEC); Method OEC D 301B, the Modified Sturm Test, developed by the Organization for Economic Cooperation and Development (OECD); and Method EPA 560/6-82-003, number CG-2000, the Shake Flask Test, adapted by the U.S. Environmental Protection Agency (EPA). These tests also determine the rate and extent of aerobic aquatic biodegradation under laboratory conditions. The Modified Sturm Test and Shake Flask Test also calculate the rate of conversion of the lubricant to CO<sub>2</sub>. The CEC test measures the disappearance of the lubricant by analyzing test

material at various incubation times through infrared spectroscopy. Laboratory tests have shown that the degradation rates may vary widely among the various test methods indicated above (US Army Corps of Engineers, 1999).

Biodegradability tests based on the CEC method described above has certain trends which indicate that mineral oils, along with alkylated benzenes and polyalkylene glycols among others, generally have poor biodegradability: between 0 – 40%. Specifically, mineral oil biodegradability varies from 15 – 35% as conducted by the CEC biodegradability test (Wiserenewables, 2006).

## BIODEGRADATION CHARACTERISTICS OF VEGETABLE OILS

The notion of biodegradability conveys the meaning of the breaking down of complex, and possibly toxic material into simple and common forms, in which the elements carbon, hydrogen and oxygen exist or are simply associated. Whenever any substance is placed in the environment, it begins to undergo degradation due to the action of relevant substrate utilizing microorganisms. Every substance, irrespective of its complexity and toxicity is subject to this process. When used in the present context, it is referenced to a time frame. That is, for a given substance to be referred to as biodegradable, a specific time limit must be used as a reference (wiserenewables.com, 2006).

According to the California advertising statute, a manufacturer cannot claim his product is biodegradable unless it has the proven capability to decompose in the most common environment where the product may be disposed within three years through natural biological processes into nontoxic carbonaceous soil, water, carbon dioxide or methane (wiserenewables.com, 2006). Biodegradation is important for the natural and industrial cycling of environmental chemicals. Government regulators and industries are always interested in the fate of industrial chemicals and waste products when discarded to the environment, either intentionally or unintentionally. This is because toxic substances in the environment eventually affect the ecosystem and humans adversely (Wackett et al., 1999).

Lipids (fats, oils and greases) form a major part of domestic and industrial waste – hence they contribute their fair share towards environmental pollution. Sources include waste water from the edible oil refinery, slaughter houses and dairy products. These waste products are responsible for clogging sewer networks and unsettling the balance of waste water treatment plants (Saifudin et al., 2006).

The first step in the degradation of vegetable based oils is the enzyme-catalyzed cleavage of the ester bond to fatty acids. The enzymes which catalyze this biodegradation reaction include esterases and lipases and these are synthesized by a wide range of microorganisms

(Broekhuizen et al., 2003). "Lipases are hydrophobic proteins that catalyze the cleavage of carboxyl ester bonds in tri-, di-, and monoacylglycerols (the major constituents of animal, plant and microbial fats and oils)" (Saifudin et al., 2006). Due to their degradative effects, lipases are applied in remediation efforts to degrade lipid rich waste. Drawbacks however include thermal instability of the enzyme and the high cost of the single use of the enzyme (Saifudin et al., 2006). Following the first step of degradation, both saturated and unsaturated fatty acids biodegrade via a process of  $\beta$ -oxidation.

Indeed, the biodegradation of materials also is dependent on the nature of the environment, as documented by Kaakinen et al. (2007) where pH adjustments of soils, for instance was found to have a noticeable effect on the biodegradation of certain compounds (Kaakinen et al., 2007). Microbial communities are also prone to adapt to a substrate when it is a regular contaminant that is, increases in rates of transformation of hydrocarbons associated with oil contaminated environments has been identified and documented (Khalida et al., 2006). Modified strains of bacteria emerge which are characterized by the ability to degrade the substances which induce the modification (Mansee et al., 2004; Abrashev et al., 2002). However, biodegradability primarily is a function of the chemical nature of the substance in question.

That natural and vegetable oils are biodegradable is not in doubt. "Vegetable oils and synthetic esters have a much better biodegradation capacity than mineral oil under aerobic as well as anaerobic conditions" (Broekhuizen et al, 2003). Tests carried out severally indicate that vegetable oils undergo about 70-100% biodegradation in a period of 28 days.

In a specific comparative study carried out by Mecurio et al. (2003), Vegetable-Derived Lubricants were established to be in fact more biodegradable than comparable Mineral-Derived Lubricants in the presence of tropical mangrove or coral reef microbial communities (Mecurio et al., 2003); while some others have examined the biodegradation of vegetable oils under spill conditions (Pereira et al., 1998; Campo et al., 2007; Al-Darbi et al., 2005). Several authors have examined the biodegradability and oxidative stability of industrial fluids obtained from vegetable oils. These include; as methyl esters (Demirba, 2009); as hydraulic fluids (Abdalla and Patel, 2006; Petyuk et al., 2004); an lubricant (Fernando and Hanna, 2002) and as dielectric fluid (McShane, 2002).

## Conclusion

The biodegradability of vegetable oils is the strongest point in the case for their industrial use. In the light of more concerns about the environmental impact of the use of industrial fuels and lubricants, they offer in theory the most plausible solution to the issue of obtaining renewable and eco friendly lubricants and fuels. With established biodegradabilities in the range of 70 – 100%,

their eco friendliness is not in doubt. The challenge is the improvement of their performance in industrial uses; specifically with reference to their oxidative stabilities and pour points which in general leave much to be desired. Improvements are inevitable and are already being recorded with increasing research directed in these areas.

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