

# CHEMICAL PROCESS INVOLVED IN THE CONVERSION OF VEGETABLE/PLANT SEED OIL INTO BIODIESEL – A REVIEW

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## ABSTRACT

*It is well known that the day to day life of human beings greatly depends on the petroleum fossil fuels for their transportation. The petroleum fuels besides transportation find vast application in helping human life. India is not rich in the source of recovering petroleum products and hence it depends on other countries for the import. The exhaust emissions released from the engines during the combustion of petroleum fuels are harmful for both human and environment. India being the importer of petroleum fuels on the other hand it is very rich in agricultural resources and also the exporter of agricultural products to other countries. Being rich in agricultural products, we can derive biodiesels easily from the vegetable/plant seeds. The only disadvantage of biodiesel is its high viscosity and ignition temperature; the both can be improved by employing it to suitable chemical process.*

**Keywords:** *biodiesel, viscosity, ignition temperature, chemical process.*

## 1. INTRODUCTION

The use of neat vegetable oils as a fuel to run diesel engine is quite difficult due to their high viscosity than the petroleum fossil fuels (Anjana srivastava et al). The Vegetable oils can be employed to suitable chemical process to reduce its viscosity and to improve its cetane number. The most commonly used chemical processes are transesterification, thermal cracking or pyrolysis and microemulsion. Out of these methods, transesterification is the most conventional and simplest way to derive biodiesel from neat vegetable oils. Transesterification is a chemical reaction between triglyceride and alcohol in presence of a suitable catalyst.

## 2. LITERATURE REVIEW

The conversion of triglycerides consists of a sequence of three consecutive reversible reactions in which initially the triglyceride is converted into diglyceride, the diglyceride is converted into monoglyceride followed by the conversion of monoglycerides to glycerol (L. Nabilah aminah et al June 2013). Theoretically the transesterification reaction is stated as an equilibrium reaction in which a larger amount of methanol was used to shift the reaction equilibrium to the right side and produce more methyl esters, the proposed product (A.V. Krishna Reddy et al 2010). It was conducted as early as 1853 by scientists E. Duffy and J. Patrick, many years before the first diesel engine

became functional (F. Ma et al 1999). During the year 1940 this process was developed in the production of soap to improve the separation of glycerin (Bradshaw, G.B et al 1942). Transesterification often called as alcoholysis is the displacement of alcohol from an ester by another alcohol. The process of transesterification is similar to hydrolysis the only difference is that an alcohol is used instead of water. This has been widely used to reduce the viscosity of the triglycerides (A.K. Azad June 2012). The methanol to oil ratio has a great influence in the yield of methyl ester. It is found that during the transesterification reaction the increase in methanol to oil ratio from 0.96:1 to 8.10:1, increases the yield of methyl ester and decreases the Saponification value. In contrary it is also found that the yield of methyl ester starts to decrease when the molar ratio is increased further beyond 8.10:1. The stoichiometric ratio of alcohol and triglyceride in the transesterification reaction requires three mol of alcohol per one mol of triglyceride to yield three moles of fatty esters and one mol of glycerol (Molla Asmare et al February 20 2014). The process of transesterification can be catalyzed by the presence of alkalis, acids or enzymes. The Alkalis include sodium hydroxide, potassium hydroxide, and alkoxides such as sodium methoxide, sodium ethoxide, and sodium propoxide and sodium butoxide. The acids such as sulphuric acid, sulfonic acids and hydrochloric acid are used as acidic catalysts. Transesterification process can be employed for the biodiesel production from the vegetable oils only if the free fatty acid composition present in the raw vegetable oil is less than 4%. For the free fatty acid composition less than 4%, the transesterification process is carried by single phase method. If the percentage of FFA present in the raw vegetable oil is more than 4% then we have to choose the two phase method of transesterification (Mohan T Raj et al 2012). The two phase transesterification method called acid catalyzed transesterification involves the use triglycerides with alcohol but instead of base an acid is used in this process. The most commonly used acid is sulfuric acid (Freedman B et al E 1986). The catalytic supercritical methanol transesterification is performed in the autoclave in the presence of 1-5% NaOH as catalyst at a reaction temperature of 520 K. In the catalytic supercritical methanol transesterification method, the yield of conversion rises to 60-90% for the first 1 minute (Demirbas A. 2002). In the transesterification of peanut oil, the 6:1 molar ratio of methanol to vegetable oil liberated significantly more glycerol than the 3:1 molar ratio. The investigators also found that the yield of glycerol increases from 77% to 95% as the sodium hydroxide catalyst increased from 0.2% to 0.8% at the 6:1 molar ratio (Lehman et al). In the separation of esters and glycerol after the successful completion of transesterification process, the recovered glycerol contains soap, catalyst, methanol and other impurities. To neutralize the catalyst and split the soap strong hydrochloric acid (HCl) was added to the crude glycerin (Asadullah Al Galib et al March 2009). In general the yield of biodiesel increases with the increase in amount of catalyst up to 1.22% and then decreases with further increase in the amount of catalyst. At lower concentration of catalyst, the rate of reaction is incomplete resulting in the lower yield, whereas at the higher concentration of catalyst, the rate of yield decreases due to the enhancement of Saponification reaction causing triglyceride to form soap faster than ester. The formation of soap in presence of high amount of catalyst increases the viscosity of the reactants and thus lowers the rate of biodiesel production (Dorado et al. 2004 and Encinar et al. 2005). The recovered biodiesel is then washed with the distilled water until the pH of the washed distilled water becomes equal to the pH of standard distilled water. After washing the biodiesel was then heated to about 110°C, to remove the moisture content (Rashmi Gadwal et al 2014).

### 3. TYPES OF CHEMICAL PROCESS INVOLVED IN THE CONVERSION

In general the chemical processes employed in the conversion of triglycerides into monoglycerides are as follows: transesterification, thermal cracking (or) pyrolysis, micro-emulsion and thermal liquefaction. Out of the above stated processes, transesterification is simplest, oldest and involves less cost and skill in the conversion.

#### 3.1. TRANSESTERIFICATION

It is the most widely used traditional and conventional chemical process used for the recovery of biodiesel from the biological matters especially plant seed, vegetable oils and fats. In general the process of transesterification is defined as the chemical process in which a triglyceride reacts with an alcohol in presence of a suitable catalyst at suitable proportion to produce esters and glycerol as the by-product. Some of the alcohols that are commonly used in the process of transesterification are ethanol/methanol/propanol/butanol and the most widely used catalysts are KOH/NaOH. The process of transesterification results in the formation of two distinct layers namely ester and glycerol. The glycerol being the byproduct settles down and is separated by gravity separation method. If the process of transesterification involves the use of base as catalyst then it is termed as base catalyzed transesterification. If the oil contains more than 1% of free fatty acid then acid catalyzed transesterification process is utilized in the conversion of triglyceride into ester and glycerol by reacting with an alcohol in presence of acid catalyst. In general

the Sulphuric acid, phosphoric acid and sulphonic acid are the most commonly used acid catalysts. The acid catalyzed transesterification is quite slow and the reaction temperature is maintained at a rate of 100°C. The water contaminants formed during the reaction of acid catalyzed transesterification should be removed immediately to avoid the formation of carboxylic acid which reduces the percentage yield of alkyl esters. If the process of transesterification is carried in the presence of an alkaline catalyst such as alkaline metal alkoxides and hydroxides as well as sodium or potassium carbonates then it is said to be alkaline catalyzed transesterification process. If the process of transesterification is carried in presence of lipase enzyme as a catalyst to form esters (biodiesel) and glycerol, then it is said to be lipase catalyzed transesterification process. The super critical transesterification process is time saving (involves only 2-4 minutes) and does not encounter problems associated in phase separation of vegetable oils as like the conventional transesterification process. Since the process of super critical transesterification is carried with the absence of catalyst, the purification of biodiesel is very easy.

### **3.2. THERMAL CRACKING OR PYROLYSIS**

Thermal cracking also called pyrolysis is defined as the process of converting complex compound into simpler compound by the application of heat. In general the process of pyrolysis reduces the viscosity and improves the flow characteristics of the fuel. The end product of pyrolysis includes alkanes, alkenes and carboxylic acids. The process of pyrolysis is simpler, free from pollution and carried in the absence of air. Thermal cracking or pyrolysis is defined as the thermal decomposition or breaking of complex structure into its simpler structure with the application of heat in the absence of air. During the process of pyrolysis the reaction temperature is maintained about 250 - 350°C. The biodiesel obtained by this method contains little and acceptable amount of sulfur, water and sediments. Depending upon the operating conditions, pyrolysis can be divided into pyrolysis/slow pyrolysis, fast pyrolysis and flash pyrolysis. Slow pyrolysis is time consuming process and results in the formation of other liquid; this makes this process not suitable for the quality biodiesel production. Fast pyrolysis is time saving process and the reaction temperature is maintained at 400°C to 600°C. The end product of fast pyrolysis includes 70-75% of oil product, 15-25% of solid phase and 10-20% of gaseous phase. The flash pyrolysis is the efficient chemical process for the recovery of oil from the feed stocks resulting in 75% of oil recovery. In flash pyrolysis the reaction temperature is maintained as high as 450°C to 1000°C. Flash pyrolysis lacks its importance because of less thermal stability, increase of oil viscosity after the process due to alkali concentration in the oil.

### **3.3. MICROEMULSION**

Microemulsion is the chemical process that is involved in the recovery of biodiesel with the use of alcohol as additive. The most commonly used additives in this process are ethanol, methanol and propanol. The additives are used for lowering the viscosity of vegetable oils, while the higher alcohols are used as surfactants and alkyl nitrates are used as cetane improvers. The products of microemulsion possess good spray characteristics and the disadvantage is that the long term use of oils recovered by microemulsion results in the sticking of injector needle and in incomplete combustion. In general microemulsion involves the use of vegetable oil, alcohol to increase the volatile property of vegetable oil, a surfactant and alkyl nitrate as cetane improver.

### **3.4. THERMAL LIQUEFACTION**

Thermal liquefaction process results in the production of liquid and some amounts of gaseous components at temperature range of 250–350°C and pressure range of 700– 3000 psi. The process of thermal liquefaction is carried in the presence of alkali metal salts as catalyst with the supplement of CO and H<sub>2</sub> to facilitate the reaction. The catalysts used in this process tends to hydrolyze the cellulose, hemicelluloses, and lignin macromolecules into smaller micellar-like fragments, which are further degraded to smaller compounds via dehydration, dehydrogenation, deoxygenation, and decarboxylation reactions. Thermal liquefaction can provide liquid fuels in line with petroleum products along with several high value chemicals; however, recent trends in biomass thermo-chemical conversion, liquefaction, could not be successful at commercial scale.

## **4. CONCLUSION**

The fast pyrolysis is found to be optimum as it does not involve the use of alcohol and more over it is time saving process. Followed by fast pyrolysis, the process of transesterification is found to be optimum as it requires only less

skill, simpler setup and involves less cost in deriving esters. The disadvantage of transesterification is that it is time consuming and it involves the use of methanol. The long term use of oil recovered by the process of microemulsion results in the sticking of injector needle and it also results in the incomplete combustion. The process of fast pyrolysis is quite suitable as it is time saving, involving operating temperature ranging 400<sup>0</sup>C to 600<sup>0</sup>C and resulting in the end products about 70-75% of oil product, 15-25% of solid phase and 10-20% of gaseous phase.

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