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THE EFFECT OF CATALYST PHASE ON BIODIESEL PRODUCTION (A REVIEW)

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ABSTRACT

Biodiesel is the monoalkyl esters of long chain fatty acids derived from a renewable lipid feedstock such as vegetable oil or animal fat. Biodiesel production is done by transesterification of the vegetable oil or animal fat. Transesterification reaction of vegetable oil or animal fat with alcohol is an equilibrium reaction and therefore requires the use of a catalyst to shift equilibrium to the right. Catalyst used in transesterification reactions can either be homogeneous or heterogeneous. In this paper the effects of the type of catalyst used on the quality and cost of biodiesel is reviewed. Advantages and disadvantages of using either a homogeneous or heterogeneous catalyst in biodiesel production are also highlighted.

INTRODUCTION

Biodiesel is derived from a varied range of vegetable oils (edible and non-edible), animal fats, used frying oil and waste cooking oil (Sharma et al 2008). Biodiesel is an environmentally viable fuel. It is Biodegradable and does not contribute to global warming. The biodegradable nature of Biodiesel is shown when it was observed that 90-98% of Biodiesel is mineralized in 21-28 days under aerobic as well as anaerobic conditions (Pasqualino et al 2006). Biodiesel increases the biodegradability of crude oil by means of cometabolism.

Biodiesel can be burned in internal combustion engines. It is used in Modern diesel vehicles with little or no modification to the engine(www.biodiesel.org, info@nbb.org). The major benefit of its use as fuel is the reduction in net carbon dioxide emissions, since all the carbon emitted was recently captured during the growing phase of the plant from which the biofuel was made(Das, 2008). The use of biodiesel also reduces emission of carbon monoxide and other pollutants such as Sulphur IV Oxide and unburned Hydrocarbon by 20 to 40% (Encyclopedia, 2008).

Research work on the conversion of Biodiesel into electricity utilizing fuel cells is also an area of very active work. Vegetable oils are renewable and potentially inexhaustible source of energy with an energetic content close to diesel fuel. Historically, it is believed that Rudolf Diesel himself started research with respect to the use of vegetable oil as fuel for diesel engines. In the following decades, the studies became more systematic and now much is known about its use as fuel, although direct use of vegetable oils in fuel engines is problematic. This is due to their high viscosity (about 11 to 17 times higher than diesel fuel) and low volatility, they do not burn completely and form deposits in the fuel injector of diesel engines (Murugesan et al, 2009). Furthermore, acrolein (a highly toxic substance) is formed through thermal decomposition of glycerol.

Enumerated below are ways to reduce the high viscosity of vegetable oils. They are:

- (1) Dilution of 25 parts of vegetable oil with 75 parts of diesel fuel.
- (2) Micro-emulsions with short chain alcohols (e.g. ethanol or methanol).

- (3) Thermal decomposition, which produces alkanes, alkenes, carboxylic acids and aromatic compounds.
- (4) Catalytic cracking, which produces alkanes, cycloalkanes and alkylbenzenes and
- (5) Transesterification with ethanol or methanol. (Murugesan et al, 2009).

Among all these alternatives, the transesterification seems to be the best choice(Ghaly et al, 2010),(Ma and Hanna,1999),(Akoh et al,2007), as the physical characteristics of fatty acid, esters (biodiesel) are very close to those of diesel fuel and the process is relatively simple. Moreover, the methyl or ethyl esters of fatty acids can be burned directly in unmodified diesel engines, with very low deposit formation(info@nbb.org).

TRANSESTERIFICATION OF VEGETABLE OIL TO BIODIESEL USING A LIQUID CATALYST

There are three basic routes to ester production from oils and fats. They are the basecatalysed transesterification, the acid catalysed esterification and enzymatic catalysis (Refaat et al, 2008). The use of base or acid catalyst in transesterification reaction is known as chemical transesterification, while the use of enzyme such as lipase is known as Biological transesterification(Abigor et al,2002).

The chemical transesterification, the base or acid catalyst may dissolve completely during the reaction, in which case the reaction is homogeneous. Also the base or acid catalyst may not dissolve, but remain in the solid form throughout the reaction time in which case the reaction is heterogeneous (Shuli Yan, 2007).,(Di Serio et al,2007).

In homogeneous transesterification, the base catalysed transesterification is the most commonly used as it is the most, economical process (Singh et al, 2006) for several reasons as stated below.

- 1. Low temperature $(150^{\circ}F)$ and pressure (20psi) processing.
- 2. High conversion (98%) with minimal side reactions and reaction time.
- 3. Direct conversion to methyl ester with no intermediate steps.
- 4. Exotic materials of construction are not necessary.
- 5. Reaction with base catalyst is 4000 times as fast.
- 6. Acids are corrosive.

However for the base catalysed reaction care must be taken to avoid water in the system, the reactants must be pure and anhydrous. Dehydrated oil must be used to prevent saponification reaction taking place. Saponification not only consumes the alkali catalyst, but also result in the formation of emulsions(Abigor et al 2005). Emulsion formation creates difficulties in downstream recovery and purification of the biodiesel(Michel Bloch,2006),(Fjerback et al,2009). The base or alkali catalyst used may be sodium hydroxide. 1% wt potassium hydroxide catalyst could result in successful conversion giving the best yields and viscosities of the esters (Refaat et al, 2008). The reaction requires 1mol of a triglyceride and 3mol of the alcohol (El Diwani et al,2009). The reaction is an equilibrium and transesterification occurs essentially by mixing the reactants (Noureddini and Zhu,1997). The presence of a catalyst accelerates considerably the adjustment of the equilibrium to form the desired product (Ma and Hanna, 1999).

The acid catalyst that may be used includes: Tetraoxosulphate VI acid or hydrochloric acid. Reactions with acid catalyst are much more slower than those with base catalyst (Di Serio et al, 2007).

TRANSESTERIFICATION OF VEGETABLE OIL TO BIODIESEL USING A SOLID CATALYST

The use of a solid catalyst for biodiesel production has been undertaken by researchers and scientists. Biodiesel produced with liquid catalyst contain impurities, excess alcohol and parts of the catalysts used in the process (Anton Kiss et al, 2005). The excess alcohol can be removed by using a flash evaporation process or by distillation. The glycerine can be neutralized through the use of acids and stored as crude glycerine. The biodiesel fuel after being separated from the glycerine is further purified by washing the fuel with hot water. Biodiesel produced by using liquid catalyst therefore requires the manufacturer to post process the biodiesel fuel (McNeff et al,2008). The biodiesel undergo treatment to remove the impurities and alkaline components of the fuel. This additional refining process adds to the already high manufacturing cost of biodiesel due to high cost of feedstock (Biodiesel fuel on line,2005).

Besides, the use of sodium methoxide can be serious health hazard to humans upon contact. Sodium methoxide is highly explosive and its formation is the most perilous part of Biodiesel production (Kotrba Ron,2005). The use of solid catalyst which may be solid base catalyst such as CaO, ZnO or solid acid catalyst such as zeolites (SiO_2/Al_2O_2) have major advantage over the liquid catalyst (Guoging et al,2009),(Cholada and Chuepeng,2009). Solid catalyst can be separated easily from the biodiesel fuel and thus can be removed quickly. The process of production is therefore less expensive when using a solid catalyst. The process is also more environmentally friendly. Since there is no sodium methoxide formation. Advantages of using a solid catalyst over a liquid catalyst are outlined in table 1 below:

	Transesterification using Liquid	Transesterification using Solid	
	Catalyst	Catalyst	
1	Maximum yield, 99.5%	Yield above 100%	
2	Glycerin quality high	erin quality high Higher glycerine quality	
3	Complex separation and purification	Simple separation and purification	
	steps	steps	
4	High cost of manufacturing	Lower cost of manufacturing	
5	Salt and aqueous wastes	No waste stream	
6	Consumption of chemicals	No consumption of chemicals	
7	Higher catalyst cost	Lower catalyst cost	

 Table 1:Advantages of solid catalyst over a liquid catalyst.(Michel Bloch, 2006).

TRANSESTERIFICATION OF VEGETABLE OILS TO BIODIESEL USING AN ENZYME CATALYST

Enzymes are specialised organic proteins composed of polymers of amino acids which acts as catalyst to regulate the speed of many chemical reactions (http://www.britannica.com/)(http://wiki/talk:Enzyme). Enzymes do their catalytic job well in mild pH and temperature conditions (http://C:/Index.html). Enzymes are non living substances produced by living cells such as microorganisms like bacteria, fungi and yeast. Enzymes are biotechnology in general and hence their processes are safer and and more environment friendly than the chemical methods (Fukuda et al, 2001). Lipase a group of water soluble enzymes which can be produced by popular yeast known as candida antartica have been found to be a very effective catalyst in fats/oils transesterification to biodiesel. The amount of enzymes used should be as low as necessary, e.g. 0.1g to obtain the desired product (Kuan et al, 2001).

Transesterification reaction using a Biocatalyst such as lipase have some advantages over those using chemical catalysts. The advantages are outlined in table 2 below:

Table 2: Advantages of Biocatalyst over Chemical catalyst.(Fukuda, Kondo, Noda, 2001),(Akhil Bajaj et al, 2010),(Sharma et al, 2008),(Ghaly et al, 2010).

	Chemical Catalysed Transesterification	Biocatalysed Transesterification
1	Requires mores energy.	Consumes less energy.
2	Formation of soap if little water molecules is present and this inhibits transesterification.	No soap formation.
3	Further purification of biodiesel may be required.	Further purification of biodiesel is not required.

	Chemical Catalysed Transesterification	Biocatalysed Transesterification
4	May not be used for oils with high free fatty acid content except free fatty acid content of the oil/fat has to be reduced to 1 or 2 % by acid esterification with H_2SO_4 .	Can be used for oils with high free fatty acids.
5	Chemical catalyst are not biodegradable	Biocatalysts are biodegradable
6	Process involves too much disposal or treatment of waste water.	Little or no waste water disposal or treatment.

Biocatalyzed transeterification however have some drawbacks which make the process non economical and difficult to commercialise. These drawbacks are as follows:

- 1) Longer reaction time, minimum of eight hours and above.(Abigor et al,2002)(Refaat 2010),(Shweta Shah et al,2003)(Ghaly et al,2010).
- 2) Methanol the popular alcohol used in transetrification reaction inhibits lipase activity.(Abigor et al,2002).If ethanol is used, it is more expensive and methy ester biodiesel is a better biodiesel in quality than ethyl ester which is obtain from ethanol usage(Abigor et al,2005).
- 3) Although the inhibition of lipase activity by methanol may be overcome by adding it to the reaction mixture in a stepwise manner, as glycerol begins to accumulate in the reaction mixture, it also inhibit lipase activity by covering it, hence the lipase activity may be lost.(Marchetti et al,2008),(Robles et al,2009).
- 4) Higher catalyst concentration is required for completion of reaction and enzyme is more expensive(\$1000 US per Kg whereas sodium hydroxide is only \$0.62 US per Kg and

heterogeneous chemical catalyst like calcium oxide is less than \$60 US per Kg). Although repeated use of the lipase is possible after immobilisation of lipase on carrier, it loses its activity in 100days of application(Bacovsky et al,2007), (Leong and Park, 2008), (Fjerback et al, 2009).

Therefore the whole process of lipase or biocatalyzed transeterification is highly costly, uneconomical and unpopular in Industrial applications. The advantages of the chemical Solid catalyzed process over biocatalyzed process is outlined in table 3 below:

Heterogeneous Chemical Catalyzed	Biocatalyzed transeterification.				
transeterification					
Short reaction time, usually between	Long reaction time, minimum of 8hours.				
1hour to 4hours.					
Requires low catalyst concentration,	Requires high catalyst concentration.				
about 1%.					
Catalyst is cheaper.	Enzymes are very expensive.				
No inhibition of reaction takes place.	Inhibition of enzyme activity by methanol				
	and glycerol formation.				

Table 3: Advantages of chemical solid cat	talvst over biocatalvst
Table 5. Advantages of chemical solid cat	Laryst over biocataryst.

CONCLUSION

All plant oils, animal fats, waste cooking oils and greases have been used for biodiesel production through transesterification. Chemical transesterification using acids and alkali catalysts have been used traditionally and commercially. The difficulty and high cost purification of the products of chemical transesterification has made way to the less energy and more active enzymatic transesterification. It has been shown that enzymatic transesterification can be carried out successfully with variety of lipases, with higher yield of oils, fats and acyl acceptors. Higher free fatty acids and water content of oils can be catalysed with complete conversion to alkyl esters with significantly condensed amount of wastewater. The process is however limited by its high cost, high reaction time and amount of water and organic solvents in the reaction mixture.

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