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Effect of Different Catalysts and their Performance In Extracting Bio Diesel –An Experimental Study

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ABSTRACT

In this contemporary world, due to the increasing population, the use of fossil fuels has increased very tremendously. This lead to the need of alternative fuels which would cater the increasing energy needs of the world. Bio diesel proved to be a promising fuel and the best substitute to the non renewable fossil fuels. Since its advent in 19th century there has been an extensive research and several methods have been invented to produce bio dieseland alter its chemistry.with the advancement in technology many new compounds have been tested as catalysts for production of bio diesel. The following discussion makes a Comparison between different catalysts and their effect on reaction parameters is reviewed. The effect of quantity of catalysts on yield,problems faced in using a particular catalyst are studied . trans esterification process is the best method and widely used for production of bio diesel hence all the catalysts discussed are with respect to this process.

Keywords :alternative fuels,bio diesel ,catalyst,transesterification process

INTRODUCTION

Today Fossil fuels account to nearly 85% of energy consumption needs of the world.But the main problem being their liberation of hazardous gases harmful to ecosystem and the urge to find an alternative fuel which could meet the future energy needs .In this area biodiesel has proven to be promising fuel which made it a challenging aspect to researchers around the globe efforts are being made to commercialise biodiesel by decreasing production cost, usage of various catalysts, design of cheaper production plants .The present paper discusses the various advancements in the catalysts used for production of bio diesel .All the catalysts mentioned will be the ones used in transesterification method which is most suitable for production of biodiesel.The various catalysts being used their effects on reaction parameters are studied below.

TRANSESTERIFICATION

Animal and plant fats and oils are composed of triglycerides, which are esters formed by the reactions of three free fatty acids and the trihydric alcohol, glycerol. In the transesterification process, the added alcohol (commonly, methanol or ethanol) is deprotonated with a base to make it a stronger nucleophile. As can be seen, the reaction has no other inputs than the triglyceride and the alcohol. Under normal conditions, this reaction will proceed either exceedingly slowly or not at all, so heat, as well as catalysts (acid and/or base) are used to speed the reaction[1].

CATALYSIS IN TRANESTERIFICATION

The following discussion summarizes the catalysis techniques used for transesterification process and their potential for being used in bio diesel industry.

The homogenous base catalyst are widely used in industry due to their ability to catalyse at low reaction temperatures and atmospheric pressure ,high conversion in minimal time, economical[2].some researchers reported that base catalyst can tolerate high FFA content .If an oil containing high FFA content is used to

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produce Biodiesel the alkali catalyst will react to form soap which is highly undesirable[3,4,5] .Since liquid base catalyzed reactions pose different problems especially with oils having high FFA, acid catalysts are introduced which are insensitive to FFA and Water content in feed stock .However acid catalyzed reaction is not suitable for industrial applications due to slow reaction rate, difficulty in separation of catalyst , high reaction temperature etc. Both acid and base catalysts have their own advantages and disadvantages hence some researchers experimented with the combination of two and it was observed that although a good yield is produced in the two step process the rate of FFA esterification was slow which required excess of acid and also the separation of catalyst posed a problem in both stages[6].Many heterogenous catalysts like zeolites, alkaline earth metal oxides and hydro silicates have been used for production of biodiesel.Frequently used heterogenous catalysts are ZrO_2,TiO_2,SnO_2,Zeolites,Sulfonic exchange resin,sulfonic modified meso structure silica ,Sulfonated carbon based catalyst,enzyme catalyst[7].

ENZYME CATALYSED TRANSESTERIFICATION

In recent times, enzyme catalyzed reactions have been a subject of interest for researchers around the globe. Enzymes such as lipases have proven to be most suitable catalysts for production of bio diesel.The advantages of this type of reaction over chemical catalyzed reaction

includes the generation of no by-products,easy product removal,mild reaction conditions

(temperature 35-45^{0}C) and catalyst recycling[8].Nelson et al[6] tested four lipases namely *MucorMeihi(lipozyme IM60),candida antartica (SP435),Geotrichum candidum and Pseudomonas cepacia(PS30)* as catalysts for transesterification of olive oil,soybeanoil,tallow with short chained alcohols.The reaction conditions developed for tallow were effective for transesterification of cooking oil optimized conditions were temperature 45^{0}c;stirring speed 200 rpm;12-25% enzyme concentration and reaction time 4-8 hrs(primary alcohols), 16 hrs (secondary alcohols) .The same conditions were proved suitable for trans estifying vegetable oils and high fatty acid containing oils. Enzymatic reactions are reported to be insensitive to FFA and water content in waste cooking oil[8,10,11].

ACID CATALYSED TRANS ESTERIFICATION

The main advantage of acid catalyzed transesterification is that they are insensitive to FFA and better than alkalicatalysts for oils having FFA (>1%).The main advantage of Acid catalyzed transesterification is that it occurs in a single step with alcohol acting both as solvent and esterification reagent[12].Experiments conducted by researchers[13,14,15] have shown that with sulfuric acid catalyst methanol to oil ratio of 50:1 acid conc.1.5-3.5 mol% was completed at 70^{0}C and if it carried out at pressure of 170-180 kPa and speed of 400 rpm the reaction was completed at 80^{0}C. Al-widyan and Al-shyoukh[16] studied the esterification of waste palm oil under different conditions. Sulfuric acid and different concentrations of hydrochloric acid and ethanol at different excess levels were used. Using higher catalyst concentrations in range of 1.5-2.25M produced biodiesel with lower specific gravity in a shorter reaction time than low concentrations.

In recent times attention on biodiesel research focused on use of solid acid catalyst knowm as heterogenous catalyst lotero et al.[2] have reported that the ideal solid catalyst for transesterification of used cooking oil should have characteristics such as inter connected system of large pores ,moderate to high concentrations of strong acid site and hydrophobic surface .

Wang et.al[17] performed a two step transesterification process in which a feedstock used cooking oil had acid value of approx.75.92mg KOH/g. it was observed that ferric sulfate which acted as solid catalyst in first step and triglycerides in UCO wetre transesterified with methanol catalyzed KOH in second step. The end result high activity of ferric sulfate as catalyst in trans esterification.

ALKALI-CATALYZED TRANSESTERIFICATION

The use of alkali catalyst in the transesterification of used cooking oil is somewhat limited because the FFA in used cooking oil reacts with the most common alkaline catalysts (NaOH, KOH and CH_3ONa) and

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forms soap. Because the water makes the reaction partially change to saponification, the alkali catalyst is consumed in producing soap and reduce catalyst efficiency. The soap causes an increase in viscosity, formation of gels which reduced ester yield and makes the separation of glycerol difficult. These two problems notwithstanding , literature is replete with studies on the transesterification of waste cooking oil using alkaline catalyst.

NaOH has been used by many researchers for the transesterification of used cooking oil despite its slow reaction rate.

KS Chen et al[18] carried out various experiments using different catalysts in order to determine influence of catalyst on yield it was observed that the yield increased with increasing amount of catalyst for 0.5%-0.75% wt of NaOH and then it decreases similar results were observed using CH_3ONa it was also reported that use of excess catalyst increased the yield of biodiesel but there was also increase in glycerin produced due to saponification.Dorado et al [19] concluded addition of excessive amount of alkali catalyst leads to formation of emulsion which increases viscosity and leads to formation of gels.

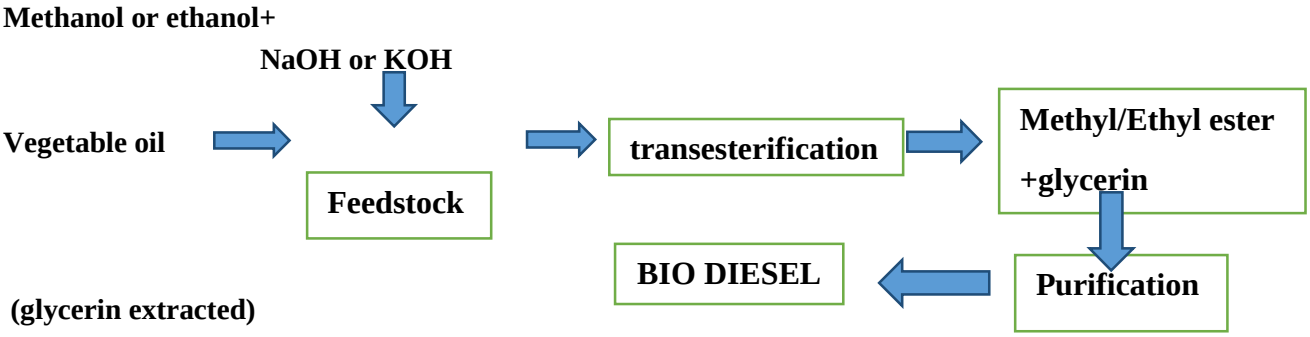

Fig.1 Extraction of Bio Diesel from Crude Oil

SUPERCRITICAL ALCOHOL

This is an alternative method for biodiesel production where no additional catalyst is required but

The alcohol itself is added under critical conditions in transesterification process.Ahyan demirbas[20] after experimentation with super critical alcohol concluded increasing reaction temperature to super critical conditions increased the yield.It was also observed that the ill effects due to presence of water with methyl ester were removed using supercritical methanol method moreover it had a positive effect on yield

Table1 Comparision of various parameters of bio diesel production using different catalysts

Variable	Alkali catalysis	Acid catalysis	Enzyme catalysis	Supercritical alcohol
Reaction temperature(C)	60-70	55-80	30-40	239-385
Free fatty acids in raw materials	Saponified products	Esters	Methyl esters	esters
Water in raw materials	Interference with reaction	Interference with reaction	No influence	----
Yield of methyl esters	Normal	Normal	Higher	Good
Recovery of alcohol	Difficult	Difficult	Easy	----
Purification of methyl esters	Repeated washing	Repeated washing	None	----
Production cost of catalyst	Cheap	Cheap	Relatively expensive	Medium

CONCLUSION

Experimental results indicate that the reaction time was reduced significantly and yield of bio diesel was improved due to the use of microwave instead of conventional heating method. The base catalyzed reaction is useful for industrial production but it cannot be used for oils with high FFA .here acids can be used but have a slow reaction rate.These take longer reaction time hence research should be done on

1) heterogenous catalysts acid or base type that require optimum reaction time

2) enzyme catalysts that require mild reaction conditions and no by products are produced

3) supercritical alcohol method which will remove the ill effects of water content in feed stock and increase the yield

Though thse methods individually have their own problems they can be efficient based on the requirement of products for instance if a need arises that no by products should be produced than using enzyme catalyst is effective.Thus a number of catalysts have been discovered and the number will go on increasing with advancement in technology hence the selection of catalyst should depend on the conditions available and the requirement of the products.

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