

Transesterification by Reactive distillation for characterization and synthesis of biodiesel

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Abstract— The awareness in alternative fuels has increased dramatically in recent years due to the rising cost and the environmental concerns related to fossil fuels use. Biodiesel represents a more environmentally friendly and cost-effective fuel produced from the reaction of various alcohols with triglycerides found in commonly available oils to produce methyl esters. Use of biofuels such as biodiesel for transportation produces no net output of carbon in the form of CO₂ and achieves 30-50 % greenhouse gas savings. The techno-economic analysis of biodiesel production has indicated that cost of biodiesel will vary from Rs. 25.70 to Rs. 56.70 per liter with cost of oil ranging from Rs. 25/- to 55/- per Kg compared to Rs.36.5/- per liter for diesel. With further availability of cheap oils and taking into consideration the carbon credits earned due to green fuel under CDM mechanism, the biodiesel costs will further reduce and be more competitive with diesel.

In this paper an optimized process have been investigated for biodiesel production and a case study of an innovative clean

technology for production of biodiesel by transesterification using reactive distillation have been illustrated. The strong base or acid typically used to catalyze this transesterification reaction is not recovered and extensive post-reaction processing is therefore required to produce the final product.

By using reactive distillation technique, energy conservation is achieved along with reduction of carbon footprints. Thus, dramatic results were obtained by using reactive distillation for biodiesel production.

Keywords: Biodiesel, transesterification, reactive distillation.

I. INTRODUCTION

1.1 Energy crisis and Biodiesel

Increasing uncertainty about global energy production and supply, environmental concerns due to the use of fossil fuels, and the high price of petroleum products are the major reasons to search for alternatives to petrodiesel. The global supply of oil and natural gas from the conventional sources is unlikely to meet the growth in energy demand over the next 25 years. Biodiesel fuel has become more attractive because of its environmental benefits, due to the fact that plants and vegetable oils and animal fats are renewable biomass sources.

Biodiesel is defined as the mono-alkyl esters of fatty acids derived from vegetable

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oils or animal fat. Biodiesel is an alternative fuel similar to conventional or ‘fossil’ diesel. It can be produced from straight vegetable oil, animal oil/fats, tallow and waste cooking oil. The process used to convert these oils to Biodiesel is called transesterification. Pure biodiesel (B100) needs to meet the requirements of ASTM D-6751 to avoid engine operational problems.

Table I

Biodiesel: ASTM D-6751 Standards

Flash point (closed cup)	130°C min. (150°C average)
Water and sediment	0.050% by vol., max.
Kinematic viscosity at 40°C	1.9-6.0 mm ² /s
Ramsbottom carbon residue, % mass	0.10
Sulfated ash	0.020% by mass, max.
Sulfur	0.05% by mass, max.
Copper strip corrosion	No. 3 max
Cetane	47 min.
Carbon residue	0.050% by mass, max.
Acid number – mgKOH/g	0.80 max.
Free glycerin	0.020 % mass
Total glycerine (free glycerine and unconverted glycerides combined)	0.240% by mass, max.
Phosphorus	0.001 max. %

content	mass
Distillation	90% @ 360°C

1.2 Key Advantages Of Biodiesel:

1. BD is the only alternative fuel that runs in any conventional unmodified diesel engine and can be stored anywhere that petroleum diesel is stored.

2. BD can be used alone or mixed in any ratio with petroleum diesel.

3. BD is 11% oxygen by weight and contains no sulfur.

4. Use of BD produces approximately 80% less CO emissions and almost no SO₂.

5. BD can be made from domestically produced, renewable oilseed crops such as soybeans.

6. BD is a proven fuel with over 30 million successful US road miles, and over 20 years of use in Europe.

7. When burned in a diesel engine, biodiesel replaces the exhaust odor of petroleum diesel with the pleasant smell of popcorn or French fries.

8. Biodiesel is biodegradable in water, up to 98% in three weeks.

9. Biodiesel is neutral with regard to CO₂ and therefore does not contribute to global warming.

10. Flash point is above 360⁰ F so no risk of explosion caused by fumes.

11. A secondary benefit of biodiesel production is that it creates more employment as it is three to six times more

labour intensive per unit of production than fossil fuels.

1.3 Transesterification for Biodiesel

Transesterification is a process of exchanging the alkoxy group of an ester compound by another alcohol where reaction is catalyzed by acid or base. It is the main reaction for converting oil to biodiesel in which an alcohol reacts with the triglyceride oils contained in vegetable oils, animal fats, or recycled greases, forming fatty acid alkyl esters (biodiesel) and glycerin. The reaction requires heat and a strong base catalyst, such as sodium hydroxide or potassium hydroxide. The simplified transesterification reaction is shown below

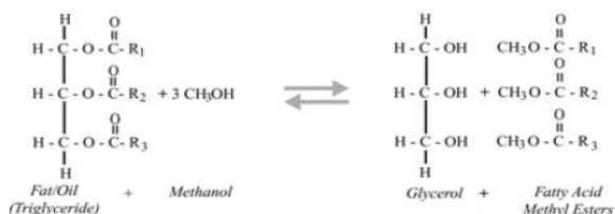


Fig.1. Transesterification process

A fat or oil is reacted with an alcohol, like methanol, in the presence of a catalyst to produce glycerin and methyl esters or biodiesel (BD). The methanol is charged

in excess to assist in quick conversion and recovered for reuse.

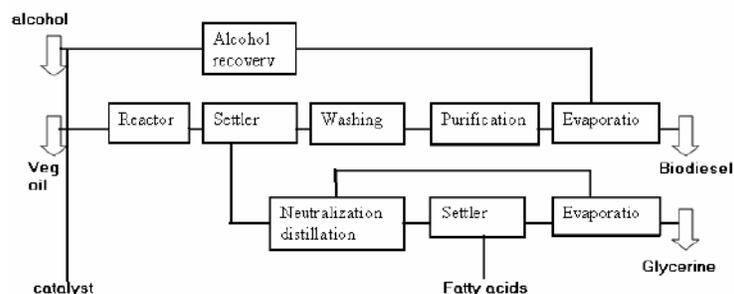


Fig.2. Schematic process for biodiesel

The catalyst is usually sodium or potassium hydroxide which has already been mixed with the methanol. Product recovery is separated into phases which provides for easy removal of glycerol, a valuable industrial by-product, in the first phase. The remaining alcohol/ester mixture is then separated and the excess alcohol is recycled. Then the esters are sent to the clean-up or purification process which consists of water washing, vacuum drying, and filtration.

2. Transesterification by reactive distillation for biodiesel production

2.1 Reactive Distillation:

The reactive distillation is a hybrid process that combines the reaction and separation in a single equipment. The product is retired at the same it is formed. This characteristic does possible to overcome the equilibrium thermodynamic of the reaction, reaching best conversions and selectivities. Distillation with chemical reaction has received attention as an alternative to conventional processes;

reactive distillation has proved to be an economical alternative in many applications (e.g. MTBE and TAME synthesis, production of methyl acetate, manufacture of di-isopropyl ether, oligomerisation of linear butenes and removal of butadiene through dimerisation).

Some works exist in which the production of biodiesel by reactive distillation is reported, as the one developed by Omata (Omata et al, 2003).

In biodiesel preparation from vegetable oils and alcohol through transesterification process in the presence of a catalyst, excess alcohol, typically 100% more than the theoretical molar requirement, is used in existing batch and continuous-flow processes in order to drive the reversible transesterification reaction to a high enough conversion rate. The excess alcohol needs to be recovered in a separate process which involves additional operating and energy costs.

2.2 Why Reactive Distillation?

The current biodiesel production processes face the problems in its separation and purification. Therefore, new alternatives are needed to be explored like non-conventional separation processes among which reactive distillation can be considered.

Recently the esterification of lauric acid with 2-ethyl hexanol and methanol by reactive distillation was reported. However these reports are totally based on experiments without a good analysis of the process technology. In this paper

theoretically the possibility of producing the corresponding ester with oleic acid and lauric acid is investigated.

Biodiesel production by transesterification using reactive distillation is one of the most promising clean technologies which involve less energy for production of biodiesel fuel from waste/nonedible/edible vegetable oils and it reduces carbon footprints to the large extent. Reactive distillation involves simultaneous reaction and separation in a single piece of process equipment. It is applicable to equilibrium limited reactions where one product is the most volatile component. Process intensification results in lower energy and capital costs. Each reaction system requires a unique approach for successful design and operation. Biodiesel, a mixture of mono-alkyl esters of fatty acids, is currently manufactured by trans-esterification of triglycerides with methanol using NaOH or KOH as liquid base catalyst. This catalyst is corrosive to the equipment, but this is easily overcome with little cost penalty, by constructing the reaction vessels out of stainless steel. However, the main drawback is that the liquid base catalyst has to be neutralized afterwards— typically using HCl—thus producing waste salt streams. Moreover, due to the presence of free fatty acids it reacts to form soap as unwanted by-product hence requiring more expensive separation. Another method to produce these fatty esters is the batch-wise esterification of fatty acids using H_2SO_4 as catalyst. However, the problem here is the batch operation mode that is not suitable for very large-scale production and again it involves

costly neutralization and separation of the homogeneous catalyst.

3. Experimental Investigations:

For achieving more benefits transesterification can be coupled with reactive distillation. In the first phase of experimentation transesterification was performed to obtain biodiesel from non edible vegetable oil (jatropha oil). The reaction conditions such as reactants ratio, temperature and pressure determine the phase equilibrium.

3.1 Transesterification Experiment:

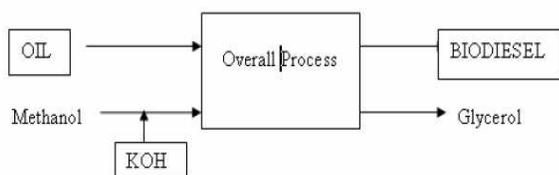


Fig.3 Overall Reaction

The overall reaction involved in whole process is:



3.2 Experimental Procedure

A known quantity of Jatropha oil is taken inside the reactor and heated at about 70°C. This temperature is maintained throughout the reaction by the thermostat inside the heat jacket. Preheating is used to remove unwanted moisture present in the oil. The transesterification is carried out in basic medium and to achieve it, KOH is used as a catalyst. Catalyst is dissolved in alcohol.

Once the oil temperature reaches 70 °C, alcohol solution (containing dissolved catalyst) is added to the reactor and an equilibrium temperature is maintained.

During the reaction, alcohol gets vaporized. To prevent any reactant loss condenser is used to condense the alcohol vapor and reflux it back into the reactor. Once the reaction is over the products are taken out through the outlet in the lower side of the reactor and put in the separating funnel. Two phases (having different density) are formed as a result of transesterification.

Separation is done using a separating funnel. Upper layer consists of bio-diesel, alcohol, and some soap (formed

as a result of side reaction saponification - free fatty acids get converted to soap). Lower layer consists of glycerin, excess alcohol, catalyst, impurities, and traces of unreacted oil. Purification of upper layer (to obtain bio-diesel) is done in two steps.

(i) Removal of alcohol – by keeping mixture at elevated temperature ~80 °C.

(ii) Removal of saponified products – by washing with warm water. Water is immiscible with bio-diesel, hence can be easily separated from bio-diesel.

3.3 Experimental Set-Up

Trans-esterification is carried out in a reactor which consists of spherical flask, which is put inside the heat jacket. Oil is used as a medium of heat transfer from heat jacket to the reactor. Thermostat is a part of heat jacket, which maintains the temperature of oil and in turn the temperature of the reactants at a desired

value. The reaction is carried out at around 65-70 °C. Spherical flask consists of three openings. The center one is used for putting stirrer in the reactor. The motor propels the stirrer. Thermometer is put inside the second opening to continuously monitor the temperature of the reaction. Condenser is put in the third opening to reflux the alcohol vapors back to the reactor to prevent any reactant loss.

3.4 Representative values of experimental observation:

Jatropha oil: 181 gm ; Methanol : 78 gm ;
 KOH : 1.0 gm ; Time taken: 3.0 hrs ;
 Temperature of Reaction: about 65° C ;
 Time for separation: 24 Hrs.

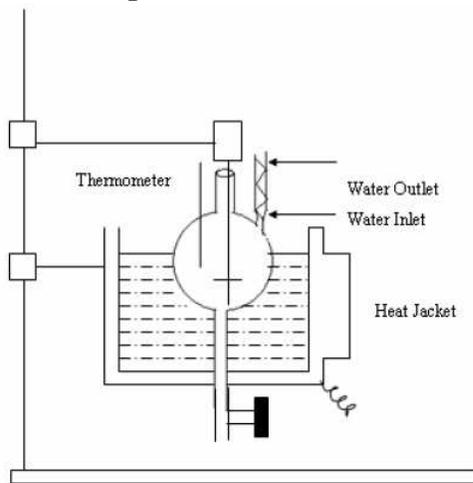


Fig.4 Experimental Set up

Results in this study can be summarized as follows:

- * The best time of reaction is 1 hr
- * Optimum catalyst is 1.0 gm per 181 gm of oil.
- * Optimum amount of methanol is 39 gm per 181 gm of oil.

* The Rate expression shows the dependence of initial rate on reaction conditions.

Notations

BD = Biodiesel

DG = Diglyceride

Gl = Glycerol

HP = Heavy Phase

k = Rate Constant (mol. min)⁻¹

LP = Light Phase

MG = Monoglyceride

4.Reactive distillation for biodiesel production:

In this study, a novel reactor system using reactive distillation (RD) technique was developed and studied for biodiesel preparation. The main objective was to dramatically reduce the use of excess alcohol in the feeding steam, which reduces the cost in downstream alcohol recover processes, and meanwhile maintain a high alcohol-to-oil molar ratio inside of the RD reactor, which ensures the completion of the transesterification of seed oil to biodiesel. For temperatures below 100°C, only low conversions can be achieved and an excess of alcohol is required to have only one liquid phase. For stoichiometric reactants ratio, two liquid phases exist at temperatures below 100°C. If temperature exceeds 100°C and the system is closed at over pressure then three phases exist: vapours–liquid–liquid. Liquid separation is undesirable due to catalyst deactivation in the presence of water. The best solution is working at temperatures above 100°C, in a system

with continuous water removal. By removing water as by-product the equilibrium is shifted towards ester formation.

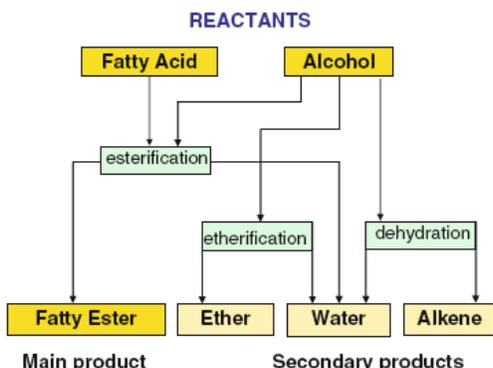


Fig.5 Reaction pathways and possible products

Hence, the ester will always be separated in the bottom of the reactive distillation column (RDC). Water is present as side product, and typically is removed as top product due to its lower boiling point, together with the alcohol if it is volatile (and not completely converted) or if it forms azeotropes with water.

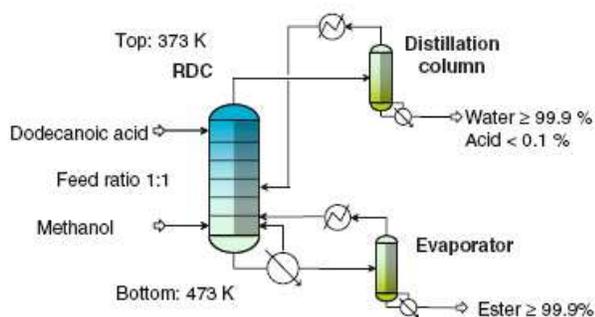


Fig.6 Biodiesel Production-Fatty acids esterification with methanol

Fig.6 presents the flow sheet for esterification of dodecanoic acid with methanol. High purity final products are feasible. Note however that pure fatty acid esters cannot be the bottom product of the reactive distillation column because of the high boiling points and lower thermo-stability. By allowing 1–2% of alcohol in the bottom stream, the reboiler temperature in the RD column can be kept below 200°C. An additional evaporator is used for further ester purification. When an excess of alcohol is used the maximum reaction rate is located at the top of the column, with total acid conversion in the bottom but partial conversion of alcohol in the top. For the optimal reflux ratio the maximum reaction rate is located in the centre of the column, providing complete conversion of both reactants at the ends of the column. The composition and temperature profiles in the reactive distillation column are shown in fig. 7 and Fig.8

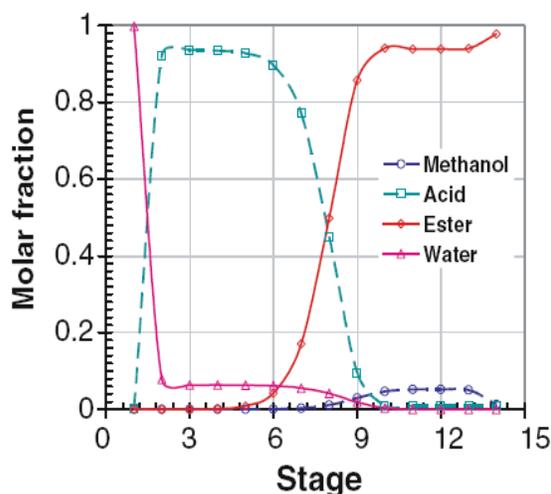


Fig.7.Reactive distillation column profiles- Liquid composition

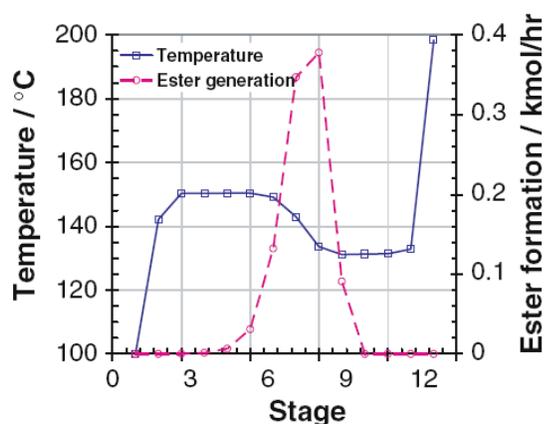


Fig.8 Reactive distillation column profiles- Temperature & ester generation

Manufacturing of fatty acid esters by reactive distillation can be applied to a variety of alcohols and fatty acids, as a multifunctional reactor, the actual applications depending on the feedstock at hand.

Conclusions

From the above work it can be concluded that biodiesel fuel can be produced by a sustainable continuous process based on catalytic reactive distillation. The process proposed here can dramatically improve the economics of current biodiesel synthesis and reduce the number of downstream steps. The key benefits are:

1. High unit productivity, up to 6–10 times higher than of the current process.
2. Lower excess alcohol requirements.
3. Reduced capital and operating costs, due to less units and lower energy consumption.
4. Sulfur-free fuel, since solid acids do not leach into the product.
5. No waste streams because no salts are produced.

The integrated design in above case study ensures the removal of water by-product that shifts the chemical equilibrium to completion and preserves the catalyst activity.

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