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Research Article

A Review on Rejuvenated Techniques in Biodiesel Production from Vegetable Oils

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Abstract

In recent years, significant research and development activities for biodiesel production have been undertaken throughout the world, in order to support the fuel requirements without further deteriorating the global climate. The biodiesel produced from a specific feedstock may have distinct advantages over others, but the practical problem concerning its availability in terms of adequate quantity and consistent quality is a concern. Hence, blending with multiple oils obtained from non-conventional non-edible biomass feedstock including algae may be considered as appropriate strategy for producing biodiesel at commercial scale. Recently, R&D endeavours are being directed towards exploring the blends of different non-edible oils as biodiesel feed-stock. This article attempts to cover all possible techniques in production of biodiesel from single and mixed feed stock.

Keywords: *Rejuvenated Techniques, Biodiesel etc.*

Introduction

To meet the ever challenging energy needs in a sustainable way, the commercial potentials of various biomass feed-stocks for clean and renewable fuels are being investigated. The research challenge here is to develop a judicious mix of the oils that exhibit the right combination of fatty acids for desired biodiesel quality as per the ASTM and European Standards. To date, edible oils such as rapeseed, sunflower, palm and soybean contribute more than 95% of biodiesel production, mostly in the US and Europe (Khan *et al,*2014). European Union (EU), Brazil, Canada and other countries have already mandated the use of bio fuels as transportation fuels (Mabee *et al,* 2007). The National Oilseeds and Vegetable Oil Development (NOVOD) Board, Government of India, highlighted the importance of non-edible feed-stocks for biodiesel production. Moreover, many Indian states agreed to reserve the land for cultivation of certain non-edible oil producing plants and trees for biodiesel production (Khan *et al*., 2014).

The major non-edible feed stocks used for biodiesel production purpose are *Jatropha curcas* (Jatropha), *Pongamia pinnata* (karanja), *Calophyllum inophyllum* (Polanga), *Hevea brasiliensis* (rubber seed), Cotton seed, *Simmondsia chinesnsis* (Jojoba), *Nicotianna tabacum* (tobacco), *Azadirachta indica* (Neem), *Linum usitatissimum* (Linseed) and *Maduca indica* (mahua) etc. The advantage of using non-edible oils as biodiesel feed-stock is their non-edible nature due to the toxic substance released by these plants and hence, no competition with food products. The major drawbacks with these non-edible oils are that they are region specific, have high free fatty acid content and high viscosity (Atabani *et al*, 2013). Hence, mixed non-edible oils can be regarded as a sustainable feed-stock for biodiesel production.

A hybrid feedstock for biodiesel production was conducted (Sharma & Singh *et al*, 2010) from karanja and mahua (50:50 v/v). A high yield in the range of 95–97% was obtained with hybrid feed-stocks and it indicates that the reaction was not selective for any particular oil. This result signifies that both types of oil can be blended, in order to maintain the constant supply of the feedstock (Yathish *et al*, 2013). It was found that the viscosity of the mixed oil biodiesel was low as compared to the karanja oil biodiesel. The flash point of the mixed oil biodiesel was found to be increased. The cost of the mixed biodiesel was observed to be very competitive 60–70% less when compared to other biodiesel produced from edible and non edible fat and oils. Under optimal conditions, mixed oil methyl esters yield of 95.1%, was achieved and all the measured properties of mixed oil biodiesel met the ASTM standards. Biodiesel production from mixture of Mahua and Simarouba oils was done by

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(Jena *et al*, 2010) by acid pretreatment followed by base trans-esterification. They observed an average yield of biodiesel conversion to around 98% following the two stage biodiesel production process.

The oil of *Simarouba glauca* was used for biodiesel production by (Garlapati *et al*, 2013), through lipase mediated trans-esterification. A maximum yield of 91.5 % fatty acid methyl esters with a 62.23 % molar conversion with respect to methyl oleate has been achieved. The feedstock, which is about 80% of the total operating cost, is the major economic factor (Demirbas *et al,* 2009) and hence, selection of suitable feed-stock is the most important step in achieving cost-effective biodiesel outlook.

Biodiesel

The name bio-diesel was introduced in the United States during 1992 by the National Soy Diesel Development Board (presently National Bio-diesel Board) which has pioneered the commercialization of biodiesel in the US. Chemically, bio-diesel is referred to as the mono-alkyl-esters of long-chain-fatty acids derived from renewable lipid sources. Bio-diesel is the name for a variety of ester based oxygenated fuel from renewable biological sources. It can be used in compression ignition engines with little or no modifications by(A.S. Ramadhas *et al*,2004).

Major problems associated with the use of pure vegetable oils as fuel is viscosity in compression ignition engines.

- Micro-emulsification,
- pyrolysis
- Transesterification

Above are the remedies used to mitigate the problem of viscosity.

Micro-emulsification

To solve the problem of high viscosity of vegetable oil, micro emulsions with solvents such as methanol, ethanol and butanol have been used.

Cracking or pyrolysis

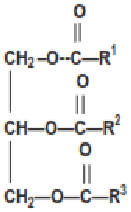
It involves heating in the absence of air or oxygen and cleavage of chemical bonds to yield small molecules.

Transesterification

Transesterification is otherwise known as alcoholysis. It is the reaction of fat or oil with an alcohol to form esters and glycerin. A catalyst is used to improve the reaction rate and yield. Among the alcohols, methanol and ethanol are used commercially because of their low cost and their physical and chemical advantages. To complete a transesterification process, 3:1 molar ratio of alcohol is needed. Enzymes, alkalis or acids can catalyze the reaction, i.e. lipases, NaOH and sulphuric acid, respectively.Among these, alkali transesterification is faster and hence it is used commercially.

Chemical composition

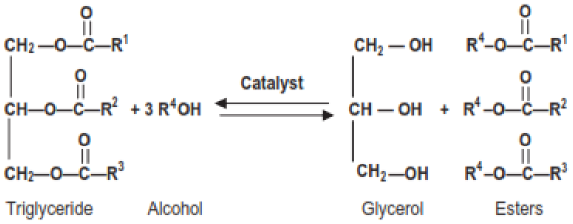
The structure of typical vegetable oil molecule is given below:



Here R¹, R2 and R³ represent straight chain alkyl groups. The large molecular sizes of the triglycerides(vegetable oil) results in higher viscosity and low volatility compared to mineral diesel. Proportion and location of double bonds affects cetane number of vegetable oils .

Transesterification reaction

The chemical reaction of the transesterification process is shown below:



Problems associated with vegetable oils during engine tests can be classified into two broad groups, namely,

- Operational
- Durability problems.

Operational problems are related to starting ability, ignition, combustion and performance. Durability problems are related to deposit formation, carbonization of injector tip, ring sticking and lubricating oil dilution.

Different feedstocks for production of biodiesel

Conventional feedstock	Non-conventional feedstock
Mahua Soybean Nile tilapia Rapeseed Palm Babassu Tobacco seed Brassica carinata Rubber plant Brassica napus Rice bran Groundnut Sunflower Cynara cardunculus Barley Cottonseed Coconut Pumpkin Jojoba oil Used cooking oil Camelina Linseed Peanut	Lard Tallow Poultry fat Fish oil Bacteria Algae Fungi Micro-algae Tarpenes Latexes Pongamina pinnata Palanga Jatropha curcas Sea mango Okra Kusum, Simarouba Karanja Polang, Argemone (our patented work), Olax Microalgae.

Homogeneous catalytic transesterification

Alkali catalyzed

The Use of alkali catalysts (NaOH, KOH, CH3-ONa) for production of biodiesel are cheap and readily available (Atapour M, Kariminia *et al,* Demirbas *et al,* 2011). The limitations of this process are as high energy consumption which in turn causes a substantial increase in capital equipment costs and safety issues. In addition, this process is highly sensitive to water and free fatty acid (FFA) content in the feedstock. High water content can change the reaction to saponification, which causes reductions of ester yield, difficult separation of glycerol from methyl ester, increment in viscosity, and the formation of emulsion (Liu KS *etal1994,* Basu HN, Norris *etal*1996) all of which create many problems in downstream purification and methyl ester recovery. There are various reports about the effect of oil FFA content in reaction with alkali catalysts as shown in Table 1.

(Arquiza *et al,* 2000) investigated biodiesel production from used coconut oil with methanol and NaOH as catalyst. They also evaluated the effects of some operating parameters such as the reaction temperature (30–65^0 C), the molar ratio of methanol to oil (3:1,6:1, and 9:1), and the catalyst weight (0.1%, 0.5% and 1%). The results were 94% yield at optimum condition of 60–65^{0}C reaction temperature, 0.5% catalyst weight and 6:1 molar ratio of methanol to oil.

Table-1 Possible FFA content for alkali catalyzed transesterification

Type of catalyst	FFA content	References
Alkali catalyst	Less than 0.5 wt%	Jeromin L *etal* 1987
	Less than 1.0 wt%	Fangrui M *etal* 1999
	Greater than 1 wt%	Crabbe E *et al,* 2001
	Less than 2 wt%	Fukuda H *et al,* 2001
	Less than 3 wt%	Dorado MP *et al,* 2003
	Up to 5 wt%	Gerpen JV *et al,* 2005

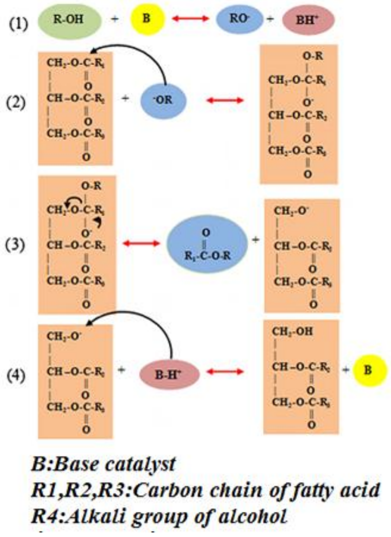


Fig.1 Reaction mechanism of homogenous base catalyzed transesterification

Acid catalyzed transesterification reaction

Acid catalysts are insensitive to free fatty acids, and they have better results for vegetable oil with FFA greater than 1% (Freedman B *et al,* 1984).However, acids can produce a large number of salt interaction,which is a cause of corrosion. Some researchers have used inor-ganic acids such as sulfuric acid, phosphoric acid, sulfonated acid and hydrochloric acid in the transesterification process. The acid is mixed directly with vegetable oil. Esterification and transesteri-fication steps occur in single stage because acids have esterification reagents and play a solvent role in this single process (Cervero´ PJM *et al,* 2008).These types of catalysts have a very slow reaction thus the reaction time is increased.(Nye *et al* 1983).

(Nye *et al*,1983)used different types of alcohols such as methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, 2-ethoxy ethanol,H2SO4 and KOH as catalysts with waste cooking oil. They reported that acid catalyzed esters had higher yield compared to alkali catalyzed reaction. However, this reaction increased the reaction time. Recently, a large number of researchers utilized Lewis or Bronsted acids as a catalyst for biodiesel production in both kinds of homogenous and heterogeneous processes (Nestor Jr US *etal*2009).

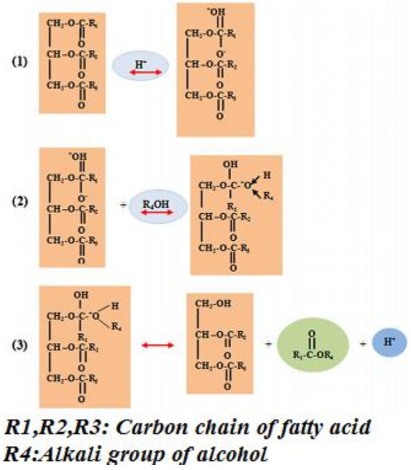


Fig.2 Reaction mechanism of homogenous acid catalyzed transesterification

Acid and alkali catalyzed two-step transesterification

The problems associated with acid and alkali catalyzed transesterification are slow reaction and separation of methyl ester and glycerol (saponification), respectively. Many researchers try to use two-step acid and alkali catalyzed transesterification to eliminate these problems. In the first step, the esterification of FFA with acid catalysts to decrease FFA levels to lower than 1% and in the second step, the transesterification of the oil with alkali catalysts.

(Fan *et al,* 2009) investigated the biodiesel production from recycled canola oil with a two-step acid and alkali catalyzed reaction. In the first step, they considered some variables for acid catalyzed esterification such as molar ratio of alcohol to oil (4.5:1–18:1), catalyst concentration, reaction temperature, and reaction time. The optimum condition was 40:1 molar ratio of methanol to oil and 5% sulfuric acid. The FFA level was reduced from 11% to 0.41% around 96.3% reductions at 55^0C temperature for 1.5 h. After esterification, transesterification was carried out at 6:1 molar ratio of methanol to oil with 1% potassium hydroxide.

Heterogeneous catalyzed transesterification

Solid catalyst

The homogenous reaction has some disadvantages such as low tolerance towards FFA, and water content and the purification pro-cess is complicated. Meanwhile, researchers have focused on the heterogeneous reaction with solid catalysts to eliminate these factors. Ideally, solid catalyst should have characteristics such as an interconnected system of large pores (Brito YC *etal* 2008, Islon AP *etal* 1994), a medium to high concentration of strong acid sites, hydrophobic surface (Dalai AKMG *et al,* 2006), and the ability to regulate the hydrophobicity of the surface to prevent the deactivation process(Lotero E *et al*,2005, Miao S *et al,* 2009).

Various types of heterogeneous catalysts such as ion exchange resins (Marchetti *et al, 2008,* Park YM *etal*2008,Furuta S *et al,* 2006 Park YM *et al,* 2008), sulfated oxides (Sakai T *etal* 2009, Holser Ronald *etal*2006, Alba-Rubio *et al*, 2010), and heterogeneous base catalysts like transition metal oxide and derivatives (Sreeprasanth *et al,* 2006, Antunes WM *etal*2008), boron group base heterogeneous catalyst (Umdu ES *et al,* 2009, McNeff CV *et al,* 2008, Xu L *et al,* 2008, Boz N *et al,* 2009, Noiroj K etal2009, Guo C *et al,* 2011, Ilgen O *et al,* 2011), alkaline earth metal oxides and derivatives (Wang L *et al,* 2007 Lopez DE *et, al,* 2005, Yoo SJ *et al,* 2010), mixed metal oxides and derivatives (McNeff CV *et al,* 2008, Xu L *et al,* 2008 Wang L *etal*2007), al-kali metal oxides and derivatives (Ebiura T *et al,* 2005, Arzamendi G *et al,* 2007), waste material based heterogeneous catalyst , carbon based heterogeneous catalyst (Shu Q *et al,* 2010, Dehkhoda AM *et al,* 2010), and enzyme based heterogeneous catalyst.(Hama S *etal*2005, Du W *et al,* 2005), have been used in various biodiesel production processes.

Solid acid catalysts

(Wang *et al,* 2006, Meher LC *et al,* 2006) investigated biodiesel production with two methods. The first method, involved FAME production from waste cooking oil with solid acid catalyst in a two-step process and the second feature, FAME production in a conventional acid catalyst system. Meanwhile, they compared the results of these two methods.

The two-step process had 97.02% conversion with 10:1 molar ratio of methanol to oil, 4 h reaction time, and reaction temperature were 95 and 65^0C for the first and second steps, 2 wt% ferric sulfate and 1 wt% KOH as catalysts in the first and second steps.

However, the conventional method had around 90% conversion with 20:1 molar ratio of methanol to oil and 10 h reaction time.

The two-step system had major advantages such as absence of acidic wastewater; low equipment costs, easy recovery of catalyst, and high efficiency. The conventional method had some limitations such as no reusability of catalyst and high equipment costs.

Solid base catalyst

There are different types of solid base catalysts such as calcium oxide, (Meher LC *et al*,2006), MgAZr, (Li Y *et al* 2011), nano-magnetic KF/CaOAFe3O4 (HuS *et al*,2011) modified CaO by trimethylchlorosilane (TMCS) (Tang Y *et al* 2011) , and sup-ported solid base catalyst such as EU2O3/Al2O3(Li X *et al* 2007), La/bZeolite (Shu Q *et al* 2007), KI/Al2O3 (Xie WL *et al*2006) , Na/NaOH/c-Al2O3, (Kim HJ *et al*,2004) which researchers have used for transesterification reaction of biodiesel production.

These catalysts are inexpensive and have high yield but there has been limited research on FAME from oil using these types of catalysts.

(Guo *et al*,2002)investigated the use of solid base catalysts in biodiesel production and demonstrated that more than 95% yield can be achieved at optimum conditions of 3.0 wt% sodium silicate catalysts, 7.5:1 molar ratio of methanol to oil,60^{0}C reaction temperature, 60 min reaction time, and 250 rpm mixing intensity.

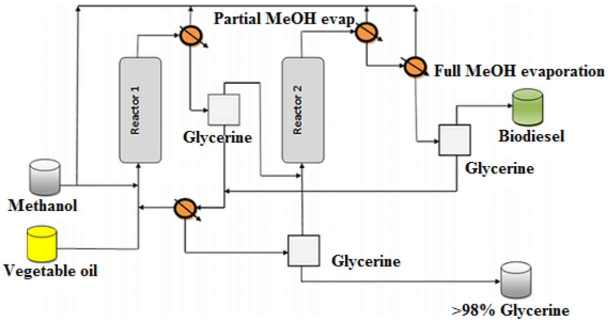


Fig.3 Flow diagram of biodiesel production using heterogeneous catalyst

Enzymatic catalyzed transesterification

Recently, it has been found that enzymatic catalyst (immobilized lipase) can be used in transesterification reaction. No by-product, easy product removal, reusability without any separation step and lower operating temperature are the key advantages of this method. However, it is found to be very expensive (Shimada Y *et al,* 2002, Robles-Medina A *et al,* 2009). The enzymatic reaction is insensitive to water and FFA content in waste cooking oil (Robles-Medina A *et al,* 2009, Hsu A *et al,* 2001).

(Ranganathan *et al*. 2008) compared the alkali and enzymatic transesterification process in biodiesel production. They construed that the utilization of biocatalyst can produce very high pure FAME with lower or no downstream process compared to alkali catalysts.

Some factors have significant influence on the biodiesel production with lipase such as number of cycles, types of alcohol, ratio with oil and type of lipase. There are different types of lipases that can be used as the catalyst such as: Rhizaopusoryzae, Candida rug-osa, Psuedomonas fluorescens, Burkholderia, Cepacia, Aspergillusniger etc.

The non-enzymatic heterogeneous catalyst

This method is relatively new and includes ZrO2, ZnO, SO4, 2-/SnO2,SO4 2-/ZrO2, KNO3/KL, zeolite and KNO3/ZrO2. The main advantages of these types of catalysts are: less corrosion and being more environments friendly. These properties can reduce the cost of biodiesel production. Furthermore, they can reduce the formation of soap even in low quality oils. However, this type of reaction was carried out at 200^{0}C and pressure level of 50 bars, with 6:1molar ratio of methanol to oil and 3% catalyst weight for maximum efficiency. (Vasudevan PT *et al,* 2008).

Non-catalytic production

There are a large number of drawbacks in biodiesel production using conventional methods (alkali and acid catalyzed processes) such as: requires high energy to conduct, difficult recovery of glycerol, high sensitivity to water and FFA content in raw material (feedstock), and very low reaction rates. Meanwhile, the utilization of lipase (enzymatic catalyzed) has their own disadvantages such as having a high price of catalyst and being time consuming (Mamoru I *et al,* 2001, Orcaire O *et al,* 2006).

Researchers have attempted to find novel methods that do not need catalysts to eliminate or decrease these types of obstacles in biodiesel production (Niza NM *et al,* 2013) . Saka was the first scientist who proposed that FAME can be produced by supercritical method (Saka S *et al,* 2001).

The supercritical method requires no catalyst and can achieve near complete conversion in a relatively short time. This method is not feasible for large scale production because it requires high temperature and pressure for biodiesel production.

These reasons dramatically increase the equipment and production costs. Thus, most researchers have focused on finding new approaches in this method to decrease the reaction temperature and pressure.

The utilization of co-solvents such as carbon dioxide,hexane and calcium oxide are the key components to overcome these obstacles (Han HW *et al,* 2005, Demirbas A *et al,* 2005) .

Supercritical method

(Jian-Zhong *et al*, 2008) investigated biodiesel production with a conventional supercritical method and a supercritical coupled with co-solvents methods. The conventional method was carried out at various reaction temperatures (260, 300, and 350^{0}C), constant molar ratio of methanol to oil 42:1, 300 rpm mixing intensity, and different pressure up to 20 Mpa. The results showed that at 350^{0}C reaction temperature, the highest yield was 95% in 10 min. Mean-while, alcohol and oil do not mix to form a single phase; therefore, hexane was added to the mixture to solve this problem. The results indicated that the reaction yield without hexane was 67.7%, but the yield reached 85.5% with 25 wt% of hexane. The researchers concluded that mutual solubility between methanol and oil was improved with the addition of hexane.

The supercritical CO_2 is a suitable solvent for moderate and small organic molecules, because it has low cost and available material. The supercritical condition of CO_2 is 31^{0}C and 7.38 Mpa which it is lower than the supercritical methanol conditions (239^{0}C and

8.09 Mpa). The reaction condition for supercritical CO_2 was 300^0C reaction temperatures, 0.2 ratio of CO_2 to methanol, and 42:1 molar ratio of methanol to oil. The highest yield achieved was 90.6% FAME in 30 min.

Reactive distillation method

Reactive distillation is the process where chemical reaction and distillation separation occur simultaneously in the single equipment (Kiss AA *et al,* 2007). This process has some advantages for special reactions such as: the reaction needs one or more reactant, the reaction needs to remove some of the products for completion, and the co-product recycling or product recovery process is complicated or has the possibility for azeotrope formation (Perry RH *et al,* 1997). A variety of reactions such as homogenous catalyst, heterogeneous catalyst and noncatalyst can be carried out in reactive distillation process, in which the reaction must show reasonable data for conversion at pressure and temperature levels that are similar (compatible) to distillation conditions (Da Silva ND *et al,* 2010, Tuchlenski A *etal*2001).

Moreover, this process can eliminate the need for a reheating because in exothermic reactions, the heat of vaporization provides the heat of reaction. The reactive distillation includes a smaller amount of equipment, hence a lower number of connections between instruments, reducing safety issues.

(Wang *et al*, 2001)evaluated the reactive distillation process for methyl acetate hydrolysis process. The results indicated a 10% reduction in energy consumption and a 50% increase in production, compared to conventional fixed bed reactor.

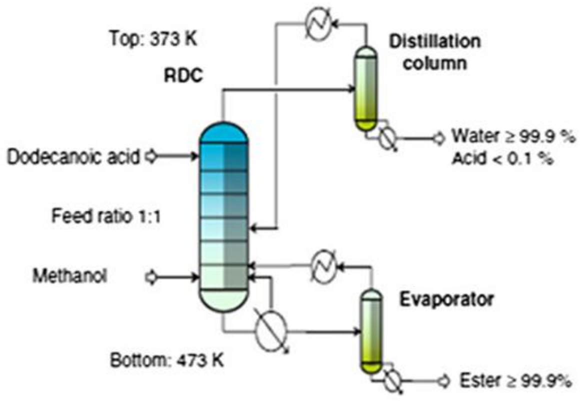


Fig.4 Flow diagram of reactive distillation method for biodiesel production

Dual reactive distillation

The catalytic reactive distillation method allows more opportunities in biodiesel production and special chemicals. Effective water removal for protecting the solid catalyst against deactivation and avoiding costly recovery of the excess alcohol are the most important problems to overcome.

(Dimian *et al*, 2009) investigated a novel approach based on dual esterification of fatty acid with light and heavy alcohols. The methanol and long chain alcohol 2-ethyl hexanol have an equivalent reactive function but synergistic thermodynamic features. The reaction process takes place at moderate pressure, 130 and 200^0C temperatures compared to high pressure and vacuum by single light and heavy alcohol.

Reactive absorption

Reactive absorption is a novel biodiesel process that offer more advantages compared to conventional methods. The advantages are: high conversion and selectivity, simple and robust process,no thermal degradation of product, omits regular catalyst-related operations and no waste streams. It can also decrease capital and operational costs. Researchers use water tolerant solid acid for catalysts in this method, so they can eliminate additional separation steps and salt waste streams (Kiss AA *et al,* 2006, Okuhara T *etal*2002, Kiss AA *et al,* 2008).

Kiss and Bildea (Kiss AA *et al,* 2011)evaluated the integrated reactive absorption process for biodiesel production with solid acid catalyst and the simulation of the process. The results illustrated that the purity of production was higher than 99.9% when the productivity of reactive absorption unit was 19(kg FAME/kg catalyst h).

Continuous flow biodiesel production

The conventional transesterification process uses batch operation, which has some disadvantages such as: poor adaption to automation, tedious, and labour-intensive. However, a continuous flow biodiesel production has significant benefits that include low production costs and time in small-scale plant, the ability to produce higher quality biodiesel per unit of labor, and the capacity to improve the equipment design to optimize the quality of biodiesel (Noureddini H *et al,* 2005).

The Rotating Packed Bed (RPB) has been designed to increase the micro-mixing efficiencies and mass transfer by the utilization of great centrifugal force. Various applications of this method have been reported such as the utilization of RBP as gas liquid contact in absorption (Chen YH *et al,* 2010, Lin CC *et al,* 2003, Chen YH *et al,* 2004, Chen YS *et al,* 2008), distillation (Ramshaw C *et al,* 1983, Kelleher Y *et al* 1996), stripping (Singh SP *et al,* 1992, Liu HS *et al* 1996), and ozonation (Lin CC *et al,* 2003, Chang CC *et al,* 2009, Chen YH *et al,* 2005, Chen YH *et al,* 2005). Meanwhile, the RPB method has a high micro-mixing ability and can be used in a large number of applications.

(Chen *et al*, 2010) investigated biodiesel production with rotating packed bed reactors. They evaluated the effects of variables such as molar ratio of alcohol to oil (4:1, 6:1, 12:1, 18:1 and 24:1), reaction time (0.43–1.67 min), mixing intensity (150, 300,900, 1500 rpm), reaction temperature (34, 42, 60, 65^{0}C), and catalyst weight (0.1, 0.24, 1, 2, 3, 5%w/w). The results of this research showed a wide range of (55–97.3%) conversion. The optimum condition was 0.72 min reaction time, 900 rpm mixing intensity, 6:1molar ratio of alcohol to oil, 3%w/w catalyst weight and 60^{0}C reaction temperature which produced the highest conversion of 97.3% ester.

Membrane reactormechanism

The most important issues in biodiesel production are the removal of residual impurities such as free glycerol, catalyst, un-re-acted methanol, bound glycerol, un-reacted triglycerides(TG), diglycerides (DG), monoglycerides (MG), and small amounts of soap and water because these types of impurities affect engine performance significantly (Saleh J *et al,* 2010).

The novel method for purification and separation of biodiesel is the utilization of membrane reactors. Methanol and vegetable oils are not miscible and membrane reactors take advantage of this immiscibility to create a better purification process. The separation by membrane is useful for water purification, protein separation and gas separation. The commercial application of this method is separation that involves aqueous solutions and relatively inert gases(Kim IC *et al,* 2002, White LS *et al,* 2000).

There are two types of membrane, organic and inorganic. The inorganic membranes are suitable for use with organic solvents because they have high thermal stability and can be used at high temperatures and continuous processes. Fig. shows a schematic view of prototype biodiesel membrane separation plant (Sdrula N *et al,* 2010).

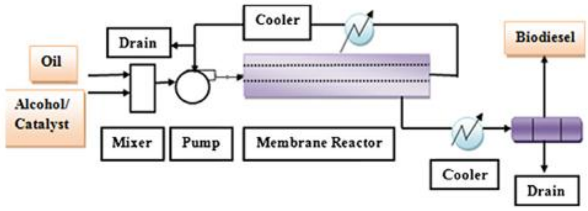


Fig.5 Flow diagram of biodiesel membrane separation prototype plant

(Dube' *et al,* 2007) reported that micro-porous inorganic membrane reactor could remove FAME, glycerol, and methanol during the transesterification reaction of triglycerides.

(Cao *et al, 2008*) investigated the utilization of membrane technology for biodiesel production and reductions in required molar ratio of methanol to oil. The results showed that the highest conversion was (85.7–92.4 wt%) and significant reduction for molar ratio from 15:1 to 10:1 methanol to oil.

(He *et al, 2006*) compared three conventional methods of washing with distilled water, washing with acid (HCL) and extracting with solvent (n-hexane or petroleum ether) with a novel technology of hollow fiber membrane extraction. All conventional methods produced 97.5% purity biodiesel. However, the membrane reactor obtained around 99% purity and other properties of biodiesel such as kinematic viscosity, acid value and density were similar to standard values.

Ultrasonic method

Ultrasonic process using sound wave energy vibrates more than 20,000 times per second. These waves are in the range of 20–100 kHz that is beyond the human hearing limit (10–12 kHz). Medical research and detection was the first application of ultrasonic waves in 1930–1940 (Newman PG *et al,* 1998).

Ultrasonic irradiation improves the reaction characteristics by formation of smaller droplets (146–148 nm by 50–70 W) compared to conventional stirring system (340 nm by 1000 rpm) by improving the contact area between oil and alcohol (Mikkola JP *etal*2001, Stavarache C *et al,* 2006). Besides, ultrasonic energy can break catalyst to smaller particles to form new sites for subsequent reaction. Therefore, researchers concluded that solid catalysts are suitable choice for this process because the catalysts stability is expected to last longer (Mootabadi H *et al,* 2010).In addition, ultrasonic irradiation can enhance the enzyme catalyst activity (Sinisterra JV *et al,* 1992, Lin G *etal* 1995). There are some reaction parameters that significantly influence the ultrasonic irradiation process: (1) ultrasonic power, (2) frequency effect, (3) catalyst type, (4) alcohol type.

The main advantages of ultrasonic irradiation process are: (1)shorter reaction time, (2) lower molar ratio of alcohol to oil, (3) less energy consumption (50%), (4) lower amount of catalyst utilization (enzyme), (5) increased reaction rate, (6) enhanced conversion, (7)improved yield, (8) different reaction path way, (9) simpler equip-ment setup, (10) better process economy, (11) simpler separation and purification processes, (12) higher quality glycerol production.

In contrast, this process has some disadvantages such as (1) the reaction temperature was slightly higher for long reactions, (2)higher catalyst loading compared to conventional processes, (3)the ultrasonic power must be under control due to the soap formation in fast reaction. Therefore, FAME yield can be reduced by higher frequencies (40 kHz).

(Yu *et al* 2010) investigated the production of biodiesel from soybean oil and an immobilized form of Novozym 435 as catalyst. The transesterification reaction was carried out by two different methods (ultrasonic irradiation and ultra-sonic irradiation with vibration). The enzyme activity and reaction rate are dramatically increased by ultrasonic irradiation with vibration. Some variables such as water content, ratio of solvent to oil, enzyme dosage, organic solvent, ultrasonic power, ratio of methanol to oil, and temperature were investigated in this research. The results indicated that the 96% yield of FAME was obtained under optimum conditions of 50 rpm mixing intensity,0.5% water content, 1:1 tert-amyl alcohol to oil volume ratio, 6:1methanol to oil molar ratio, 40^{0}C reaction temperature, 50% of ultrasonic power and 4 h reaction time.

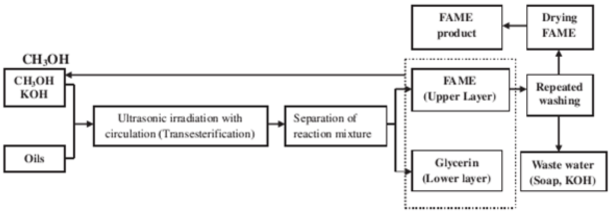


Fig.6 Flow diagram of ultrasonic irradiation process for biodiesel production from vegetable oil in presence of base catalyst

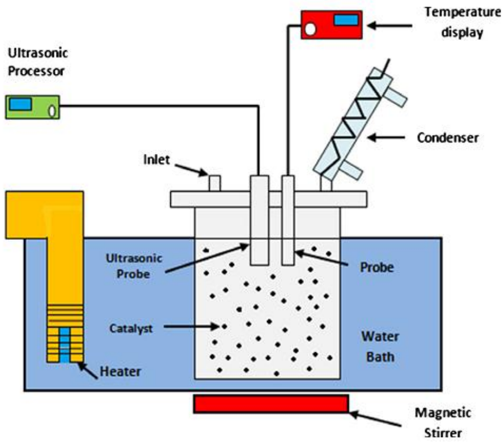


Fig.7 Schematic diagram of an experimental setup used for ultrasonic assisted biodiesel production process

Microwave mechanism

Microwave ovens entered households in 1954 and the utilization of this equipment has increased in recent years. Microwaves can heat matter faster than conventional ovens, and this is the most important property of this type of oven.

Microwaves transfer energy to samples directly and this energy completes the reaction. Microwave irradiation has a higher frequency than radio waves and much lower than X-rays with wave-length of 1 mm–1 m and 300 MHz to 300 GHz frequency (Orchard B *et al,* 2007). There are three microwave heating equipments patents in use in bio fuel manufacturing (WO03/014272 A2, 2003; US 2005/0274065 A1, 2005; US 2006/0162245 A1, 2006). The implementation of multiple microwave process has a significant effect on land, time saving and energy in comparison with conventional single large reactor tank system.

The main advantages of microwave process are: (1) higher quality and yield product, (2) minimum energy consumption (23 times lower than conventional methods) (Patil PD *et al,* 2010), (3)environmental friendly, (4) shorter reaction time, (5) lower molar ratio of alcohol to oil, (6) less quantity of by-products, (7) more effective heat transfer system (conventional methods transfer heat to the reaction by convection, conduction, and radiation from reactor surface but, microwaves transfer energy in a form of electromagnetic and not thermal heat reflux.) The microwave energy is directly delivered to the reactant and preheating step is eliminated.

(Refaat *et al*, 2008) obtained the optimum parametric conditions for conventional method with application of microwave irradiation for production of biodiesel from neat and waste vegetable oil with a high FFA content. Meanwhile, the results indicated that micro-waves can easily route fuel with the added benefits of increasing the reaction reactant and improving the separation and purification process.

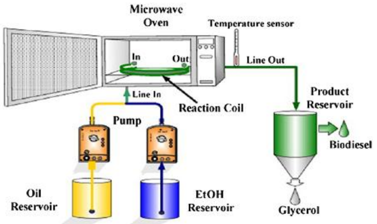


Fig.8 Schematic diagram of continuous microwave biodiesel production process

Conclusions

Alternative fuel production from renewable resources poses many challenges. Depletion of fossil-fuel resources, unstable price of crude oil, and environmental concerns are the main reasons for finding a new fuel which should be environ-mentally friendly, cheap, widely available, and technically acceptable. Biodiesel is one of the best fuel alternatives that researchers are focused on and efforts are being made to produce it at a lower cost and with outstanding fuel properties. The transesterification reaction is the best method for production and modification of bio-diesel. Acid, alkali, or enzymatic catalyzed, and non-catalyst transesterification are different approaches that have been tried for biodiesel production. However, all of them have their own advantages and disadvantages. The type of feed stock is the most important factor in the production of biodiesel. There are various types of vegetable oils and animal fats that can be used in this pro-cess. Hence, blending with multiple oils obtained from non-conventional non-edible biomass feedstock including algae may be considered as appropriate strategy for producing biodiesel at commercial scale.

The transesterification with alkali catalysts is the conventional method for bio-diesel production, but this method causes serious problems in the purification part since they are highly sensitive to FFA and water content in the raw material. The acid catalyzed process is not sensitive to FFA and water content like base catalysts. How-ever, the production process is much longer. The utilization of enzymatic catalysts showed very good results, but they are expensive and for the industrial production of biodiesel, this is not acceptable. In addition, the non-catalyst method or supercritical method requires high temperature and pressure, and this is obviously not economical. Therefore, scientists focus on the utilization of heterogeneous acid and base catalysts in biodiesel production since the catalysts may be reusable many times. The reusability of catalyst is the most important property which can make them economical for industrial production in a continuous process. Hence, various methods such as membrane reactor, reactive distillation, reactive absorption, microwave, and ultrasonic to reduce production costs, reaction time, catalyst and alcohol requirements have been used in transesterification reactions. These methods can increase the quality of FAME for applications to diesel engines without any kind of engine modification.

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