2. Production of Biodiesel from waste cooking oil

Review Article

Dipak Dadaso Pukale
Final Year Bachelor of Technology
Department of Oils, Oleochemicals and surfactant Technology

Abstract

High variation in global price of petroleum crude oil has an inauspicious impact on national economy of crude oil dependant countries like India. As per the survey, petroleum crude oil consumption in India was 3.182 million barrels/day in 2010 and oils consumption is growing fast, in 2002 consumption rate increases by 3.28% while in 2010, it increases by 6.77%. Therefore, looking for the eco friendly alternative path to produce replacement for the petroleum based fuel like diesel is the recent task for green technologists. Transesterification reaction of frying oil generally known as waste cooking oil with alcohol (methanol or ethanol or both) in presence of various different catalysts to synthesis transesterified product i.e. biodiesel is the future need as the alternative energy source because of depletion of fossil fuels.

The comparisons of the biodiesel production from waste cooking oil using various methods were also reviewed in this paper. This paper reviews the work that has been already studied in biodiesel production technologies from waste cooking oils.

Keywords: Biodiesel, waste cooking oil, Trans-esterification, frying oil etc.

1. Introduction

Currently, intensive efforts to reduce green house gases (GHG) emission from petroleum-based diesel usage have initiated vast production of biodiesel worldwide. It is biodegradable in which the fuel is derived from renewable sources; non-toxic, less emission of hazardous gases during combustion and has been categorized as the most promising substitute to petroleum-based diesel [1]. However, the bottleneck to produce

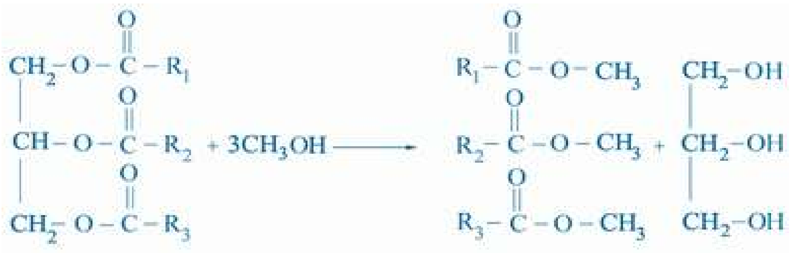

Figure 1: Transesterification reaction [5]

biodiesel in commercial scale is the high cost of edible virgin oil, in which account for more than 70% of the overall biodiesel production cost. In addition, using edible virgin oil such as rapeseed, sunflower, soybean and palm oil in biodiesel production has raised the concern of food versus fuel debate. Thus, recent biodiesel development has shifted to use non-edible and waste cooking oil (WCO) as a new and sustainable feedstock for long term production [2]. It is strongly believed that using these oils will help in improving economical feasibility of biodiesel and minimize the hurdle of food versus fuel phenomena. See Table 1 for physical and chemical properties.

Table 1. Physical and chemical properties of waste cooking oil. [3]

Properties	WCO
Physical	
Density at 27^{0}C, g cm^{-3}	0.9168
Acid Value, mg KOH g^{-1}	5.0
Free fatty acid, %	2.54
Moisture content, %	0.162
Saponification value	183.5
Chemical	
Fatty acid composition, wt.%	
C16:0	39.3
C16:1	0.18
C18:0	2.3
C18:1	46.3
C18:2	11.9

2. Transesterification

The most common way to produce biodiesel is by transesterification, which refers to a catalyzed chemical reaction involving oil and an alcohol to yield fatty acid alkyl esters (i.e. biodiesel) and glycerol. Triglycerides, as the main component of vegetable oil, consist of three long chain fatty acids esterified to a glycerol backbone [4]. When triacylglycerols react with an alcohol (e.g., methanol or ethanol or both), the three fatty acid chains are released from the glycerol skeleton and combine with the alcohol to yield fatty acid alkyl esters. Glycerol is produced as a by-product.

Methanol is the most commonly used alcohol because of its low cost and is the alcohol of choice in the processes developed. In general, a large Excess of methanol is used to shift equilibrium towards the product side.

A simple molecular representation of the reaction is shown in Fig. 1.

3. Various methods to produce Biodiesel from WCO

3.1 Alkali catalyzed transesterification reaction

In alkaline catalyzed transesterification process, Strong base catalysts e.g. sodium methoxide, sodium hydroxide, potassium hydroxide and potassium methoxide are used. This process is most effective in converting triglycerides into esters when free fatty acid level is less than 1%. It is the most widely used process because this reaction happens at moderate temperatures and lower pressures and also there is high conversion efficiency (98%). This process requires only a small time and there is a direct conversion of biodiesel without any intermediate steps. However, it becomes less effective when the free fatty acid level exceeds 1% because the FFA reacts with the most common alkaline catalysts (NaOH, KOH, and CH3ONa) and forms soap which adversely affects on the separation of ester from glycerin i.e. ultimately reduces the conversion rate. Certain amount of alkaline catalyst is consumed in producing soap and hence, catalyst efficiency decreases [6].

3.2 Acid catalyzed transesterification reaction

In acid transesterification process, acidic catalysts like, sulfuric acid, phosphoric acid, hydrochloric acid and organic sulfonic acid are used. In this process, a strong acid is used as a catalyst for esterification of the FFAs and the transesterification of triglycerides [8]. This process does not yield soap due to the absence of alkali material. The esterification rate of the FFAs to alcohol esters is relatively fast however; the transesterification of the triglycerides is very slow, taking several days to complete.

3.3 Two step method

The combined process with acid catalyzed pretreatment is developed to improve the yield of biodiesel by the WCO. The pretreated step of this process is to esterify the FFA with methanol by acid catalysis. When the FFA content is lower than 0.5%, the sulfuric acid drained and the solid alkali is introduced into the system to complete the transesterification [10].

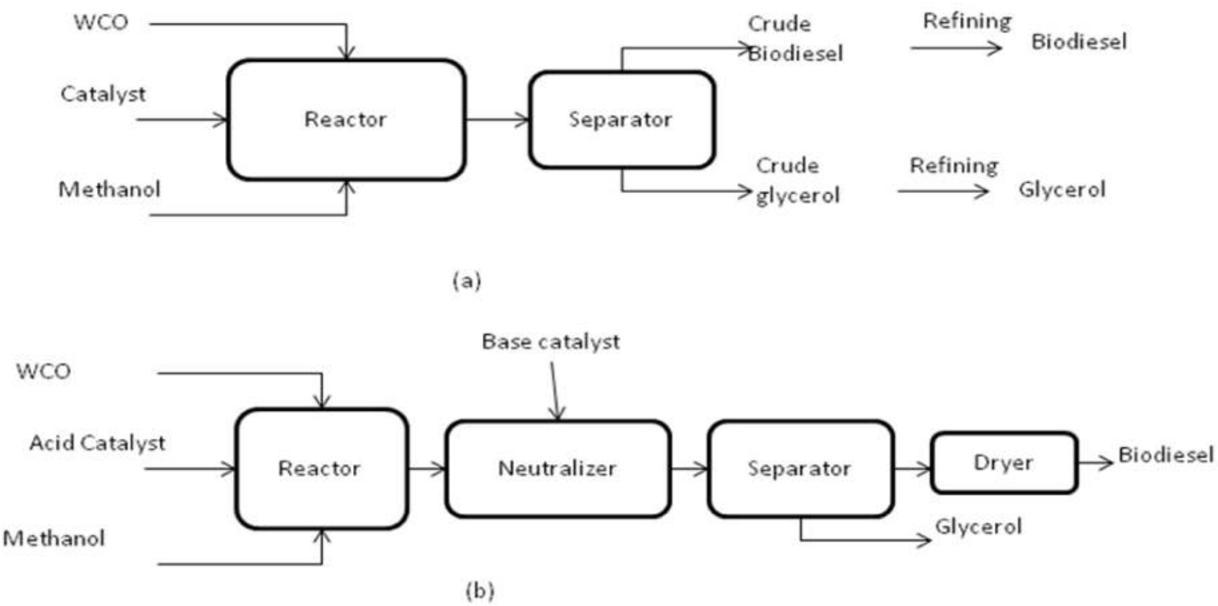

Figure 2: a) Alkali catalyzed method [7], b) Acid catalyzed method [9]

However, long reaction time, no recovery of catalyst and high cost of reaction equipment are disadvantages of this process. To overcome the disadvantages of acid catalyzed process or pretreatment, the homogeneous Lewis acid catalyst (carboxylic salts) is used [11]. However, the reaction temperature is too high (≤200 ◦C), and the conversion ratio is relatively low (≤90%). That is why heterogeneous catalyst is used in this method and also this catalyst can be recycled and reused. At the first step, ferric sulfate introduced to catalyze the esterification reaction in which FFA in the WCO reacted with methanol. The ferric sulfate that has very low solubility in the oil is separated from the liquid after the methanol recovery, and could be recovered by ashing process [12]. At the second step, potassium hydroxide is added to catalyze the transesterification reaction in which triglyceride (TG) reacted with methanol. Without wastewater, reusable catalyst and low cost of reaction tank, this two-step catalyzed process exhibits potential application in the biodiesel industry. At the first step, ferric sulfate introduced to catalyze the esterification reaction in which the Fig. 3. Mechanism of synthesis biodiesel by two-step catalyzed process. FFA in the WCO reacted with methanol. The ferric sulfate that has very low solubility in the oil is separated from the liquid after the methanol recovery, and could be recovered by ashing process [13]. At the second step, potassium hydroxide is added to catalyze the transesterification reaction in which triglyceride (TG) reacted with methanol. Without wastewater, reusable catalyst and low cost of reaction tank, this two-step catalyzed process exhibits potential application in the biodiesel industry.

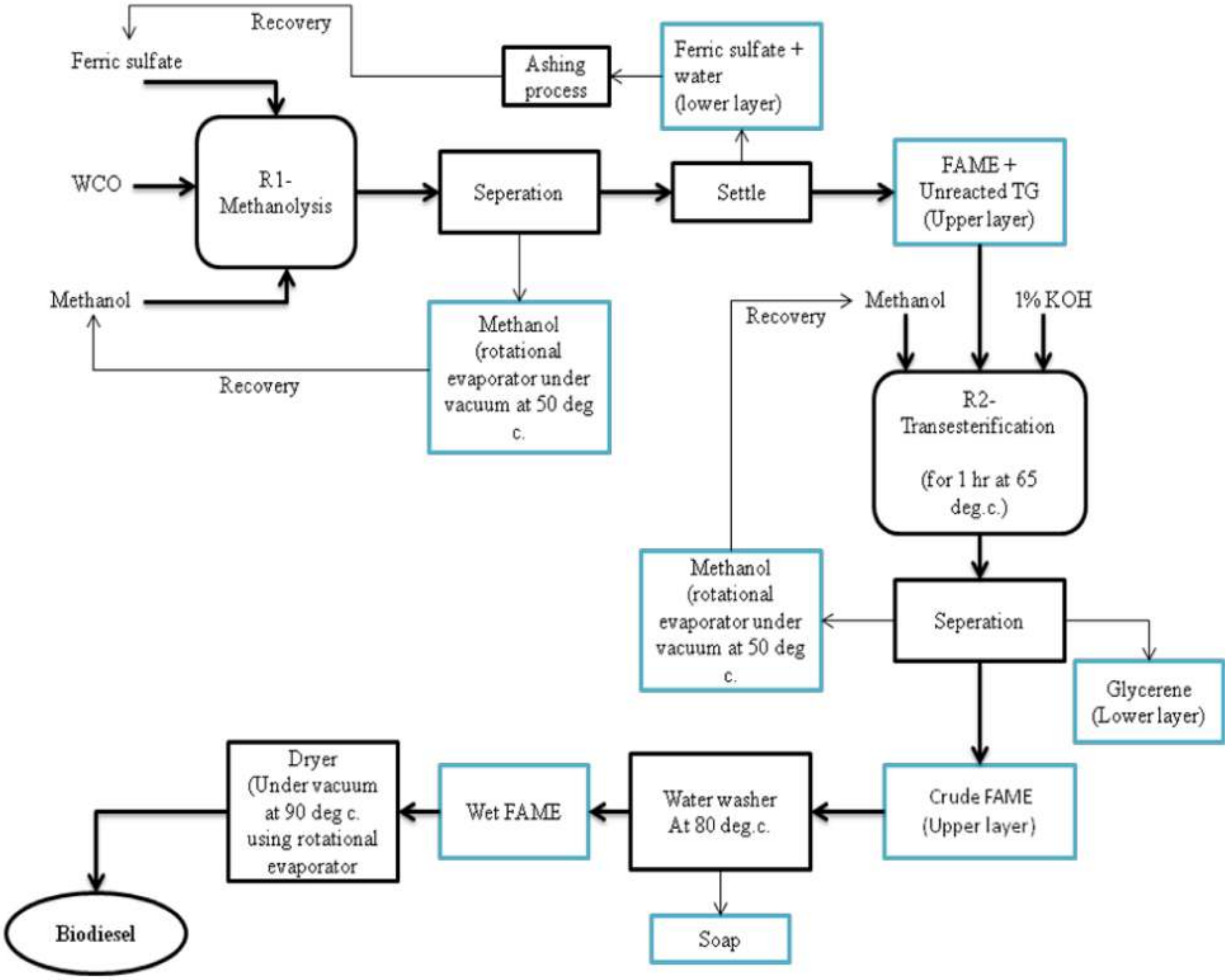

Figure 3: Two step method

3.4 Supercritical Method

A combination of acid- and alkali-catalyzed processes has been developed to overcome disadvantages of Alkali and acid catalyzed method caused by the presence of FFA and water; these can be essentially overcome if a non-catalytic biodiesel production is realized [14]. In such a situation, supercritical fluid has received a special attention as a new reaction field due to its unique properties.

Following figure 4(a) shows a schematic diagram of the supercritical methanol method. In supercritical methanol, TG in oils/fats is found to be converted to FAME without any catalyst due to its methanolysis ability. Compared to the alkali-catalyzed method, there are some advantages, the production process becomes much simpler the reaction is so fast, FFA in oils/fats can be converted to FAME through methyl esterification and Yield of FAME is higher. This method, therefore, offers potentially a simple process for producing biodiesel fuel [15]. Although this process has many disadvantages, it requires restrictive reaction conditions. In such conditions, special alloys (e.g.Inconel and Hastelloy) are required for the reaction tube to avoid its corrosion. In addition, FAME particularly from poly-unsaturated fatty acids, such as methyl linolenate, are partly denatured under this severe condition [10].

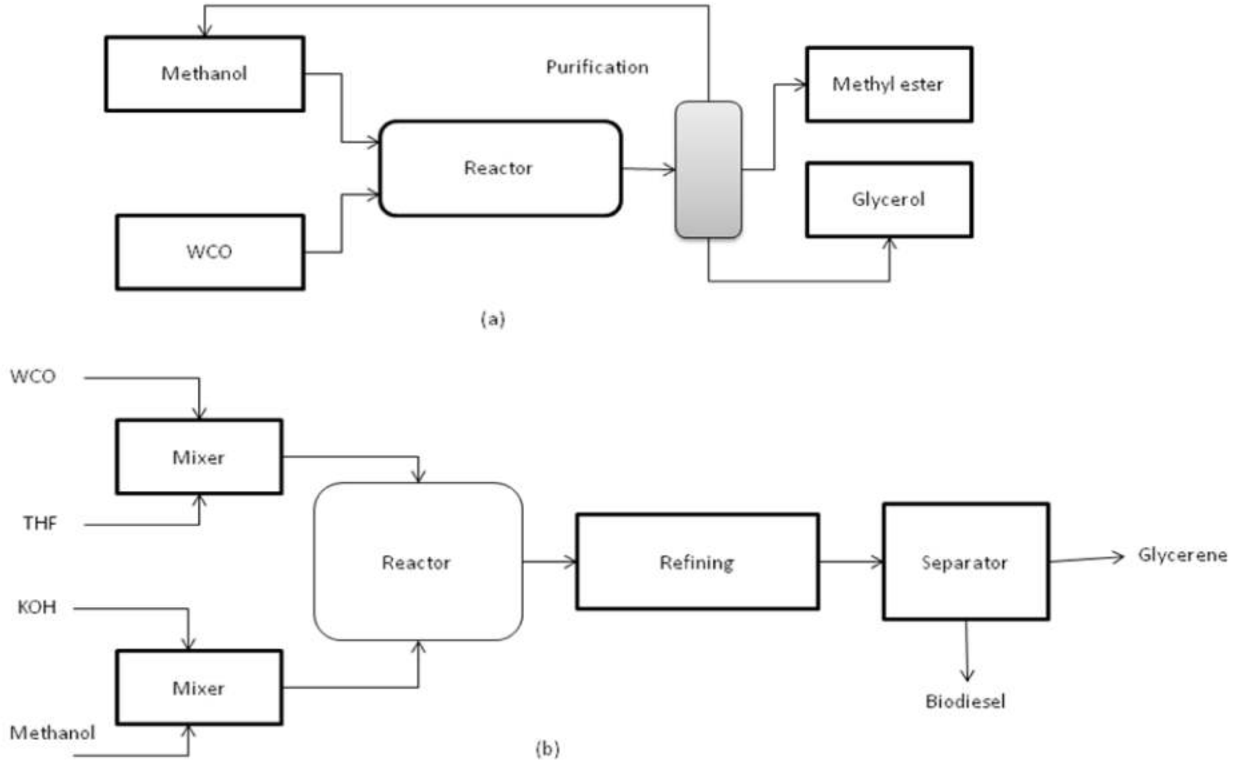

Figure 4: (a) Supercritical method [16], (b) Biox method [19]

3.5 Biox Method

The main problem for the lower rate of transesterification is that the reaction mixture is not homogeneous because the oils and alcohols are not miscible each other because of their chemical structures. Oil disperses in the methanol medium, so the probability and the rate of collision of the glyceride and the methoxide (the mixture of methanol and the alkaline catalyst KOH or NaOH) molecules becomes lower. This lowers the rate of collisions of molecules and so the rate of reaction causes longer reaction times, higher operating expenses and labor [17].

To overcome this difficulty of the heterogeneous mixing of the reactants, a single phase reaction has discovered. The proposed model includes a cyclic solvent introduced into the reaction mixture which makes both the oil and methanol miscible. This solvent can be a numerous of different solvents with the boiling point up to 100°C. THF (tetrahydrofuran) is preferred because of close boiling point to that of methanol so that after reaction both methanol and THF can be recycled in a single step to use again [18]. This process uses a co-solvent, tetrahydrofuran to stabilize the methanol. It requires only 5–10 min to complete the reaction. This system requires low operating temperature 30 °C [18].

Tetrahydrofuran is the most extensively used co-solvent because; its boiling point is close to that Tetrahydrofuran is the most extensively used co-solvent because; its boiling point is close to that of methanol. Firstly the process converts the free fatty acids (up to 10% free fatty acids contents) followed by the triglycerides through the addition of a cosolvent in two steps, single phase continuous process at atmospheric pressure and temperature within 90 min of reaction time. The co solvent is then recycled and reused continuously in the process. A lot of research work has been carried out to produce biodiesel that is cost competitive with conventional diesel by using this method. See table 2 for overview of parameters involved in all the above processes.

4. Conclusion

The objective of this paper is to review the work that has been already done in the technologies of conversation of triglycerides into biodiesel. The following specific conclusions are based on the review from this paper.

4.1 Selection of a transesterification process depends on the amount of free fatty acid and water content of the feedstock.

4.2 Alkaline catalyzed transesterification process is most effective in converting triglycerides into esters when free fatty acid level is less than 1%. KOH is the most commonly used alkaline catalyst for producing biodiesel from waste cooking oil.

4.3 When the FFA content of feedstock is >1 wt. %, then an acid catalyzed transesterification process is most effective. However, this process requires high catalyst concentration and high molar ratio leading to corrosion problems.

4.4 A new technology (Biox process) is developed in order to overcome the problem low homogeneity of reactants, methanol and oils. This process uses a co-solvent to stabilize the methanol. THF is most commonly used co solvent and this method is commercialized.

Table 2: Overview of parameters involved in all the above processes.

Reaction Variable	Acid catalyzed	Simple base catalyzed	Two step reaction	Biox method	Supercritical method
Feedstock	WCO	WCO	WCO	WCO	WCO
FFA content	High	Low (<1%)	High	High	High
Reaction time (min)	240	60	90	10-15	30
Temperature (d. C.)	55-80	60-70	60-70	30	350
Catalyst used	H_2SO_4	NaOH	1- Ferric sulfate 2-NaOH	Catalyst- NaOH Co solvent- THF	No catalyst
Catalyst loading	1.3:1	1%	1% ferric sulfate	-	-
Conversion (%)	91.7	98.4	99.3	>99	90
Glycerine recovery	Difficult	Difficult	Easy	Easy	Easy
Purification	Difficult	Difficult	Easy	Difficult	Difficult
Cost of catalyst	Cheap	Cheap	Costly	Costly	-

4.5 Problems which are occurred during alkali and acid catalyst process, two step process is used to overcome. In this case heterogeneous catalyst is used in first step which can be recycled and reused while in second step solid alkali catalyst is used.

4.6 Non-catalyzed supercritical methanol transesterification process has been developed in order to overcome the limitations of catalyzed transesterification process. It requires very short time under supercritical conditions (temperature 350–400 °C and pressure more than 80 bar. However, it requires a high alcohol to oil (42:1) ratio and higher capital and operating cost. It also consumes more power

4.7 Currently the cost of biodiesel is high as compared to conventional diesel oil because most of the biodiesel is produced from pure vegetable oils. However, it can be reduced by using low cost feedstock such as animal fat and used cooking oil.

4.8 The fuel properties of biodiesel derived from used cooking oil are in accordance with biodiesel standards. Thus, biodiesel produced from used cooking oil can be used in diesel engines without any engine modifications.

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