

## Processing of vegetable oil for biofuel production through conventional and non-conventional routes



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### ABSTRACT

Ever growing world energy demands, depletion and price of petroleum reserves, and environmental concerns are enormous challenges in today's scenario. For meeting the demand, alternate fuels are considered as an obvious choice owing to their renewability and environmental friendliness. Among the possible alternatives, processing of vegetable oil for biofuel production has gained considerable attention due to its ease of operation and integration with existing oil refining processes. Typically, transesterification based processes have been developed for production of biodiesel whereas hydroprocessing routes are developed to convert vegetable oil to green diesel and Bio-aviation turbine fuel (Bio-ATF) fraction using non-edible/edible vegetable oils as a feedstock. Accordingly, the present review is aimed at understanding of process aspects of various available processes. Based on the reviewed processing options, the merits and demerits of the developed routes have been highlighted and possible approaches for development of glycerin free biodiesel routes are envisaged.

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### Introduction

Today, stringent environmental norms and depletion of oil reserves have added impetus for development of eco-friendly and sustainable fuel options. This has resulted into emergence of biofuels from sustainable bio-resources. In this context, fuels of bio-origin, such as bio-alcohols, biodiesel, biogas, green diesel and Bio-aviation turbine fuel (Bio-ATF) are found to be potential alternatives and are increasingly becoming important. Among these, vegetable oil based biofuel options i.e. biodiesel, green diesel and bio-ATF have become more attractive in recent time because of their ease of production from available vegetable oil feedstock options.

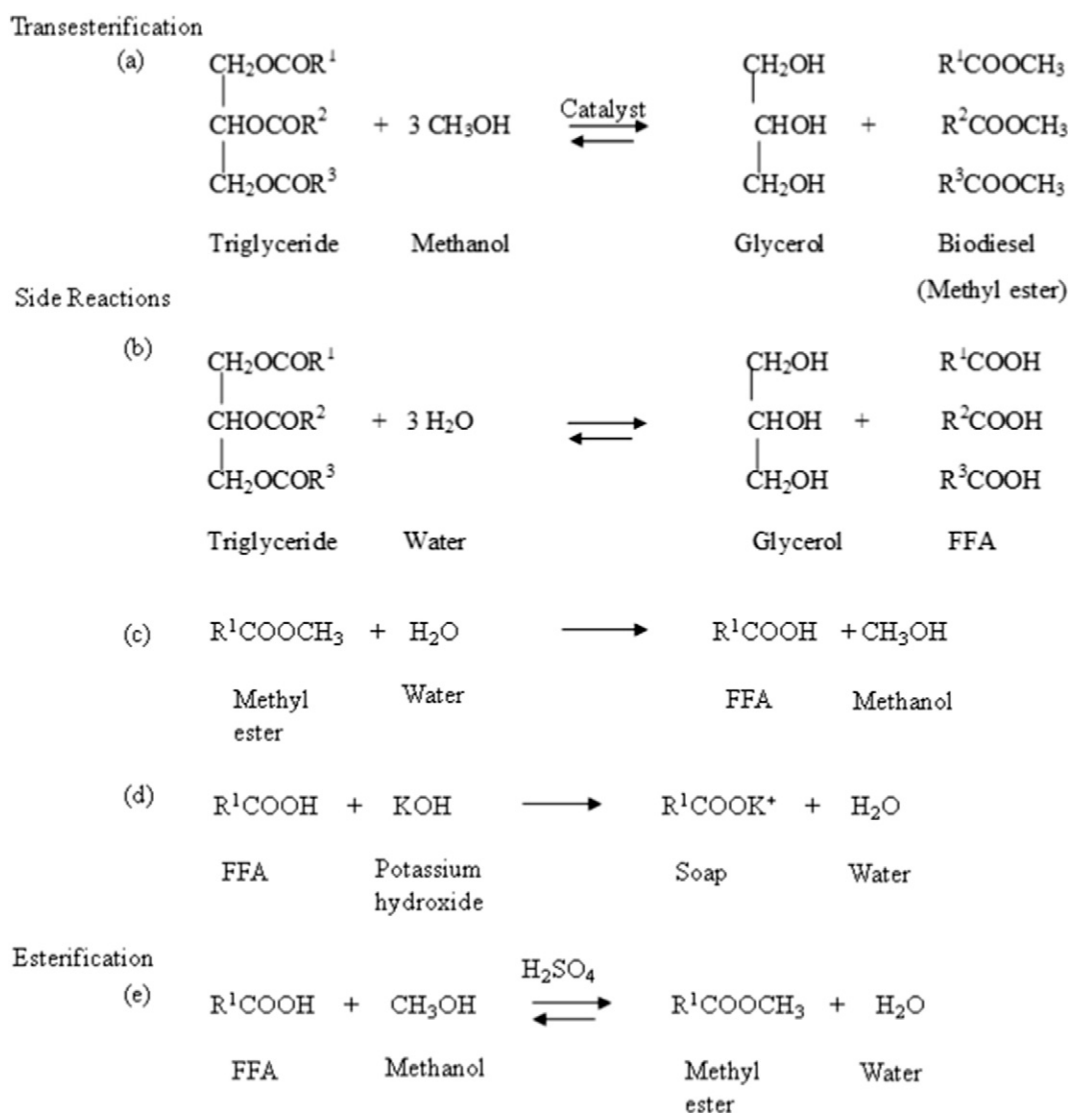
The direct use of vegetable oil as an alternative for diesel has been attempted in the past due to its portability, heat content (80% of diesel fuel), ready availability and renewability. However, its major disadvantages namely high viscosity, lower volatility and presence of unsaturated hydrocarbon have hampered its direct use as a diesel fuel (Pryde, 1983). Therefore, different ways have been evolved to transform vegetable oil to compatible diesel fuel option. This has led to development of (a) dilution, (b) micro-emulsions, (c) pyrolysis, (d) catalytic

processing and (e) transesterification approaches to convert vegetable oil to viable biofuel option (Ma and Hanna, 1999). Among all these alternatives, transesterification of vegetable oil with methanol leads to fatty acid methyl esters (biodiesel) formation and their physical characteristics that are very close to the diesel fuel (Selmi and Thomas, 1998; De et al., 1999). Typically, oil/triglycerides undergo transesterification reaction with low molecular weight alcohols such as methanol in the presence of catalyst as shown in Fig. 1a. For this purpose, alkali catalyst viz. sodium or potassium hydroxide prevails as the cheapest catalyst. However, reaction of sodium and potassium hydroxides produces water while reacting with alcohol in the formation of their alkoxide (Ma and Hanna, 1999). This reaction is naturally undesirable, because water can react with triglycerides, fatty acids, or esters in hydrolysis reactions as presented in Fig. 1b & c. In fact, the presence of water competes with alcohol which inhibits transesterification, thereby promotes ester hydrolysis, leading to formation of FFAs (Haas, 2005). The formed FFA favors saponification, leading to soap formation as shown in Fig. 1d. Hence, performance of alkali catalyzed transesterification are majorly affected by the presence of water by various side reactions which turns into loss of methyl ester to glycerol phase, and often result into high purification costs and less biodiesel yield (Zadra, 2006; Singh and Singh, 2010; Huang and Chang, 2010). Therefore, feedstocks containing considerable amount of water (>0.06 wt.%) and FFA (>3 wt.%) prior to transesterification undergo pre-treatment via esterification reaction using acid catalyst (H<sub>2</sub>SO<sub>4</sub>) as shown in Fig. 1e. The product (refined feedstocks) obtained with less FFA content (≤3 wt.%) and water content (<0.06 wt.%) is then used for alkali-catalyzed transesterification to produce biodiesel.

*Abbreviations:* VO, vegetable oil; WCO, waste cooking oil; WFO, waste frying oil; FO, frying oil; UCO, used cooking oil; IS, Indian Standard; TG, triglyceride; FAMES, fatty acid methyl esters; FFA, free fatty acid; DMC, dimethyl carbonate; DEC, diethyl carbonate; FAGC, fatty acid glycerol carbonate; GDC, glycerol dicarbonate; GC, glycerol carbonate; ATF, aviation turbine fuel.

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**Fig. 1.** Various reactions involved in Biodiesel production (a) transesterification; (b) triglyceride hydrolysis; (c) ester hydrolysis; (d) saponification; (e) FFA esterification. R<sup>1</sup>, R<sup>2</sup> & R<sup>3</sup> fatty acid chain of triglyceride.

Conventionally, transesterification of vegetable oils with methanol is performed in the presence of homogeneous or heterogeneous alkali/acid as catalysts (Serdari et al., 1999; Aksoy et al., 1990). Such processes are highly complex in nature due to the downstream separation and purification steps to produce biodiesel of requisite quality. Due to this, pre-treatment of vegetable oil feedstock is highly recommended to overcome the problems associated with downstream processing. Typically, downstream treatments involve separation of reaction product viz. biodiesel and glycerin from contaminants i.e. excess alcohol, soap formed (due to the presence of free fatty acid, FFA, in vegetable oil) and catalyst. Although the removal of the excess alcohol from both phases is achieved by distillation, the removal of catalyst and soap is more complicated, time consuming, and often leads to lower biodiesel yields (Fukuda et al., 2001). Thus, the overall performance of conventional process is mainly governed by impurity levels present in the vegetable oil as well as in the processed product. Therefore, to optimize the product yield and meet desired purity, process advances are made over the period in vegetable oil processing. Such advancement involves the use of pre-treatment steps, modified reactor designs and integration of non-conventional process intensification steps. This has resulted into development of various processing technologies for biodiesel production, which have been widely adopted (Serio et al., 2007; Bournay et al., 2005; Gogate and Kabadi, 2009). In this context, use of

supercritical conditions, enzymatic catalyzed, membrane and microwave assisted transesterification have been explored (Saka and Kusdiana, 2001; Du et al., 2004; Refaat et al., 2008; Georgogianni et al., 2009; Cao et al., 2007). In spite of advancement in conventional process technology, the overall economic viability of biodiesel production has been in question due to inferior glycerin quality and its over supply. This in turn demands intense and complex purification steps to upgrade glycerin quality [Hawash et al., 2009; McCoy, 2005, 2006]. Hence, it is utmost important to balance glycerin's availability, quality and demand. Therefore, attempts have been reported either to valorize glycerin stream by converting it to fuel additives (glycerin ethers), speciality chemicals (propane diols) etc. or to eliminate glycerin formation during biodiesel process (Leoneti et al., 2012; Fabbri et al., 2007).

The production of glycerin free biodiesel is conceptualized through two pathways namely hydroprocessing route and replacement of methanol as a reactant. The development hydroprocessing route has added impetus for integration of vegetable oil processing in existing oil refining processes. Such route offers platform for production of diesel and jet fuel fraction namely "Green Diesel" and "Bio-ATF", respectively. The green diesel fuel fraction produced is found to have excellent cetane number vis-à-vis mineral oil based diesel fraction (Choudhary and Phillips, 2011; Lestari et al., 2009). On the other hand, replacement of methanol with dimethyl carbonate (DMC) and methyl acetate (Fabbri

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