

Synthesis of Linseed oil Biodiesel using a Non-Catalytic Supercritical Transesterification Process

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ABSTRACT

Due to high energy demand and limited availability of fossil fuels, the energy necessity becomes a point of apprehension as it results in hike of fuel prices. It is essential to develop renewable energy resources while considering the impact on environment. In the last decade, demand of alternative fuels has increased a lot. Therefore, researchers have already started working on the aim of developing a green fuel to overcome the future energy demand. And as we know that the biodiesel is generally prepared from the non-edible and renewable resources thus, it can be among the competitive alternative future fuels. Besides that, it does not require any prior engine modifications for its usual advantage among other alternative fuels while using it within certain boundaries. However, the process biodiesel production is in itself time consuming which increases the cost of production while decreasing the yield. Supercritical method is drawing major attention for its efficient means with overcoming the negatives of conventional production processes. This method generally results in a high conversion rate of triglycerides into the FAME's (fatty acid methyl ester). But, it is confined to vegetable oils having low FFA content. Hence, in the present study, a non-catalytic supercritical trans-esterification process was utilized to produce biodiesel from Linseed oil. The analysis for the influence of temperature and time of run was done on the yield of FAME's, DG and TG. Results revealed that FAME's content increases with increase in temperature and the time of run. However, the pattern was uniform for all initial range of temperatures though a slight decrement was observed at higher temperature due to the thermal degradation of esters.

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INTRODUCTION

Energy production and consumption are the most crucial aspects for the development of any country. In a row of development; presently, all the countries are passionate towards growth. Subsequently, this appetite of evolution requires a huge amount of energy to fulfill the desire of entire world. Most of the energy is derived from the fossil resources which are extracted from the earth and these resources are depleting day by day because of its in-determinate need for growth and development of any country. Transportation and industrial sector are the key exploiters of fossil derivatives for generation of energy while playing a vital role in the economic growth of the country. As these sectors mainly require crude oil for the energy generation; which is being consumed at an exponential scale comprehending the need of alternative fuels to cope up for further energy demand.

Considering the world's insatiable desire for petroleum, one of the best renewable resources available are vegetable oils derived from plant seeds. Biodiesel (fatty acid esters) is

derived from triglycerides (oils and fats) by trans-esterification process with the use of methanol or ethanol and has attracted considerable attention as a renewable fuel due to its non-toxic and biodegradable properties [1, 2, 3, 4]. As we know that transportation sector is a huge contributor of emissions and is responsible for the global climate change. Currently, one fifth of the global CO₂ emissions are from the transport sector. The global outlook for reduction of emissions from this sector does not look promising, as the number of light motor vehicles on the roads are going to increase over 2 billion by 2050 [5].

Even the recent oil and gas discoveries in India have failed to keep pace with the energy demand. Besides having a high rate of economic growth, and 15% of the world's population, it is currently dependent on imports for 68% of its oil use and is expected to become the fourth largest net importer of oil in the world by 2025, behind the United States, China, and Japan [6]. In addition of receiving ample comfort from petroleum product, the humans are critically affected by its detrimental by-products which are usually released in the atmosphere. Therefore, to get

rid of from these problems; a shift is required towards the fuels having less harmful product which do not affect the environment much as well as our living organism.

Hence, alternative fuels like vegetable oils are considered to be the most promising ones and will play an important role in meeting the world's energy requirement [7-8]. The direct uses of vegetable oils in diesel engine possess many problems on their long run. Efforts have been made to develop vegetable oil derivatives that have approximated the properties and performance of mineral diesel [9-10]. The problem of substituting vegetable oil for diesel engine as a fuel is mostly associated with high viscosity, low volatility and polyunsaturated characters. These can be changed in at least four different ways: Pyrolysis, Micro-emulsion, Dilution and Trans-esterification [11-12].

Bio-diesel can be prepared by various methods such as Acid catalyzed, base catalyzed, supercritical trans-esterification etc. out of which the supercritical trans-esterification process is considered as a best from the production point of view [13].

The performance of vegetable oil can be improved by amending it through trans-esterification process. The purpose of this process is to lower the viscosity of the oil. Vegetable oil consists of three carbon back bones with long chain fatty acids and bio-diesel is composed of fatty acid chains that are chemically bonded to one methanol molecule [14]. It is a chemical process in which triglyceride is reacted with an alcohol [15]. It is displacement of alcohol from an ester by another alcohol in a process similar to hydrolysis except that an alcohol is used instead of water. The reaction can be represented as shown below: chemical reaction of synthesis of bio-diesel [16].

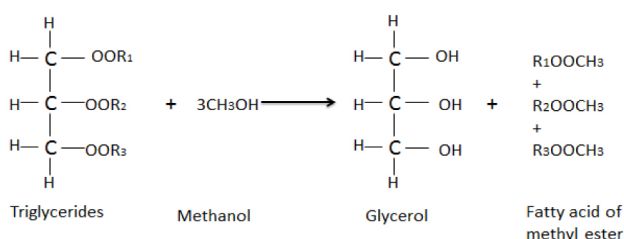


Figure 1. Supercritical Trans-esterification reaction of vegetable oil.

Trans-esterification of vegetable oils using alcohol (Methanol) in a catalytic environment is a chemical process to produce diesel-like liquid, biodiesel. Chemically, biodiesel is mono-alkyl esters (fatty esters) of long chain fatty acids. This method has however, some drawbacks such as difficulties in the recovery of glycerol, production process to be longer and reduces the conversion yield. The main factors affecting trans-esterification are the amount of alcohol, free fatty acid content, presence of water, catalyst reaction, temperature, pressure and time [17, 18, 19]. Furthermore, oils containing free fatty acids tend to form soapy products with alkaline catalyst. This problem has

been greatly reduced by applying a novel method which is catalyst free and the alcohol (Methanol) is used at its supercritical conditions.

An alternative, catalyst-free process for trans-esterification uses supercritical methanol. The purification becomes much simpler, and it produces higher yield [20, 21]. In this process, free fatty acids are converted to methyl esters instead of soap, so a wide variety of feed stocks can be used. Also, the catalyst removal step is eliminated. Energy costs of production are similar or less than catalytic production routes [22].

Due to the limitations of homogeneous and heterogeneous catalytic reactions, an ideal technology that can produce biodiesel in a sustainable and environmental-friendly method has been the motivation of many researchers. For instance, it must be energy-efficient and does not produce unnecessary wastes in the processing steps. Besides, it must have high tolerance towards impurities (FFA and water) to allow wider range of feedstock application. The absence of catalysts makes this process relatively easy and simple in terms of separation and purification of biodiesel. Besides, it was reported that this process only required a small amount of reaction time to achieve a significant yield of biodiesel [18]. Due to its enormous advantages, several researchers have carried out thorough investigations on this process concerning reactivity and kinetics [23].

Pilar et. al. [24] conducted an experiment in which one- step supercritical methanolysis of refined soybean oil has been done and found that the yield of methyl ester can be maximized at different reaction temperature and time. The best reaction condition for highest yield of fatty acid methyl ester was at 325°C temperature (which corresponding to the pressure at 35MPa) and a reaction time of 60min. Under these conditions, practically total conversion of TG (triglyceride) was reached; however, 8.1 wt. % of MG (monoglyceride) and DG (diglyceride) remained in the medium and a 7.9 wt. % decomposition of fatty acid chains was observed. Raising the temperature is the only way to reduce these glycerides and increase the yield of biodiesel in catalyst free one-step supercritical process. And the other way to reduce content of these glycerides in the catalyst-free one-step supercritical process is to reduce the thermal decomposition of the FAMES.

Kok Tat Tan et. al. [25] has discussed SCM (super critical methanol) and SCE (super critical ethanol) reactions involving palm oil by RSM (Response surface methodology) analysis and the effect of alcohol in supercritical trans-esterification reaction was investigated and elaborated thoroughly. Apart from that, the effects of variables involved on the yield of biodiesel in SCM and SCE processes were studied and compared. After that concluded that for SCM reaction, temperature is the most important parameter whereas for SCE reaction, reaction time seems to be the most influencing variable. In addition, optimization studies of SCM and SCE