

TRANSESTERIFICATION FOR THE PREPARATION OF BIODIESEL FROM CRUDE-OIL OF PONGAMIA PINNATA

by

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Biodiesel was prepared from the non-edible oil of Pongamia pinnata L. by transesterification of the crude-oil with methanol in the presence of NaOH as catalyst. Vegetable oils can be transesterified by heating them with a large excess of anhydrous methanol and an acidic or basic reagent as catalyst. Both the acid as well as alkaline esterifications were subsequently performed to get the final product. A catalyst is usually used to improve the reaction rate and yield. NaOH was found to be a better catalyst than KOH in terms of yield. In a transesterification reaction, a larger amount of methanol was used to shift the reaction equilibrium to the right side and produce more methyl esters as the proposed product. Several aspects including the type of catalyst (alkaline, acid, or enzyme), alcohol/vegetable oil molar ratio, temperature, purity of the reactants (mainly water content) and free fatty acid content have an influence on the course of the transesterification. A maximum conversion of 94% (oil to ester) was achieved using a 1:10 molar ratio of oil to methanol at 60 to 65 °C. Important fuel properties of methyl esters of pongamia oil (biodiesel) compare well with ASTM standards.

Key words: *Pongamia pinnata L., biodiesel, non-edible oil, base catalyst, transesterification*

Introduction

Pongamia oil is derived from pongamia tree, found everywhere in India up to an altitude of 1200 m with a maximum height of 16 m. Each shell of the fruit contains 1 to 2 kidney shaped brownish red kernels as shown in fig.1. It is a non-edible oil [1]. The oil is squeezed from the seeds (nuts) of pongamia contains in a shell. The oil content of the kernel is 30-40 %. In all oils two saturated acids, palmitic and stearic, and two unsaturated acids, oleic and linoleic, are commonly present. Pongamia oil contains oleic acid (44.5-71.3%) as the major fatty acid followed by linoleic (10.8-18.3%), palmitic (3.7-7.9%), and stearic (2.4-8.9%) acids.

The most commonly used oils for the production of biodiesel are soybean, sunflower, palm, rapeseed, cotton seed, and jatropha. Most of these oils are edible except jatropha [2]. From the beginning of diesel engines the various possibilities of using pongamia oil as a fuel has been investigated [1, 3-8]. Pongamia oil is popular due to its low cost and ready availability. However, as for other oils there are limitations in the use of this non-edible oil as fuel. Its high viscosity and poor combustion characteristics can cause poor atomization, fuel injector blockage, and excessive engine deposit, and engine oil contamination. With the esterification of oil we can get better fuel properties [9] rather than using straight vegetable oil (SVO) as a fuel.

In India the ever increasing demand of edible oils for the food prevents their use in biodiesel preparation. However, non-edible oils are affordable for biodiesel production. Biodiesel



Figure 1. Shape of pongamia kernels

is synthesized from oils and fats [9] by using either chemical or biocatalysts. Chemically, the reaction is catalyzed by either an acid or a base. The transesterification reaction of triglycerides is known to be a three step process. The kinetic studies of transesterification of soybean, sunflower [10], palm [11], rapeseed [12], and monoglycerides of pongamia oil [13] have been reported. More recently research on alcoholysis of oil has focused on the use of heterogeneous catalysts. Zeolites and metal catalysts have also been used for the transesterification of soybean oil [14]. Even though base catalyzed transesterification of oils is the widely accepted method of preparing biodiesel, the chemical properties and purity of oil warrants complete optimization of the reaction conditions. This

paper reports for the first time details of the process of base catalyzed transesterification of crude pongamia oil with methanol. The fuel properties of pongamia oil methyl esters (biodiesel) on comparison with those of accepted biodiesel standards indicate that esterification of oil does improve its properties making it similar to diesel.

Methods

The production processes for biodiesel are well known. Different ways to reduce viscosity include dilution, microemulsification, pyrolysis, catalytic cracking, and transesterification [15, 16]. Because of the simple process and glycerol obtained as byproduct, which has a commercial value, transesterification is preferred over others.

There are three basic routes to biodiesel production from oils and fats:

- base catalyzed transesterification of the oil,
- direct acid catalyzed transesterification of the oil [17], and
- conversion of the oil to its fatty acids and then to biodiesel.

Most of the biodiesel produced today is done with the base catalyzed reaction for several reasons:

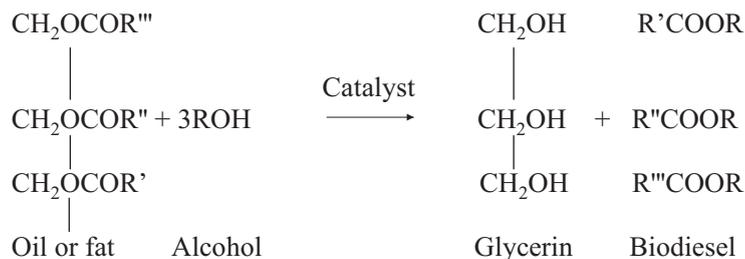
- it is carried at low temperature and pressure,
- it yields high conversion (98%) with minimal side reactions and reaction time,
- it is a direct conversion to biodiesel with no intermediate compounds, and
- no exotic materials of construction are needed.

Base catalyzed transesterification

The chemical reaction for base catalyzed biodiesel production is depicted below. One hundred liters of fat or oil (such as soybean oil or pongamia oil) are reacted with 18-20 liters of a short chain alcohol in the presence of a catalyst to produce 18-20 liters of glycerin and 100 liters of biodiesel. The short chain alcohol, signified by ROH (usually, methanol, but sometimes ethanol) is charged in excess to assist in quick conversion. The catalyst is usually sodium or potassium hydroxide that has already been mixed with the methanol (called as sodium methoxide).

R', R'', and R''' indicate the fatty acid chains associated with the oil or fat which are largely palmitic, stearic, oleic, and linoleic acids for naturally occurring oils and fats.

The biodiesel reaction



Transesterification of crude-oil of pongamia pinnata

Transesterification of crude pongamia oil using NaOH

To one litre of crude pongamia oil, a known amount of catalyst NaOH, 8 to 10 g (1 wt. %) dissolved in the required amount of methanol was added [13, 18]. The temperature *i. e.* 45 or 60 °C was maintained as desired throughout the experiment. Samples were taken in to decant and allowed to settle down glycerin at the bottom as shown in fig. 2. The oil from decant is collected after the removal of glycerin and washed with water (500-2000 ml) to remove unreactive base, glycerin, and trace amount of soap. The collected pongamia methyl ester may vary from 700 to 950 ml.



Figure 2. Settling of glycerin after base treatment

Water Washing

The sample is collected in to a glass cup and in to it 500 ml of water is added. An ortho-phosphoric acid of 5 to 10 drops are added into it to avoid soap formation. With the help of air bubbles the above mixture is washed. This process is repeated till we can see clear water in the mixture, is separated and formed as a bottom layer when it is again taken into decant as shown in fig. 3.

The amount of glycerin collected varies from 200 to 350 ml based on the methanol ratio with respect to pongamia oil.



Figure 3. Pongamia oil collected at the top

Results and discussion

Effect of molar ratio of oil: methanol and temperature on transesterification of pongamia oil

The stoichiometry of the transesterification reaction requires 3 moles of alcohol per mole of triglyceride to yield 3 mole of fatty esters and 1 mole of glycerol [19]. To estimate the molar ratio the molecular weight of crude-oil is taken as 887.5 [20] and the density is 0.925 kg/l.

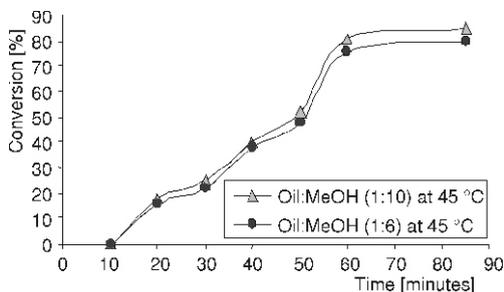


Figure 4. Conversion of pongamia oil to fatty acid methyl esters at two different molar ratio of 1:10 and 1:6 (oil:methanol) at 45 °C

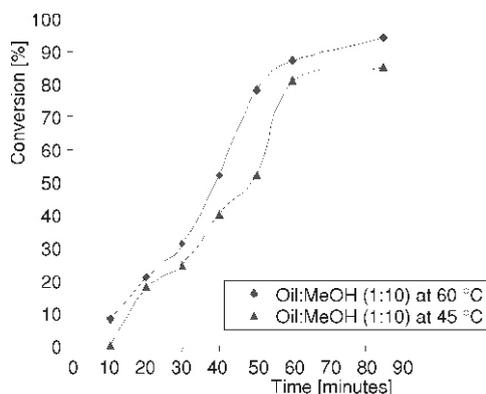


Figure 5. Conversion of pongamia oil to fatty acid methyl esters at two different temperatures 45 and 60 °C at 1:10 (oil:methanol) molar ratio

97.3% at a residence time of 60 minutes. Biodiesel from rapeseed oil [12] was prepared in supercritical methanol at a molar ratio of 1:42 (oil:methanol) in the absence of catalyst where the temperature was as high as 240 °C. The conversion was 95% after 240 s. Fatty acid methyl esters from jatropha oil were prepared (92% yield) in a two step process with an oil to methanol molar ratio of 1:4.5 at 30 °C and reaction time of 10 hours. The optimized conditions for transesterification of heated refined sunflower oil and used frying oils were reported recently [23-24]. The methanolysis of different used frying oils were performed at 25 °C with 0.5-1.5% (KOH or NaOH) with a molar ratio of oil to methanol as 1:4.5, 1:6, and 1:9 and 1% KOH, 25 °C, 1:6 molar ratio was found to be optimum.

Fuel properties of fatty acid methyl esters in comparison with pongamia oil and diesel

The two important fuel properties are viscosity and flash point of methyl esters of pongamia oil were found to be 4.71 Cst (40 °C) and 170 °C (tab. 1), respectively. Pongamia oil itself has a high viscosity of 74.14 Cst (30 °C) which drops down dramatically on transesterification to 4.71 Cst (40 °C). Both these properties meet the specifications of ASTM and German biodiesel standards.

With two different molar ratios of pongamia oil to methanol (1:6 and 1:10) at 45 °C during transesterification of pongamia oil was studied (fig. 4). At a molar ratio of 1:6 a maximum conversion 80% was observed whereas at 1:10 molar ratio the conversion was 85% with an initial lag time.

The initial lag phase is usually attributed to transport effects required to transfer the methanol into the oil phase. At a molar ratio of 1:10 (oil: methanol), increasing the reaction temperature from 45 to 60 °C resulted in a significant increase in conversion from 85 to 94% (fig. 5).

It is important to note that crude pongamia oil was used in this study for biodiesel preparation. The degree of refinement of the vegetable oil affects the yield of ester formation [18, 21, 22]. The conversion can only be expected to improve when refined pongamia oil is used. Using alkaline catalyst (0.5% of NaOH or methoxide) at 60 °C and a molar ratio of 1:6 (oil:methanol) with fully refined oils resulted in complete conversion to methyl esters in 1 hour but at a moderate temperature (32 °C) these oils were transesterified up to 99% in 4 hours. Palm oil was transesterified with 1 wt.% KOH at 60 °C and a molar ratio of 1:6 (oil:methanol), using a continuous stirred tank reactor [11, 21] to give a yield of 58.8% of methyl ester at a reactor residence time of 40 minutes which increased to

Table 1. Fuel properties according to pongamia FAME, ASTM, and German biodiesel standard

Parameters	Pongamia FAME	ASTM standard for 100% biodiesel	German biodiesel standard DIN V51606
Viscosity [Cst]	4.71 (40 °C)	1.9 to 6.0	3.5 to 5.0 (40 °C)
Acid value [mg KOHg ⁻¹]	0.62	0.80 maximum	0.5
Flash point [°C]	170	130 minimum	100 minimum
Cetane number	57	48-65	>51
Density [gcm ⁻³]	0.885	0.875-0.89	0.82-0.86 at 15 °C

Conclusions

Crude pongamia oil was transesterified using NaOH as catalyst and methanol to form biodiesel. The conversion was 94% at 60 °C with 1:10 molar ratio (oil:methanol) for NaOH (1 wt.%) catalyzed transesterification. The fuel properties especially viscosity (4.71 Cst at 40 °C) and flash point (170 °C) of the transesterified product (biodiesel) compare well with accepted biodiesel standards *i. e.* ASTM and German biodiesel standards.

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