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Biodiesel production from *Trichilia emetica seeds* using in-situ transesterification

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The main purpose of this research work was production of biodiesel from trichilia emetic seeds by in-situ transesterification. The process was studied at reaction temperature 80°C and reaction time 100min. The physico-chemical parameters of the biodiesel were checked by ASTM D 6751 standards. In this study, copper strip corrosion, kinematic viscosity, cloud point, ash content have 1a, 5.44mm^2/s, 18^{0}C and 0.062% respectively. These values satisfy the quality criteria of biodiesel set by ASTM D6751. However, the flash point and the acid values of biodiesel don't meet the quality criteria set by ASTM D6751, due to the presence of unreacted (residual) alcohol and residual mineral acids from the production process respectively. In other words, 60% the physico-chemical properties of the biodiesel satisfies the quality criteria set by ASTM D6751 and pretreatment of the seeds is necessary to increases the quality of biodiesel.

Keywords: Biodiesel, in-situ transesterification, trichilia emetica seeds, physico-chemical parameters

INTRODUCTION

Biodiesel obtained from vegetable oil can be used as conventional diesel in diesel engines, because its properties are very close to petroleum diesel. For example, biodiesel has the proper viscosity; high flash point; high cetane number and no engine modification are required when using biodiesel [1]. Several biodiesel production methods have been developed, among which in-situ transesterification in the preference of alkali catalyst gives high level of conversion of triglycerides to their corresponding methyl ester in short reaction time. The process of in-situ transesterification is affected by the reaction condition: molar ratio of alcohol to oil; type of alcohol; type and amount of catalysts; reaction temperature and pressure; reaction time and contents of free fatty acids; particle size and water in oils or fats [2]. In-situ transesterification is the direct transesterification of ground oil bearing materials instead of purified oils with alcohol and catalyst, to produce alkyl fatty acid esters. The efficiency or yield of in-situ transesterification is defined as the percentage of biodiesel–rich phase over oil content in raw material which is determined by hexane soxhlet extraction.

Biodiesel has a higher cetane number than petroleum diesel fuel, no aromatics, and contains 10-11 % oxygen by weight. These characteristics of biodiesel reduce the emissions of carbon monoxide, hydrocarbons, and particulate matter in the exhaust gas compared with diesel fuel. However, NO_X emissions of biodiesel increase, because of combustion and some fuel characteristics' [3]. Biodiesel has been mainly produced from edible vegetables oils all over the world. More than 95% of global biodiesel production is made from edible vegetable oils. The largest biodiesel producers were the European Union, the United States, Brazil, Indonesia, with a combined use of edible oil for biodiesel production of about 8.6 million tons in 2007 compared to global edible oil production of 132 million tons [4]. Rapeseed and sunflower oils are used in EU, palm oil predominates in biodiesel production in tropical countries, and soybean oil is the major feedstock in the United States [5].

The preparation of biodiesel from various vegetable oils based on alkaline transesterification of triglycerides with polyhydric alcohol has been studied for several decades, and a major amount of industrial production has been achieved with this method [6]. However, the transformation of jatropha seed in oil industry requires extra steps during the extraction and refining processes. As the cost of the vegetable oil production contributes to approximately 70% of the biodiesel production cost [7], there is a need for the development of a new biodiesel production process that is simple, compact, efficient, low-cost, and that consumes less energy. On the other hand, the preparation of biodiesel based on in situ transesterification has been successfully carried out from various oilseeds [8]. In situ transesterification is a biodiesel production method that uses the original agricultural products as the source of triglycerides

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instead of purified oil for direct transesterification, and it works virtually with any lipid-bearing material. It can reduce the long production system associated with pre-extracted oil, and it maximizes ester yield. The objective of this study was to investigate the in situ transesterification allowing producing directly biodiesel from trichilia emetica seed and evaluate the properties of biodiesel by ASTM D6751.

Experimental Materials

The major feedstock used in this work was Trichilia emetica seeds, locally available in Ethiopia. It was purchased at the local market in Tepi, South-west of Ethiopia and cleaned with tap water to remove impurities (Fig. 1 & 2).

Fig. 1. Trichilia seed before removing the husk (Directly collected from local market)

Fig. 2. Trichilia seed after removed the external cover, cleaned with water & dried

By the stoichiometric equation of the process, 1 mol of Trichilia emetica seeds is required to react with 3 moles of butanol to produce 3 moles of the biodiesel and 1 mole of glycerol. 100g Trichilia emetica seeds were used for the in-situ transesterification process. Reaction temperature for the process must be below the boiling point of alcohol used. The butanol used, manufactured by Aldrich Chemicals Co. Ltd, England has a boiling point of 117°C; therefore, a reaction temperature of 80°C was selected. Different researchers have reported different reaction times for in-situ transesterification process as well as the entire biodiesel production process. The reported reaction time ranges from less than 30 minutes to more than 2 hours. Reaction time of 100 minutes was therefore selected. KOH used was manufactured by Aldrich Chemicals Co. Ltd, England.

Experimental Procedures

Potassium Butoxide Production

1000.0g of butanol was measured and poured into a plastic container a funnel and the lid of the butanol container was tightly replaced. 4.0g of KOH was carefully added to the plastic container via a second funnel. The bung and the screw on the cap were replaced tightly. The container was shake a few (about ten) times by swirling round thoroughly for about 2 minutes until the KOH completely dissolved in the butanol, forming potassium butoxide (Fig. 3).

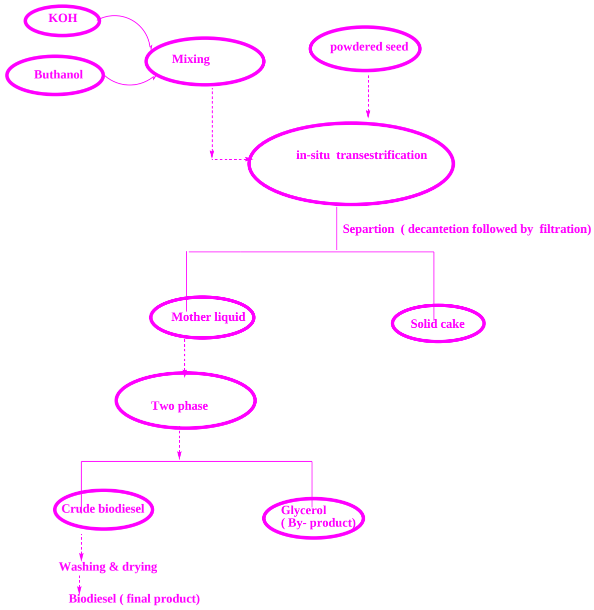

Fig. 3. Flow chart of biodiesel production and purification processes.

In-situ transesterification reaction

100.0g of Trichilia emetica seeds powder was measured out in a beaker, pre-heated to the required temperature (80°C) and poured into the blender. With the blender still switched off, the prepared potassium butoxide from the plastic container was carefully poured into the Trichilia emetica seeds. The mixture was left to blend for the 100minutes at moderate speed before the blender was switched off. Detail information of in-situ transesterification reaction was presented in Fig. 3.

Settling

The mixture was poured from the blender into a 250ml separator funnel for settling and the lid was screwed on tightly. The reaction mixture was allowed to stand overnight while phase separation occurred by gravity settling into biodiesel on the top and glycerol at the bottom of the bottle (Fig.4). The next day, the Trichilia emetica seeds biodiesel/ester at the top was carefully decanted into a volumetric flask leaving the glycerol at the base.

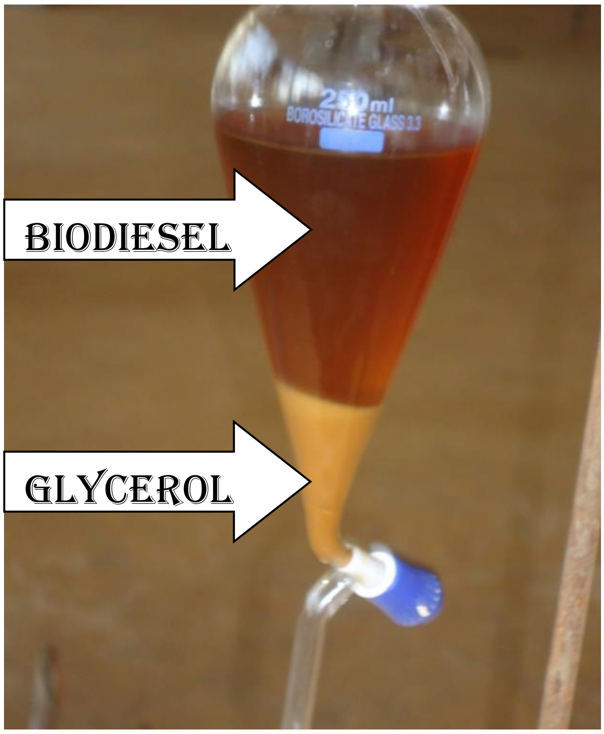

Fig. 4. Phase separation stage (biodiesel from glycerol)

Washing and purification

When biodiesel was first made it was quite caustic with a pH of between 8.0 and 9.0.Washing with water neutralized the product. Traces of butanol along with the catalyst were washed with hot water (45°C) and 0.1% phosphoric acid solution. Since biodiesel has a lower specific gravity than water, the water was sinking to the bottom and the biodiesel was remaining over the water.

After about 40 min the butanol has boiled off to remove the unreacted alcohol then dried with anhydrous MgSO4 to get rid of any water (Fig. 5).

Biodiesel yield

The biodiesel yield (% wt) after the post-treatment stage, relative to the amount of Trichilia emetic seeds poured into the reactor, was calculated from the butyl ester and weights of seeds.

$$\text{Biodiesel yield} = \frac{\text{Mass of butyl ester}}{\text{Mass of seeds powder}} \text{x100}$$

Biodiesel quality analysis

The pure biodiesel obtained through the above procedure gave the ester yield, measured on weight basis. The experiment was replicated three times and average experimental parameters recorded. ASTM D6751 standard fuel characterization was subsequently carried out on the Trichilia emetica seeds biodiesel. The physico-chemical properties of biodiesel such as kinematic viscosity (ASTM D445); flash point (ASTM D93); cloud point (ASTM D2500); conradson carbon .residual (ASTM D189); copper strip corrosion ((ASTM D130); total acidity (ASTM D974) and ash content (ASTM D482) was determined by ASTM D6751 standard method [10].

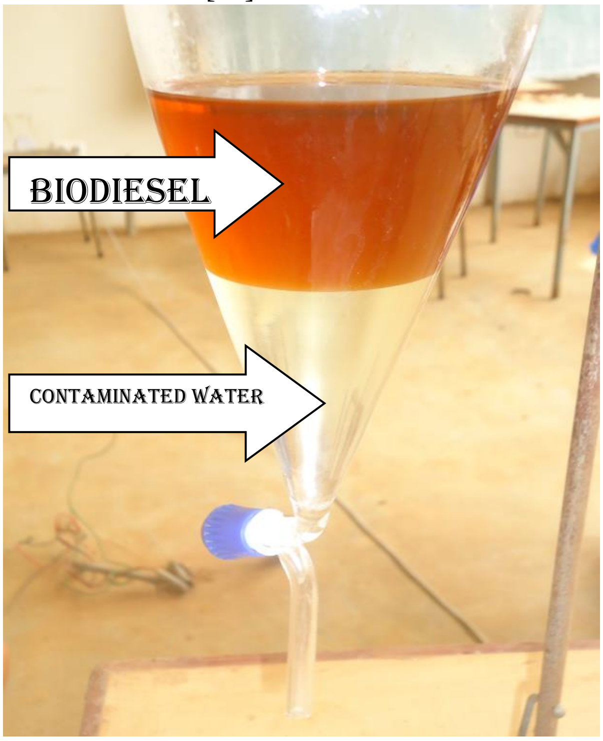

Fig. 5. Purification of biodiesel by hot distilled water (slightly acidic) to remove excess alcohol, soap, catalyst

RESULTS AND DISCUSSIONS

For the alkali-catalysed in-situ transesterification experiment conducted using the stated reaction parameters, the experiment was triplicate and average experimental results evaluated. The physico-chemical parameter of the biodiesel was characterized by Ethiopian petroleum supply enterprise laboratory, Addis Ababa, Ethiopia and the result was presented in **Table 1.** The butyl ester of Trichilia emetica seeds biodiesel prepared using 100g Trichilia emetica seeds powder, 1000.0g butanol, 4.0% KOH at 80°C and 100 minutes reaction time yielded 84.0g Trichilia emetica seeds biodiesel which is a satisfactory result and the seed is promising in the production of biodiesel in large industrial scale.

Table 1. Physico-chemical parameter of biodiesel

No	Property	Test method ,ASTM	Test ASTM 6751 limit	Biodiesel
1	Flash point (PMCC), ^{0}C	D 93	Min. 93	49
2	Cloud point, ^{0}C	D 2500	report	18
3	Kinematic viscosity, mm^2/s	D 455	Min. 1.9 Max. 6	5.44
4	Conradson carbon residue	D 189	Max.0.05	0.33
5	Total acidy, mgKOH/g	D 974	Max.0.5	6.28
6	Ash content	D 482	Max.0.02	0.062
7	Copper strip corrosion	D 130	Max.No.3	1a

Kinematic viscosity

Viscosity, the measurement of the internal flow resistance of a liquid, constitutes an intrinsic property of vegetable oils. It is of remarkable influence in the mechanism of atomization of the fuel spray. In-situ transesterification is the most common way to lower this high viscosity. From the result presented in Table 1, the viscosity of Trichilia emetica seeds biodiesel (5.44 mm2/s) fall within the range prescribed by ASTM D6751 standard (1.9 – 6.0) mm2/s for biodiesel [11]. This implies that the Trichilia emetica seeds biodiesel satisfies the fluidity requirement of an alternative biodiesel.

Copper strip corrosion

This parameter characterizes the tendency of a fuel to cause corrosion to copper, zinc and bronze parts of the engine and the storage tank. This corrosion resulting from biodiesel might be induced by some sulfur compounds and by acids, so this parameter is correlated with acid number. Some experts consider that this parameter does not provide a useful description of the quality of the fuel, as the results are unlikely to give ratings higher than class 1. In this study, the copper strip corrosion was 1a which lies in the biodiesel quality requirement criteria set by ASTM D6751 (Max.No.3). This reveals that, the biodiesel is not producing any rust on the machine engine.

Cloud Point

The cloud point is "the temperature at which a cloud of wax crystals first appears in a liquid when it is cooled down under conditions prescribed in this test method." The cloud point is a critical factor in cold weather performance for all diesel fuels. Because of climate diversity in different places, the American and European standard, haven't set any limitations for flow properties. The saturated fatty acid compounds have significantly higher melting points than unsaturated fatty acid compounds [12]. In this study the cloud point of the biodiesel was 180C which is higher than that obtained for the conventional petroleum diesel.

Ash content

The Ash content or mineral content is a measure of the amount of metal contained in the fuel. From the result the ash content of biodiesel is 0.062% slightly greater than the standards. Biodiesel burnt with very low smoke. This implies that biodiesel emissions from exhaust of vehicles will help reduce the pollution introduced to the atmosphere.

Carbon residue

The parameter serves as a measure for the tendency of a fuel sample to produce deposits on injector tips and inside the combustion chamber when used as automotive fuel. It is considered as one of the most important biodiesel quality criteria, as it is linked with many other parameters. So for biodiesel, carbon residue correlates with the respective amounts of glycerides, free fatty acids, soaps and remaining catalyst or contaminants [12]. The carbon residue of the biodiesel 0.33% was higher compared to 0.050max documented. This could be due to the contaminant which might have entered the sample during the heating in the production of biodiesel and the presence of small amount of glycerol left in the final product.

Acid value

Acid value or neutralization number is a measure of free fatty acids contained in a fresh fuel sample and of free fatty acids and acids from degradation in aged samples. The acid value of the present study was 6.28mgKOH/g which is higher than with the ASTM D6751 standards. The acidic compounds that could possibly be found in biodiesel are: 1) residual mineral acids from the production process, 2) residual free fatty acid from the hydrolysis process or the post- hydrolysis process of the esters and 3) oxidation byproducts in the form of other organic acids. Therefore, the trichilia emetica seeds need acid pretreatment before using for the production of biodiesel.

Flash point

In general, the flash point value specified by the quality standards is relatively high, for safety reasons regarding storage and transport and also to ensure that the alcohol is removed from the finished product. Low flash points may indicate alcohol residue in biodiesel. The flash point for the biodiesel obtained in this study was 490C which is lower than the minimum requirement set by ASTM D6751. This is due the presence of residual alcohol left in the biodiesel during drying processes.

Conclusion

This study has shown that most of the physico-chemical properties evaluated for the biodiesel conform to the ASTM D 6751 standard values. It could be concluded from this study that the biodiesel produced from trichilia emetica seed using in-situ transesterification is a potential replacement for fossil diesel and effective usage of biodiesel will help to reduce the cost of protecting the atmosphere from the hazards in using fossil diesel and hence will boost the economy of the country.

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ПОЛУЧАВАНЕ НА БИОДИЗЕЛ ОТ СЕМЕНА НА *TRICHILIA EMETICA* ЧРЕЗ *IN-SITU* ТРАНСЕСТЕРИФИКАЦИЯ

Б. Адиню

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(Резюме)

Основната цел на тази изследователска работа бе производството на биодизел от семена на trichilia emetica чрез in-situ трансестерификация. Процесът е изследван при реакционна температура 80 °C и време за реакция 100min. Физико-химичните параметри на биодизела са били проверени чрез ASTM D 6751 стандарти. В това проучване, корозията на медна пластина, кинематичния вискозитет, точката на помътняване, пепелно съдържание имат стойностти 1a, 5.44 mm^2/s, 180C и 0.062% съответно. Тези стойности отговарят на критериите за качество на биодизел, определени чрез ASTM D6751. Въпреки това, точката на възпламеняване и киселинните стойности на биодизел не отговарят на критериите за качество, определени от ASTM D6751, което се дължи на присъствието на нереагирал (остатъчен) алкохол и остатъчни минерални киселини от производствения процес, съответно. С други думи, 60% от физико-химичните свойства на биодизела отговарят на критериите за качество, определени от ASTM D6751 и е необходимо предварително третиране на семената, за да се повишава качеството на биодизела.