

Performance Characteristics of Biodiesel Produced from Waste Groundnut Oil using Supported Heteropolyacids

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Abstract—Contribution of petroleum sourced fuels to accumulation of carbon dioxide in the environment necessitated an alternate renewable, carbon neutral transport fuel. Raw and spent vegetable oils have attracted attention as a potential renewable resource for the production of biodiesel. Supported heteropolyacids mainly Cesium Tungstophosphoric acid catalysts are an excellent alternate to the existing homogeneous catalysts for transesterification reaction in biodiesel production. CsTPA was supported externally and as a composite (internal and external) onto the support SBA15 and the parameters were optimized. It was found that the composite loaded catalyst system gave a maximum yield of 90.5% for 0.3% catalyst concentration, 6.6:1 methanol:oil molar ratio for 1 hour and 60°C. The methyl esters obtained from WCO were found to meet the ASTM standards for bio diesel. Performance characteristics of bio diesel with diesel were studied on a four stroke diesel engine under loaded conditions. Mechanical (67.79%), Brake and Indicated thermal efficiencies are better for biodiesel obtained from WCO than diesel (64.3%) thus making it a promising candidate as an alternate fuel.

Index Terms—Heteropolyacid, Biodiesel, CsTPA, Transesterification, SBA-15

I. INTRODUCTION

The worldwide worry about the protection of environment and the conservation of non-renewable natural resources, has given rise to alternate development of sources of energy as substitute for traditional fossil fuels. The major part of all energy consumed worldwide comes from fossil sources (petroleum, coal and natural gas). However, these sources are limited and will be exhausted in the near future. Thus, looking for alternative sources of new and renewable energy such as hydro, biomass, wind, solar, geothermal, hydrogen and nuclear is of vital importance. Alternative new and renewable fuels have the potential to solve many of the current social problems and concerns, from air pollution and global warming to other environmental improvements and sustainability issues. Vegetable oils have become more attractive recently because of its environmental benefits and the fact that it is made from renewable resources.

The use of vegetable oils as alternative renewable fuel competing with petroleum was proposed in the beginning of 1980s. The advantages of vegetable oils as diesel fuel are:

liquid nature-portability, ready availability, renewability, higher heat content, lower sulfur content, lower aromatic content and biodegradability. The high cost of biodiesel is mainly due to the cost of virgin vegetable oil. Therefore, it is not surprising that the biodiesel produced from vegetable oil (for example, pure soybean oil) costs much more than petroleum-based diesel [1, 2]. Hence, it is necessary to explore ways to reduce the production costs of biodiesel. The use of waste frying oil, instead of virgin oil, to produce biodiesel is an effective way to reduce the raw material cost because waste frying oil is estimated to be about half the price of virgin oil [2,3]. In addition, the utilization of waste frying oils diminishes the problems of contamination, because reusing them can reduce the burden on the government in disposing of the waste, maintaining public sewers, and treating the oil wastewater. The fact is, so far, that only a very small percentage of these oils have been collected and used for soap production.

Generally, biodiesel is produced by means of transesterification. Transesterification is the reaction of a lipid with an alcohol to form esters and a byproduct, glycerol. It is, in principle, the action of one alcohol displacing another from an ester, referred to as alcoholysis (cleavage by an alcohol). Transesterification consists of a sequence of three consecutive reversible reactions. The first step is the conversion of triglycerides to diglycerides, followed by the conversion of diglycerides to monoglycerides, and finally monoglycerides into glycerol, yielding one ester molecule from each glyceride at each step. The reactions are reversible, although the equilibrium lies towards the production of fatty acid esters and glycerol [5,6].

Base-catalyzed transesterification, however, has some limitations among which are that it is sensitive to FFA content of the feedstock oils [3]. A high FFA content (> 1 % w/w) will lead to soap formation which reduces catalyst efficiency, causes an increase in viscosity, leads to gel formation and makes the separation of glycerol difficult. Also, the oils used in transesterification should be substantially anhydrous (0.06 % w/w). The presence of water gives rise to hydrolysis of some of the produced ester, with consequent soap formation. Other drawbacks of the base-catalyzed transesterification is that the process is energy intensive, recovery of glycerol is difficult, alkaline catalyst has to be removed from the product and alkaline waste water requires treatment.

Keggin type heteropolyacids (HPAs) have been widely used in acid-catalysed reactions as well as oxidation reactions

both in the heterogeneous and homogeneous systems [7-13]. Heteropolyacids have been pointed out lately as versatile green catalysts for a variety of reactions: alkylation and acylation of aromatics, esterification and liquid bi-phase processes [14-15]. There is an interest to substitute liquid catalysts (e.g. H₂SO₄, HF, p-toluenesulphonic acid) – which are corrosive, toxic and difficult to separate from reaction solution by more environment friendly solid acids. Among many possible forms of heteropolyacids used as catalysts, there are their salts and supported heteropolyanions. Pure HPAs generally show low catalytic reactivity owing to their small surface area. In order to be more effective for catalytic reactions, HPAs are usually impregnated on different porous materials. The type of carrier, textural and structural properties influence the thermal stability and the catalytic activity of Keggin-type heteropolyacids. Out of the heteropolyacids, Cesium substituted Tungstophosphoric acid has been tested for Transesterification reactions. The surface area of the catalyst was increased by supporting it on to SBA15, a mesoporous material.

This is an attempt to explore potential alternative to the current biodiesel production methods, thus contributing to biodiesel commercialization. In this article, CsTPA supported on SBA15 catalyst system was synthesized and tested for Transesterification reaction using spent groundnut oil as a feedstock. The reaction parameters were optimized. Properties of biodiesel were found to be in accordance with ASTM standards. Performance characteristics were tested on a four stroke diesel engine.

II. EXPERIMENTAL PROCEDURE

A. Preparation of Catalyst system

SBA-15 was prepared according to the procedure presented in [16] by crystallization from acidic solutions of Poly (Ethylene glycol) – block – Poly (Propylene glycol) – block – Poly (Ethylene glycol) copolymer (Aldrich) and TEOS (Aldrich). The composite with high loading of Cs-TPA externally and as a composite (external and internal) on SBA – 15 was prepared according to the procedure described in [17].

B. Reaction Procedure

Transesterification reactions were carried out in a 250 ml glass reactor with a condenser. Used Groundnut oil/Waste Cooking Oil which was heated to 100°C was got from a sweet stall. First, a known quantity of the catalyst system loaded externally was dispersed in methanol under magnetic stirring. Then Waste Cooking Oil (WCO) in the molar ratio of 6:1, methanol to oil was added to the mixture and heated to about 60°C. The reaction was allowed to take place for two hours after which the two phase product formed as a result of transesterification was separated using a separating funnel. Upper layer consists of biodiesel, alcohol and some soap (formed as result of side reaction saponification – free fatty acids get converted to soap). Lower layer consists of Glycerin, excess alcohol, Catalyst, impurities, and traces of unreacted oil. Purification of the upper layer was done by washing with warm water. As water is immiscible with Biodiesel it can easily be separated from biodiesel.

Experiments were repeated to optimize the catalyst concentration, methanol to oil molar ratio, reaction time and reaction temperature.

C. Performance test on constant speed engine

The biodiesel synthesized was tested for its performance in a 3.7 kW, vertical automatic governing mechanical brake diesel engine. The effective maximum load that can be applied to the brake drum was calculated. The fuel supply, cooling water supply and the lubricating oil level were all checked. The engine was then started and brought to the rated speed. The cooling water was then allowed to the brake drum, the engine was then loaded and the time taken for 20 cc of fuel consumption was noted.

III. RESULTS AND DISCUSSION

A. Optimization of Catalyst concentration

Fig.1 shows the influence of catalyst concentration on methyl esters yield. Methanol: oil molar ratio, Reaction time and temperature were fixed at 6:1, 2h and 60°C respectively. The catalyst concentration was varied from 0.004 – 0.05% for external loading and 0.004 – 0.04% for composite loading. It is seen that the composite loaded catalyst system gave the maximum yield of 88.9% for a catalyst concentration of 0.03%. This can be attributed to an increase in the availability and number of catalytically active sites.

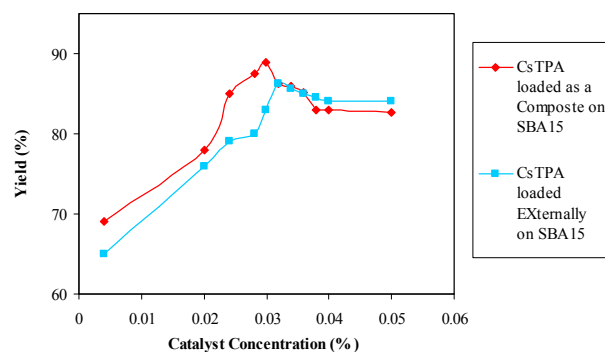


Figure 1. Optimization of Catalyst Concentration

B. Optimization of Methanol:Oil Molar ratio

The stoichiometry of the reaction requires 3 moles of methanol per mole of triglyceride to yield 3 moles of biodiesel and 1 mole of glycerol. It was varied from 5.6 – 7.8:1 for both the catalyst systems. Biodiesel yield could be elevated by introducing an excess amount of methanol to shift the equilibrium to the right hand side.

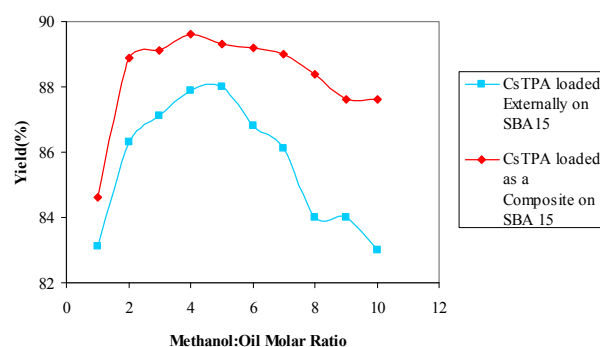


Figure 2. Optimization of Methanol:Oil Molar Ratio

C. Optimization of Reaction Time

In the present work, reaction time was varied between 0.25 – 2.25 h respectively for the catalyst systems. It is seen that the composite loaded catalyst system gave a maximum yield of 90.5% at a reaction time of 1h.

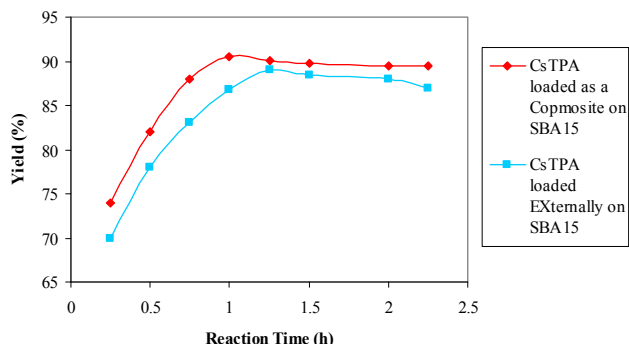


Figure 3. Optimization of Reaction Time

D. Optimization of Reaction Temperature

Reaction temperature can influence the reaction rate and bio- diesel yield. The reaction temperature was varied between 40–65°C while keeping the other parameters constant. The primary advantage of higher temperatures is a shorter reaction time. However, higher reaction temperatures causes methanol to vaporize resulting in decreased yield.

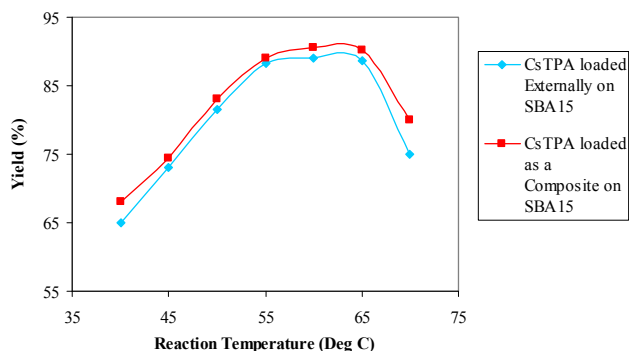


Figure 4. Optimization of Reaction Temperature

E. Biodiesel Properties

Bio-diesel separated from the reaction mixture with both Groundnut oil and Waste cooking oil source was washed with water to remove the methanol traces in it and was analyzed for its properties. Table 1 lists the properties of raw feedstock and the methyl esters obtained from it. It is seen that the biodiesel obtained by using waste cooking oil meets the standards specified by ASTM.

Amongst the various properties measured for biodiesel, cetane number is the indicator of effective ignition of the diesel fuel. The higher the cetane number, higher will be the ignition efficiency. Because of the higher oxygen content, biodiesel has a higher cetane number compared to petroleum diesel. Another important parameter that helps to decide the suitability of the oil for transesterification reactions in

biodiesel synthesis is the acid value. In general, an acid value less than 2 mg of KOH/g of oil is normally recommended for the production of biodiesel. It is evident from table 1 that biodiesel obtained from waste cooking oil using supported tungstophosphoric acid is several times less than conventional biodiesel, which was found promising.

TABLE 1. PROPERTIES OF RAW OIL AND METHYL ESTERS

S.NO	Properties	Raw WCO	ASTM Standards	Diesel	Bio Diesel from WCO
1.	Sp.Gravity (28 °C) (g / ml)	0.887	-	0.85	0.89
2.	Kinematic Viscosity (CSt)	35.3	2.52 – 7.5	2.049	4.6
3.	Flash Point (° C)	155	Min 130	78	130
4.	Fire Point (° C)	160	Min 53	82	135
5.	Cetane No	40	Min 45	47.73	49.5
6.	Calorific Value (MJ / kg)	36.7	Min 33	42.57	40
7.	Iodine Value	101	Max 135	102	106
8.	Saponification Value (mg / g)	220	Min 180	224	202
9.	Diesel Index	40	Min 45	47.73	47.9
10.	Acid Value (mg / g)	3.1	0.8 max	0.72	0.007
11.	Cloud Point (°C)	13.5	-3 to 12	<10	10.7
12.	Pour Point (°C)	-4	-15 to 10	-6	-6

F. Performance Characteristics of Biodiesel

The Bio-diesel got by using waste Cooking oil as source was tested in a Four stoke diesel engine. Load was varied from 0 to 10 kg. Ambient temperature of the test laboratory was maintained at 30°C while carrying out the work.

It is observed from the characteristic Fig 5 that SFC is more for Diesel when compared to Bio-diesel from WCO. For the fuels tested, brake specific fuel consumption decreased with increase in load. One possible explanation for this reduction could be due to higher percentage of increase in brake power with load.

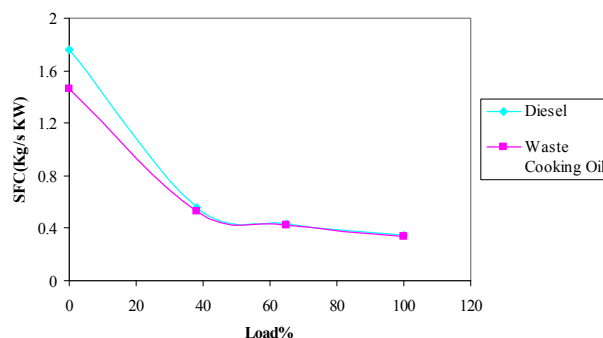


Figure 5. SFC Vs Load %

In Fig. 6 it is observed that the Brake Thermal Efficiency increased with increase in load percent. This was due to reduction in heat loss and increase in power with increase in percent load. Brake Thermal efficiency is more for Bio-diesel obtained from Waste cooking oil when compared with Diesel. The improved thermal efficiency for lower concentrations of WCO is due to more complete combustion and additional lubricity of oil. The lower brake thermal efficiency obtained for diesel could be due to reduction in calorific value and increase in fuel consumption.

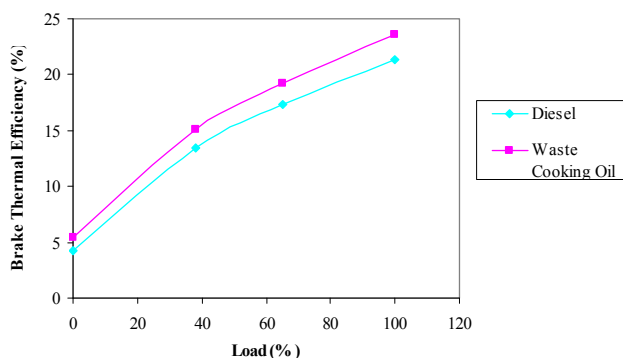


Figure 6. Brake Thermal Efficiency Vs Load %

It is observed from the characteristic curve Fig 7 that Mechanical Efficiency (77.1%) is more for varying loads of Bio-diesel obtained from groundnut oil when compared to diesel (64.3%). Even the mechanical efficiency from WCO was better than diesel. This may be due to better lubricating property of the oil which reduces frictional losses.

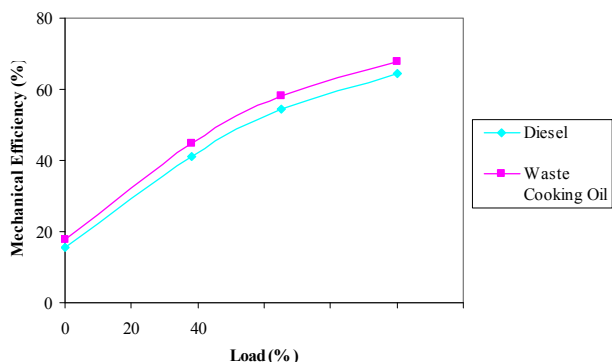


Figure 7. Mechanical Efficiency Vs Load%

From Fig.8 it is observed that for varying loads, the Indicated Thermal Efficiency is greater for bio-diesel obtained from waste cooking oil when compared to diesel. The indicated thermal efficiency (33.3%) is the least for diesel.

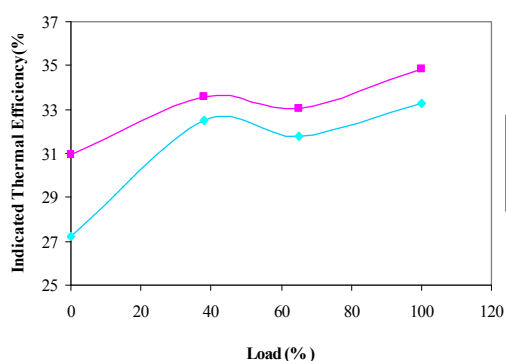


Figure 8. Indicated Thermal Efficiency Vs Load%

IV. CONCLUSION

With exception of hydropower and nuclear energy, the major part of all energy consumed worldwide comes from petroleum, charcoal and natural gas. However, these sources

are limited, and will be exhausted on the near future. Thus, looking for alternative sources of energy is of vital importance. Vegetable oils are a renewable and potentially inexhaustible source of energy with energy content close to diesel fuel. The maximum yield obtained for WCO was 90.5%, with the composite loaded catalyst system of 0.03% concentration, methanol: oil molar ratio of 6.6: 1 for 1 h at 60° C.

The properties of raw vegetable oil and waste cooking oil were analysed. High viscosity and cloud point makes the vegetable oil not compatible to be used raw in the engine and hence justifies the need for transesterification. The methyl esters obtained from GO and WCO were found to meet the ASTM standards for bio diesel. It can be inferred that CsTPA supported internally and externally on SBA 15 is the best alternate for the trans-esterification of waste cooking oil to produce biodiesel. The high catalytic activity, re-usability, lower emission rates, improved engine performance and environmentally benign nature makes it a promising candidate when compared with conventional catalysts.

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