COMPARISON OF CATALYTIC PERFORMANCE OF TPA AND MPA FOR THE PRODUCTION OF BIODIESEL FROM WASTE COOKING OIL

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Abstract

An environmentally beneficial ,facile and clean method for the production of Biodiesel from waste cooking oil has been developed. Solid acids namely do-decatungstophosphoric acid (TPA) and do decamolybdophosphoric acid (MPA) have been used as heterogeneous catalysts for the production of Bioidesel with Methanol. A study for optimizing the reaction conditions such as the methanol to oil ratio, amount of catalyst, reaction time , temperature and the usage times of the catalyst has been performed for TPA and MPA solid acid catalysts. Though both are environmental friendly comparison of the yield for varying reaction conditions proves keggin type 12 Tungstophosphoric acid to be promising in Biodiesel production via the transesterification route. Moreover TPA shows a very high catalytic activity under the optimized reaction conditions when compared to a conventional homogenous catalyst such as Sodium hydroxide and can easily be separated from the product and reused for several more runs. The fuel properties of WCO Biodiesel were found to be in agreement with ASTM standards.

Keywords : Biodiesel, Transesterification, Heteropolyacid, Waste cooking oil, Optimization

I. INTRODUCTION

Energy use is the most fundamental requirement for human existence. Consumption of fossil fuels has increased to a greater extent and the use of these energy resources is seen as having major environmental impact. From the point of view of protecting the global environment and the concern for long-term supplies of conventional diesel fuels [Krawczyk, 1996],it becomes necessary to develop alternative fuels comparable with conventional fuels. Alternative fuels should be, not only sustainable but also environment friendly. For developing countries, fuels of bio-origin, such as alcohol, vegetable oils, biomass, biogas, synthetic fuels etc. are becoming important. While some fuels can be used directly, others need some modification before they can be used as a substitute of conventional fuels.

Vegetable oils have become more attractive recently because of their environmental benefits and because it is made from renewable resources. Since plants remove Carbon dioxide from the atmosphere during photosynthesis, the net production of CO2 is arguably zero. The levels of other pollutants (unburnt hydrocarbons, carbon monoxide and particulate matters) are also generally lower with biofuels than with petroleum [Krawczyk, 1996]. It has almost no sulphur, no aromatics and has about 10% built in oxygen, which helps it to burn fully. Its higher cetane number improves the combustion. The advantages of vegetable oils as diesel fuel are: i) Portability ii) Capacity to displace petroleum based diesel fuel iii) High heat content , about 80% of diesel fuel iv) Ready availability v)Renewability vi) Energy efficient vii)

However, the direct use of vegetable oils and/or oil blends is generally considered to be unsatisfactory and impractical for both direct-injection and indirect type diesel engines. The problems include i) Higher viscosity ii) Lower volatility iii) Reactivity of unsaturated hydrocarbon chains iv) Coking and trumpet formation on the injectors to such an extent that fuel atomization does not occur properly or is even prevented as a result of plugged orifices v) Oil ring sticking vi) Thickening and gelling of the lubricating oil as a result of contamination by the vegetable oils.

Environmental considerations and handling difficulties have led to sustained efforts in recent years to replace homogeneous acid catalysts, both Bronsted and Lewis types with Solid acid catalysts. Catalysis by heteropolyacids (HPAs)[4] of the Keggin's structure is one of the most important and growing areas of research in recent years. They have been used in both homogeneous and heterogeneous catalysis. They are better active catalysts for various reactions in solution than conventional mineral acids. The present investigation is to use solid acid catalysts namely Do –Deca Tungstophosphoric acid (TPA) and Do-deca Molybdophosphoric acid (MPA) as transesterification catalysts for the production of biodiesel from waste cooking oil. Methanol to oil molar ratio, catalyst to oil weight ratio, reaction time and temperature are the parameters to be optimized for all the oil samples.

The product obtained was subjected to purification and analysed to measure several properties like density, viscosity, acid value, saponification value, cetane number, iodine value, flash point, fire point and calorific value to compare if the biodiesel obtained met the ASTM standards.

II. EXPERIMENTAL PROCEDURE

Transesterification reactions were carried out in a 250ml glass reactor with a condenser. First a known quantity of the catalyst (TPA) 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 60C. The reaction was allowed to take place for two hours. Once the reaction was over 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 a result of side reaction). 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 amount of catalyst, methanol to oil molar ratio, reaction time and temperature. The procedure was repeated using MPA as a catalyst.

Experiments were carried out to test the re-usability of the catalysts for repeated use. The performance of the catalysts was compared with conventional catalyst Sodium Hydroxide. The fuel properties were tested and compared with ASTM standards.

III. RESULTS AND DISCUSSION

A. Optimization of Methanol: Oil Molar ratio:

Waste cooking Oil from a sweet stall was subjected to trans-esterification process using Methanol from the molar ratios of 3:1 to 10:1.It is seen that the yield of biodiesel is comparatively high for TPA as catalyst in the molar ratio of 7:1.

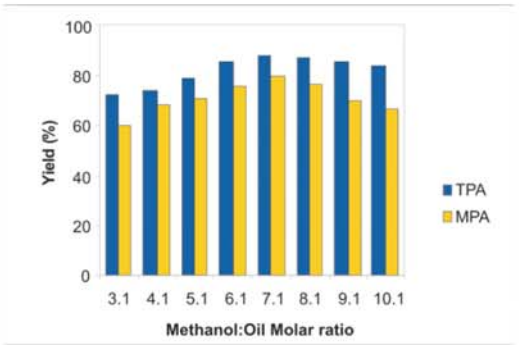

Fig. 1. Optimisation of Methanol: Oil Molar ratio

B. Optimization of Catalyst: Oil weight ratio:

The biodiesel yield improved with increasing catalyst addition and the maximum biodiesel yield was obtained for TPA at weight ratio of 0.07:1 as shown in figure2.

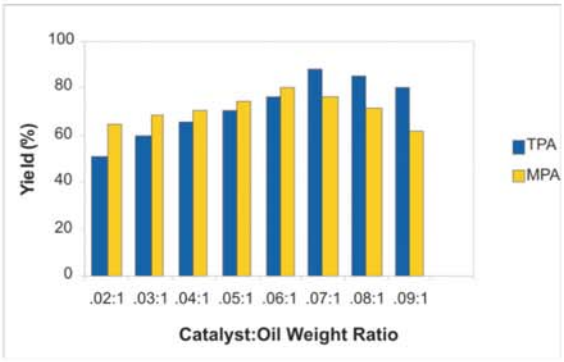

Fig. 2. Optimisation of Catalyst: Oil weight ratio

I*C. Optimization of Reaction Time:*

In the present work the reaction time was varied from 0.25 to 3 hours. The effect of reaction time on biodiesel yield is shown in figure 3.The performance of TPA as a catalyst is better in comparison with MPA for waste cooking oil.

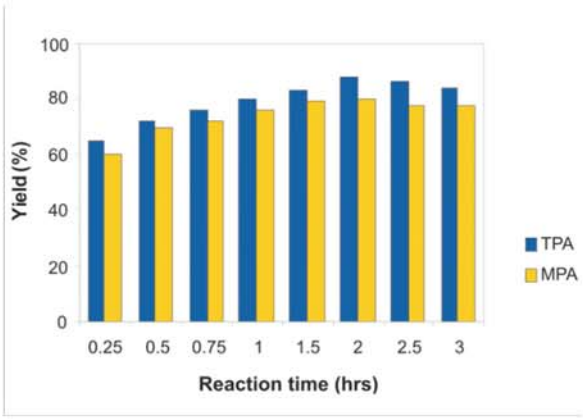

Fig. 3. Optimisation of Reaction time

C. Optimization of Reaction Temperature:

The reaction temperature was varied from 37 °C to 60°C. The biodiesel yield increased with increase of reaction temperature as shown in figure 4. The optimum temperature for trans-esterification reaction is found to be 55°C for the maximum yield using TPA as catalyst.

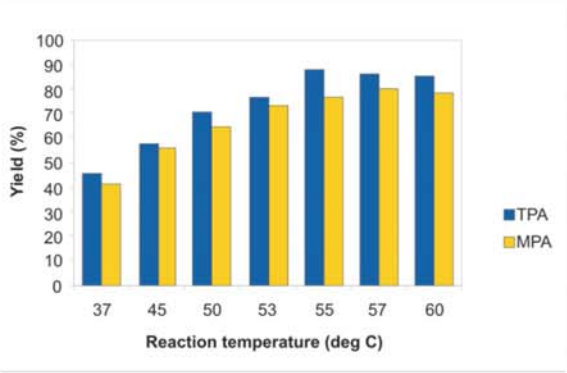

Fig. 4. Optimisation of reation temperature

D. Effect of Recycling of used catalyst on biodiesel yield:

The advantage of the solid acid catalysts are that they can be recovered from the reaction mixture and recycled. Both TPA and MPA were tested for their reusability as shown in figure 5.

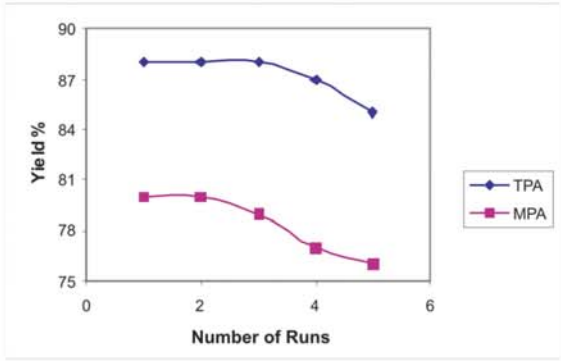

Fig. 5. Re-usability Studies

F. Comparison of Catalytic Performance with Conventional Catalyst:

A comparative study of TPA and MPA with conventional catalyst NaOH was done for the optimized conditions. The results illustrated in fig 6 indicate that TPA is a better catalyst for transesterification reaction using waste cooking oil.

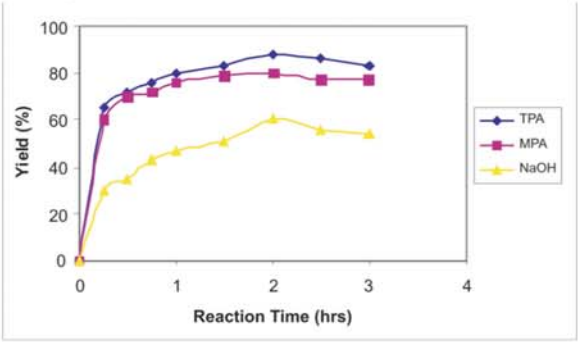

Fig. 6. Optimisation of reation temperature Catalyst

Table 1. Physical Properties of Waste cooking oil ester:

S.NO	Properties	ASTM Standards	Bio Diesel using TPA	Bio Diesel using MPA
1.	Sp.Gravity (28 °C) (g / ml)	-	0.88	0.89
2.	Kinematic Viscosity (CSt)	2.52 – 7.5	4.5	4.6
3.	Flash Point (° C)	Min 130	140	130
4.	Fire Point (° C)	Min 53	145	135
5.	Cetane No	Min 45	51	49.5
6.	Calorific Value (MJ / kg)	Min 33	48.23	40
7.	Iodine Value	Max 135	105	106
8.	Saponification Value (mg / g)	Min 180	195	202
9.	Diesel Index	Min 45	52	47.9
10.	Acid Value (mg /g)	0.8 max	0.003	0.007
11.	Cloud Point (°C)	-3 to 12	10	10.7
12.	Pour Point (°C)	-15 to 10	-7	-6

IV. CONCLUSION

The experimental results show that solid acid catalysts are a promising alternative for Trans-esterifcation reaction when compared to the conventional catalysts. The reaction yield shows that Do-Deca Tungstophosphoric acid is a better catalyst for the production of biodiesel from methanol using waste cooking oil. Moreover the catalyst can be reused effectively for 3 runs without any decrease in the yield. The properties of the methyl esters obtained are found to be in accordance with the ASTM standards.

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