

Transesterification of Used Cooking Oils Catalyzed by CsTPA/SBA15 Catalyst System in Biodiesel production

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Abstract—An environmentally beneficial, facile and clean method for the production of Biodiesel from Used Cooking Oils have been developed. Owing to corrosion and re-usability problems associated with the alkali catalysts like NaOH and KOH, a novel Heteropolyacid Cesium substituted do-decatungstophosphoric acid (CsTPA) on SBA 15 was synthesized. A process for the production of Biodiesel from Used Groundnut Oil(UGO), Used Sunflower Oil(USO) and Used Palm Oil(UPO) has been studied and the reaction conditions that affect the yield and purity of product esters like the concentration of catalyst, methanol:oil molar ratio, reaction time and temperature were optimized. Performance of the catalyst was compared with that of the conventional alkali catalysts and it was found that the proposed heteropolyacid catalyst system gave higher yield of 91.5% for UPO. The catalyst activity did not vary much even after reusing the recovered catalyst system for up to three runs. The fuel properties for the Used Cooking Oil esters produced were found to be in agreement with ASTM standards. Comparative performance and emission study of UCOs with diesel was carried out to check the effect of CO, CO₂ and NO_x.

Index Terms—Biodiesel, CsTPA/SBA15, heteropolyacid, optimization, transesterification, used cooking oils.

I. INTRODUCTION

There is increasing worldwide concern for environmental protection and for the conservation of non-renewable natural resources. Fatty acid methyl esters (FAME) show great potential as diesel substitutes, and they are known to be sources of biodiesel. Biodiesel is synthesized from direct transesterification of vegetable oils, where the corresponding triglycerides react with a short-chain alcohol in the presence of a catalyst [1]. Transesterification of vegetable oils to biodiesel with methanol can be carried out using both homogeneous (acid or base) and heterogeneous (acid, base and enzymatic) catalysts [2]. Homogeneous base catalysts provide much faster reaction rates than heterogeneous catalysts in transesterification. However, a large amount of water is required to transfer the catalysts from the organic phase to a water phase [3],[4]. Therefore, it is considerably costly to separate homogeneous catalysts. Heterogeneous catalysis is an economically and ecologically important field in catalysis research because these catalysts have many advantages: they are non-corrosive, environmentally benign and present fewer disposal problems. They are also much easier to separate from liquid products and they can be designed to give higher activity, selectivity and longer

catalyst lifetimes [5].

In search for water tolerant acid catalysts Heteropolyacids [6]-[8] appear to be the most appropriate choice. CsTPA catalyst has been chosen on the basis of high activity, water tolerance, re usability and eco friendly nature of these materials for Biodiesel production. Silica has been widely favored as a supporting material for CsTPA since it interacts weakly with the Keggin anions and thus preserves their structure. A larger pore diameter (7 – 9 nm) and comparable internal surface of SBA – 15 relative to MCM – 41 enables higher loading of catalytic phase with little pore blockage and improved control of its location. Hence SBA – 15 is a proper support for Cs- TPA.

A Major hurdle towards wide spread commercialization is the high price of biodiesel. One of the means to address the higher priced hurdle is to develop methods to reduce the cost of biodiesel [9],[10]. A reduced cost option is to produce biodiesel from waste fats and oils. Another option for cost reduction is to reduce the cost of processing through optimizing the process variables that affect the yield and purity of bio - diesel.

Biodiesel possess several distinct advantages over petro – diesel in the following safety, bio-degradability and environmental aspects: Renewable fuel with a net gain of energy producing it ; Higher flash point makes it safer in transport and storage ; greatly reduces particulate matter and carbon monoxide emissions; reduces carcinogenic polycyclic aromatic hydrocarbons (PAH) and nitrated PAH; contains essentially no sulfur, therefore greatly reduces sulfur- dioxide emissions from diesel vehicles; biodegrades as fast as dextrose [11],[12].

In the present work SBA-15 was employed as a support for preparation of high loading composite CsTPA on the external surface of the support. The catalytic activity of the novel catalyst was tested and optimum reaction conditions were determined for the transesterification of waste cooking oil to produce methyl ester (Biodiesel). The variables were a) Concentration of catalyst b) Methanol to oil molar ratio, c) Temperature of the reaction and d) Reaction time. The fuel properties of the obtained biodiesel were found comparable with the standards for Bio Diesel based on American Society for Testing and Materials. Reusability studies were carried out to test the stability of the catalyst system for repeated usage.

II. MATERIALS AND METHODS

Used frying Sunflower oil, Palm oil and Groundnut oil were collected from local restaurants and were used as feedstocks. Prior to transesterification, the UFO samples were dried over calcium chloride (CaCl₂) and filtered through a cellulose filter to remove any suspended matter and CaCl₂

crystals. All chemicals were obtained from Aldrich.

A. Preparation of CsTPA /SBA 15 Catalyst System

The bulk CsTPA was prepared from aqueous solutions of CS_2CO_3 (Aldrich) and $\text{H}_3\text{PW}_{12}\text{O}_{40}$ (Aldrich) by previously reported procedure [13]. SBA-15 was prepared according to the procedure presented in [14] by crystallization from acidic solutions of Poly (Ethylene glycol) – block – Poly (Propylene glycol) – block – Poly (Ethylene glycol) copolymer (Aldrich) and TEOS (Aldrich). CsTPA was deposited on the external surfaces on SBA 15 by dispersing as – synthesised surfactant containing SBA 15 (1gm) in aqueous solution of CS_2CO_3 (0.03 gm in 10 ml), drying at 383 K for 2 h and calcination in air at 773 K. It resulted in simultaneous decomposition of CS_2CO_3 to CS_2 and removal of surfactant. The solid was subsequently reacted with methanolic solution of TPA (0.6 gm in 10 ml) followed by drying and calcination at 573 K for 2 h. The sample was then stirred in excess of methanol (to remove free TPA) for 2 h, filtered and dried overnight at 373K. The CsTPA / SBA 15 thus prepared were used as the catalyst system.

B. Reaction Procedure

Transesterification reactions were carried out in a 250 ml glass reactor with a condenser. The reaction procedure was as follows. First, a known quantity of the catalyst system (Cs-TPA/SBA15) was dispersed in Methanol under magnetic stirring. Then Used Groundnut oil (UGO) in the molar ratio of 6:1, methanol to oil was added to the mixture and heated to about 60 deg Celsius. 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. Experiments were repeated to optimize the amount of catalyst, methanol to oil molar ratio, reaction time and temperature using UPO and USO also. The catalyst in the lower phase was separated by centrifugation. Experiments were also conducted to test the reusability of catalyst for consistent yield.

C. Exhaust Emission Analyzer

The Exhaust Emission Analyzer used was a rugged portable gas analyzer with PC software. The analyzer has a measuring range of 0 -25% with a resolution of 0.01%. No external display is required and this makes the emission analyzer the most cost effective choice for a high quality emission analyzer. The software included makes this a complete stand alone unit when connected to any PC running on windows.

III. RESULTS AND DISCUSSION

A. Optimization of Catalyst Concentration

A catalyst possessing large surface area exhibits high activity. In this study, catalyst concentration was varied within a range of 0.01-0.08% for all the oil samples. The biodiesel yield improved with the addition of catalyst and it was found that the yield was maximum at 91% for UPO at a catalyst concentration of 0.03% as shown in Fig.1. The increase in conversion with an increase in the catalyst concentration can be attributed to an increase in the availability and number of catalytically active sites.

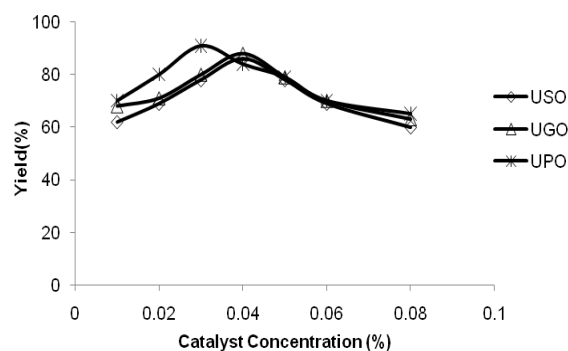


Fig. 1. Optimization of catalyst concentration

B. Optimization of Methanol: Oil Molar Ratio

The transesterification reaction requires 3 mol of alcohol per mole of triglyceride to give 3mol of fatty esters and 1 mol of glycerol. In order to shift the reaction to the right, it is necessary to either use excess alcohol or remove one of the products. A molar ratio of 6:1 is normally used in industrial processes to obtain higher methyl ester yields. Methanol:Oil Molar Ratio was varied from 5.3 - 6.9:1 for all the oil samples as shown in Fig.2. However with the addition of increased methanol quantity glycerol separation becomes more difficult thus decreases the biodiesel yield.

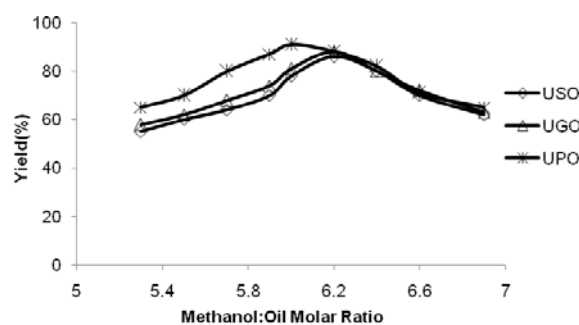


Fig. 2. Optimization of methanol: oil molar ratio

C. Optimization of Reaction Time

In order to determine the effect of reaction time on the yield of biodiesel, reactions were carried out for different reaction times, by keeping the optimized catalyst concentration, Methanol: oil molar ratio and reaction temperature constant. The time of the reaction was varied between 0.25-2.0 h for the catalyst system. It is seen from Fig.3 that UPO gave the maximum yield of 91.5% at a reaction time of 1h.

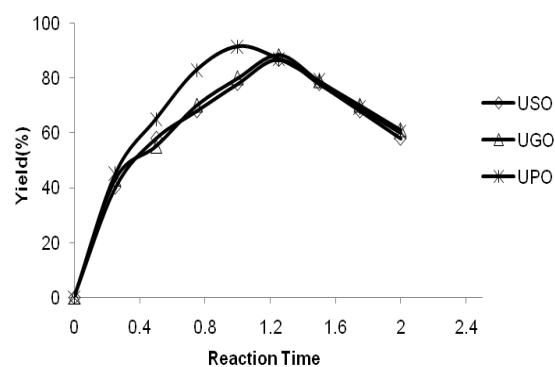


Fig. 3. Optimization of reaction time

D. Optimization of Reaction Temperature

The rate of reaction is strongly influenced by the reaction temperature. The methanolysis was carried between 40-75°C for UPO, USO and UGO in order to determine the effect of the reaction temperature on methyl ester formation. It is seen from Fig. 4 that UPO gave the maximum yield at 60°C. The other optimized parameters were kept constant. However when the reaction temperature exceeds the boiling range of methanol, methanol vaporizes and forms a large number of bubbles, which inhibit the reaction on the three phase inter phase.

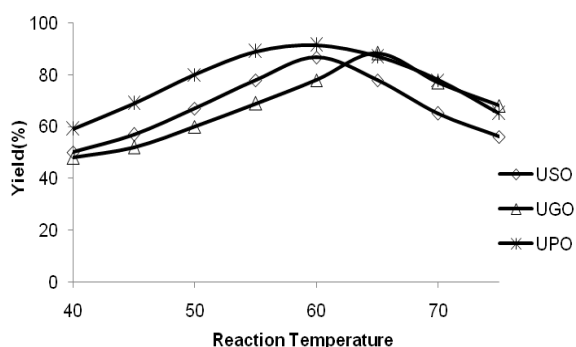


Fig. 4. Optimization of reaction temperature

E. Effect of Recycling of Used Catalyst on Biodiesel Yield

One of the characteristic features of the catalyst system is its re-usability. As mentioned above, the catalyst was easily separated from the production mixture, because at the end of the reaction, the catalyst settled at the bottom of the reactor and was used one more time without any treatment.

Experiments were repeated by using the separated catalyst system for all the oil samples. It can be seen that there is no considerable change in the catalytic yield up to three reaction cycles and it decreased only slightly with increasing runs as shown in Fig.5. The main reason resulting in the minor decrease in catalytic activity was due to the catalyst loss during the repeated experiments. From an economic point of view, the cost of the catalyst accounts for a large part of the cost of Biodiesel production. Therefore the stability and sustained activity of the catalyst are of great importance for industrial applications.

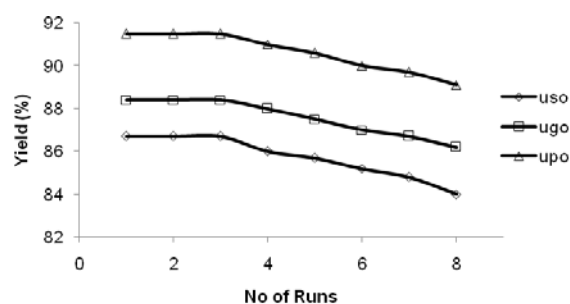


Fig. 5. reusability studies

F. Biodiesel Properties

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

TABLE I: PROPERTIES OF RAW FEEDSTOCK AND METHYL ESTERS

S.NO	Properties	UGO	USO	UPO	BD UGO	BD USO	BD UPO	Diesel	ASTM Standards
1.	Sp.Gravity (28°C) (g / ml)	0.887	0.93	0.92	0.89	0.87	0.88	0.85	-
2.	Kinematic Viscosity (CSt)	35.3	41.4	45.2	4.6	5.5	5.1	2.049	2.52 – 7.5
3.	Cetane No	40	49.1	71.4	49.5	50	52	47.73	Min 45
4.	Calorific Value (MJ / kg)	36.7	38	39.7	40	44	46	42.57	Min 33
5.	Iodine Value	101	120	60	106	110	100	102	Max 135
6.	Saponification Value (mg / g)	220	196	197	202	198	200	224	Min 180
7.	Acid Value (mg / g)	3.1	3.82	1.90	0.007	0.1	0.15	0.72	0.8 max

G. Emission Test

Comparative performance and emission study using an exhaust analyser with USO, UPO and UGO was carried out to check the effect of CO, CO₂ and NO_x.

CO Emission

The variation of CO produced by running the diesel engine using bio-diesel obtained from used cooking oils is compared with diesel in Fig. 6. The emission levels of diesel are higher when compared to used cooking oils. This is because even though diesel engines are operated with lean mixtures, some local rich mixtures will always be present in the cylinder. As a result CO formation occurs. But in the case UCOs, oxygen is available in it (fuel bound) and hence most of the CO that is formed during combustion will be oxidized to carbon dioxide.

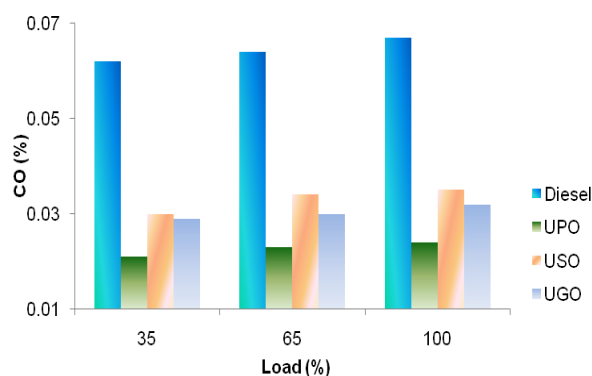


Fig. 6. Variation of CO emission with Load

CO₂ Emission

Emission rates of CO₂ at various loads are shown in Fig. 7.

Bio diesel from UCOs gave higher emission rates than diesel because as mentioned earlier most of the CO that is formed during combustion is oxidized to carbon dioxide.

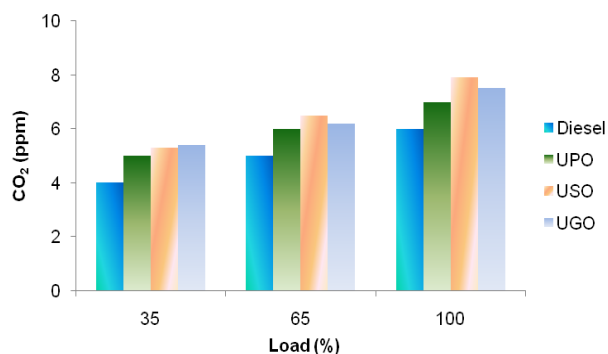


Fig. 7. Variation of CO₂ emission with Load

NO_x Emission

The NO_x emission is strongly related to lean fuel with high cylinder temperature or high peak combustion temperature. A fuel with high heat release rate at premix or rapid combustion phase and lower heat release rate at mixing will produce NO_x emissions. The variation of NO_x emission with engine load for bio diesel and diesel is shown in Fig. 8. NO_x emission depends upon the maximum combustion temperature. Reason for decreasing NO_x is due to lower combustion temperature. However, biodiesel's lack of sulfur allows the use of NO_x control technologies that cannot be used with conventional diesel. So, biodiesel NO_x emissions can be effectively managed and efficiently eliminated as a concern of the fuel's use.

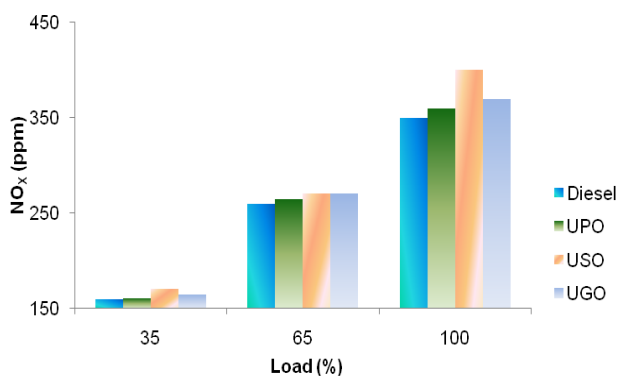


Fig. 8. Variation of NO_x emission with Load

IV. CONCLUSION

The experimental results show that the supported solid acid catalyst system demonstrated excellent catalytic activity and stability for transesterification of used cooking oils to biodiesel. It is found that used palm oil gave the maximum yield of 91.5% at 60°C, catalyst concentration of 0.03%, methanol: oil molar ratio of 6:1 and reaction time of 1 hr. Since it is a solid acid catalyst, it was recovered at the end of the reaction and used for up to 3 reaction cycles without any

decrease in the catalytic yield. Cs-TPA loaded externally on SBA15 has increased potential as green catalyst for transesterification reactions due to the decreased CO emission levels in comparison with diesel.

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