SYNTHESIS OF BIO-DIESEL AND BIO-LUBRICANT BY TRANSESTERIFICATION OF VEGETABLE OIL WITH LOWER AND HIGHER ALCOHOLS OVER HETEROPOLYACIDS SUPPORTED BY CLAY (K-10)

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Abstract: The use of different lower and higher alcohols *viz*; methanol, ethanol, n-propanol and n-octanol, for the synthesis of methyl, ethyl, propyl and octyl fatty acid esters by transesterification of vegetable oil (triglycerides) with respective alcohols also known as 'Bio-diesel' and 'Bio-lubricants' was studied in detail. The reactions were carried out in a batch process. The activity with different supports like clay (K-10), activated carbon, ZSM-5, H-beta and TS-1 were compared. The superacids (heteropolyacids, HPA) *viz*; Dodeca-Tungstophosphoric acid $[H_3PO_4 \cdot 12\ WO_3 \cdot xH_2O]$ (TPA) and Dodeca-Molybdo phosphoric acid ammonium salt hydrate $[H_{12}Mo_{12}N_3O_{40}P + aq]$ (DMAA) was used to increase the acidity and so the activity by loading on the most active support *viz*; clay (K-10). These HPA loaded on clay as a catalyst was used for the following study: effect of percent HPA loading on clay, effect of different vegetable oils, effect of different alcohols on the triglyceride conversion based on glycerol formation and selectivity based on alkyl esters formation. The data is compared at the best-optimized identical set of operating reaction conditions: 170°C, 170 rpm, catalyst loading: 5% (w/w of reaction mixture), molar ratio (oil : alcohol): 1:15 and time on stream of 8 h. The generated data is also evaluated based on the reported one.

Keywords: vegetable oil (triglyceride); alcohol; heteropolyacid; clay; ester; bio-fuel.

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INTRODUCTION

The major part of all energy consumed worldwide comes from fossil sources. Diesel fuels have an essential function in the industrial economy of a developing country. Economic growth is always accompanied by commensurate increase in the transport. Because of the acute shortages, dramatic price increase and high level emission of certain pollutants of conventional petroleum-based fuels, there has been a renewed interest in alternative cleaner burning fuels. One possible alternative to petroleum-based fuels is the biofuels. Biofuels are fuels derived from renewable sources such as naturally occurring fats and oils, which may be obtained from variety of plants and animals. The products such as bioethanol, biodiesel, biogas, biomethanol, biodimethylether, bio-ETBE (ethyl-tertio-butyl-ether), bio-MTBE (methyl-tertio-butyl-ether), synthetic biofuels, biohydrogen and pure vegetable oil are considered as biofuels. Biodiesel relates to specific application to diesel fuel and usually they are derived from fatty acid glycerides, which are major components of an oil or fat. The biodiesel find application as either replacement for, or a blending component for use with, fossil derived diesel. Direct use or blending, microemulsions, thermal cracking and transesterification of vegetable oils have been explored as potential alternatives to diesel. The transesterfication process can make use of alcohols such as methyl, ethyl, butyl and isopropyl alcohol. Methanol, ethanol and isopropanol are most common alcohols with methanol having the highest demand followed by the other two. Among these alcohols, isopropanol is the only one with a branched structure. Butyl esters and isopropyl esters crystallized at 12–15°C and 7–11°C lower, respectively, when compared to methyl esters of the same source material. The cold flow properties of these branched-chained esters are further improved when blended with diesel fuel (Demirbas and Balat, 2007; Wang, 1998).

Although, there are many ways and procedures to convert vegetable oil or animal fat into a diesel-like fuel, transesterification is the key and foremost important process to produce the cleaner and environmentally safe fuel. Transesterification significantly reduces oil viscosity, thereby improving fuel atomization and consequently fuel combustion characteristics. Transesterification or alcoholysis is the displacement of alcohol from an ester by another in a process similar to hydrolysis, except than alcohol is used instead of water. In other words, transesterification is the process of using an alcohol (e.g., methanol, ethanol, propanol, butanol, pentanol, hexanol, heptanol, octanol), in the presence of a catalyst to chemically break the molecule of the raw renewable oil into alkyl esters of the renewable oil with formation of glycerol as a by-product. Several aspects including the type of the catalyst, alcohol/vegetable oil or animal fat molar ratio, temperature, time, water content and free fatty acid content have an influence on the course of transesterification. Although, methanol is commonly used in this process due to its lower cost than other alcohols, ethanol is the preferred alcohol as it is derived from agriculture products and it is renewable and biologically less objectionable in the environment. Biodiesel produced by transesterification reactions can be catalysed with alkali (e.g., alkaline metal alkoxides and hydroxides as well as sodium and potassium carbonates), acid (e.g., Bronsted acids, preferably sulfonic acid and sulfuric acid) or enzyme (e.g., lipase). A catalyst is usually used to improve the reaction rate and yield.

Base catalysed transesterification reaction is the most economical and in fact, is in practice in several countries for bio-diesel production (Schuchardt *et al.*, 1998; Lang, 2001; Vicente *et al.*, 2004; Barnwal and Sharma, 2005). Alkaline metal alkoxides (as CH_3ONa for the methanolysis) are the most active catalysts, since they give very high yields ($>98\%$) of fatty acid alkyl esters in short reaction times (30 min) even if they are applied at low molar concentrations (0.5 mol%) (Brat and Pokorny, 2000). However, they require high quality oil and the absence of water, which makes them inappropriate for typical industrial processes. Alkaline metal hydroxides (NaOH and KOH) are cheaper than metal alkoxides but require increasing catalyst concentration (1–2 mol%). NaOH is more superior to KOH as the latter and other alkali hydroxides yield more soponified products than the bio- fuel. Leclercq *et al.* (2001), studied the transesterification of rapeseed oil in the presence of Cs-exchanged NaX and commercial KW2200 hydrotalcite catalysts. At a high methanol to oil ratio of 275 and 22 h reaction time at methanol reflux, the Cs-exchanged NaX gave a conversion of 70%, whereas 34% conversion was obtained over hydrotalcite. ETS-4 and ETS-10 catalysts gave conversions of 85.7% and 52.7%, respectively at 220°C and 1.5 h reaction time (Srinivas, 2007). Suppes *et al.* (2001), achieved a conversion of 78% at 240°C and $>95\%$ at 260°C using calcium carbonate rock as catalyst. Of late, Suppes *et al.* reported the use of Na, K and Cs exchanged zeolite X, ETS-10, NaX occluded with NaOx and sodium azide in the transesterification of soybean oil with methanol. Furruta *et al.* (2004), describe biodiesel production from soybean oil and zirconium oxides with oil conversions over 90%. Use of tin complexes immobilized in ionic liquids for vegetable oil alcoholysis was reported by Abreu *et al.* (2004, 2005). The transesterification process can also be catalysed by acids, preferably by sulphonic and sulfuric acids. Acid catalytic transesterification of vegetable oil were reported (Schuchardt *et al.*, 1998) to give very high yields in alkyl esters. However, in presence of homogeneous acid catalysts, the reactions are slow and hence take longer time as compared to alkaline catalysts. Moreover, acid-catalysed transesterification also needs extreme temperature and pressure conditions but soap formation and side reactions are avoided. As for the solid catalysts, the reports on the uses of acid catalysts are few in contrast to solid bases. Solid superacid catalysts of sulfated tin, zirconium oxides and tungstated zirconia were used in the transesterification of soybean oil with methanol at 200–300°C and the esterification of n-octanioc acid with methanol at 175–200°C. Tungstated zirconia-alumina was reported (Furruta *et al.*, 2004) to be a promising catalyst for the production of biodiesel fuels from soybean oil because of its high activity for the transesterification as well as the esterification.

The present paper relates to a reaction for the preparation of alkyl esters by transesterification process. It deals with the work for producing methyl/ethyl/propyl fatty acid esters also called as biodiesel, octyl fatty acid ester called as biolubricants, which comprises contacting fatty acid glycerides/triglycerides with or without free fatty acids of vegetable oil with alcohols in the presence of a solid heteropolyacids catalyst which is substantially insoluble in the reaction mixture under reaction conditions. The present work eliminates most of the above said drawbacks. The feedstock oil is a triglyceride or a mixture of fatty acids and glycerides. The heteropolyacids (HPA) catalysts usually have the general formula $H_nXM_{12}O_{40}$ where X is the central metal atom and M is the peripheral atom normally numbering 12 surrounding the central metal atom. Since these materials are stable, they are efficient to transform feedstocks containing fatty acids in a single step to fatty acid alkyl esters by transesterification. The catalyst could be separated easily by centrifugation or by simple filtration and reused. Most importantly, the catalyst is highly efficient and only a small amount is needed to carry out the reaction. The process is atom-efficient and the reaction conditions like temperature and pressure are only moderate. Unlike the conventional base catalysts, the catalyst of the present work is more efficient even in the presence of water impurity in oil. Hence, there are no limitations on the quality of oil that should be used with the catalysts presented in this paper.

EXPERIMENTAL

Catalyst Synthesis and Characterization

The commercial grade monmorillonite clay (K-10) and activated carbon supplied by fluka was used as a support without further purification. The other supports *viz*; ZSM-5, TS-1 and H-beta was prepared in the laboratory as per the procedure (Kasture *et al.*, 2004; Sharanappa *et al.*, 2004). The super acids (heteropolyacids, HPA) *viz*; Dodeca-Tungstophosphoric acid [$H_3PO_4 \cdot 12WO_3 \cdot xH_2O$] (TPA) and Dodeca-Molybdo phosphoric acid ammonium salt hydrate [$H_{12}Mo_{12}N_3O_{40}P +$ aq] (DMAA) was supplied by M/s Loba Chemie and used as such without further purification. The HPA on support was prepared by incipient wetness technique prepared in our laboratory (Yadav and Bokade, 1996). Typically for 10 gm scale catalyst preparation: Take 10 gm of different types of support *viz*; clay (K-10), ZSM-5 (Si/Al: 250),