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HIGHLY EFFICIENT AND SOLVENT-FREE TRANSFORMATION OF GLYCEROL OVER A HETEROGENEOUS SOLID ACID CATALYST

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ABSTRACT
Aluminophosphate ($AlPO_4$) has proved to be a highly efficient and reusable heterogeneous solid acid catalyst for glycerol etherification without any solvent in the synthesis of additives of diglycerol (DG), triglycerol (TG), and polyglycerol. The optimum reaction parameters of reaction contact time, temperature, monomer dosage of glycerol, and catalyst dosage were investigated. A maximum of 96 % of glycerol conversion was achieved at 60 °C for 2 h over 0.5 g $AlPO_4$.

KEYWORDS: Aluminophosphate, Heterogeneous, solid acid, glycerol, diglycerol, triglycerol

1. INTRODUCTION
To produce biodiesel from vegetable oils or animal fats, fatty acids are transesterified with methanol or ethanol, which transforms them into fatty acid methyl esters with glycerol as a co-product[i]. Biodiesel processing in large quantities will result in an excess of glycerol. Glycerol-based fuel additives are one way to use the substance. In general, glycerol etherification with alcohol, acetic acid has been developed to convert glycerol into oxygenated fuel. Glycerol has been converted into additives of glycerol using different catalysts[ii]. In the esterification of glycerol with acetic acid, heterogeneous solid catalysts such as sulfonic acid functionalized mesostructured silicas [iii] and acid ion exchange resins and zeolites [iv] have been investigated. Sulfated-based superacids[v-vi], heteropolyacid-based catalysts [iv, vii], Amberlyst-15 [viii-ix], tin chloride[x], Y/ SBA-3 [xi], and ZrO_2 based solid acids [xii] have all been used as glycerol esterification catalysts. The etherification reactions can be carried out effectively and with high yields in catalytic homogeneous systems, but long purification procedures are unavoidable, and the expensive catalysts are usually difficult to recover and recycle [xiii-xiv]. The catalyst for successfully converting glycerol into value-added additives is produced in this process.The glycerol polymerization reaction in the previous literature needed a lot of toxic solvents and catalysts, which resulted in contamination and corrosion [xv]. This study aims to examine the highly effective and solvent-free transformation of glycerol in the presence of environment friendly Aluminophosphate ($AlPO_4$) as a catalyst.

2. EXPERIMENTAL PROCEDURE

The glycerol esterification catalytic tests were performed in a 100 ml two-necked round bottom flask with a condenser on a magnetic stirrer. Typically, 20 ml glycerol and 0.5 g $AlPO_4$ were applied to the catalytic reactor, and the mixture was then heated to the appropriate temperature for a set amount of time. The mixtures are refluxed and optimized over contact time, reaction temperature, monomer dosage, and catalyst dosage of glycerol. Finally, the product mixture was filtered and distilled to isolate the products, which were then quantified and analyzed using HPLC. The conversion and selectivity equations of glycerol were used to quantify glycerol-based fuel additives.

$$\text{Conversion (\%)} = \frac{\text{Converted glycerol (\%)}}{\text{Total glycerol}} \times 100$$

$$\text{Selectivity \%} = \frac{\text{Moles of one product}}{\text{Moles of all product}} \times 100$$

2.1 HPLC Analysis

The glycerol-based additives are formed during etherification reactions were quantified using a High-Performance Liquid Chromatographic System (HPLC Model - LC 20 AD Prominence, Shimadzu). A set of analyses were carried out on a shim-pack GIST column of 250 x 4.6 mm. Acetonitrile used as a mobile phase was filtered through a 0.45 µm membrane filter (Millipore), and then degassed ultrasonically before use. The flow rate was 0.6 mL min-1 and the analysis time is 30 mins, the volume of injections was 10 µL. In the analyzed samples, each attribute was defined by comparing its retention time with that of the respective standards.

3. RESULT AND DISCUSSION

3.1 Optimization process parameters

3.1.1 Effect of reaction time

Initially, the effect of reaction time on the etherification of glycerol with 0.5 wt % $AlPO_4$ of the catalyst at 60 °C for 1 to 5 h was studied. The product composition of the mixture (Diglycerol (DG), Triglycerol (TG), and polyglycerol) obtained was analyzed by HPLC. From this study, complete glycerol etherification with $AlPO_4$ resulting in DG, TG, and polyglycerols was observed every 1 h. It is shown in figure 1. The reaction contact time increases glycerol conversion also increases up to 2 hours after increasing reaction time decreases glycerol conversion gradually. However, maximum selectivity of DG, TG, and polyglycerol was obtained for 2 hours reaction time. It was found that the optimum reaction time for the complete glycerol conversion to glycerol-based additives is 2 hours.

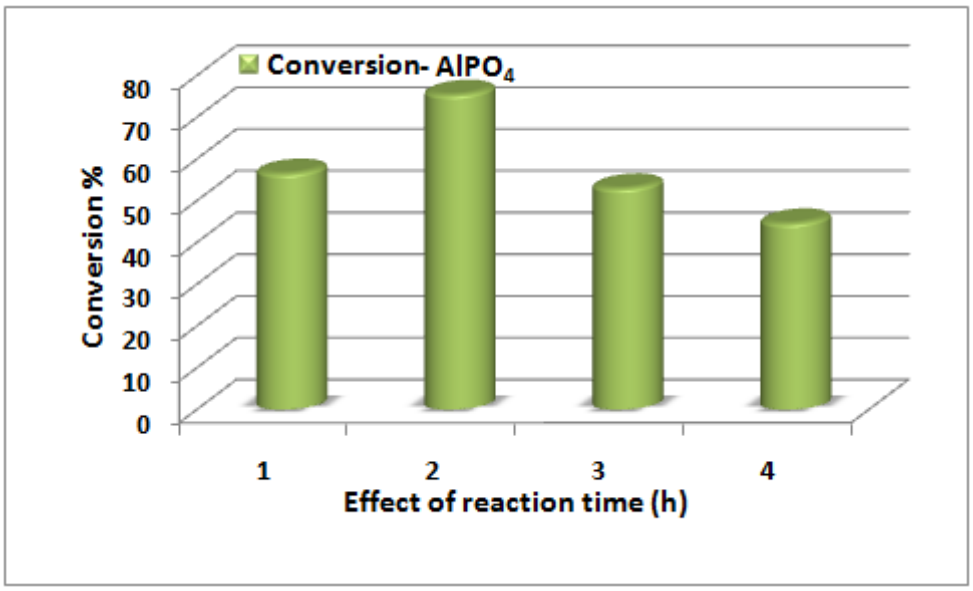


Figure 1. Effect of reaction time on glycerol conversion over $AlPO_4$

3.1.2 Effect of reaction temperature

Reaction temperature has played a key role in the catalytic glycerol conversion. As shown in Figure 2, glycerol conversion improved remarkably with the increasing reaction temperature and reached maximum at 60°C over $AlPO_4$ catalyst. Simultaneously, as the temperature rises, the conversion of glycerol increased drastically. Glycerol conversion and selectivity decrease after 60°C. Since consecutive etherification of glycerol is a highly endothermic reaction, raising the temperature allows for further etherification [xvi].

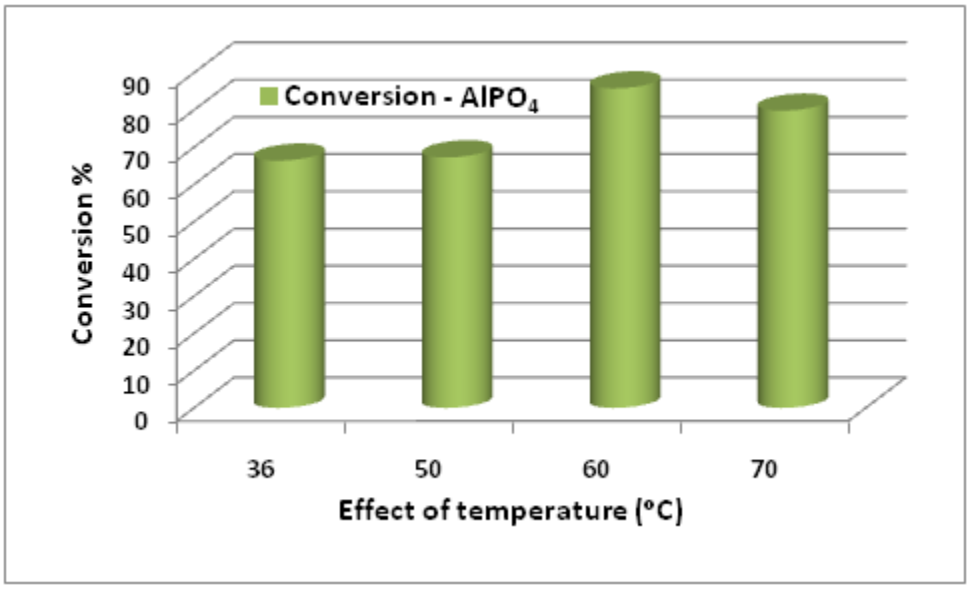


Figure 2. Effect of temperature on glycerol conversion over $AlPO_4$

3.1.3 Effect of monomer dosage

The effect of monomer dosage on the etherification reaction was studied using different monomer dosages were studied within the range of 10, 20, 30, 40, and 50 ml. The impact of monomer dosage on glycerol conversion and selectivity is revealed in Figure 3. The maximal glycerol conversion is observed at a 20 ml glycerol dose, after which it gradually decreases with increasing monomer dosage.

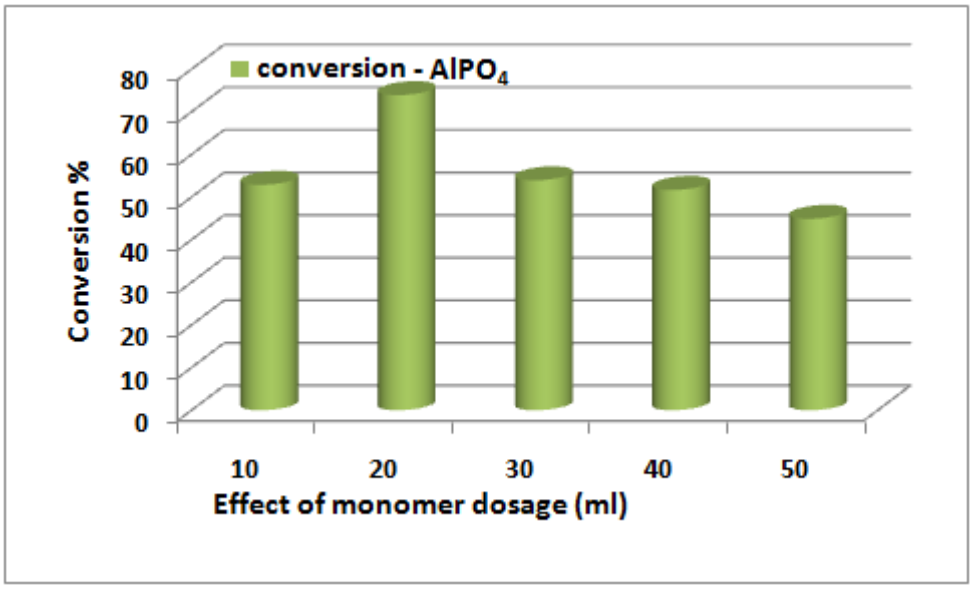


Figure 3. Effect of monomer dosage on glycerol conversion over $AlPO_4$

3.1.4 Effect of Catalyst dosage

Catalyst dosage has an important effect on the activity of catalyst and distribution of a product. The effect of catalyst dosage on the total glycerol conversion to DG, TG, and polyglycerol was investigated by varying from 0.5 to 2.0 wt % for 2 hours at 60°C. As shown in Figure 4, glycerol conversion improved initially with the increasing catalyst loading and reached maximum at 0.5 wt% over $AlPO_4$ catalyst. After increasing catalyst loading, the glycerol conversion getsdecreases.

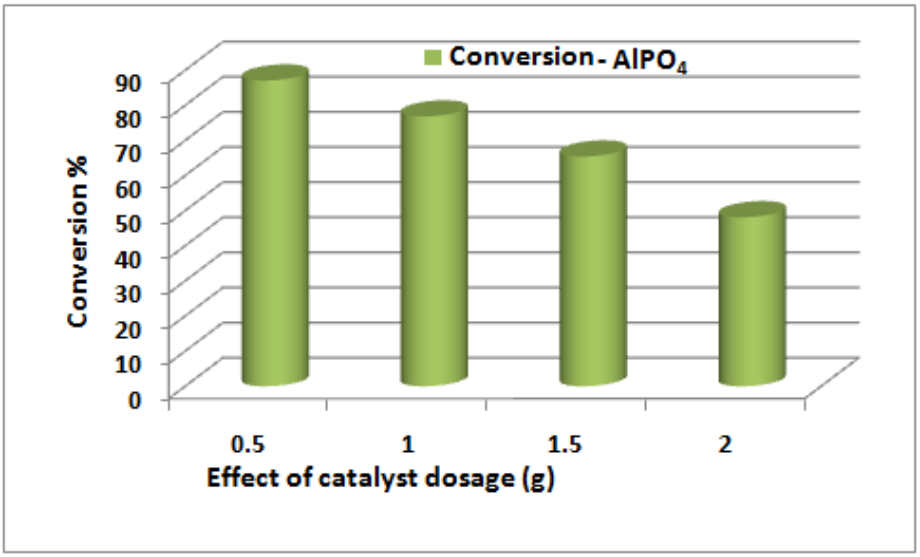
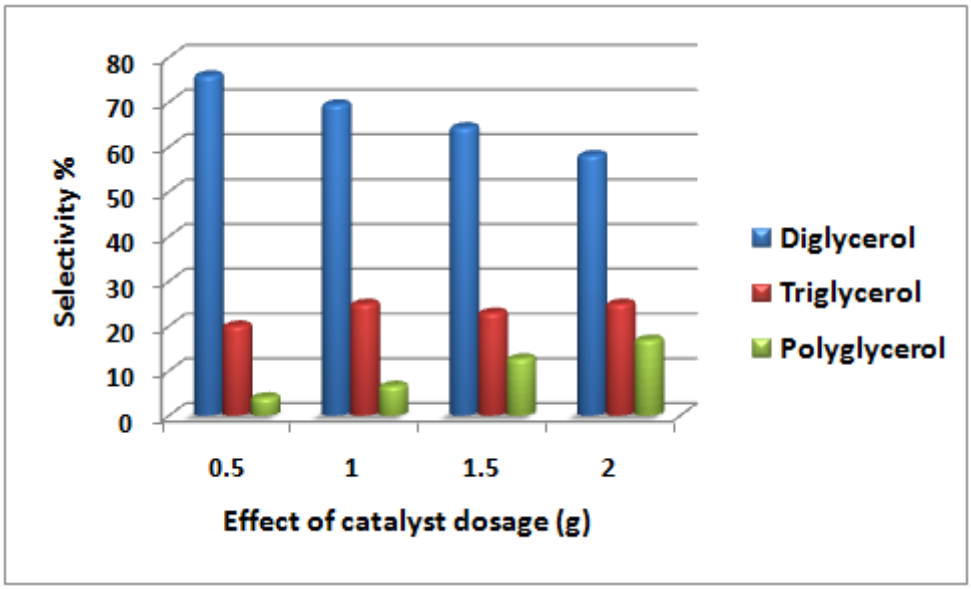


Figure 4. Effect of catalyst dosage on glycerol conversion over $AlPO_4$

The experimental conditions like temperature, time, monomer dosage, and catalyst dosage are optimized for maximum conversion of glycerol into value-added fuel additives. The maximum conversion of glycerol into fuel additives (diglycerol andtriglycerol) is 96% at 0.5 g catalyst dosage. This proved that $AlPO_4$ is the suitable catalyst for etherification process.



Reaction Condition: 2 h time, 60ºC temperature, 20 ml glycerol, 0.5g catalyst

Figure 5. Selectivity of glycerol conversion over $AlPO_4$ under optimized condition

The optimized parameters of this study results, the combined yield to DG, TG, and polyglycerol over AlPO are higher than that of already reported catalysts $PrSO_3H$-SBA15, sulfated zirconian, Y/SBA-3, andM_oO_x/TiO_2-ZrO_2[v-vi, xi-xii]. After the completion of the reaction, the $AlPO_4$ catalyst was first filtered and washed in ethanol, and dried for 3 hours at 120 °C before being calcined to make it moisture-free for reuse. The ALPO was recovered and reused two or three times without catalytic activity loss.

4. CONCLUSION

As compared to traditional solid acid catalysts, is a highly effective acid catalyst for the glycerol conversion to use value-added additives. AlPO's excellent efficiency, the entire glycerol conversion with combined selectivity to DG and TG of 96 %. Furthermore, $AlPO_4$ demonstrated consistent conversion in several catalytic studies. It's easy to see how a low-cost, high-capacity solid acid catalyst might be useful for a wide variety of etherification reaction.

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