

Oxygenated Additives Production for Diesel Fuel by Glycerol Etherification

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Introduction

It is well known that the blending of oxygenated additives with diesel fuels could be a promising way of improving the combustion efficiency of internal combustion engines with a significant reduction of pollutant emissions. Among several proposed oxygenated additives to blend with diesel, the ethers of glycerol could hold a prominent role [1]. The etherification reaction of glycerol can be catalyzed by solid acids, especially by strong acid ion-exchange resins [2].

The synthesis of *tert*-butyl ethers from isobutene and glycerol on ion exchange resins has been already investigated [2]. However, a problem with GTBE production from isobutene is that isobutene is a petroleum refining product, so GTBE production by the etherification of glycerol with *tert*-butanol (TBA), which can be considered a bio-source, should appear more attractive.

This study aims to investigate the etherification of glycerol with *tert*-butyl alcohol over different solid acid systems. Attention was focused on isolating the primary factors that limit large scale process development.

Materials and Methods

Two solid acid supported catalysts were prepared by the incipient wetness impregnation method, using a silica carrier (S.A.-BET, 250 m² g⁻¹) and two solutions containing 17 wt% of *Nafion*[®] ionomer (N-17) and 17 wt% of *tungstophosphoric heteropoly acid* (HPW-17) respectively. A catalyst was also prepared by the partial exchanging of H⁺ ions of HPW-17 sample with cesium (Cs-HPW). In addition, two commercial acid ion-exchange resins, *Nafion*[®] on amorphous silica (SAC-13) and *Amberlyst*[®] 15 dry (A-15), were used as reference catalysts.

The etherification reaction between glycerol and *tert*-butyl alcohol was carried out in a liquid phase in a 100 cm³ stainless steel “jacketed-batch reactor” under different reaction conditions: *i*) under pressure; *ii*) at T_R, 303-363 K; *iii*) by operating at different reaction times and *iv*) at different catalyst/glycerol and alcohol/glycerol ratios.

Results and Discussion

From Fig 1 a linear relationship between catalyst acidity and glycerol conversion is observed. Cs-HPW and Amberlist samples characterized by the higher surface acidity are the most active systems. The increasing of reaction temperature from 303 to 363K affect significantly both glycerol conversion and products distribution. Reaction occurs with a *consecutive* mechanism and the primary product formed is 3-butoxy-1,2-propandiol (mono-ether). Di-ether slowly forms while tri-ether never forms probably due to steric hindrance phenomena.

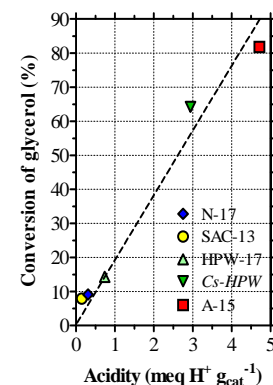


Figure 1. Glycerol conversion as a function of catalyst acidity

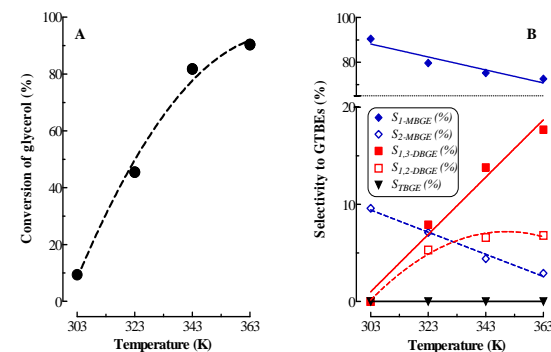


Figure 2. Glycerol conversion and product distribution as a function of reaction temperature
Amberlist catalyst; P = 1bar; R_{Alcoh/Gly} = 4;

To address the reaction to the formation of DBG (di-butoxy-glycerol) water, formed during reaction must be continuously removed form the reaction medium.

Combustion tests performed in an internal combustion engine, not reported here for brevity, demonstrated that DBG is a suitable oxygenated additive for diesel fuel.

References

1. R.S. Karinen, A.O.I. Krause, Appl. Catal. A: General, 306 (2006) 128-133
2. K. Klepáčová, D. Mravec, A. Kaszonyi, M.Bajus, Appl. Catal. A: General 328 (2007) 1-13