



ISCRE 23



APCRE 7

ISCRE 23 & APCRE 7
Bangkok, Thailand

September 7-10, 2014

Etherification of Glycerol with C₄ and C₅ Reactive Olefins*

Burcin Ikizer¹, Nuray Oktar², Timur Dogu^{1,*}¹Department of Chemical Engineering, Middle East Technical University,
Ankara, Turkey²Department of Chemical Engineering, Gazi University, Ankara, Turkey

*Corresponding author: tdogu@metu.edu.tr

Highlights

- Max. glycerol conversion recorded at 90 °C with C₄ olefin
- Dowex DR-2030 was the best catalyst for etherification of glycerol with C₄ olefin
- Increasing amount of catalyst increased conversion of glycerol with C₅
- Max. glycerol conversion (about 80%) obtained with 1g of Dowex DR-2030 at 120 °C, with C₅ olefin in an autoclave batch reactor
- Glycerol conversion reaches to equilibrium after 6 hour with Amberlyst-36 at 140 °C, with C₅ olefin

Summary

In this study etherification of glycerol, with C₄ (isobutylene) and C₅ (2 Methyl 2 Butene) olefins was investigated for the production of transportation fuel additives. The etherification reactions were carried out in a stainless steel autoclave reactor. Activities of acidic resin catalysts, Amberlyst-36, Dowex DR-2030 and Dowex M-31 were compared. Especially in the absence of any published work for the investigations of experimental conditions on glycerol conversion and product distributions in etherification of glycerol with C₅ (2 Methyl 2 Butene) olefin results obtained with C₄ and C₅ olefins are quite promising.

Keywords

Glycerol, Etherification, C₄ & C₅ Olefins

* Financial support of Middle East Technical University Research Fund (BAP-03-04-2013-008) and Scientific and Technical Research Council of Turkey (TUBITAK-112M234) are gratefully acknowledged.

Introduction

Glycerol is the main side product of biodiesel production through transesterification of vegetable oils and fats with low molecular weight alcohols. Approximately 10 wt.% of the total product of biodiesel synthesis is glycerol [1]. Widespread use of biodiesel as a fuel alternate requires conversion of its byproduct glycerol to valuable products, such as high quality fuels and/or fuel additives [2,3]. One of the possibilities of glycerol utilization is to produce oxygenated compounds by its etherification with C₄ (isobutylene) and C₅ (2 Methyl 2 Butene) olefins. Such oxygenates are known to have high octane numbers, low atmospheric reactivities and vapor pressures [3]. The main objective of this work was to investigate the product yields and distribution in etherification of glycerol with C₄ and C₅ iso-olefins with different

solid acid catalysts. Effects of temperature, catalyst to reactant ratio and reaction time on glycerol conversion and product distribution were also investigated in a batch reactor.

Methodology

Chemicals and Catalyst

The chemicals used; isobutylene (Air Products), Glycerol (Merck), Dioxane (Merck), 2 Methyl 2 Butene (Merck), Ethanol (Merck) were of analytical grade purity.

Commercial strong acidic ion exchange resins Amberlyst-36 (Sigma-Aldrich), Dowex Monosphere DR-2030 and Dowex Monosphere M-31 (The Dow Chemical Company) were used as etherification catalysts.

Reaction Experiments



ISCRE 23



APCRE 7

ISCRE 23 & APCRE 7
Bangkok, Thailand

September 7-10, 2014

Etherification reactions were performed in a stainless steel autoclave batch reactor (75 ml) with a magnetic stirring. Due to the insolubility of C_4 and C_5 in glycerol, dioxane and ethanol were used as solvents during the etherification reactions with isobutene and 2M2B, respectively. Composition of the reactor outlet stream was analyzed by a gas chromatograph (Agilent 6890N) equipped with an FID and a capillary HP Innowax column.

Results and Discussion

Etherification of Glycerol with C_4 Olefin (Isobutylene)

Etherification of glycerol with isobutylene was performed using different solid acid catalysts.

Experimental results (Fig.1) obtained with Amberlyst-36, Dowex DR-2030 and Dowex M-31, showed an increase of glycerol conversion and ether yields with an increase of temperature in the temperature range of 70-90°C, while a decrease in conversion was observed at 120°C. The highest glycerol conversion was obtained in the presence of Dowex DR-2030 at all temperatures.

Increase in temperature increases etherification reaction rate, however rate of isobutene oligomerization was found to increase more rapidly than the glycerol etherification reaction rate, especially over 100°C, this caused a negative effect on glycerol conversion. Dowex DR-2030 and Dowex M-31 are stable only upto 130°C. However, Amberlyst 36 is more stable upto 150°C. Product distributions showed formation of mono-ethers, di-ethers and trace amount of tri-ethers.

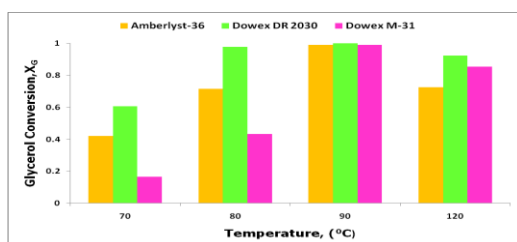


Figure 1: Glycerol conversion values at different Reaction temperatures with different catalyst. (Reaction time =6h, m_{cat} =0.3 g)

Etherification of Glycerol with C_5 Olefin (2M2B)

To our knowledge there is no published work for the investigations of experimental conditions on glycerol conversion and product distributions in etherification of glycerol with 2M2B.

Experimental results obtained at 120°C with Amberlyst-36 and Dowex DR-2030 (Fig.2) showed an increase of glycerol conversion with an increase of amount of catalyst charged to the reactor. The highest glycerol conversion was obtained by using 1 g of Dowex DR-2030, which is about 80%. This conversion level is highly promising.

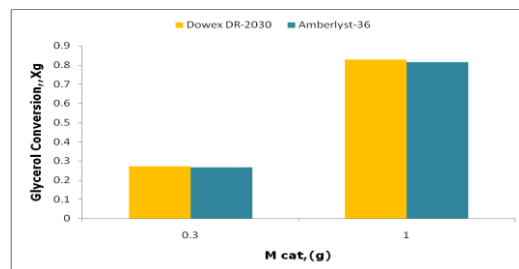


Figure 2: Glycerol conversion values with different amount of catalyst (Reaction Temperature=120 °C, Reaction time =6h,)

Experimental results obtained at 140 °C with Amberlyst-36 (Fig.3) showed an increase of glycerol conversion with an increase in reaction time up to 6 hours. After this time glycerol conversion reaches to a constant value which did not change much after this time. This maximum (equilibrium) conversion of glycerol was about 0.98 with Amberlyst-36 at the specified experimental conditions.

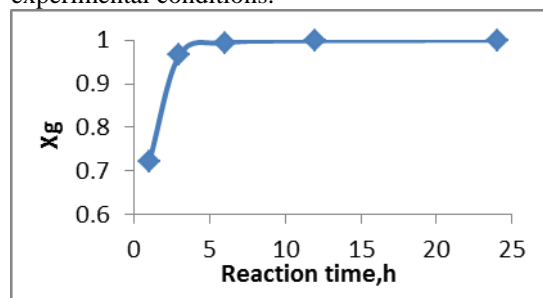


Figure 3: Glycerol conversion values with different reaction times (Reaction Temperature=140 °C, m_{cat} =1 g, Catalyst=A-36)

Conclusion

In this study etherification of glycerol with C_4 and C_5 olefins to produce oxygenated compounds were studied. Results obtained with C_4 olefin are quite promising. Very high glycerol conversions reaching to 99% were obtained using acidic ion-exchange resin catalysts. Conditions on etherification of glycerol with C_5 olefin are likely to be improved with further studies. Preliminary results on the topic showed that increasing amount of catalyst had increased glycerol conversion and Dowex DR-2030 had shown the highest activity at 120°C. Besides glycerol conversion at 140 °C in case of 1 g Amberlyst 36 showed an increasing trend up to 6 hours of reaction time, reaching to a constant value which did not change much after this time.

References

- [1] Karinen, R.S., Krause, A.O.I., Appl. Catal. A-Gen., 306 (2006) 128-133
- [2] Ozbay, N., Oktar, N., Dogu, G., Dogu, T., Int. J. Chem. React. Eng., 8 (2010), Article A18
- [3] Ozbay, N., Oktar, N., Dogu, G., Dogu, T., Top Catal., 56 (2013) 1790-1803