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CATALYST PERFORMANCE TESTING: CATALYTIC CONVERSION OF DILUTED GLYCEROL TO HIGHER VALUE ADDED PRODUCT

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ABSTRACT

Glycerol production has increased dramatically over the passed few years as a result of tremendous biodiesel demand. Glycerol can be converted to various higher value added products. One of the products that can be converted from glycerol is olefin. Olefin has numerous benefits as it is tough, light and stain resistant. This study will focus on the analysis of the effect of reactant and catalyst bed dilution on the conversion of glycerol to olefin. The temperature for this reaction is set at 700°C as high temperature will favour high olefin production. Feed of glycerol/water mixture are varied at from 5 to 60wt%. The dilution of well mixed catalyst bed was varied to different degree of dilution to observe the conversion of glycerol using glass pellet as the inert material. Highest conversion was obtained when the catalyst and diluents were very well mixed. With higher degree of catalyst dilution, the yield of olefin increase as the dilution fraction approaches one.

Keywords: glycerol; production; olefin;

INTRODUCTION

Glycerol, a chemical compound also commonly called glycerin, is colorless, odorless, viscous liquid that is widely used in pharmaceutical formulations. In organic chemistry, an alkene or olefin is an unsaturated chemical compound containing at least one carbon-to-carbon double bond, no other functional groups, form a homologous series of hydrocarbons with the general formula C_nH_{2n} [1, 2].

At 2008, glycerol became valuable byproduct of biodiesel production with a refined value close to $1/kg [3, 4]. As biodiesel production increases, the price of glycerol is expected to drop significantly from the actual cost and it has already decreased by half in the last few years [5]. Such an inexpensive feed makes the development of processes for the conversions of glycerol into other higher value added product increasing and have high demand.

Olefin is a one of valuable chemicals which can be produced from conversion of

glycerol. Olefin has various benefit and uses. It has good characteristics which contribute to its strength, colorfastness, comfort, stain, mildew, abrasion and sunlight resistance, good bulk and cover [6].

Traditionally, glycerol is obtained as a by-product in four different processes which include soap manufacture, fatty acid production, fatty ester production and microbial fermentation [7]. A wise used of this byproduct will give positive impact in economy and encourage cleaner environment as glycerol has a good potential to produces valuable chemicals substances.

Research shows olefin as by-product was obtained by reacting gas-phase glycerol/water mixtures with zeolite catalysts. Glycerol was converted through a series of reactions involving dehydration, cracking, and hydrogen transfer and catalyzed by the acid sites of the zeolite [8]. In this research, with increasing reaction temperature, the yields of light olefins increased. This research also shows feed dilution concentration has little effected on conversion of glycerol. These findings indicate that the high-temperature operation is ideal operating condition for light olefin production.

Since, catalyst bed dilution technique has found widespread useful applications as a means of producing reliable and reproducible results; it was adopted in this study. Catalyst bed dilution ensured uniform catalyst distribution along the bed, and reproducing such uniformity is essential to avoid channeling and segregation [9]. High degree of dilution will give high conversion of reactant. Low-surface-area materials such as glass, quartz, and silicon carbide (SiC) are preferred as dilution because of their relative inertness and good heat transfer properties. Dilution may also significantly reduce the conversion due to local bypass effects. If the catalysts and the diluting particles are not well mixed, the conversion reduces significantly due to bypassing and axial dispersion [10].

MATERIALS AND METHODS

Sample and materials

Chemicals used in this investigation were liquid glycerol, HZSM-5 zeolite catalyst, water and glass pellet. Glycerol reagent vial (85wt %) was purchased from Merck KGaA Company while zeolite reagent vial (30 wt%) was obtained from Zeolyst International Company. Stainless steel reactor was used throughout the experiment. An electrical furnace (carbolite), a 500 ml rounded bottom flask three neck, glass bits (4mm), heating mantle, thermometer 360°C, silicon stopper, condenser, water bath, 200ml rounded bottom flask and conical flask were also used in the experimental set-up.

Catalyst characterization

X-Ray diffraction

X-Ray diffraction was performed using the Siemens Diffractometer D5000 (Software Diffract Plus) with CuK α radiation, λ = 1.54056A° at 40kV and 30mA in the range of

2θ = 5° to 80° at a screening speed of 0.05° per seconds, with a vertical goniometer at room temperature (20°C). The sample was held on mountain sample holder and then grounded before mounting on glass.

Fourier Transform Infra Red (FTIR)
The existent of the impregnated metal in zeolite catalysts will analyzed by Fourier Transform Infra Red (FTIR). Spectrum one FTIR Spectrometer and spectrum 20 explorer with instrumentation model spectrum one was used to characterize the catalysts.

Experimental procedure
The study of glycerol conversion to olefin was divided into two sections, where the first part was to study the effect of glycerol in different degree of dilution and the second part was to study the effect of catalyst bed dilution. Helium was applied prior to running the experiment to activate the catalyst for 1 hour at 500°C. Then, the experiment was continued with different feed glycerol solution (5, 15, 30, 45 and 60wt %) at 700°C for two hours at fixed 0.1g zeolite catalyst. For the study of the effect of catalyst bed dilution, different degree of catalyst bed dilution (0.998752, 0.999167, 0.999375 and 0.999500) was prepared with fixed 45wt% glycerol solution. The product is kept in universal bottle and directly analyzed using gas chromatography flame ionization detector (FID) capillary column DB-1 with methanol solvent.

RESULTS AND DISCUSSION

Catalyst Characterization
Figure 1 shows the XRD pattern of HZMS-5 (30wt %). Notably, the HZMS-5 shows well resolved peaks in the 5-35° characteristic for the MFI structure. The peaks suggesting that amorphous aluminosilicate macroporous wall converts into MFI structure. A Fourier Transform Infrared (FTIR) spectrum of HZMS-5 is presented in Figure 2. HZSM-5 shows three significant broad bands at 1230 cm^{-1}, 1100 cm^{-1} and 796 cm^{-1} which associated with asymmetric and symmetric stretching vibrations of the Si-O-Si. These bands also related to internal linkages in SiO_2 or Al_2O_3 of zeolite lattice [11].

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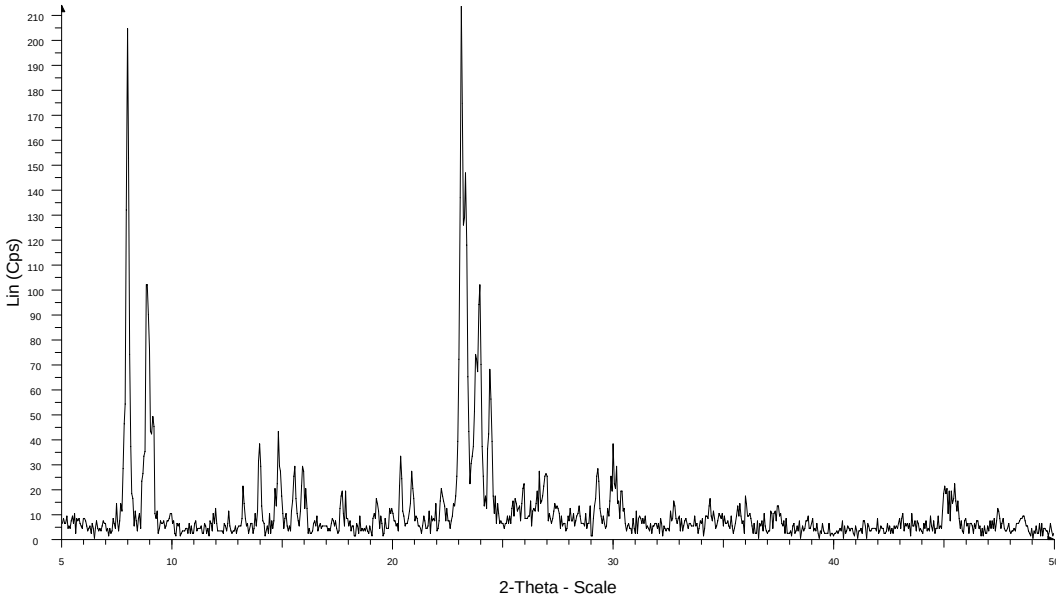

Figure 1: XRD pattern of HZSM-5 zeolite sample

Analysis of effect of reactant dilution on conversion glycerol to olefin

The results of conversion of glycerol, liquid product selectivity and yield of olefin for reactant dilution study is illustrated in Figure 3. It was reported earlier that different feed dilution slightly affects experimental result [8]. Hence, the result of glycerol conversion and olefin selectivity did not significantly differ in all experiments.

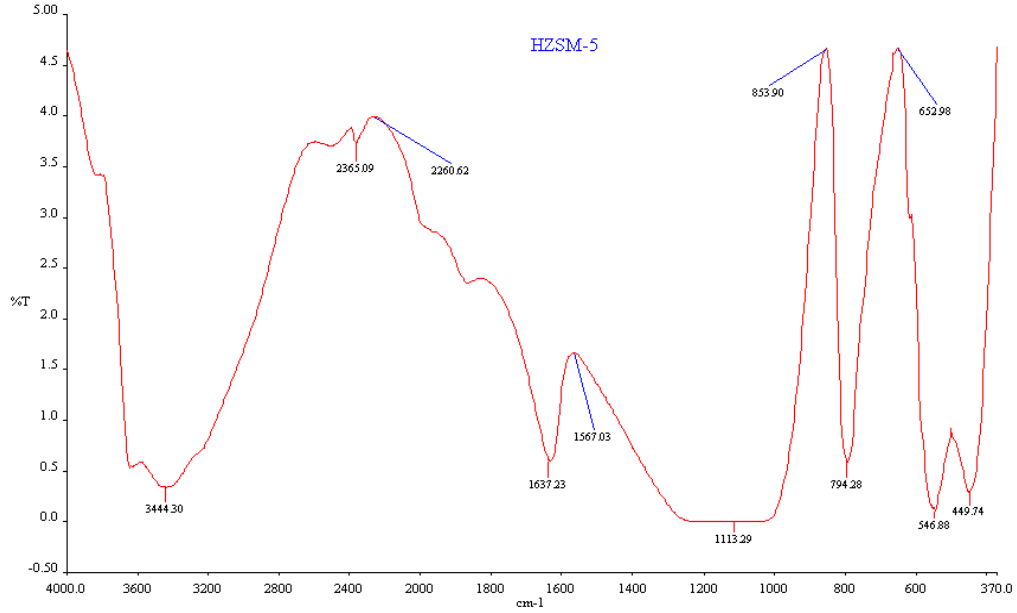

Figure 2: FTIR spectra of HZSM-5 zeolite

Glycerol conversion obtained for all experiments is 100%. This result is supported by Corma [8] who stated that glycerol conversion with zeolite catalyst is 100% as reaction temperature is above 300ºC. For the selectivity, it decreases at feed dilution 15wt%, and then sharply increases at 45wt%. Finally, at 60wt%, the selectivity significantly decreases and approach olefin selectivity of 14%. The olefin formed during these reactions may once oxidize to carbon monoxide, carbon dioxide and char. Similar effect and trends applies to olefin yield.

Analysis of effect of catalyst bed dilution on conversion glycerol to olefin
Results of glycerol conversion, olefin selectivity and olefin yield are tabulated in Table 1 and displayed graphically in Figure 4. Higher olefin selectivity was expected to be obtained if the catalyst and diluents are very well mixed. In the other hand, insufficient attention to the mixing procedure of catalyst bed will result to lower olefin selectivity and yield. The investigation has shown positive outcome as it appears that increase in degree of dilution has increase the olefin selectivity and yield when degree of dilution *(b)* approaches one [10]. For practical application, the relative deviation in conversion, b can be estimated from observable parameters as shown in the equation below:

$$b = \frac{V_{dil}}{V_{cat} + V_{dil}}$$

where V_{dil} is volume of glass pellet and V_{cat} is volume of catalyst.
In all catalyst bed dilution experiments, 100% glycerol conversion was achieved. Selectivity increases as degree of bed dilution increases, which aggress well with the study reported by Berger [10]. Unlike olefin selectivity, olefin yield shows consistent reading (0.99 to 1.63%) without any significant percentage increment. This was possibly due to the negative effect of high dilution as channelling and by-passing.

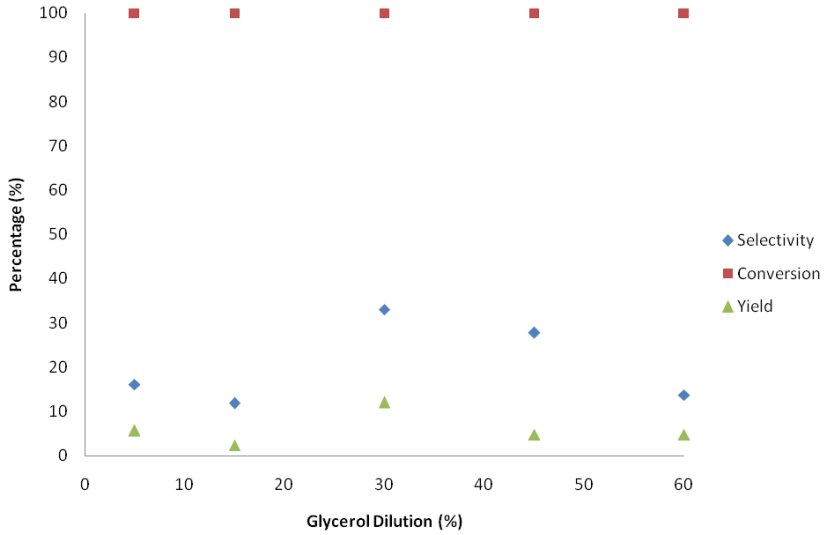

Figure 3: Conversion of glycerol, olefin selectivity and olefin yield versus glycerol dilution

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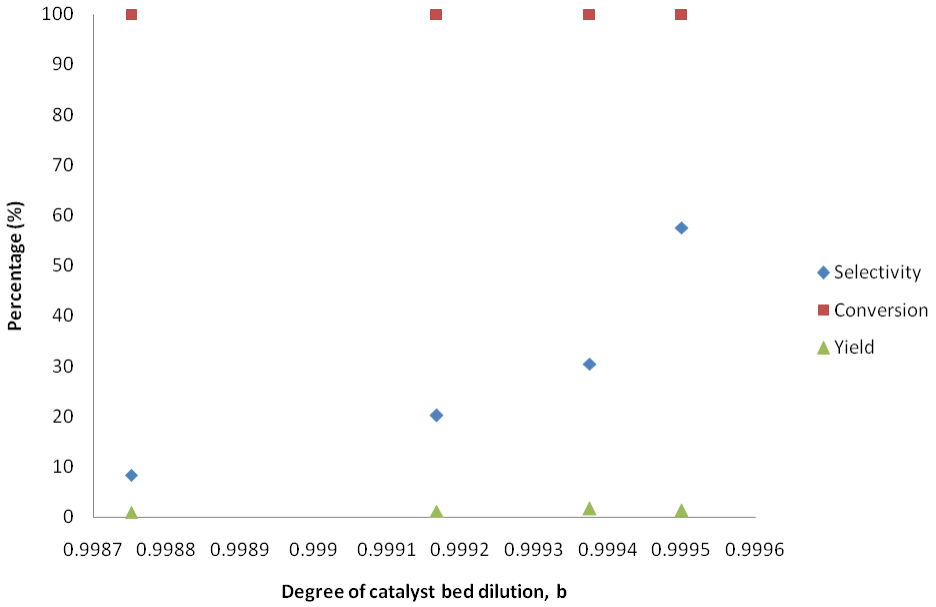

Figure 4: Conversion of glycerol, olefin selectivity and olefin yield versus degree of catalyst bed dilution

Table 1: Analysis of effect of catalyst bed dilution on conversion glycerol to olefin

Experiment	Degree of dilution, b	Conversion of glycerol, X (%)	Liquid product selectivity, S (%)	Yield of olefin, Y (%)
1	0.998752	100	8.367	0.9980
2	0.999167	100	20.231	1.1299
3	0.999375	100	30.460	1.6315
4	0.999500	100	57.572	1.29485

CONCLUSIONS

High reaction temperature of glycerol with zeolite catalyst gave 100% conversion. Different aqueous glycerol dilution gave slight affect on olefin selectivity and olefin yield. Highest conversion is expected for well mix catalyst bed dilution. It also appears that conversion of glycerol, olefin selectivity and olefin yield increases when dilution fraction increases and these increases enhances strongly when dilution fraction approaches 1.

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