

## Alkylation of ethylene with zeolite Beta

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**Abstract**—The Fischer-Tropsch process converts biomass into liquid hydrocarbons. The gas phase form this process contains a lot of light alkenes depending on the temperature used. In this investigation a model feed of Ethylene is used for alkylation over a hydrogen beta zeolite catalyst. Experiments were carried out at different flow rates of Ethylene (45 to 180 ml/min) and at different temperatures (350-450°C) in a continuous flow packed bed cylindrical reactor.

Maximum conversion of Ethylene was 13% at flow rate of 45 ml/min and temperature of 400°C. High reactivity was seen around the operating temperatures of 375 to 425°C. Considerable unsaturated alkenes groups were observed. There was a considerable formation of methane at lower flow rates. Except Acetylene no major triple bond carbon molecules were present in the products. Liquid products were only obtained at lower flow rates; however the amount of liquid was not sufficient enough to treat as a good conversion. Other than alkanes and alkenes there were also Isomeric and aromatic products observed.

**Keywords**—component; Alkylation, ethylene, hydrogen zeolite Bet, diesel fuel.

### I. INTRODUCTION

An ever increasing demand for energy sources in the world and the rapid depletion of fossil fuels has brought up the urgent need to find other sources of energy. If we are not careful today we will be facing an energy crisis in the future; to prevent this from happening politicians worldwide are drafting and making new policies. The European Directive 2009/28/EC states that by the end of year 2020 traffic fuels should contain 10% bio-fuels (in energy content). To successfully achieve this target new means of biofuel production which differs from existing commercial methods is required.

The Fischer-Tropsch process converts biomass into liquid hydrocarbons. The gas phase form of this process contains considerable amount of light alkenes. In this investigation a model feed of ethylene is used for alkylation over a Hydrogen Beta Zeolite catalyst.

Alkylation can be described as a process of introducing an alkyl group into a molecule. In industry, a variety of alkylation reactions are carried out. For example, in petroleum refining, isobutane is alkylated with low-molecular weight alkenes in the presence of a strong acid catalyst, either sulfuric acid or hydrofluoric acid. The resulting product mixture is Alkylate which is a premium

gasoline blending stock. Moreover, Ethylbenzene is produced from alkylation of benzene with various alkenes over a Zeolite catalyst, this is known as the Mobil-Badger EB process.

Although Alkylation reactions can be carried out thermally by free radical pathways, all commercial alkylation reactions use catalysts<sup>[1]</sup>. Friedel-Crafts catalysts (Metal Halides) have been used for alkylation of aromatics in the past. Mineral acids are used in the oil refining industry for alkylation to produce a premium gasoline blend<sup>[2]</sup>. These two types are very active and allows reactions to be carried out in liquid phase at low temperatures. A new development is solid alkylation catalysts i.e. Zeolites<sup>[3-7]</sup>. Zeolites are desirable because they are non-corrosive. They combine high acidity with shape selectivity and have a high surface area and high thermal stability. The objective with this study is to use ethylene as a model feed and to use zeolite beta as an alkylation catalyst.

### II. EXPERIMENTAL

The catalyst Hydrogen Beta Zeolite ( $\text{SiO}_2/\text{Al}_2\text{O}_3$  mole ratio: 360 and  $\text{Na}_2\text{O}=0.05$  weight %) was provided in the laboratory. One gram of the catalyst was mixed with four grams of silicon. This mixture was then calcinated at 350°C in the furnace for a minimum of six hours. The catalyst was then added to the reactor. Before the experiment was started the reactor was heated to the reaction temperature using a heating jacket. After that, the ethylene was pressurized into the system operating at atmospheric pressure at a specific flowrate controlled by the Flow Controller. The products were collected in a trap with cool glycerol and were analysed. The experiment was left running for four to six hours.

Figure 1 shows the process diagram. There is an ethylene supply on the right then a control valve. Then there is a flow meter which is connected to the flow controller to control the flow rate of Ethylene entering the reactor. The reactor is a packed bed reactor partially enclosed by a heating jacket which is connected to the temperature controller to keep the desired temperature. The cooling system is a trap with cool glycerol in a beaker and a sidearm test-tube where the liquid is collected and gas passes through to the GC.

In Figure 2 the reactor is presented. Catalyst placed in between nylon wool over which glass pellets are placed. The tip of the thermocouple is pointed exactly at the middle of the catalyst bed.

### Procedure

Flowrate (ml/min)	Catalyst	Temperature
180	1 g B-Z/4 g Si	400
180	1 g B-Z/4 g Si	450
180	1 g B-Z/4 g Si	425
180	1 g B-Z/4 g Si	350
170	1 g B-Z/4 g Si	350
135	1 g B-Z/4 g Si	400
45	1 g B-Z/4 g Si	400
90	1 g B-Z/4 g Si	400

### Analysis

The gaseous products were analysed using FID (Flame Ionization Detector) on the Gas Chromatograph Clarus 500. The Liquid product analysis performed with a Gas Chromatograph Varian 3400 coupled with Varian 4270 Integrator.

### III. RESULTS & DISCUSSION

Different experiments were carried out at a variety of different conditions, the temperature was varied from 350°C to 450°C and similarly the flow rate of Ethylene was varied from 45 to 180 ml/min. A brief overview of all the different experiments which were carried out is given below (sorted Date wise).

In Figure 3 the conversion to gas products is shown for four flows. In this experiment the conversion seems to go through a maximum dependent on the flow. At high flow the conversion maximum comes early and it also as expected have a low conversion compared to the other. The general trend is the lower flow the higher conversion. The fall in activity is expected to be catalyst deactivation. Maximum conversion was 13 % after 6 hours at flow rate of 45 ml/min. Moreover the least overall conversion was at flow rate of 180 ml/min. This low conversion could be increased if a longer reactor is employed. The n-C<sub>4</sub> is formed in the reaction and not iso-C<sub>4</sub>. This can be seen on the small values in the ratio in Figure 4. The formation of benzene ring is interesting since it can be further alkylated<sup>[8, 9]</sup>.

### IV. CONCLUSION

The experiments were carried out at different flow rates and reaction temperatures. The primary objective was to alkylate Ethylene to as heavy molecules as possible, although this was achieved the conversion was not good enough. Maximum conversion was 13% at flow rate of 45 ml/min and temperature of 400°C. High reactivity was seen around operating temperatures of 375 to 425°C but more experiments are required to confirm this. Moreover lots of unsaturated alkene groups were observed. There was a considerable formation of methane at lower flow rates. Except Acetylene, no major triple bond carbon molecules were present in the products. Liquid products were only obtained at lower flow rates; however the amount of liquid was not sufficient enough to treat as a good conversion. Other than alkane and alkene groups, Isomeric and aromatic products were also observed. After six to eight hours of experiment, the overall conversion decreased due to coke formation on catalyst.

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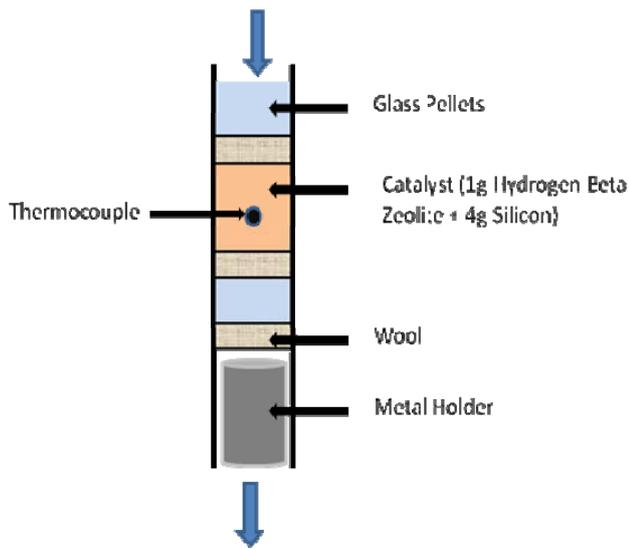


Figure 1. Process setup. The reactor is in red colour.

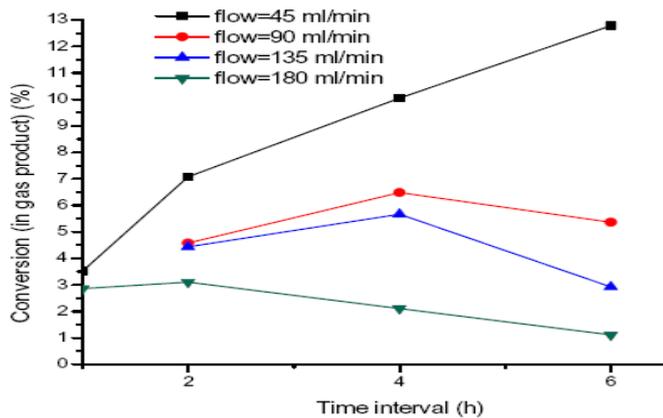


Figure 3. Conversion at different times with constant temperature (400 °C).

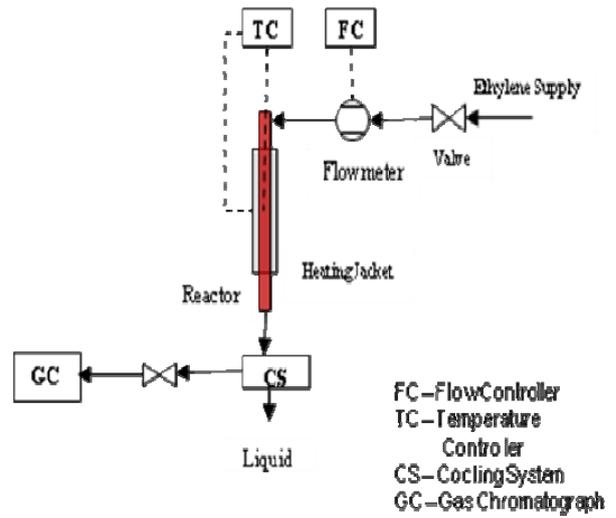


Figure 2. Details of the reactor

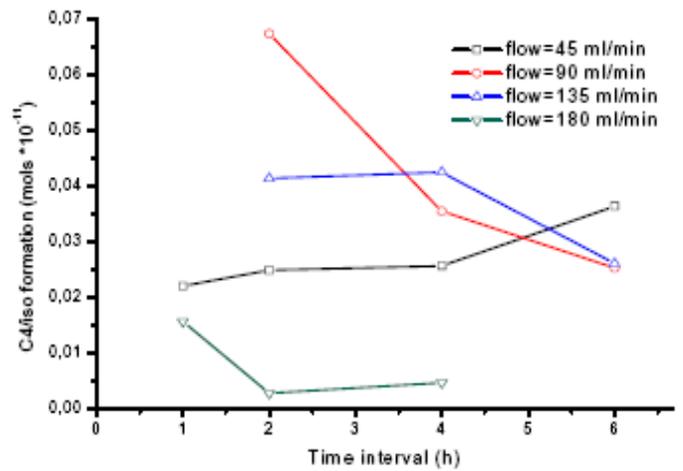


Figure 4. Formation of C<sub>4</sub>s.