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## Alkylation of ethylene as self-alkylating agent over H-beta zeolite.

Master of Science Thesis [in the Master Degree Program, Innovative and sustainable  
chemical engineering]

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Göteborg, Sweden, 2011

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## Abstract

Alkylation of ethylene as self-alkylating agent was studied over beta zeolite catalyst in a fixed bed reactor. Ethylene was used as model for fuel gas from the Fischer-Tropsch process. The Fischer-Tropsch process can convert biomass into liquid hydrocarbons. The gas phase from this process contains some amount of light alkenes. The possibility to produce fuel gases, both gasoline and diesel, from ethylene as a self-alkylation agent was the main objective. Experiments were carried out between the flow rates of ethylene 30 and 45 ml/min and at different temperatures (300-480°C) in a continuous flow packed bed cylindrical reactor at the ambient atmospheric pressure (1 bar). There were two experimental sets; one with single catalytic bed reactor and the other with double catalytic bed reactor.

The selectivities from this experiment were gaseous products formed through the alkylation and liquid products which have their boiling point in a range of the gasoline and diesel. The alkylation process gives some side reactions which lead to dimerization, oligomerization, isomerization and cracking.

Maximum conversion of ethylene was 65% which was observed at the operating condition (30 ml/min, 480 °C) on the single catalytic bed reactor. In the case of the double catalytic bed reactor, the higher conversion was 70% at the condition (45 ml/min, 480 °C). Differences in the results between these two experimental sets were observed. The maximum conversion of ethylene was found at the beginning of the experiment on the single bed reactor while on the double bed reactor, the maximum was observed after the running time passed one hour. Several types of alkenes were detected in the gaseous products for all experiments. Methane was an interesting compound observed in a significant amount only at the high temperature. Except acetylene, no major triple bond carbon molecules were present in the products. Liquid products were obtained at almost every operating condition. However, the amount of liquid was not sufficient enough to be regarded as a good conversion. These liquid samples had a boiling point range between 170 and 300 °C. Some catalyst samples were also analyzed to show how temperatures and flow rates affected the coke formation.

**Keywords:** alkylation, beta zeolite, ethylene, GC, catalyst

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## ***1. Introduction***

Increasing worldwide energy demand over last two decades is leading to the energy crisis in the future. Gasoline and diesel are significant in the transportation sector for the future energy security. Both can be produced conventionally via distillation of crude oil. In addition, a chemical process called cracking can break the long chain hydrocarbon to the shorter ones, allowing the refinery to turn diesel to gasoline for practical instance. The world is combating with the crude oil shortage in the coming years while the energy demand is still considerably growing. Consequently, the rise needs to be compensated through utilizing light hydrocarbons, which can be gained from the nature or by-products from other hydrocarbon processes, to heavier paraffin. This can be achieved with several processes like alkylation, oligomerization, isomerization, and etc. In addition, the environmental concerns due to global warming impact and running out of conventional energy source such as crude oil have recently issued globally in order to combat the future negative consequences and next generation burdens. Transforming to non-hazard catalyst process can delight the future path on one way.

In 1877, the first alkylation reaction was discovered when benzene was alkylated with amyl chloride in the presence of aluminum chloride performing as catalyst to produce amyl benzene or officially known as pentyl-benzene in IUPAC name. This experiment was conducted by Charle Friedel and his collaborator James Mason Crafts. So, this alkylation reaction was named as Friedel-Crafts alkylation reaction (1). Various types of catalysts and their applications have been discovered and synthesized for over last century, and they have well documented (2-4). The alkylation process over zeolite catalyst is one of the promising choices to solve the energy shortage and environmental problems. Currently, aromatic compounds and light alkenes were used as substances in most commercial alkylation processes with the presence of acid catalyst. Unlikely, the production of alkylated gasoline is manufactured by alkylating one light hydrocarbon with another. Hence, the alkylation product naturally depends on the catalyst used. Each catalyst provides difference properties, affecting directly the output product. Zeolite contains several advantage properties which are strong and thermally stable, shape selective and non-corrosive. If feed stream in the alkylation process can partly or totally gained from by-products of other processes, utilizing them through catalytic reactions would give some benefits to both economic and environment.

The Fisher-Tropsch process converts the mixture of carbon monoxide and hydrogen to liquid hydrocarbon in the presence of cobalt and iron catalyst such products from this process are methane, alcohols, gasoline and waxes. As by-products, water and carbon dioxide are also generated. Petroleum substitute normally from coal, natural gas and biomass for examples is produced by the process as the key component of liquid to gas technology. Apart from liquid hydrocarbon produced, light hydrocarbon gases and waxes are also generated. Waxes can be separated and delivered to a cracking unit while light hydrocarbons are possibly sent to alkylation unit. Thus, utilization of light alkenes from the Fisher Tropsch process to perform in the alkylation process is feasible. In this study, the system was modeled that ethylene was derived from the Fisher Tropsch unit and then used it as feed-stock to the alkylation unit.

## 2. Zeolite

### 2.1 General catalytic properties of zeolite

Zeolite is crystalline aluminosilicate compounds which have vast three dimension network structure of tetrahedral coordinated  $\text{SiO}_4$  and  $\text{AlO}_3$ , producing low density microporous structure with ranging about 1.9-2.3 g/cc (5). Generally, zeolites with alkaline metal cations are colorless powder. Color appearance on catalyst may occur due to transition metals or modifying zeolite by an ion-exchange method. Most zeolites can be dehydrated by calcination at temperature between 350- 500°C without a collapse of framework or structural change. In 1962, zeolite was used as cracking catalyst in oil refinery technology, introduced by Mobil oil Company and has several industrial applications which provide many benefits to the refinery industry until now. Zeolite itself contains particular properties which has led zeolite to play the essential role in some processes in the conversion of a wide variety of hydrocarbons to selective products. Those properties are ion exchange, shape selective, selective absorbent, highly thermal stability, high activity, and selectivity in a wide range of products, and non-corrosive.

-Normally, synthesized zeolite contains cations such as  $\text{K}^+$ ,  $\text{NH}_4$  and  $\text{Na}^+$  for example. The mentioned ions are needed to balance negative charge as result in aluminum cations, coordinated the tetrahedral structure of zeolite by oxygen anions. The sodium cation can perform the ion exchange with other cations by explosion of a sodium contain zeolite to solutions containing other cation types. The cations of several zeolites locate inside the pore channel. Moreover, the structural framework of zeolite does not change after undergoing ion-exchange. Thus, zeolite as ion-exchanger can remove undesired components to soften water where  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  are removed from the water (6).

-The shape selectivity of zeolites is the ability of zeolite to catalyze selectively reagents or reactants. This ability is achieved through their pore structure. Thus, if the molecules are small enough to pass through pore size, zeolite can absorb the molecules inside. Comparing the size of reactant and product molecules with the pore size of zeolite, reaction proceeds in a particular manner. So, zeolite shows selective catalysis reaction due to their unique pore structure and size (7).



-According to acidic property of zeolite, particularly beta zeolite has Lewis acid sites predominantly in the internal microporous surface and Brønsted acid sites on both internal and external surfaces (8).

-The high thermal stable characterization of zeolite has well known. Zeolite is also thermal stable up to 600 °C and some studies found that there is minor destruction of the framework structure caused by dealumination which leads to slightly decrease pore volume. Moreover, a severe dealumination can be found at the temperature above 760 °C. This severe operating condition directly involves breaking 12-membered rings resulting in a drastic decrease of pore volume. Consequently, when regeneration temperature is taken into account, operating temperature in the regeneration of zeolite catalyst should not be more than 760 °C to avoid the collapse of original zeolite structure. Another thermal stability study on zeolite was also reported by Murphy in 1996. The study presented that the thermal stability of zeolite increased when  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio was increased and the decomposition of zeolite occur near a temperature around 700 °C, supported by Liu's study (9). In high  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio, the decomposition can occurs at the temperature above 1300 °C. The acidic property of zeolite changes when  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio varies. At high  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio, zeolite is stable in concentrated mineral acid while at low  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio it is rather delicate in the presence of acid. In contrast, the high  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio is unstable in the basic solution but the low  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio presents an increase of stability. So, the acidic property of zeolites mainly depends on  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio and also reacting temperatures. In zeolite structure shown on Figure 1, acid sites are classified due to the classical Brønsted and Lewis acid models (10). Brønsted acidity corresponds to proton donor acidity, while Lewis acidity corresponds to electron pair acceptor. Brønsted acidity occurs when the cations used to balance the negatively charged framework are protons ( $\text{H}^+$ ). The trigonally coordinated aluminum atom possessing a vacant orbital that can accept an electron pair, behaves like a Lewis acid site (5).

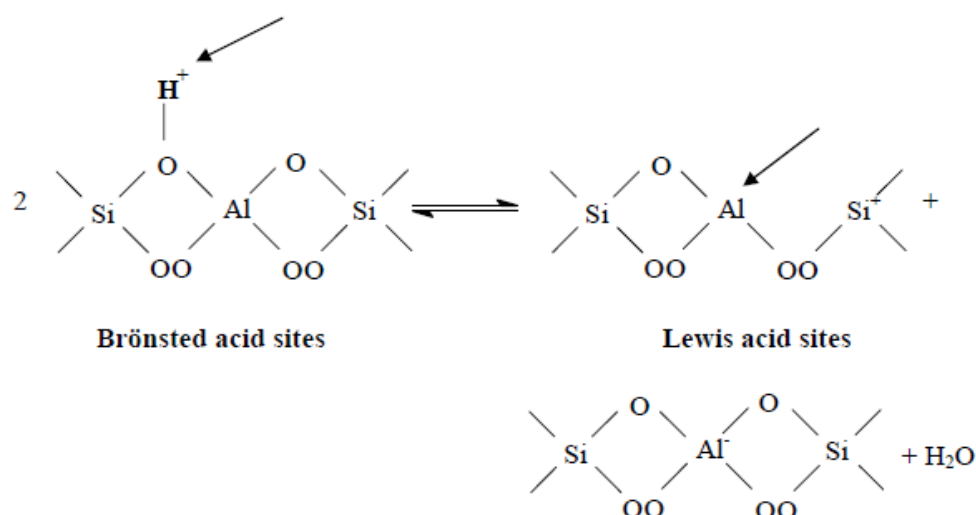


Figure 1 Brønsted and Lewis acid sites in zeolite framework (10)

## 2.2 Beta zeolite

Beta zeolite has been used as an acid catalyst in hydrocarbon conversion such as alkylation, acylation. The shape of beta zeolite is random fashion. The three-letter code is preceded to indicate the framework type. Beta zeolite was named as BEA. The units are connected to one another via 4-rings to form several layers with saddle-shaped 12 rings as shown on Figure 2. The sequence is 3-dimensional 12 ring channel system. Beta zeolite itself has a high silica ratio with  $\text{SiO}_2/\text{Al}_2\text{O}_3$  between 10 and 200. Beta zeolite was first synthesized and reported officially by Wadlinger. The synthesized zeolite was made from gel, organic template (tetraethyl ammonium cations), and alkali metal (11). Beta zeolite has the potential acid, the high acid strength and the hydrophobic high thermal stability, described as a potential acid catalyst (12). Aromatic alkylation of biphenyl with propylene, aromatic nitration and aliphatic alkylation are successful applications of beta zeolite over Friedel-Craft alkylation reaction. Isomerization of normal chain olefins to their branched-isomers over beta zeolite is more effective than cracking them to lower molecules (5). Specifically, H-beta zeolite has been widely used as acid in organic chemical reaction as mentioned above in this section while it has not been widely used in the organic transformation reaction on the solid catalyst support. Basically, beta zeolite has Brønsted acid sites inside the micropores and also on the external surface, and Lewis acid sites locate mostly at the internal surface. This catalyst is not corrosive to equipments and friendly to environment. On the other hand, it can be categorized as a poisonous material.

According to hazard identification, H-beta zeolite is a poisonous material causing irritation to human-body. It should be kept in the closed container in order to avoid contact with skin, eyes and clothing. Safety goggles such as chemical resistant gloves, is also necessary when the material is handled.

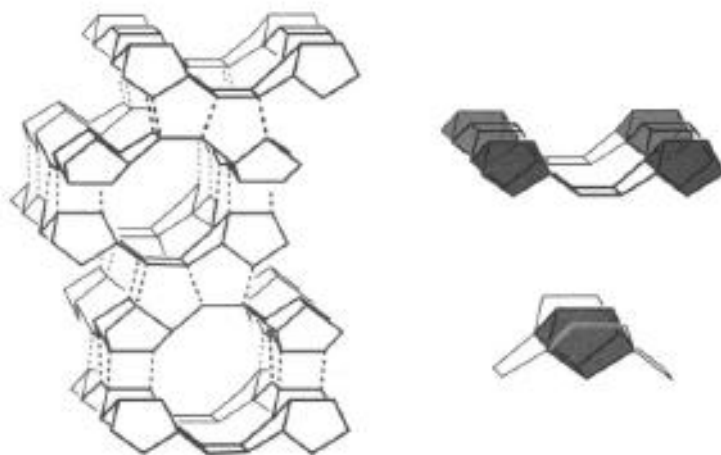


Figure 2 the idealized \*BEA framework type with all layers related to one another via a counterclockwise rotation (the dotted lines show the connections between layers)

### 3. Alkylation

Acid catalysts have been used in several alkylation processes. Typically, acid catalysts used are Bronsted acids which contain acidic proton also including acidic halides in catalyst site. Aluminum Chlorides, acidic oxides and zeolites are some examples of acid catalyst used in the alkylation process. For instance, the alkylation of benzene with light olefin has been established as commercial way to produce many petrochemical products for over last 20 years. This alkylation has been operated commercially to replace earlier processes which operated on liquid phase by using aluminum chloride as catalyst. By the way, this route generated some environmental problems concerning disposal of aluminum chloride waste and corrosion to equipments (13). The special properties of zeolite are strongly and thermally stable, shape selective and non-corrosive. These have led zeolite to play the essential role in some processes for the conversion of a wide variety of hydrocarbons to selective products. The current method in transformation of light hydrocarbons to gasoline process with liquid acid catalyst is going to be replaced with solid acid catalyst which can provide more advantages. Non-toxic, non-corrosive, environmental friendly and easily regenerable solid acid catalysts are benefits from the use of solid catalyst.

#### 3.1 The Mobil-Badger EB process

In the middle of 1980s, ethyl-benzene commercial production process was announced and named as Mobil- Badger EB process. According to EB process, the zeolite, ZSM-5, substituted the acid catalyst and operated in vapor phase at high temperature. Interestingly, the corrosion and waste disposal problem were eliminated and its selectivity of ethyl benzene was improved, achieving over 99% with high energy efficiency. The EB process was announced by using a zeolite as a fixed bed reactor. However, the initial problem of this process related to the rapid deactivation of catalyst by coking deposition. Consequently, catalyst is needed to regenerate for several weeks during the operation before change it to fresh catalyst (14).

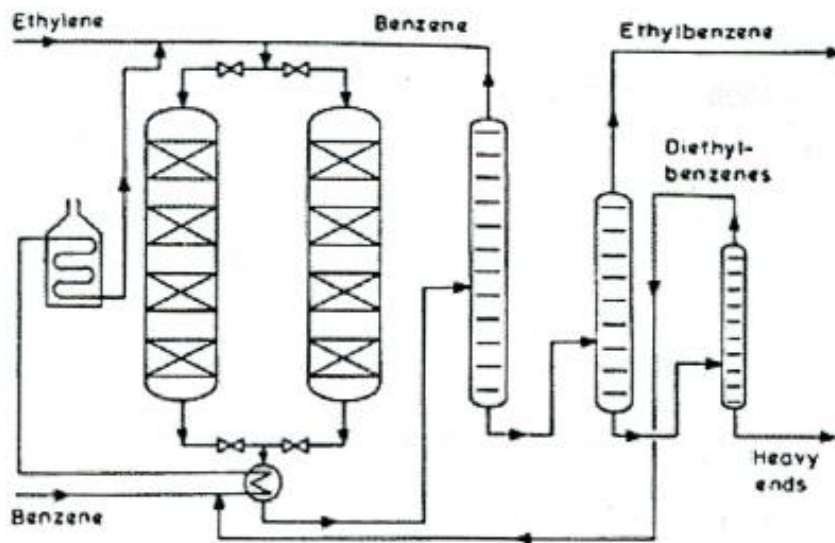


Figure 3 The Mobil-Badger ethylbenzene (15)

### 3.2 UOP Processes (16)

The UOP has some commercial processes to produce gasoline from light olefin. Catalytic condensation process and alkylation are well-known because of high purity of product provided. At first, this catalytic process was utilized to use economically the light olefin by-products gases from hydrothermal processing. Those light hydrocarbon compounds were converted to high octane vehicle fuel. As a development, the current UOP hydrofluoric acid catalyzed alkylation process uses propylene and butylenes to produce the high octane gasoline. There is also technological flexibility to produce wide range olefin products. This process operates on solid phosphoric acid catalyst. Its application comprises of the condensation of light olefins to form nonene, propylene tetramer and wide boiling range gasoline. This process is needed to operate at high pressure levels. The product from this process contains the mono-olefin content of poly unit heptenes and noenes which are normally greater than 99wt%. This process uses solid phosphoric acid catalyst which is non-corrosive. The UOP alkylation process is competitive and commercial in the market with availability to liquid acid technology. This process operates on hydrofluoric acid catalyst, combining isobutene and  $C_3$ - $C_5$  olefins to generate gasoline. The alkylate low Reid vapour pressure is a significant blending component for gasoline with high octane number, the low Reid vapor pressure, low sulfur contained and also low volatility. Branched paraffins are the major alkylates. For example, one of the commercial UOP alkylation processes is operated on

hydrofluoric acid (HF) as shown on Figure 4. In 2007, the company has more than 140 licenses worldwide with a combined operating capacity of more than 620,000 barrels/day of alkylate.

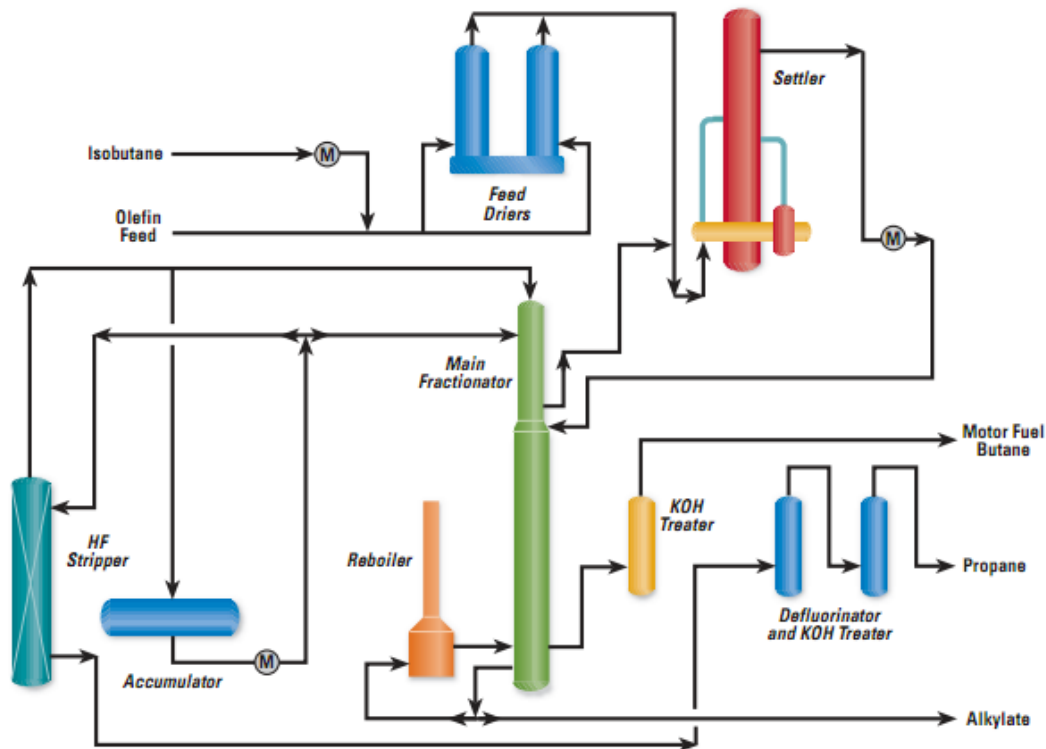


Figure 4 UOP HF alkylation process (16)

### 3.3 Other alkylation processes to generate gasoline in refinery

A definition of alkylation in refinery is a process which light olefins, particularly butenes, react with isobutane in the presences of catalyst to form iso-paraffinic gasoline. Alkylate is mainly comprised of high octane hydrocarbons, iso-paraffin but the octane number of products depends on feedstock and operating service condition. There are two commercially common alkylation processes, operating in the presence of sulfuric acid (Figure 5) and hydrofluoric acid (Figure 6). These two processes show several drawbacks even though they can produce a high-quality gasoline component. Catalyst consumption is high utility cost. Their corrosiveness and volatility has been highly concerned about their toxicity.

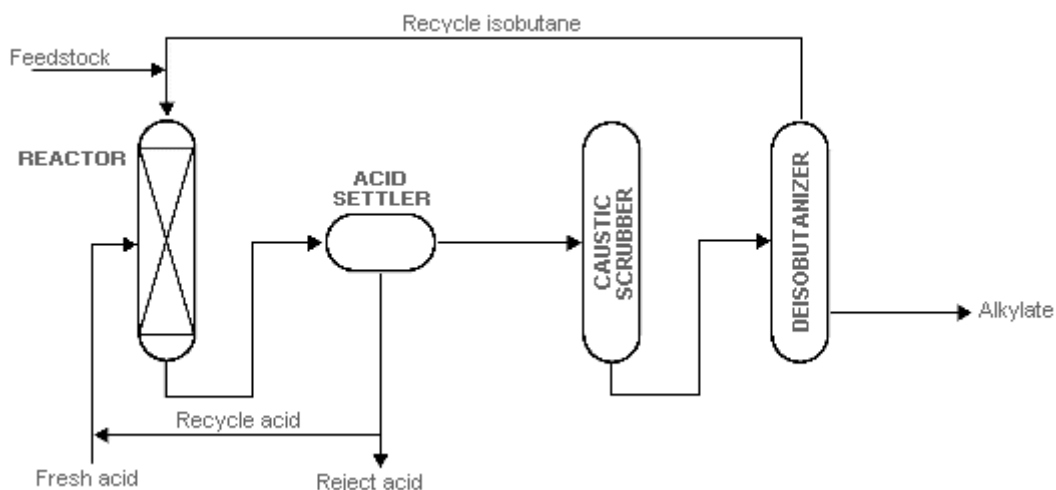


Figure 5 Schematic of sulfuric acid alkylation process (17)

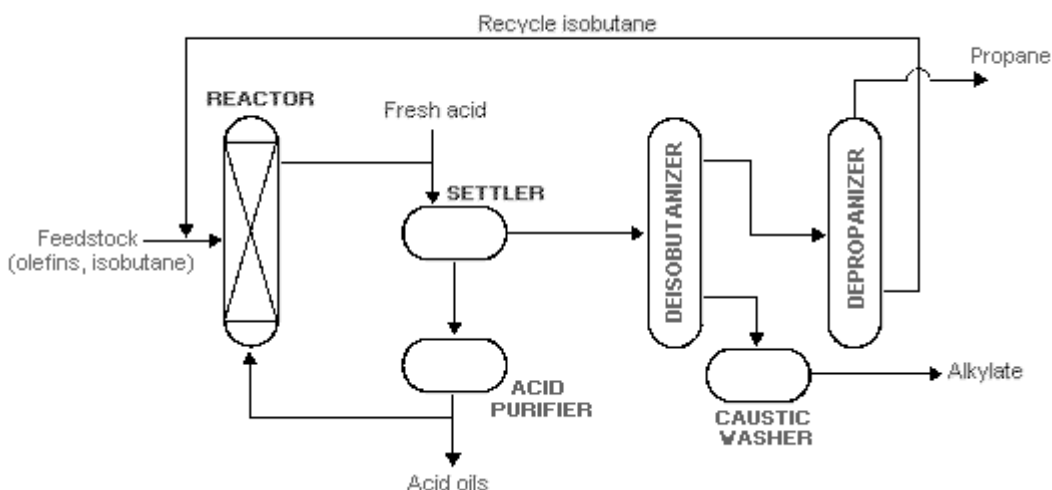


Figure 6 Schematic of hydrogen fluoride alkylation process (17)

Even though, present economical acidic processes are able to generate high yield gasoline product, those processes are potentially hazardous. Precautions for equipment and materials used are required to ensure that they can handle the acids. Some corrosion and fouling in units may occur so that frequent maintenances are required. Thus, the replacement of acid catalyzed alkylation to non-corrosive one has become interesting. Zeolite can perform as the alkylation catalyst, providing more environmental friendly and the non-corrosive process without releasing environmentally hazardous components to atmosphere. Moreover, zeolite provides the simple regeneration properties by using hydrogen as its valuable advantage. The process is comprised of combustion of coke deposited zeolite with oxygen including the presence of a halogen and followed by reducing the catalyst in the presence of hydrogen (18).

### 3.4 Alkylation of ethylene and Light hydrocarbon compounds to diesel

Ethylene has been used as alkylating agent for many years but itself as self alkylating agent, it has not officially documented. By the way, production of gasoline from light hydrocarbon molecules was well documented (19). There was a study relating to the hydrocarbon conversion of ethylene in the presence of methane over different zeolite catalysts proportion studied (20). However, alkylation of light olefin in refinery generally relates to production of gasoline while generation of diesel has rarely reported. Theoretically, the conversion of C<sub>3</sub>-C<sub>4</sub> into diesel involves three different processes; a dehydrogenation of paraffins, an oligomerization of dehydrogenated hydrocarbons and followed by a hydrogenation of gasoline range products into saturated hydrocarbons. The oligomerization of olefin to gasoline has proposed since 1970s and after 20 years later, the use of zeolite for this process was introduced. Zeolite application has some disadvantages for oligomerization process. Firstly, several steps were needed to boundary the side-reactions of isomerization and cracking. Secondly, the formation of aromatic compound lowers diesel product yield below 60% at high cetane number (21).



#### 4. *Experimental setup*

The experiment was carried out by using a small continuous flow reaction system; the fixed catalytic bed reactor. The H-beta zeolite catalyst ( $\text{SiO}_2/\text{AL}_2\text{O}_3=360$ ) was purchased from the Zeolyst international company at Kansas, USA. A summary outlining about the surface area, pore volume and pore size of the catalyst is given Table 1. The H-beta zeolite was characterized by a researcher and the result was also reported domestically in the department of Applied Surface Chemistry, Chalmers University of Technology. The H-Beta catalyst contains less than 0.05% Na and 0.5 wt% moisture. 5 grams of catalyst, consisting of 1 gram of beta zeolite and 4 grams of silica powder (0.1-0.3 mm), were weighted and consequently calcined in the furnace at the temperature of 350 °C for 6 hours before using. Then, the calcined catalyst was positioned in the middle of a fixed-bed reactor made from carbon steel with a diameter of 10 mm. The reaction temperature was controlled by electrically heating system in which the temperature was measured by the thermocouple in the middle of the reactor where catalyst was positioned. At the constant ambient atmospheric pressure, ethylene was pressurized into the system, controlled by electrical flow controller. During the operation, gaseous products went through the cooling system comprising of a trap with cool glycerol in a beaker and a side arm test-tube. The gaseous product connected to the gas chromatography for gas analysis. The collected liquid products was extracted from the glass tube and later analyzed by the chromatography instrument. The experiments were running for 24 hrs. The rearrange of an order of materials packed in the reactor was also applied to study how it affected the result. Consequently, the experiments were divided into 2 sets.

- On the first set with the ordinary packing style (Figure 7), gaseous samples were collected and analyzed periodically for 5 times; initial, 2<sup>nd</sup> hour, 4<sup>th</sup> hour, 6<sup>th</sup> hour and 24<sup>th</sup> hour while liquid product was collected at the end of experiment.
- On the second set with the modified packing style (Figure 8), gaseous samples were collected and analyzed periodically for 5 times; initial, 1<sup>st</sup> hour, 2<sup>nd</sup> hour, 4<sup>rd</sup> hour and 24<sup>th</sup> hour and the liquid samples were also analyzed in the same way as the first one.

Coke samples were analyzed by Belab AB, (Bränsle & Energilaboratoriet AB,) Norrköping) on dry basis. The gaseous products were analyzed using FID method (Flame Ionization Detector) on the Gas Chromatograph (GC) Clarus 500 and the settings for the GC are shown on Table 2. Similarly, the Liquid product analysis

performed on the Gas Chromatograph Varian 3400 coupled with Varian 4270 Integrator. The GC settings to analyze the liquid samples are shown on Table 3. The flow diagram of ethylene as self-alkylation agent can be seen from Figure 9.

**Table 1 A summary outlining the surface area, pore volume and pore size of H-Beta zeolite used.**

<b>Surface Area</b>	
<b>BET Surface Area:</b>	461.4424 m <sup>2</sup> /g
<b>t-plot Micropore Area:</b>	295.7618 m <sup>2</sup> /g
<b>t-plot External Surface Area:</b>	165.6805 m <sup>2</sup> /g
<b>Pore Volume</b>	
<b>Single point adsorption total pore volume of pores less than 1163.855 A diameter at P/Po = 0.983080432:</b>	0.363625 cm <sup>3</sup> /g
<b>t-Plot Microspore volume:</b>	0.136899 cm <sup>3</sup> /g
<b>BJH Adsorption cumulative volume of pores between 20.000 A and 30000.000 diameter:</b>	0.237940 cm <sup>3</sup> /g
<b>BJH Desorption cumulative volume of pores between 20.000A and 3000.000 A diameter:</b>	0.246046 cm <sup>3</sup> /g
<b>Pore Size</b>	
<b>Adsorption Average pore width (4V/A by BET)</b>	31.5207 A
<b>BJH Adsorption average pore diameter (4V/A)</b>	58.270 A
<b>BJH Desorption average pore diameter (4V/A)</b>	54.133 A

**Table 2. The settings for the Gas Chromatograph Clarus 500.**

<b>Initial Temperature</b>	40°C
<b>Oven Temperature</b>	60°C
<b>Holding Time</b>	15 min at 60°C
<b>Sampling Type</b>	Auto sample
<b>Carrier Gas</b>	Hydrogen (6.2bar)
<b>Detector</b>	FID
<b>Nitrogen Pressure</b>	6.2 bar

**Table 3. The setting for the Gas Chromatograph Varian 3400 coupled with Varian 4270 Integrator**

<b>Detector Temperature</b>	300°C
<b>Interface Temperature</b>	325°C
<b>Initial Temperature</b>	40°C
<b>Rate</b>	16°C / min
<b>Initial Stabilizing time</b>	2 min
<b>Final Temperature</b>	325°C
<b>Nitrogen Pressure</b>	6.2 bars
<b>Hydrogen Pressure</b>	6.2 bars

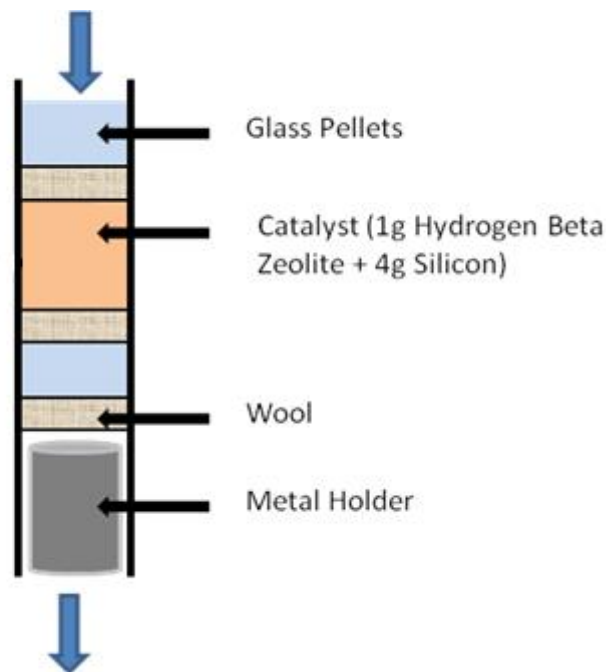


Figure 7 Packing style in the continuous flow packed bed cylindrical reactor (the single catalytic bed reactor)

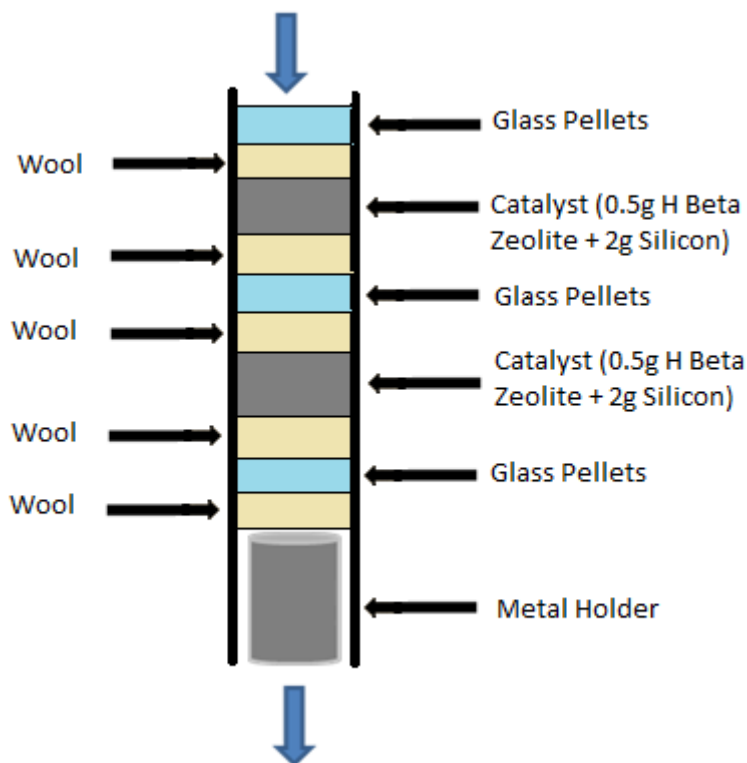


Figure 8 Modified packing style in the continuous flow packed bed cylindrical reactor (the double catalytic bed reactor)

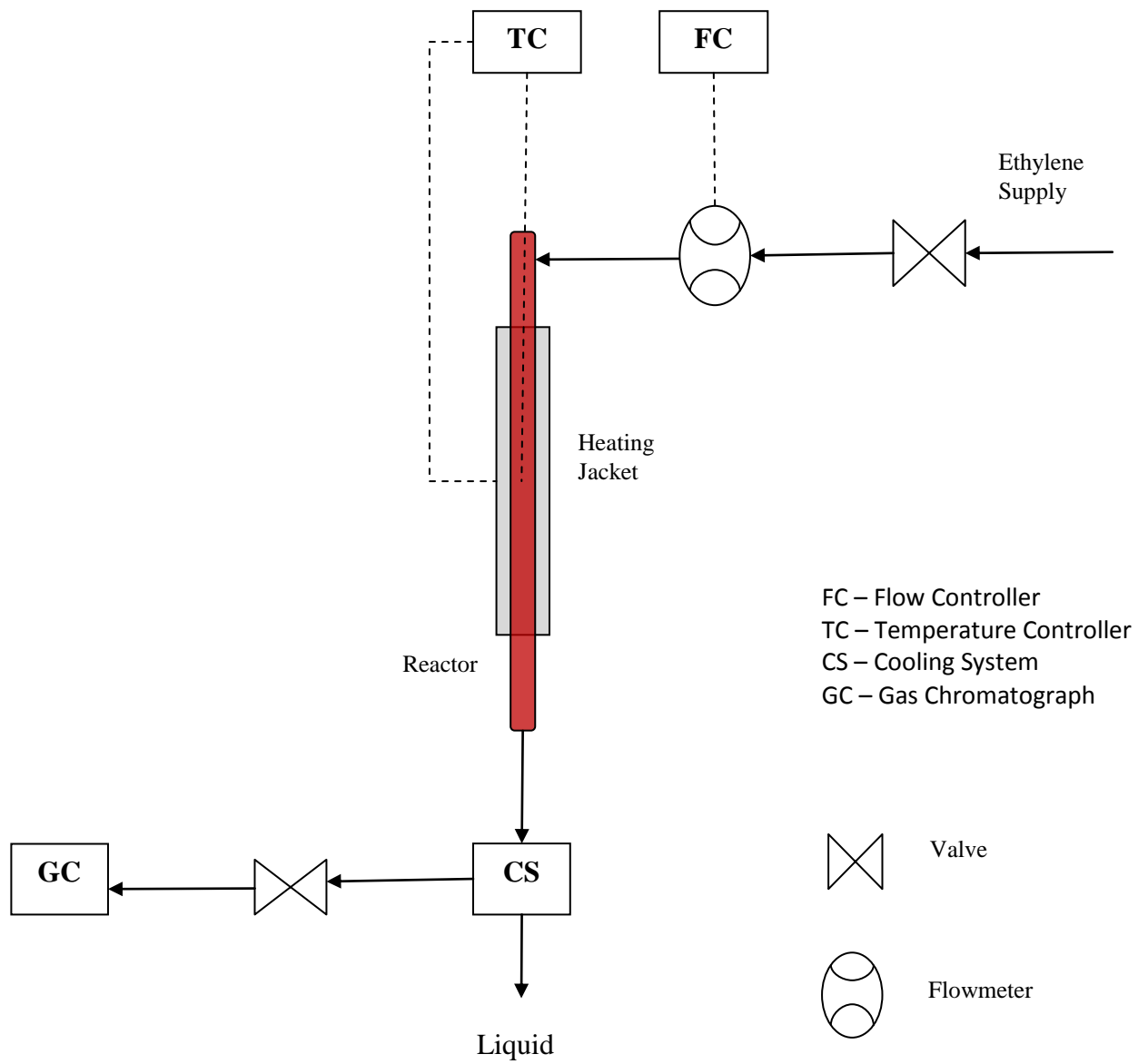


Figure 9 the process diagram of ethylene as self-alkylation agent.

## 5. Result and discussion

### 5.1 Influence of temperature and flow rate on the conversion of ethylene.

The experiments have been lasting in 24 hours and were done at different temperature (300-480 °C) and two flow rates (30, 45 ml/min). In order to avoid the change of zeolite structure, the experimenting temperature was limited below 500°C which can cause the structural change of zeolite (6). The same catalyst's type and the same preparing catalyst method were used for all experiments. Product samples were analyzed by gas chromatography (GC). Results were divided into two parts; liquid products and gas products. The results for ethylene conversion and presence of liquid products in each experiment set are listed below on the following tables. Table 4 is the result from using the single catalytic bed reactor and Table 5 is the result by using the double catalytic bed reactor. Both tables show operation conditions (flow rate and temperature), time interval, presence of liquid product, and ethylene conversion.

**Table 4 Conversion of ethylene at different temperatures and 2 flow rates over H-beta zeolite by using the single bed reactor.**

Flowrate (ml/min)	Temperature (°C)	Ethylene conversion (wt. %)					Presence of liquid product
		time interval (hrs)					
		Initial	2	4	6	24	
45	300	4.80	6.63	7.05	2.08	1.57	No
45	320	4.51	4.55	7.23	5.67	5.86	Yes
45	340	8.40	7.67	5.27	4.98	3.18	Yes
45	360	10.18	7.78	7.51	5.26	3.02	Yes
45	380	15.14	12.89	11.43	7.84	2.90	Yes
45	400	18.94	13.72	7.23	7.88	2.36	Yes
45	420	28.61	13.57	7.86	5.76	1.52	Yes
45	440	47.33	7.05	4.92	4.38	2.34	Yes
45	460	41.59	8.07	4.32	3.48	1.39	Yes (Dark)
45	480	40.83	9.13	5.35	3.71	0.93	Yes (Dark)
30	320	11.44	9.87	8.82	3.32	1.67	Yes
30	420	46.85	15.95	9.84	6.12	2.45	Yes
30	440	44.37	11.38	6.85	3.32	1.36	Yes
30	460	58.06	20.34	6.52	4.92	4.61	Yes (Dark)
30	480	64.64	8.81	6.00	3.44	1.86	Yes (Dark)

- **The single catalytic bed reactor**

Regarding influence of gas velocity by fixed temperature, there were higher conversions at lower gas velocity (30 ml/min). The percent conversions of ethylene decreased dramatically during the first 2 hours of the experiments and slightly dropped until the catalysts were almost deactivated at the end of experiment. The ethylene conversions mostly dropped to below 5% after the experiments lasted. At the gas velocity of 30 ml/min, the highest conversion was found at the temperature of 440 °C with 47.33% of the ethylene conversion. Interestingly, the highest conversion with 64.64%, at the gas velocity of 45 ml/min, was observed at the temperature of 480 °C which was the highest temperature in the experiment. There were presences of liquid products in all cases except one condition (300°C, 45 ml/min). A color of the liquid products was rather dark brownish at the temperature of 460 °C and 480 °C but the between 320-440 °C, the color of liquid products looked similar to a color of oil. Just, the amount of collected liquid products increased as seen by observing when the temperature climbed. The weight of collected liquids was not measured since they did not present in the significant amount.

- **The double catalytic bed reactor**

When modified packing style was applied by using the double beds, the maximum conversion for ethylene did not take place at the beginning of experiment similar to the first experimental set. All results shows on Table 5.

**Table 5 Conversion of ethylene at different temperatures and fixed flow rate 45 ml/min over H-beta zeolite by rearranging sequence of materials used in the reactor**

Flowrate (ml/min)	Temperature (°C)	Ethylene conversion (wt %) in each time interval (hrs)					Presence of liquid product
		time interval (hrs)					
		Initial	1	2	4	24	
45	320	35.75	31.42	20.89	11.46	2.24	No
45	420	23.65	50.09	46.78	20.34	3.79	Yes (Dark)
45	440	31.07	52.50	51.24	28.38	4.68	Yes (Dark)
45	460	25.55	68.39	49.67	26.87	4.88	Yes (Dark)
45	480	20.24	70.44	53.52	25.59	5.71	Yes (Dark)

It is obvious that the highest conversion observed after the experiment had been run for 1 hour. The percent conversion of ethylene conversion increased dramatically during the first operating hour. The highest conversion in this set of experiment was 70.44% at 480 °C. The amount of ethylene converted rose while temperature increased. The percent conversion dropped slightly after passing 1 hour until plunging below 5% in all cases except the condition at 480 °C with just above 5%.

## 5.2 Classification of gaseous products

For the single catalytic bed reactor, the catalyst was highly active at the beginning and then, it started being deactivated, interpreted from a decrease of the ethylene conversion (table 4-5). There were 8 major hydrocarbon compounds mainly dominating in the gas products for the single catalytic reactor case. These consists of methane, propane, acetylene, propylene, propadiene, 1-butene, iso-butene and  $C_5=C_6^+$ . For the double catalytic bed reactor, propadiene appeared rarely and  $C_4$  paraffins which showed up with little amount in the single bed case, were observed in the considerable amount. Non-reacted ethylene was not included in the result of gaseous products.

Due to the low activity of the catalyst at medium temperatures (300 - 400 °C), the gaseous product results, at higher temperatures (420 °C and 480 °C), were selected as examples in this section. So, an influence of temperature and flow rate on the gaseous products is mostly clarified.

## 5.3 Effect of temperature on the gaseous products

At the operating condition (45 ml/min, 420 °C) as shown in Figure 10,  $C_5=C_6^+$  and propane dominated the majority of outlet components with just above 5 wt% from total 100%, followed by propadiene, propylene and isobutene respectively. The percent weight of these detected compounds except propadiene decreased slightly during experiment had been running in the first 6 hrs. wt% of propadiene dropped sharply during first 2 hrs and later propadiene was almost undetected. Similarly, a proportion of acetylene went drastically down during the first period. Butene-1 had appeared just once at the beginning of experiment and disappeared from the detection. Surprisingly, methane was also detected but presented in very little amount. When the temperature was adjusted to 480 °C with the same flow rate as shown in Figure 11, it was more active than the previous examined condition. Acetylene had been the most dominating product

for the first analysis and the amount of that plunged to almost 0 wt% for the next consecutive analyses. Apart from acetylene, there was just propane, detected above 5 wt% at the same time. The rest components were observed at lower than 5 wt% over this operating condition. By the way, the weight percent of most detected compounds continuously dropped along 6 hrs as in the previous case. Interestingly, the observed methane with 1 wt% was detected initially this case was higher than the previous one. It can be seen that the temperature has a high effect on the output gaseous composition. Increasing temperature makes the catalyst more active but the catalyst deactivates early.

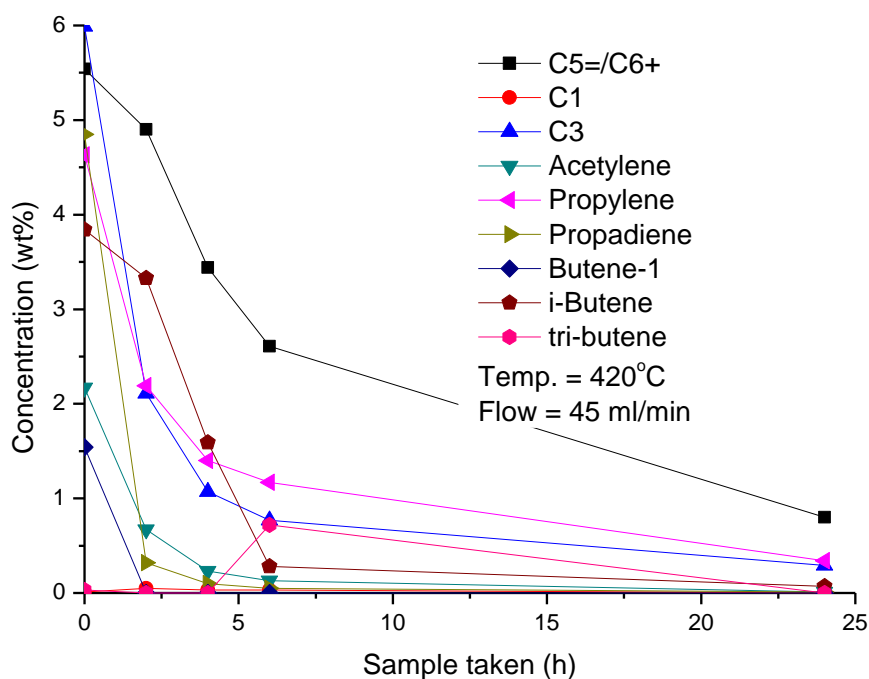


Figure 10 Gas products from the single catalytic bed reactor at the operating condition (45ml/min, 420 °C)



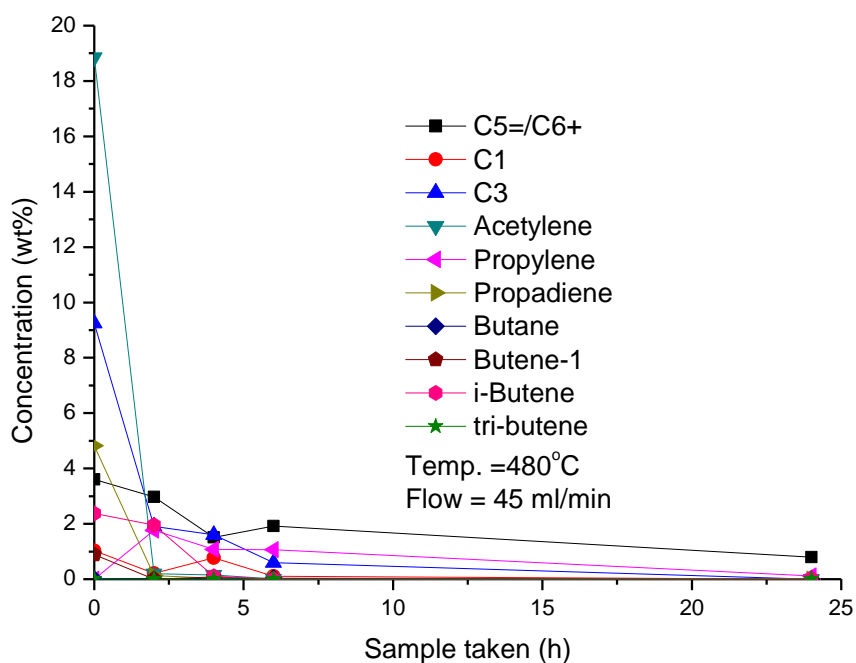


Figure 11 Gas products from the single catalytic bed reactor at the operating condition (45ml/min, 480 °C)

#### 5.4 Effect of flow rate on the gaseous products

In Figure 12 (30ml/min, 420 °C), acetylene showed a similar trend as in the case (45ml/min, 480 °C) but the observed conversion percentage was higher by around 3 % at the beginning. Propadiene and propane came closer to each other at around 7%. Acetylene and propadiene were almost unable to be detected after the first analysis, but propane was well observed with an insignificant drop of its weight percent over 6 hrs. 3 detected components, consisted of  $C_{5=}/C_6^+$ , isobutene and propylene respectively, were observed at the highest portion on the second analysis instead of on the first analysis as observed previously in this section. Regarding the weight percent, most gaseous compounds in the case (30ml/min, 420 °C) were higher than the case (45ml/min, 420 °C) while isobutene and methane did not show much different in both cases. At the condition (30ml/min, 480 °C) shown in Figure 13, the trend on changing in product proportion were almost similar to the condition (45ml/min, 480 °C). Unlikely, the most components detected in this case were higher at the start than the recently one. Concomitantly, methane appeared and its percentage almost reached 2 wt% which was higher than the case (30ml/min, 420 °C). So, it could be mention that methane existed with noticeable amount only at the high temperatures.

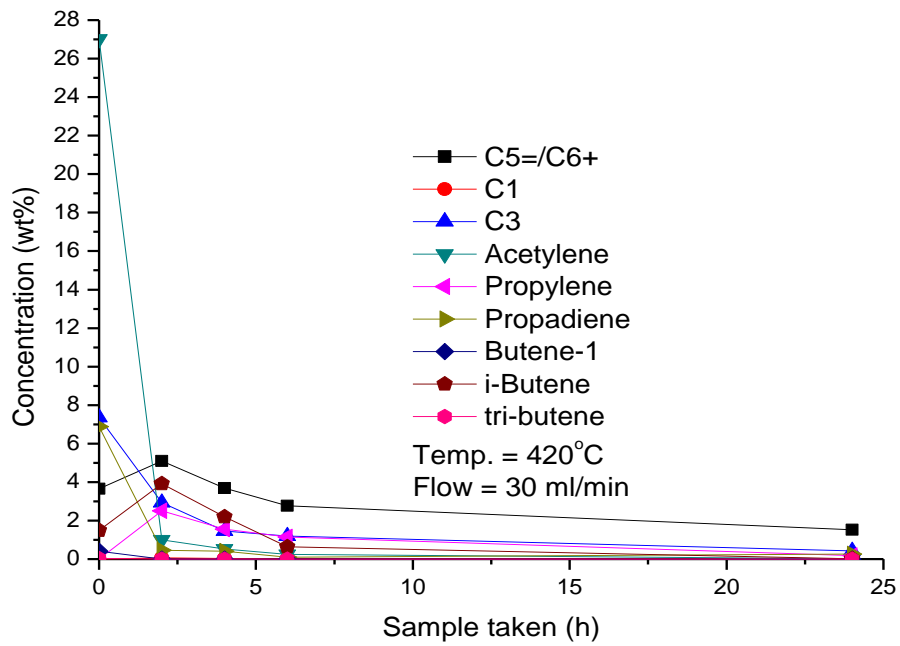


Figure 12 Gas products from the single catalytic bed reactor at the operating condition (30ml/min, 420 °C)

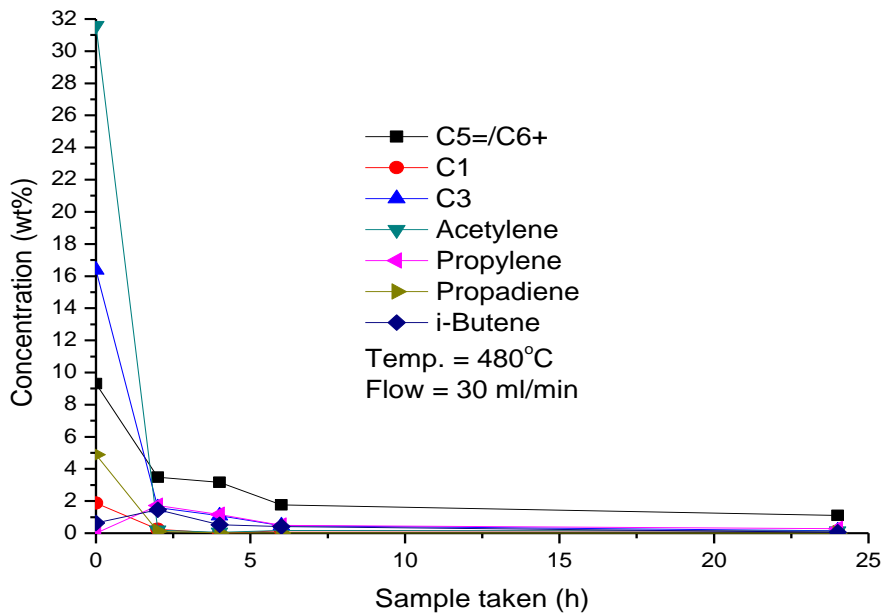


Figure 13 Gas products from the single catalytic bed reactor at the operating condition (30ml/min, 480 °C)

## 5.5 Effect of modified packing style in reactor (the double catalytic bed reactor)

The modification on packing style in the fixed reactor was done by rearranging sequence of materials packed in the reactor as shown before in Figure 8. 5 grams of the calcined catalyst was divided into a top base and a bottom base in the reactor. The reaction pattern also changed. First, the catalyst did not seem highly activate at the beginning, but it took about an hour to reach the peak. The reaction did not go so fast, comparing to the reaction from the single catalytic bed method. For this reason, the analysis of gas outlet was followed every hour until 4<sup>th</sup> hour. Mainly, the weight percent of most gas outlet compounds achieved the highest point in the second analysis at 1<sup>st</sup> hr. In Figure 14 and Figure 15; acetylene in this case still dominated the majority of detected products when the ethylene conversion reached the maximum point. This trend was similar to four recent figures from the single catalytic bed reactor method. The rearranging sequence of materials positioned in the reactor did not change the main dominating compound when ethylene had maximum conversion. Surprisingly, propadiene rarely emerge in the products on this method. From the first analysis, data in both figures showed that most gaseous products were formed with no far difference in their weight percentages from each other. They were detected around between 0-7 wt%. At 420 °C, the weight percents of acetylene and propylene increased sharply during the first hour and then started gradually decreasing. Also, that of isobutene rose and dropped slightly. On figure 14, C<sub>5</sub>=/C<sub>6</sub>+ methane, propane, and butene appeared a fluctuation of their proportions over first 4 hrs. One interesting thing, in operating the system at this condition, was the presence of butane and iso-butane which had found just in the very little amount in the single bed case. They also showed up at the other conditions (45ml/min: 320 °C, 440 °C and 460 °C) which can be seen in the appendix. When the temperature was adjusted to 480 °C (Figure 15), a proportion of butane appeared just slightly higher than what iso-butane appeared in the previous examined condition (45ml/min, 420 °C) over first 4 hrs. The modification of the sequence of materials packed in the reactor significantly affected the catalyst activity and the proportion of gaseous products. While temperature increased, the catalyst was more activated and so, ethylene was converted more. Consequently, higher amounts of gaseous products were generated and it slowed down the deactivation of catalyst.

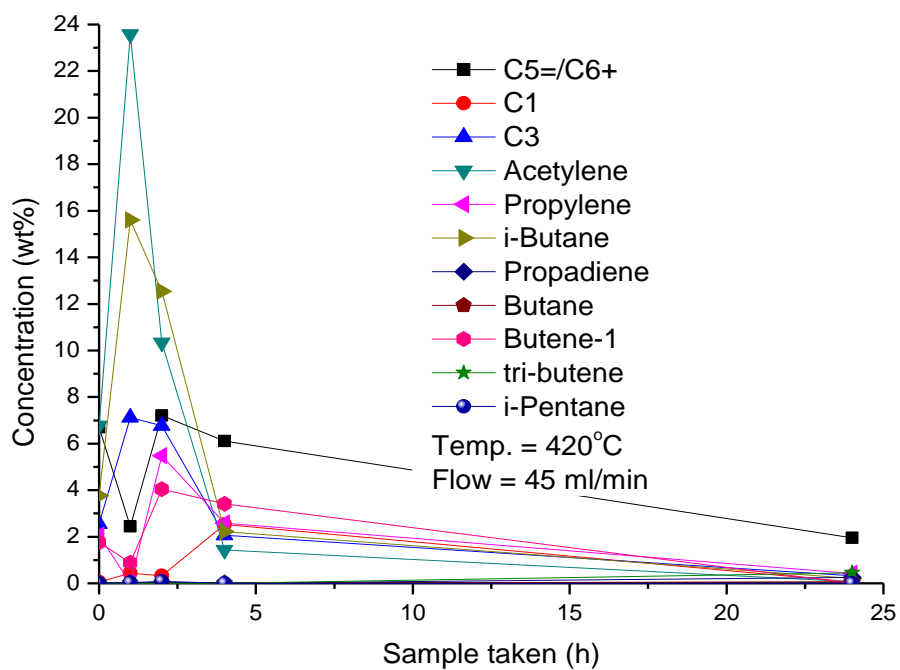


Figure 14 Gas products from the double bed reactor at the operating condition (45ml/min, 420 °C)

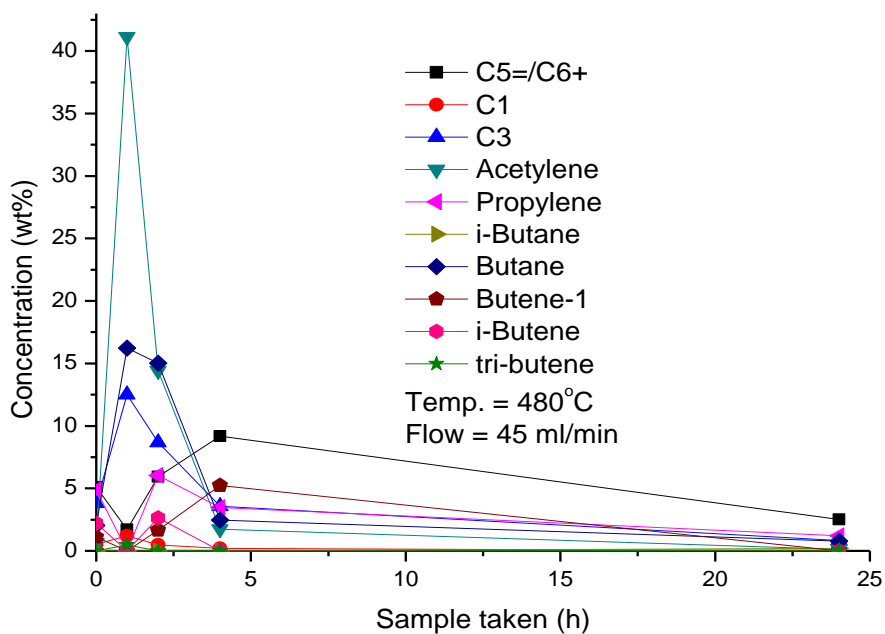


Figure 15 Gas products from the double bed reactor at the operating condition (45ml/min, 480 °C)

## 5.6 Distribution of liquid products

Liquid hydrocarbons existed in most operating conditions except the condition (30 ml/min, 320 °C) in the first method and the condition (45 ml/min, 320 °C) in the second method. According to the single catalytic bed method, at temperature below 460 °C, a color of liquid product was similar to vegetable oil generally used in household. But, the liquid products at temperatures (460 °C and 480 °C) for both flow rates were observed that the color was darker, dark brownish, and the quantity was a little higher. In this section, the result will show in a form of boiling point range as show on Table 6. Each liquid sample was analyzed by the GC and the results showed in the proportion of components divided by their boiling point. The identification of liquid paraffins and olefins was not included due to a limitation of the provided instrument.

**Table 6 boiling points of liquid hydrocarbon compounds**

Name	Boiling Point (°C)
Heptane	98
Octane	125
Nonane	151
Decane	174
Undecane	196
Dodecane	216
Tridecane	234
Tetradecane	253
Pentadecane	268
Hexadecane	287
Heptadecane	302
Octadecane	317
Nonadecane	330
Icosane	342

According to Figure 16 and Figure 17, at the operating temperature from 320 °C to 400 °C and from 420 °C to 480 °C with the fixed flow rate (45 ml/min), product samples had the boiling point range between 230 and 340. At the operating temperature between 320 °C and 400 °C, almost half of them had the boiling point between 250 °C and 270 °C. Apart from other cases at 45 ml/min, the sample from the case (45ml/min, 400°C) had the major amount at the boiling point around 330°C. Concerning the operating temperature between 420°C and 440°C, the major portion in the samples had the boiling point at around 250°C with 35% and 25 % respectively. When the operating temperature changed to 460°C and 480°C, the most quantity of samples had boiling

point between 270°C and 310°C. According to these 2 figures, it can be explained that most fraction of each sample would probably have the boiling point around between 250°C and 310 °C if the cases (380 °C and 400 °C) did not take into account. Decreasing flow rate slightly affected the boiling point of liquid samples. At the flow rate of 30 ml/min, the liquid sample in all cases showed similarly that the percentage of components was just below 20% at the boiling point of 250°C, as shown in Figure 18. The low boiling point components were also observed at the operating temperature of 440°C. They had the boiling point between 170°C and 210°C. At the operating temperatures between 460°C and 480°C, the main proportion in the samples was observed at the boiling points around 320 °C and 300°C respectively. By using the double catalytic bed reactor, low boiling point liquid compounds in samples were also observed and most of them had the boiling point roughly between 150°C and 270°C, as presented in Figure 19. It would interpret that using the double bed reactor can generate shorter hydrocarbon chains in the liquid product. Moreover, operating the system at higher temperature also produce shorter hydrocarbon chains.

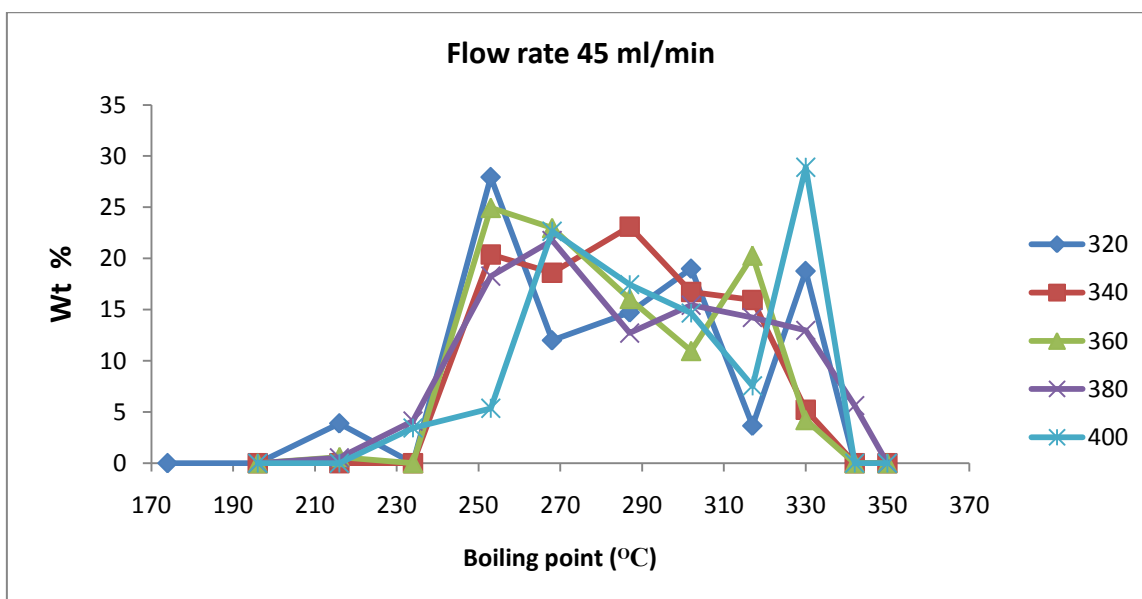


Figure 16 Liquid samples at the operation flow rate 45 ml/min and the temperatures between 320°C and 400°C

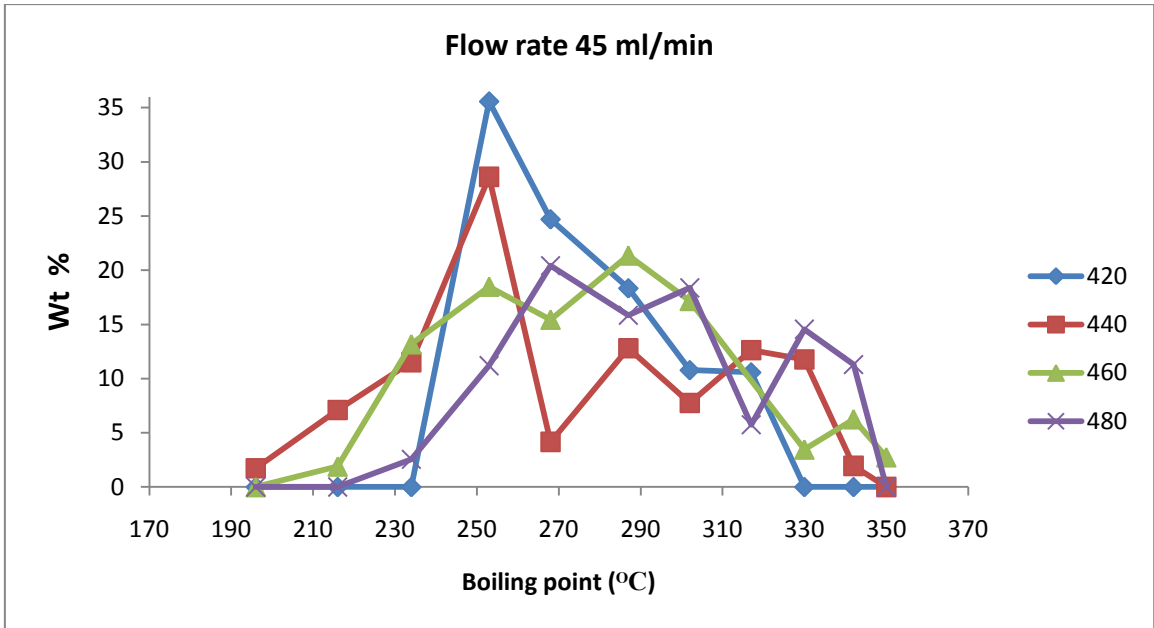


Figure 17 Liquid samples at the operation flow rate 45 ml/min and the temperatures between 420 °C and 480 °C

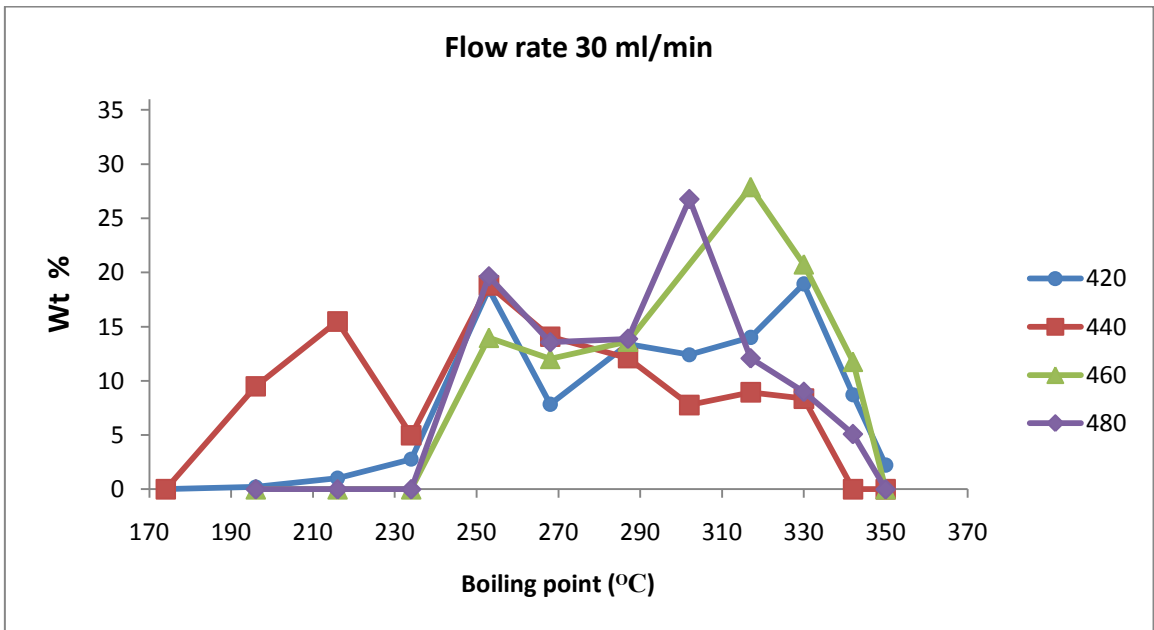


Figure 18 Liquid samples at the operation flow rate 30 ml/min and the temperatures between 420°C and 480°C

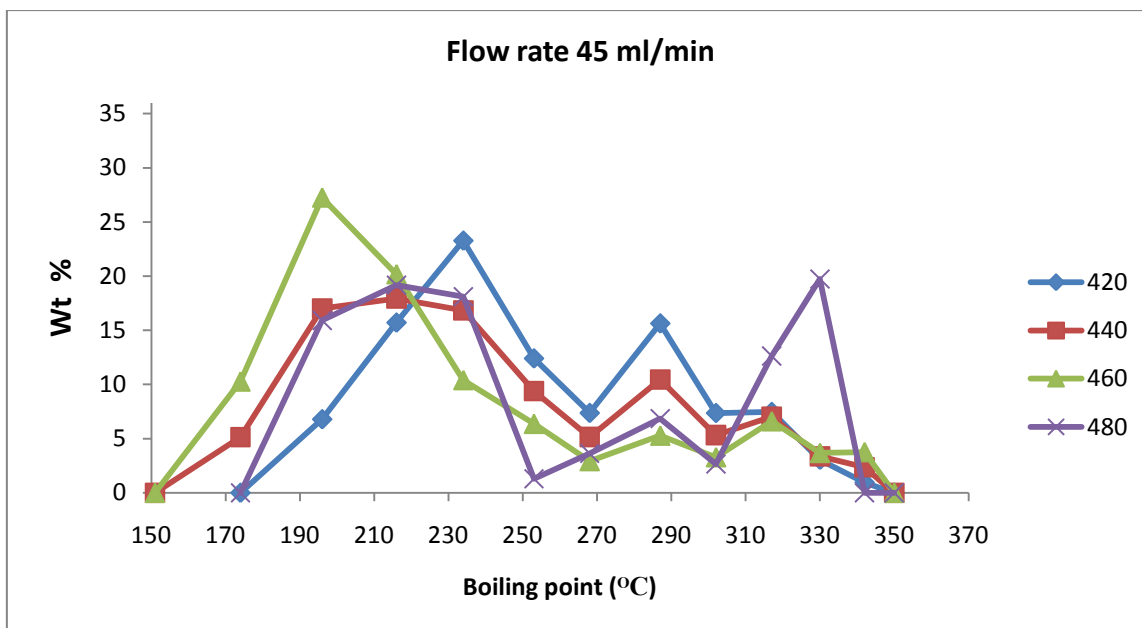


Figure 19 Liquid samples at the operation flow rate 45 ml/min and the temperatures between 420°C and 480°C (the double catalytic bed reactor)

### 5.7 Coke deposition

5 coke samples were analyzed by Belab AB, (Bränsle & Energilaboratoriet AB) Norrköping. Data of the analyzed cokes was given in Table 7. Operating at low temperature (320 °C) led to low amount of coke deposition in the catalyst. Changing flow rate from 45 ml/min to 30 ml/min caused a rise of the coke deposition in the catalyst. When the double bed reactor was used, the dry weight percents of depositing coke on the upper and lower beds were different. The lower bed had more coke deposition than the upper one by almost double.

Table 7 analyzed coke samples

Sample	Catalyst type*	Operating Temperature. (°C)	Operating pressure. (°C)	LHSV (ml/min)	Coke (dry base %)
1	Zeolite 1 g	320	1	30	1%
2	Zeolite 1 g	440	1	45	1.5%
3	Zeolite 1 g	440	1	30	3%
<b>Split type of catalyst bed in reactor – double bed catalyst in reactor.</b>					
4	Zeolite 0.5 g Upper bed	440	1	45	3%
5	Zeolite 0.5 g Lower bed	440	1	45	5.5%

\*No coke deposition on silica



## 5.8 Product selectivity of the alkylation

The selectivity from this experiment was gaseous products formed through the alkylation and liquid products which have their boiling point in a range of the gasoline and diesel. According to the limitation of instruments in the laboratory, components in the liquid samples could not be individually indentified. So, using boiling point to separate compounds in the sample was an applicable way.

## 5.9 Dimerization, oligomerization, isomerization and cracking

The possibility of alkylation reaction by the use of ethylene as self-alkylating agent was studied through the experiment. As far as we have known that ethylene by itself as alkylating agent may not be economical today. Theoretically, ethylene reacts with the lower initial rate when compares to propene and butane at the similar partial pressures. Consequently, in order to make ethylene more reactive, the experiment was set to operate at the medium and high temperature ranges and the ambient atmospheric pressure. It is noticeably seen from the results that the reaction can be speeded up by operating the system at high temperatures. By doing that, the higher activation energy of ethylene adsorption on the catalyst to form  $C^+-C$  (carbenium ion) can be achieved.  $C^+-C$  has very strong interaction with alkoxy groups on H-beta zeolite. As presented in the results, it can interpret that at medium operating temperature (below 400°C), the migration capacity of adsorbed ethylene is poor. Generally, alkylation partly involves dimerization, oligomerization, isomerization and cracking at the same time. Ethylene has the lower reactivity in a comparison to propylene and butane as shown in the previous study (19).

The initiation of the alkylation reaction requires an olefin dimerization step. When ethylene adsorbs on the catalyst and be converted to carbenium ions of ethylene, it can be reacting with another ethylene through alkenyl carbenium ion to form dimer. This step is called as the olefin dimerization step which occurred quickly during the experiment. The presence of  $C_4$  in the entire experiments demonstrates that there is the dimerization of ethylene as long as the catalyst is still activated. As shown in the figure 4-9, butenes was detected although it did not present in the high amount. It would be explained that the detected butenes by GC were not reacted further with other hydrocarbon compounds. The dimerization step was just an intermediate step before the

alkylation probably takes place. As observed experimentally, the dimer was able to either desorb from the catalyst and move out the reactor as products or subsequently participate in other reactions such as alkylation, oligomerization and isomerization.  $C_6^+$  observed was one of the expected selective product, it was formed by alkylation of  $C_2$  with  $C_4$  (dimer of ethylene). The boiling point of components detected in the liquid samples located mainly on the boiling point of diesel range but rarely existed on that of gasoline. It means that injected ethylene underwent several reactions before exist. Some of those were oligomerization and isomerization. The former made the hydrocarbon chain longer and the later transformed a compound into any of its isomeric forms. Operating system at high temperature possibly leads to higher cracking rate. Cracking of the larger alkylate is usually favored by the high temperature. The variation of gaseous product can be resulted in the cracking of both the large alkylate and oligomer.

## **6. Conclusion**

The experiments were carried out at two flow rates and different reaction temperatures. The primary objective was to alkylate ethylene with itself to heavier molecules in gasoline and diesel ranges. The achieved maximum conversion of 64.64% was observed at the operating condition (30 ml/min, 480 °C) under the single catalytic bed reactor. After the double catalytic bed reactor was used, the higher conversion was observed with 70.44% at the condition (45 ml/min, 480 °C). These two methods showed different results. On the single bed method, the maximum conversions were observed experimentally at the first analysis by GC when the experiments started. Dissimilarly, the outcome from the double catalytic bed method did not show the highest conversion on the first analyzes but it was observed on the second analyzes after the running time passed 1hr. Most liquid samples had the boiling in the diesel range. The coke deposition on the catalyst was high and the deactivation was rapid when the system was operated at the high temperature. Operating system at lower flow rate also showed the same behavior. When the double catalytic bed reactor was applied, the coke deposition was much higher than that in the single catalytic bed reactor at the same operating temperature and flow rate. The olefin dimerization step was the important step since ethylene can initially react with itself to form the dimer before longer hydrocarbons can be produced. The dimers participated in the alkylation reaction and also other reactions like oligomerization and isomerization. Cracking occurred in the entire experiments. Consequently, many types of hydrocarbon compound were detected in the entire experiment. Operating at high temperature leads to more cracking.

### ***7. Future work***

More experiments should be carried out at different temperatures and flowrates with different catalyst composition. In the current catalyst, the Silica to Aluminum ratio should be changed by lowering the ratio. The experiments should also be carried out for shorter periods of time since the deactivation of catalyst is quite rapid. The degeneration of catalyst should be looked into in the future. The cooling system should be improved in order to acquire more accurate results. Coke testing should be carried out in more detail.

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Appendix

A. Additional results of gaseous products from the single catalytic bed reactor

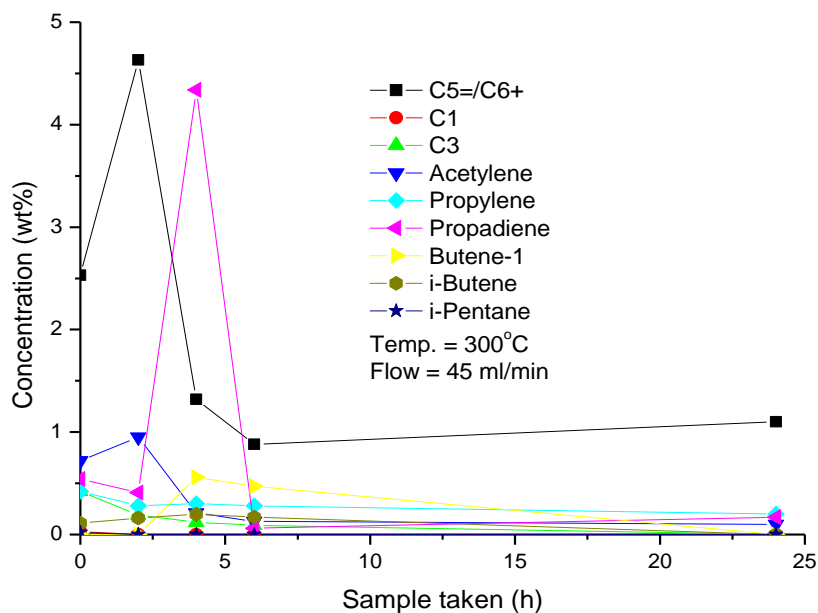


Figure 20 Gas products from the single bed reactor at the operating condition (45ml/min, 300 °C)

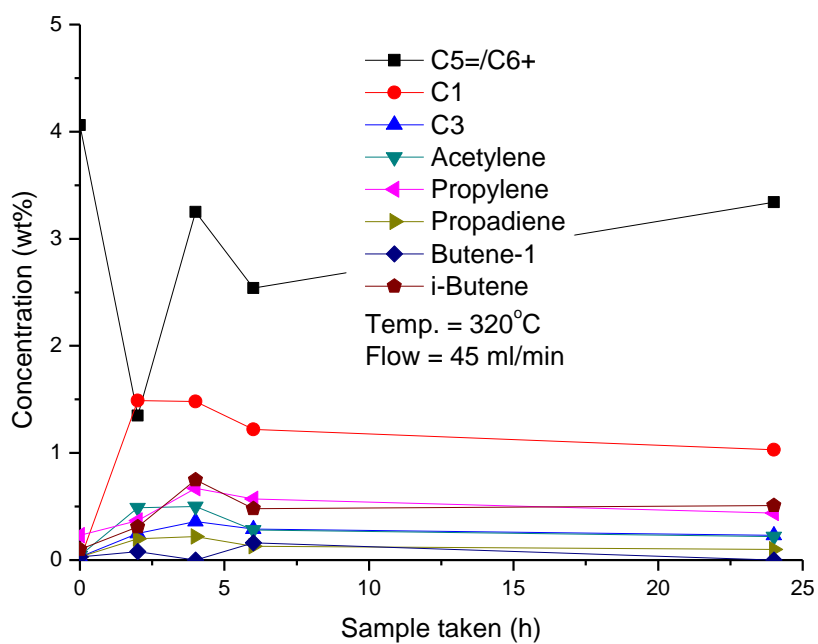


Figure 21 Gas products from the single bed reactor at the operating condition (45ml/min, 320 °C)

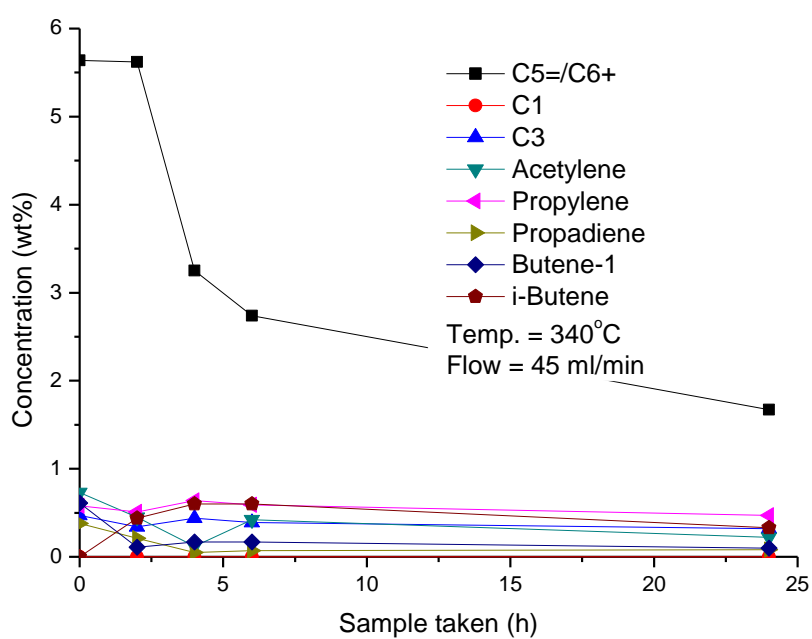


Figure 22 Gas products from the single bed reactor at the operating condition (45ml/min, 340 °C)

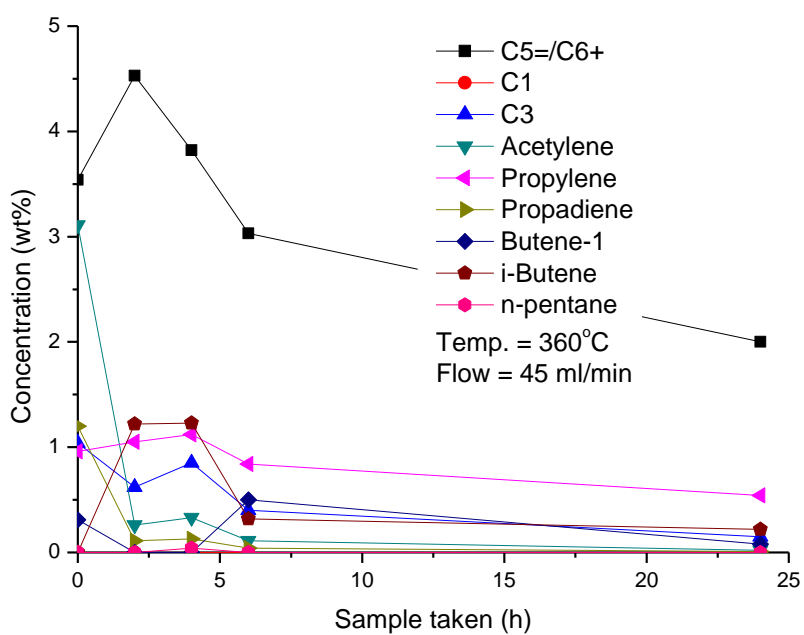


Figure 23 Gas products from the single bed reactor at the operating condition (45ml/min, 360 °C)



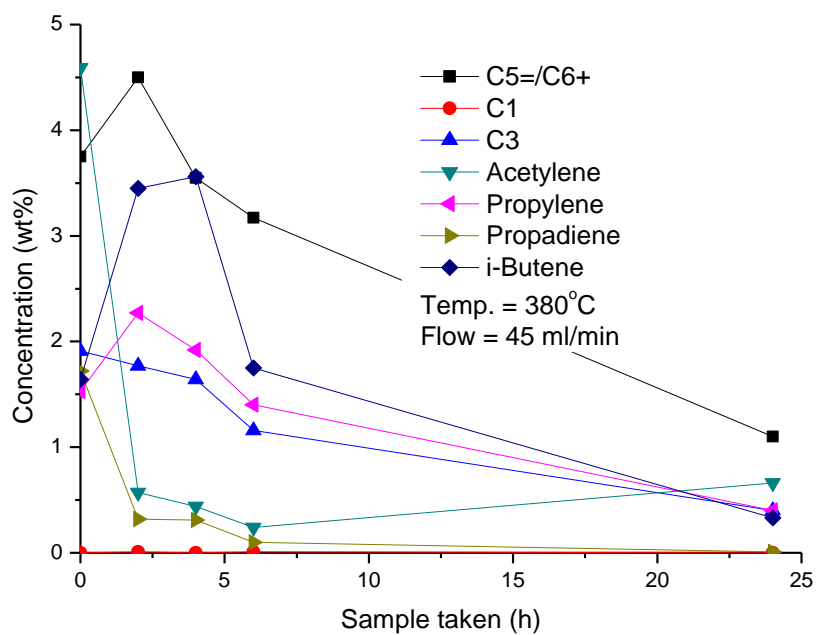


Figure 24 Gas products from the single bed reactor at the operating condition (45ml/min, 380 °C)

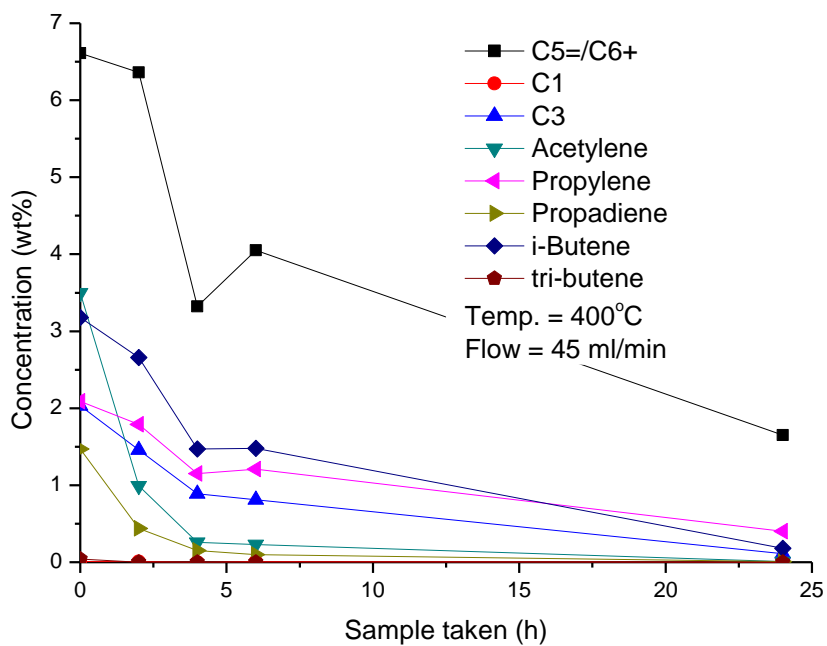


Figure 25 Gas products from the single bed reactor at the operating condition (45ml/min, 400 °C)

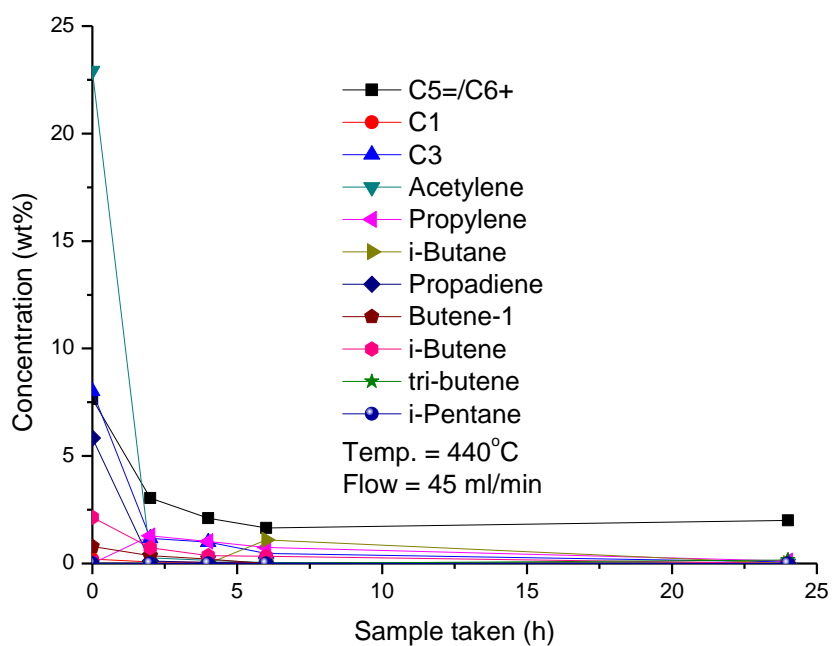


Figure 26 Gas products from the single bed reactor at the operating condition (45ml/min, 440 °C)

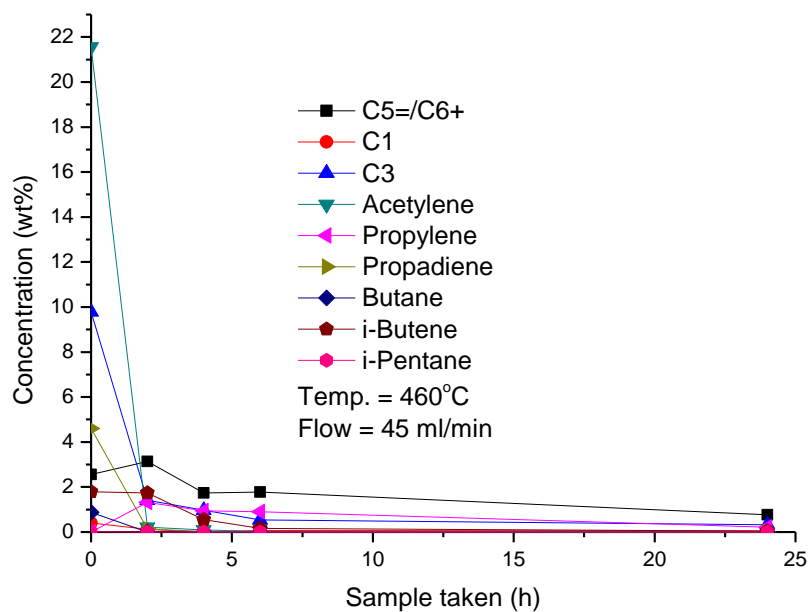


Figure 27 Gas products from the single bed reactor at the operating condition (45ml/min, 460 °C)

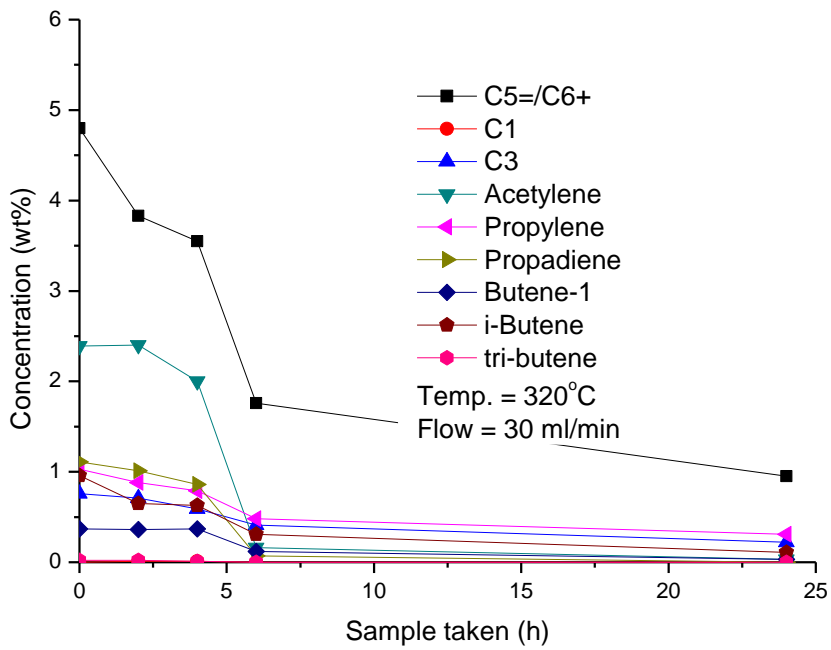


Figure 28 Gas products from the single bed reactor at the operating condition (30ml/min, 320 °C)

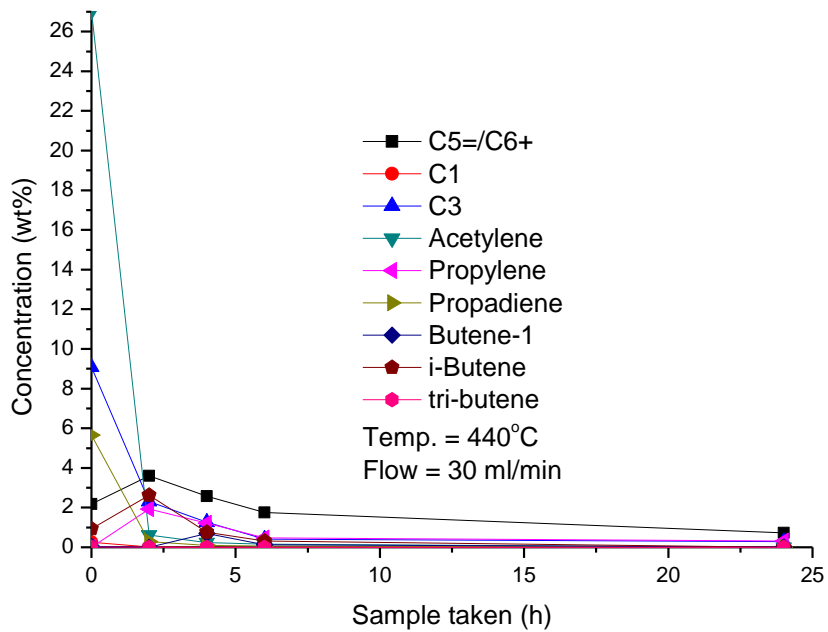


Figure 29 Gas products from the single bed reactor at the operating condition (30ml/min, 440 °C)

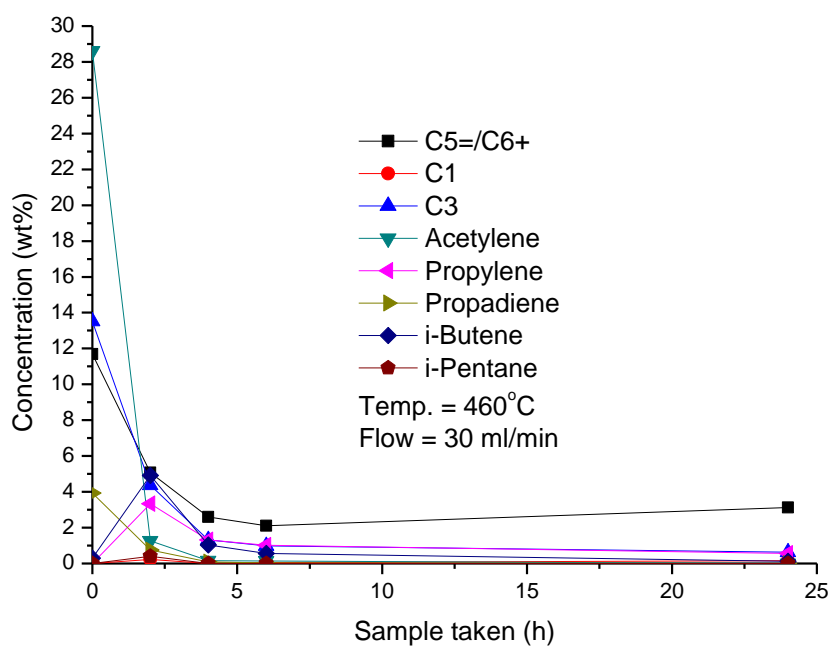


Figure 30 Gas products from the single bed reactor at the operating condition (30ml/min, 460 °C)

B. Additional results of gaseous products from the double catalytic bed reactor

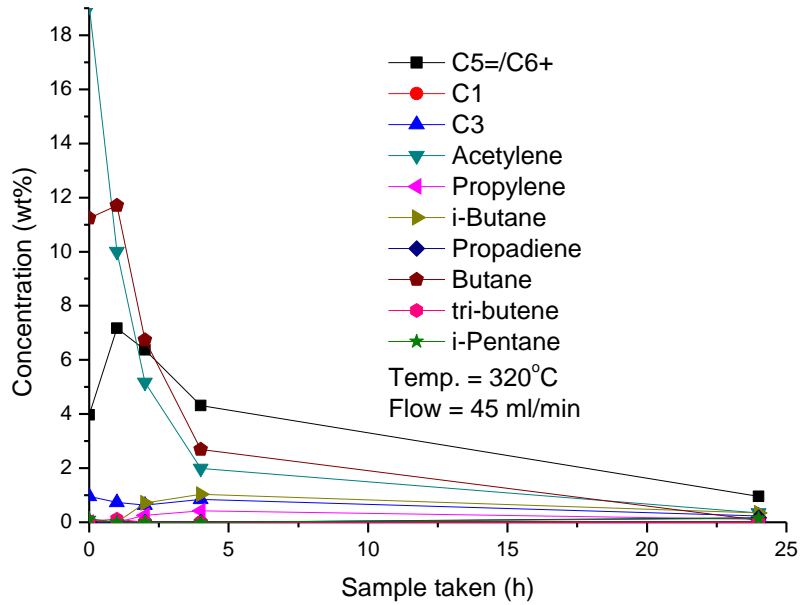


Figure 31 Gas products from the double bed reactor at the operating condition (45ml/min, 320 °C)

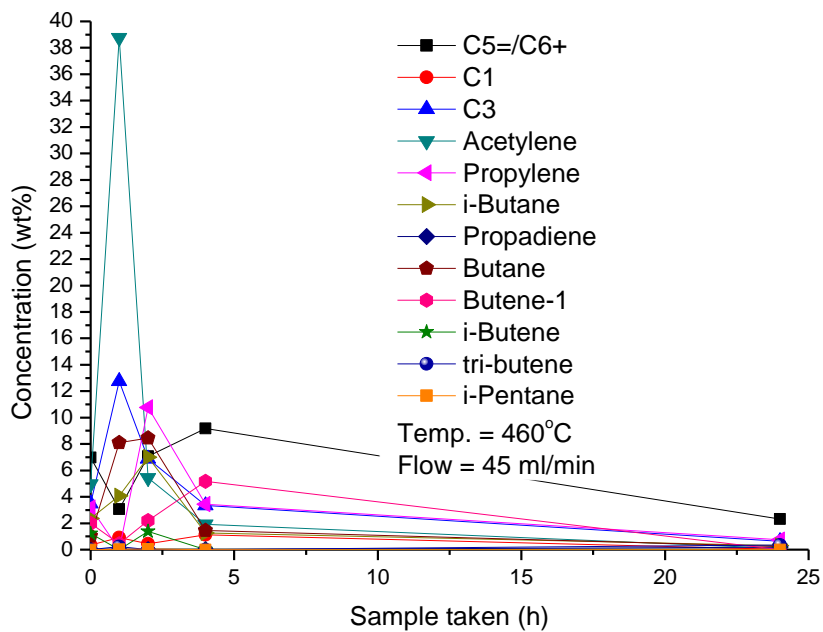


Figure 32 Gas products from the double bed reactor at the operating condition (45ml/min, 440 °C)

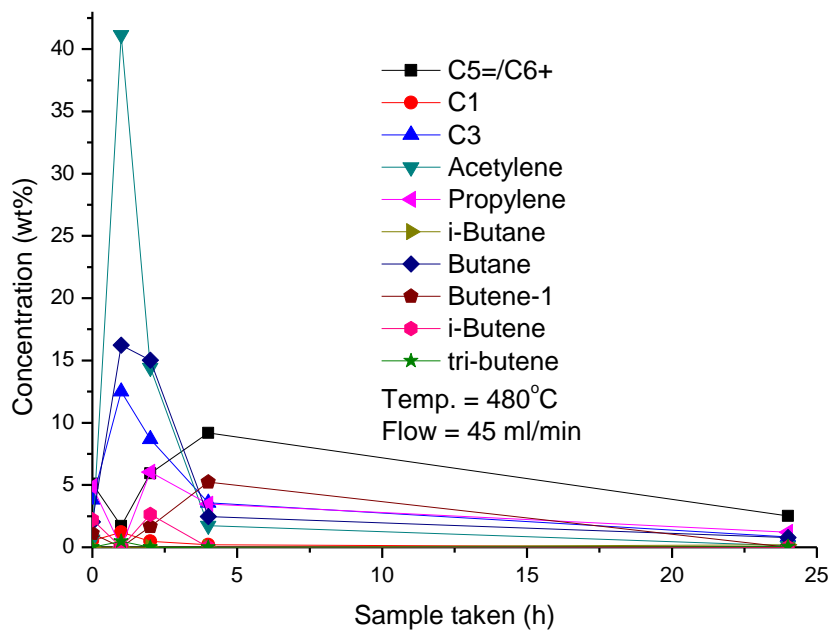


Figure 33 Gas products from the double bed reactor at the operating condition (45ml/min, 460 °C)