



CHAPTER I

INTRODUCTION

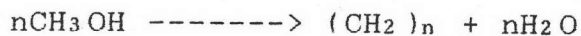
1.1 Scope of the Present Report (1) , (2) , (3)

Zeolite catalysis : Crystalline alumino silicates possessing base exchange properties have been known for well over 100 years and occur quite frequently in nature. In the mid - 1950S Union Carbide corporation first commercially produced synthetic zeolites of the X and Y type as adsorbents ; they later became ingredients of zeolite catalysis. The new zeolites cracking catalysts exhibited greater activity and selectivity than all previous catalysts. While their initial introduction was for use in TCC units in late 1961 , fluid - bed zeolite catalysts were soon manufactured and used.

A series of catalyst improvements followed the initial introduction of zeolites , each adding to stability or selectivity of the catalyst. Almost simultaneously with the introduction of zeolite-cracking catalysts came the discovery of catalytic shape selectivity by P.B. Weisz and his coworkers at Mobil. They stipulated and demonstrated that diffusional constraints prevented the entry of molecudes above certain

dimensions into the pores of certain zeolites , and introduced the concept of "molecular engineering". The zeolite suited perfectly for use in several processes for a long time in the field of petrochemical and refinery industries. The latest application of this type of catalyst , which has not yet become commercial although it has been in operation in a sizeable pilot plant is conversion of methanol to high-octane gasoline. This new chemical reaction involves an internal dehydration and polymerization with simultaneous isomerization and hydrogen transfer. Methanol goes via dimethyl-ether to an olefinic entity , which then forms isoparaffins and aromatics. The catalyst is ZSM-5 and operation can be in either fixed or fluid bed at quite mild conditions. Several reaction mechanisms have been suggested for this reaction that had not been previously observed. It is not limited to methanol , but works with higher alcohols , ethers , and other oxygenates.

Recently, the conversion of methanol to hydrocarbons over ZSM-5 zeolite catalyst was reported by Mobil Oil Co.,. Mobil has now demonstrated a simple catalytic process to convert methanol quantitatively to hydrocarbons and water as follows (2)



They showed that variation in product yields can

achievedly varying operation conditions , reactant types , and catalyst properties. With respect to catalyst properties, we have learnt to dramatically control product selectivity by varying the type of zeolites and ratio of Si/Al.

Consequently , we are interested to study the reactivities of Alcohols ($C_1 - C_4$) over zeolite catalysts for extending to the new alternatives of petrochemical feedstock such as C_2H_4 , C_3H_6 etc. and energy from natural gas and agricultural products , which show in Figure 1.1 , Figure 1.2

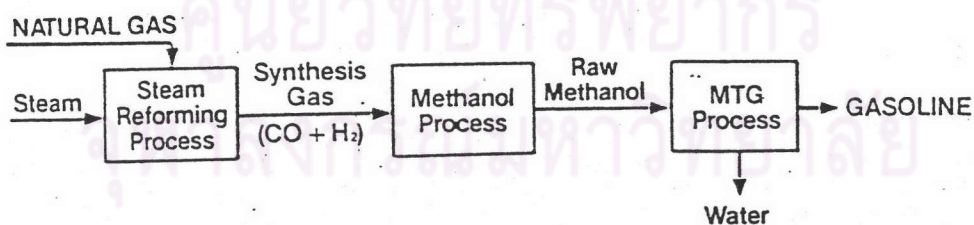


Figure 1.1 Making gasoline from natural gas via MTG (3)

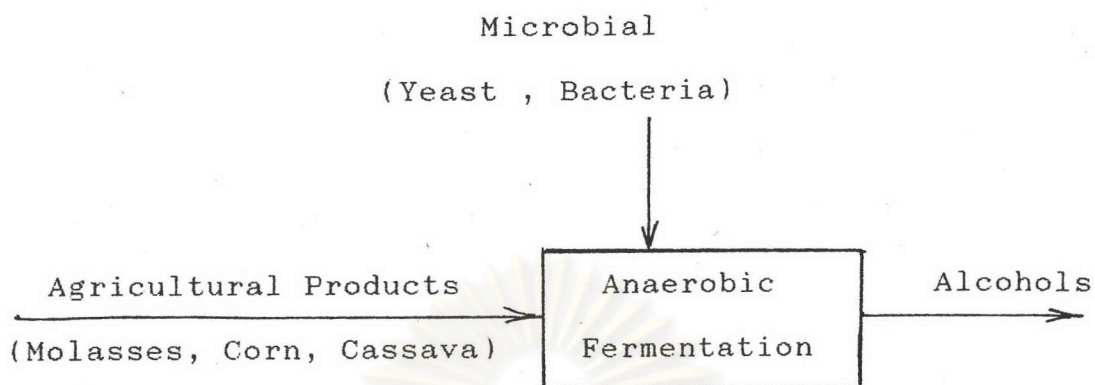


Figure 1.2 Making alcohols from agricultural products.

The production of olefins from alcohols would appear to be highly unsound from an economic standpoint. However, there are olefin plants that use alcohols as the feedstock. They are economical under special circumstances such as a country with a large amount of fermentation alcohols available.

Increasing demand for olefins, e.g. $C_2 - C_4$ olefins has, from time to time, led to periods of shortage, either due to a diminished supply of suitable feedstocks or to limited processing capacity. In any event, it is desirable to provide efficient means for converting alcohols other than petroleum to olefins.

1.2 Petrochemical Situation and Use of Olefins (4) , (5)

The three most important olefins used for the production of petrochemicals are ethylene , propylene , and butene. Ethylene is the dominant olefin with a production of 28 billion pounds in 1978. The united state name plate ethylene capacity as of January 1 , 1979 , was 32.49 billion pounds. This increased to about 40.5 billion pounds/year by January 1 , 1981. World - wide ethylene capacity on January 1 , 1986 , was about 52 milliontons/year and will increase in the future. So , the analysis of economist will be impoverished for world-wide ethylene market in 1995.

For , propylene is the second most important olefin. World - wide propylene capacity on January 1 , 1986 , was about 29 milliontons/year and will increase in the future. Its growth rate is the fastest of any petrochemical raw material , appreciably higher than growth rate of ethylene. So, the analysis will be impoverished for world - wide propylene market in 1990. And, butene is the same status.

Petrochemicals from ethylene : A basic reason why ethylene is a prime raw material for petrochemicals is that it is readily available , at low cost, and in high purity. Ethylene reacts by addition with low cost materials such as oxygen, chlorine, hydrogen chloride and

the reactions take place under relatively mild conditions and usually with high yields. All of these reactions add weight to ethylene molecule. And chemicals are sold by weight, not by mole. Ethylene also reacts by substitution to produce vinyl monomers. It enters into the production of about 30% of all petrochemicals. Derivatives of ethylene are used for the production of plastics (65%), antifreeze (10%), fibers (5%), and solvents (5%). Ethylene and many ethylene derivatives are used for the production of polymers, which account for a very large percentage of ethylene utilization. The formation of polyethylene and ethylene-related polymers are the polystyrene, polyester, and polyvinyl chloride. For, ethylene oxide dominates the individual compounds produced from ethylene with ethylene dichloride, the precursor of vinyl chloride, next in quantity of ethylene utilized. Ethylbenzene for styrene production is third in quantity. These three account for 37% of the ethylene demand. Polyethylene accounts for 44% and the remaining 19% is scattered through a wide range of compounds: Acetaldehyde, ethylchloride, vinylacetate, and many others. show in the figure 1.3

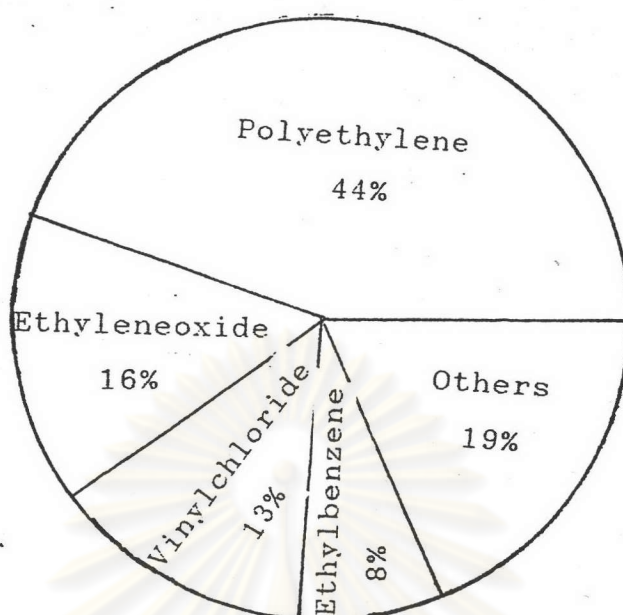


Figure 1.3 The demand pattern for ethylene. (4)

Petrochemicals from Propylene: Propylene, $\text{CH}_3\text{-CH=CH}_2$, often referred to as "the crown prince of petrochemicals," is superficially similar to ethylene, but it has many differences both in production and uses. Petrochemical demand for propylene is about one-half the demand for ethylene. This is somewhat surprising because the added complexity of the propylene molecule should permit a wider selection of end-products and markets. But this very difference can lead to the production of undesirable byproducts, and it frequently does. An appreciable amount of industrial research effort goes into developing selective catalysts and operating conditions for propylene. The propylene utilization pattern for the estimated 15.5 billion pound demand for chemical propylene in 1980 is illustrated in Figure 1.4. Polypropylene will

account for only 29 percent of the propylene demand, while the 1980 polyethylene production is estimated to be 45 percent of the propylene demand. The overall petrochemical demand for propylene will grow about 6.2 percent per year through 1985.

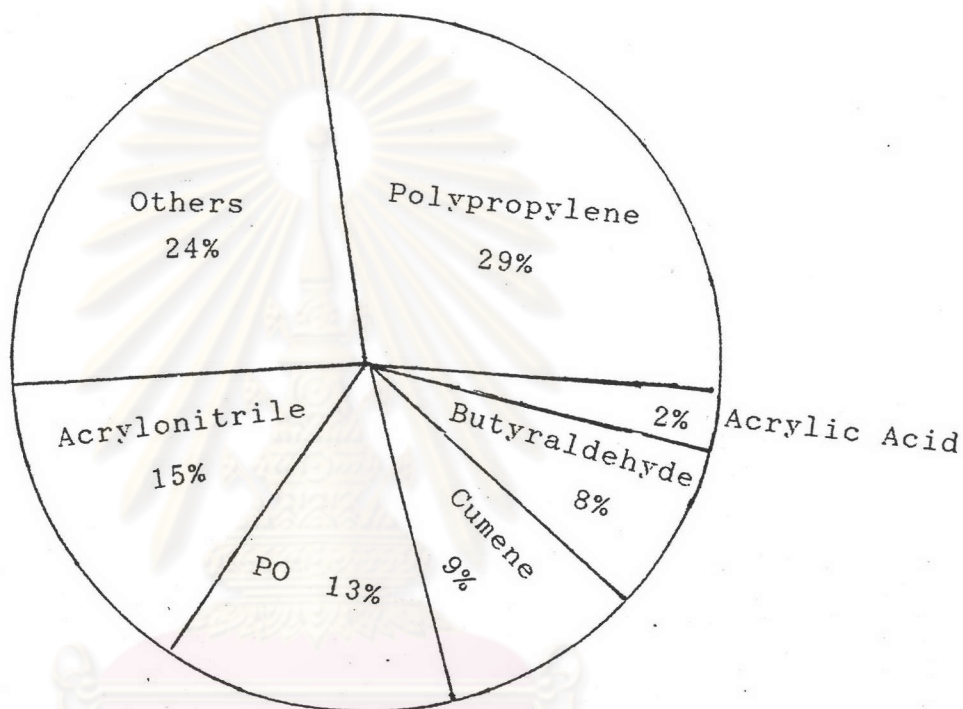


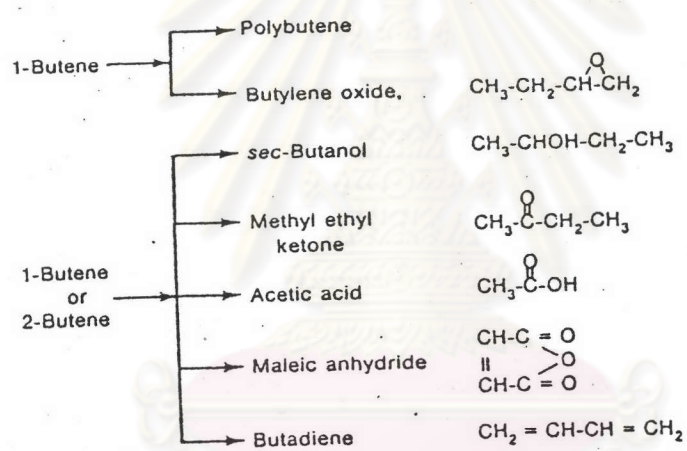
Figure 1.4 The predicted use pattern of propylene consumption in 1980. (4)

Petrochemical from Butylenes :- The butylenes and butadiene have, in general, similar chemical and physical properties. They differ, however, in their utilization with the butylenes being used more for chemical synthesis and less for polymer formation than butadiene. The structures, names and boiling points of the C₄ mono- and diolefins are given in Table 1.1

Table 1.1 The structure and names of the C₄ olefins and diolefins (4)

| Olefins ¹ | | |
|--|---|-------------------------------|
| Structure | Names ² | Boiling point °C ³ |
| CH ₃ - CH ₂ - CH=CH ₂ | 1-Butene α-Butylene | - 6.3 |
| $\begin{array}{c} \text{H} & & \text{H} \\ & \diagdown & / \\ & \text{C}=\text{C} \\ & / & \diagdown \\ \text{CH}_3 & & \text{CH}_3 \end{array}$ | <i>cis</i> -2-Butene β-Butylene 2-Butene | + 3.7 |
| $\begin{array}{c} \text{CH}_3 & & \text{H} \\ & \diagdown & / \\ & \text{C}=\text{C} \\ & / & \diagdown \\ \text{H} & & \text{CH}_3 \end{array}$ | <i>trans</i> -2-Butene β-Butylene 2-Butene | + 0.9 |
| $\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3 - \text{C} = \text{CH}_2 \end{array}$ | 2-Methylpropene Isobutylene Isobutene | - 6.6 |
| CH ₃ - CH=C=CH ₂ | Diolefins ⁴ 1,2-Butadiene Methylallene | +10.8 |
| CH ₂ =CH-CH=CH ₂ | 1,3-Butadiene Butadiene | - 4.4 |

The n-butenes are characterized by having an unbranched, straight-chain, carbon structure, C-C-C=C while isobutylene has a branched-chain structure, C = $\overset{\text{C}}{\underset{|}{\text{C}}} - \text{C}$. This makes an appreciable difference in the type of reaction, and general chemical utilization of the two types of C₄ olefins. There are also addition reactions where both 1-butene and 2-butene give the same products. Relative to the potential supply of the n-butenes, their chemical utilization is small and show in Figure 1.5



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Figure 1.5 The chemical utilization of the n-butenes (4)



Isobutylene, $\text{CH}_3\text{-C}=\text{CH}_2$, is not used extensively as a chemical precursor because many of its derivatives have the reactive tertiary structure which has a tendency to revert to isobutylene. The oxidation of isobutylene to methacrylic acid is an example. Isobutylene dimerizes readily with itself and with other olefins to form higher molecular weight olefins such as diisobutylene and heptene. Figure 1.6 indicates some of the compounds synthesized from isobutylene. These are produced in relatively small amounts. Butyl rubber and polybutenes account for about 75% of chemical utilization of isobutylene.

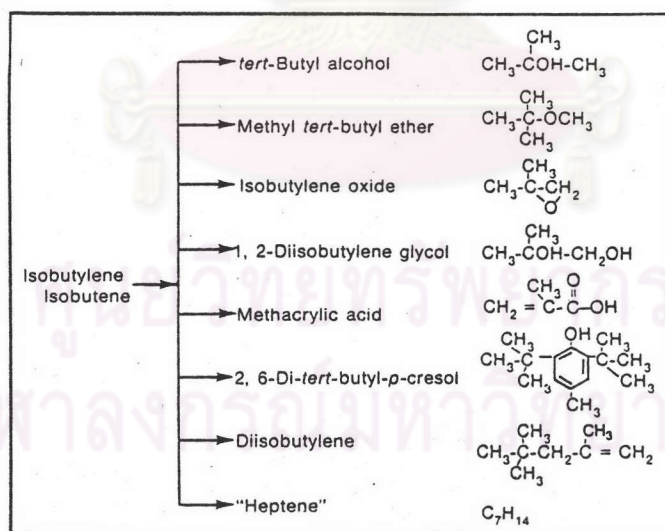


Figure 1.6 The chemical utilization of isobutylene, exclusive of polymer formation. (4)

1.3 Objective of the Research and Expectantly Get a Benefit.

We are going to study the production of light olefins from alcohols ($C_1^{OH} - C_4^{OH}$) by catalytic cracking process. The transformation of alcohols to light olefins, commercially appear to be highly unsound from economic standpoint. However, they are economical under special circumstances such as in a country with a large amount of fermentations. (5) This research is aimed in developing technology for production of light olefins from light alcohols and reducing production cost.

1.3.1 Objective

- 1) to investigate the heterogeneous process for direct dehydration of alcohols ($C_1^{OH} - C_4^{OH}$)
- 2) to study the preparation techniques and to prepare a suitable zeolite for the above process.
- 3) to study of reactivity of alcohol ($C_1^{OH} - C_4^{OH}$) over zeolite catalysts.
- 4) to investigate the effect of reaction conditions (space velocity, temperature, type of zeolites) of the above reaction.

1.3.2 Get a Benefit

- 1) for outline to choose and to improve the ability of catalysts to use industrial application.
- 2) for outline to choose and to improve the operation conditions to use industrial application

3) Experimental unit of this reserach, which is a foundation of attemption to study the above reaction in feature of Pulsed - Microcatalytic Reactor.



ศูนย์วิทยทรัพยากร
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