

## CHAPTER II

### THEORETICAL BACKGROUND AND LITERATURE REVIEW

#### 2.1 Palm Fatty Acid Distillate (PFAD)

PFAD is a by-product produced from the physical refining of palm oil. It is a light brown semi-solid at room temperature melting to a brown liquid on heating. Table 2.1 shows that PFADs comprise mainly of free fatty acid (FFA) (>80%) with palmitic acid and oleic acid as the major components. The remaining components are triglycerides, partial glycerides and unsaponifiable matters *e.g.* vitamin E, sterols, squalenes and volatile substances as show in Table 2.2.

**Table 2.1** Typical fatty acid composition (FAC) of palm fatty acid distillate (Ping, 2009)

FAC	%wt
C8:0 capric	0 – 0.3
C10:0 caprylic	0 – 0.2
C12:0 lauric	0.1 – 2.4
C14:0 myristic	0.9 – 1.6
C16:0 palmitic	43.0 – 49.1
C16:1 palmitoleic	0.1 – 0.3
C18:0 stearic	4.0 – 4.5
C18:1 oleic	34.7 – 37.2
C18:2 linolenic	8.5 – 9.7
C18:3	0.3 – 0.5
C20:0 arachidic	0.0 – 0.4
Others	0 – 0.2

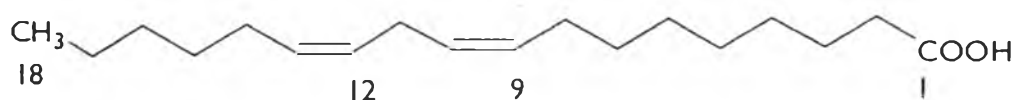
**Table 2.2** Typical composition (wt%) of PFAD (Top, 2010)

Composition	wt%
Free fatty acids	81.7
Glycerides	14.4
Vitamin E	0.5
Squalene	0.8
Sterols	0.4
Others	2.2

Fatty acid distillates are generally used in the soap industry, animal feed industry and as raw materials for oleochemical industries, *e.g.*, in the manufacture of candles, cosmetics and toiletries. Other applications include their use as food emulsifiers, and aid in rubber processing, in flavours and fragrance industries as well as in pharmaceutical products. Vitamin E has been extracted commercially from PFAD for encapsulation. Squalene is a valuable compound used in health foods, cosmetics and in the pharmaceutical industry.

### 2.1.1 Fatty Acids

Fatty Acids are the main constituents of oils and fats, whose applications are overwhelming. They possess a simple structure consisting of a long hydrocarbonate chain and one or more carboxylic groups. The broadest definition includes all chain lengths, but most natural fatty acids are  $C_4$  to  $C_{22}$ , with  $C_{18}$  most common. The simplest fatty acids are referred to as saturated fatty acids. They have no unsaturated linkages and cannot be altered by hydrogenation or halogenation. When double bonds are present, fatty acids are said unsaturated, monounsaturated (MUFA) if only one double bond is present and polyenoic (or polyunsaturated fatty acids = PUFA) if they have two or more double bonds generally separated by a single methylene group (methylene-interrupted unsaturation). Some uncommon

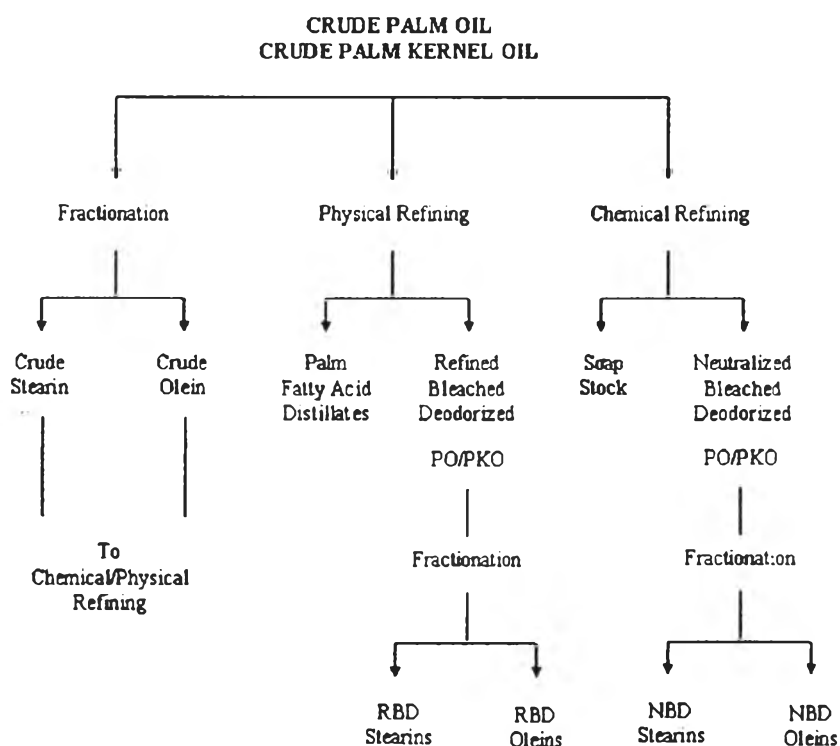


polyunsaturated fatty acids have two adjacent double bonds separated by more than one methylene group; they are named polymethylene-interrupted fatty acid.

Systematic names for fatty acids are too cumbersome for general use, and shorter alternatives are widely used. A general way to describe these compounds is using two numbers separated by a colon, which give, respectively, the chain length and number of double bonds: octadecenoic acid with 18 carbons and 1 double bond is therefore 18:1.

### 2.1.2 Physical Refinery Process

(<http://www.scribd.com/doc/120187349/17-PalmOil>)



**Figure 2.1** Fractionation and refining of crude palm oil and crude palm kernel oil

(<http://it.doa.go.th/palm/linkTechnical/oil%20palm%20processing.html>).

The raw material, which is used by physical plant, is crude palm oil (CPO) from the CPO storage tank. The initial temperature of CPO is at 40 – 60 °C. CPO is

pumped through the heat recovery system, that is plate heat exchanger to increase the temperature around 60 – 90 °C.

After that, 20% of the CPO is mixed with the bleaching earth to form slurry (CPO + Bleaching earth). The agitator inside the slurry tank will mix the CPO and bleaching earth completely. Then, the slurry will go into the bleacher.

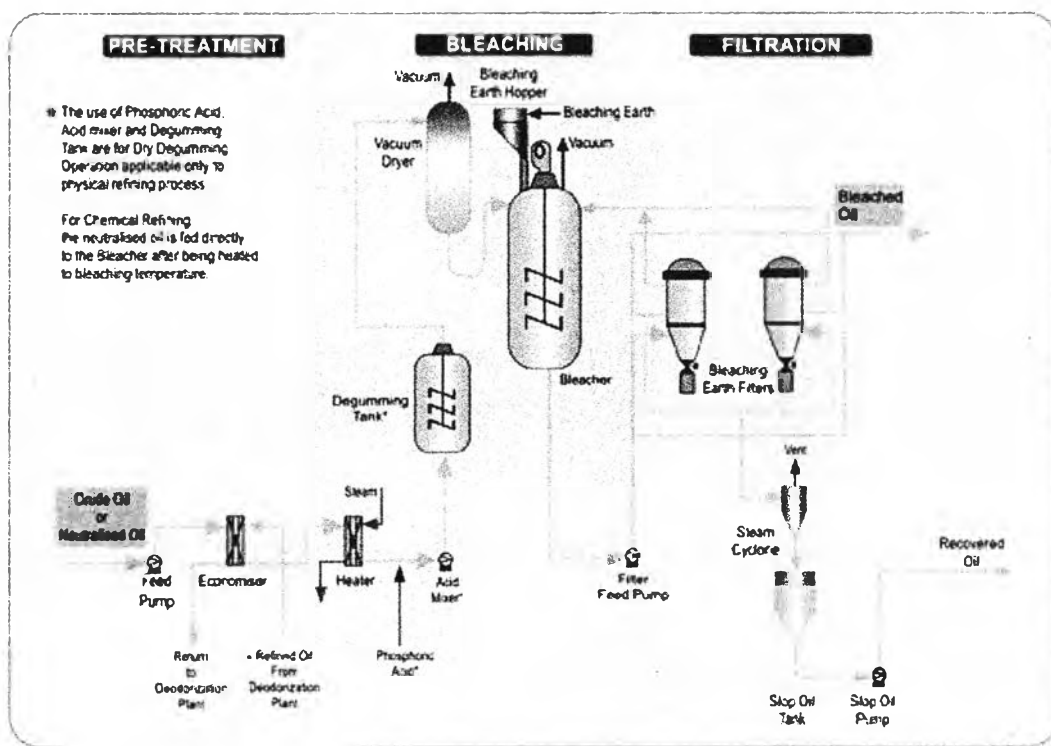


Figure 2.2 Bleacher process.

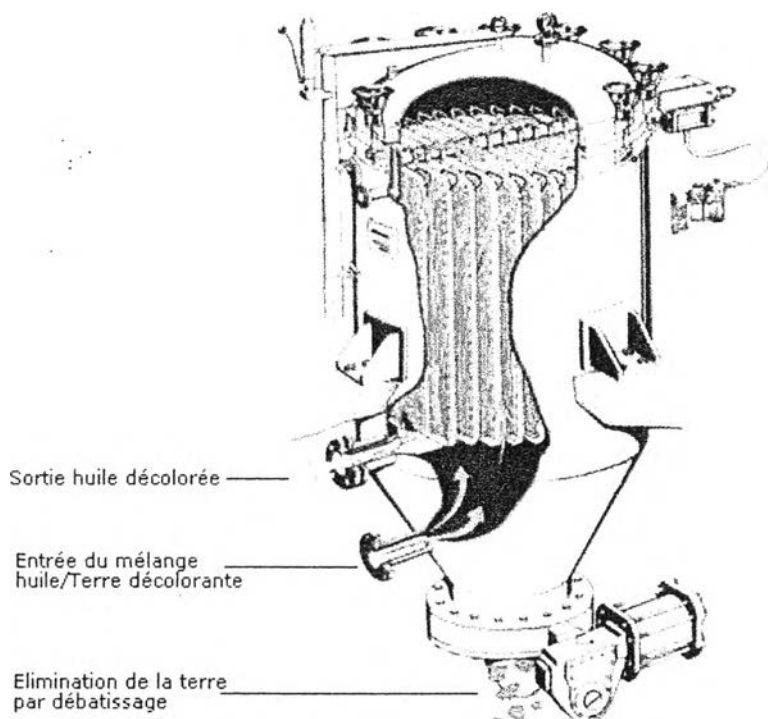
At the same time, another 80% of the CPO is pumped through another plate heat exchanger and steam heater to increase the CPO temperature to 90 – 130 °C. Then, the CPO feed is pumped to static mixers and the phosphoric acid. Inside there, the intensive mixing is carried out with the crude oil for precipitation up the gums. The precipitation of gums will ease the later filtration process, avoid the scale formation in deodorizer and heating surface. The degumming CPO then will go into bleacher.

In the bleacher, there are 20% slurry and 80% degummed CPO will mix together and the bleaching process occur. The practice of bleaching involves the

addition of bleaching earth to remove any undesirable impurities (all pigments, trace metals, oxidation products) from CPO and this improves the initial taste, final flavor and oxidative stability of product. It also helps to overcome problems in subsequent processing by adsorption of soap traces, pro-oxidant metal ions, decomposes peroxides, color reduction, and adsorbs other minor impurities. The temperature inside the bleacher must be around 100 – 130 °C to get the optimum bleaching process for 30 min of bleaching period. The low-pressure steam is purged into bleacher to agitate the concentrated slurry for a better bleaching condition.

The slurry containing the oil and bleaching earth is then passed through the Niagara filter to give a clean, free from bleaching earth particles oil. The temperature must be maintained at around 80 – 120 °C for good filtration process. In the Niagara filter, the slurry passes through the filter leaves and the bleaching earth is trapped on the filter leaves. Actually, the bleaching earth must be clear from Niagara filter after 45 min in operation to get a good filtration. Bleached palm oil (BPO) from Niagara filter is then pumped into buffer tank as a temporary storage before further processing.

Usually, a second check filter, trap filter is used in series with the Niagara filter to double ensure that no bleaching earth slips occur. The presence of bleaching earth fouls deodorizer, reduces the oxidative stability of the product oil and acts as a catalyst for dimerization and polymerization activities. So, the “blue test” is carried out for each batch of filtration to ensure the perfect filtration process. This test indicates whether any leaking is occurring in Niagara filter or trap filter. Hence, any corrective actions can be taken intermediately.

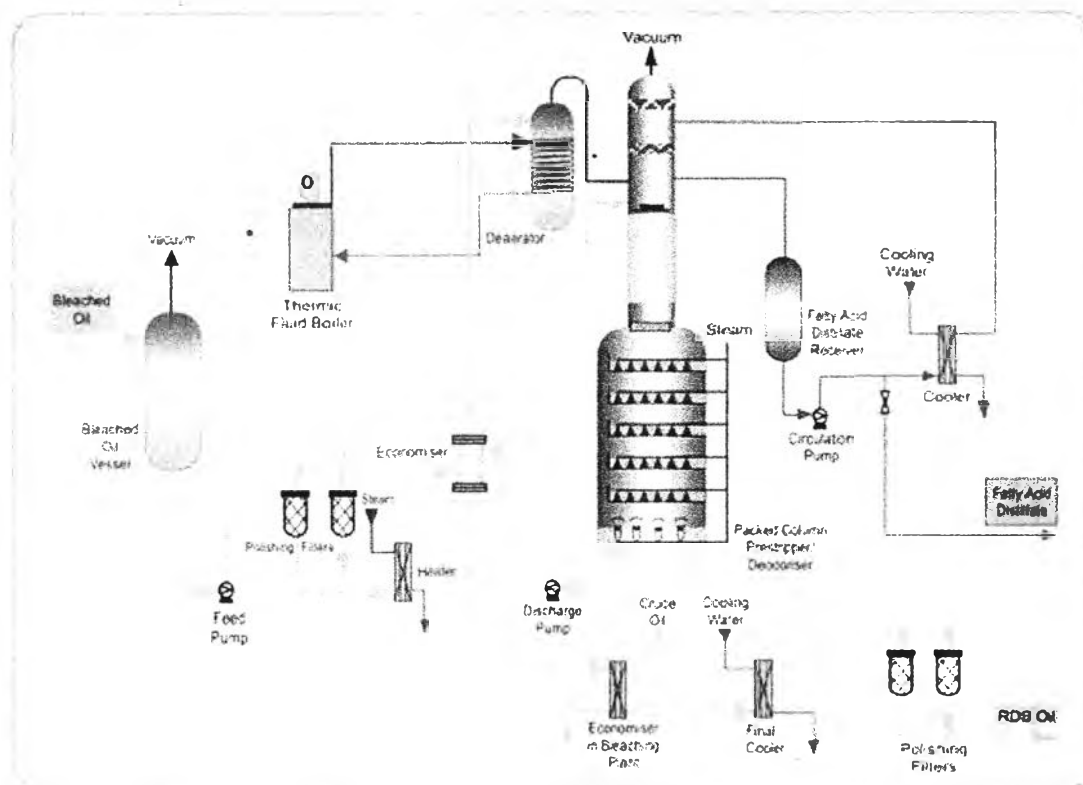


**Figure 2.3** Filtration tank.

The BPO comes out from the filter and passes through another series of heat recovery system, Schmidt plate heat exchanger and spiral (thermal oil: 250 – 305 °C) heat exchanger to heat up the BPO from 80 – 120 °C until 210 – 250 °C.

The hot BPO from spiral heat exchanger then proceeds to the next stage where the free fatty acid content and the color are further reduced and more important, it is deodorized to produce a product that is stable and bland in flavor.

In the pre-stripping and deodorizing column, deacidification and deodorization process happen concurrently. Deodorization is a high temperature, high vacuum and steam distillation process. A deodorizer operates in the following manner: (1) deaerates the oil, (2) heat up the oil, (3) steam strips the oil and (4) cools the oil before it leaves the system.



**Figure 2.4** Deodorization.

In the column, the oil is generally heated to approximately 240 – 280 °C under vacuum. A vacuum of less than 10 torr is usually maintained by the use of ejectors and boosters. Heat bleaching of the oil occurs at this temperature through the thermal destruction of the carotenoid pigments. The use of direct steam ensures readily removal of residue free fatty acids, aldehydes and ketones which are responsible for unacceptable odor and flavors. The lower molecular weight of vaporized fatty acids rises up the column and pulls out by the vacuum system. The fatty acid vapor leaving the deodorizer are condensed and collected in the fatty acid condenser as fatty acid. The fatty acids then is cooled in the fatty acid cooler and discharged to the fatty acid storage tank with temperature around 60 – 80 °C as palm fatty acid distillate (PFAD), a by-product from refinery process.

## 2.2 Aromatic

The liquid phase adsorption processes for aromatics extraction are made economically relevant by the large world demand for aromatic petrochemicals. The global per annum production rates of the highest capacity aromatic petrochemicals derived from reformat or pygas for the recent past are shown in Table 2.3.

**Table 2.3** Approximate world demand of high - volume aromatic petrochemicals (Kulprathipanja, 2010)

$10^6$ t/year (2005–2008)	
Benzene	40
<i>p</i> -Xylene	26
<i>o</i> -Xylene	5
<i>m</i> -Xylene	0.4

Benzene and *para*-xylene are the most sought after components from reformat and pygas, followed by *ortho*-xylene and *meta*-xylene. While there is petrochemical demand for toluene and ethylbenzene, the consumption of these cannot be discussed in the same way as the other four. Toluene is used in such a large quantity in gasoline blending that its demand as a petrochemical pales in comparison. Ethylbenzene from reformat and pygas is typically dealkylated to make benzene or isomerized to make xylenes. On purpose production of petrochemical ethylbenzene (via ethylene alkylation of benzene) is primarily for use as an intermediate in the production of another petrochemical, styrene monomer. Ethylbenzene plants are typically built close coupled with styrene plants.

The large demand for benzene is due to its use as a starting material in the production of polystyrene, acrylonitrile styrene butadiene rubber, nylons, polycarbonates and linear alkyl benzene detergent. All of these final chemical products that are suitable to form into consumer goods have multiple chemical transformations in various industrial processes to obtain them from benzene.



However, benzene is important to note that it is typically a large byproduct from an aromatics complex producing *p*-xylene, and its economics are important in the profitability of any aromatics complex.

### 2.2.1 Method of Production (Kulprathipanja, 2010)

The production of *p*-xylene begins with petroleum naphtha, as does the production of the other mixed xylene components, benzene and toluene. Naphtha is chemically transformed to the desired petrochemical components and the individual components are recovered at required purity in what is known in the industry as an aromatics complex. A generic aromatics complex flow scheme is shown in Figure 2.5. It is useful to briefly review the general flow scheme of this complex for subsequent discussion of the liquid adsorptive processes. The process blocks in Figure 2.5 are labeled according to the corresponding UOP process units. The columns shown are distillation columns.

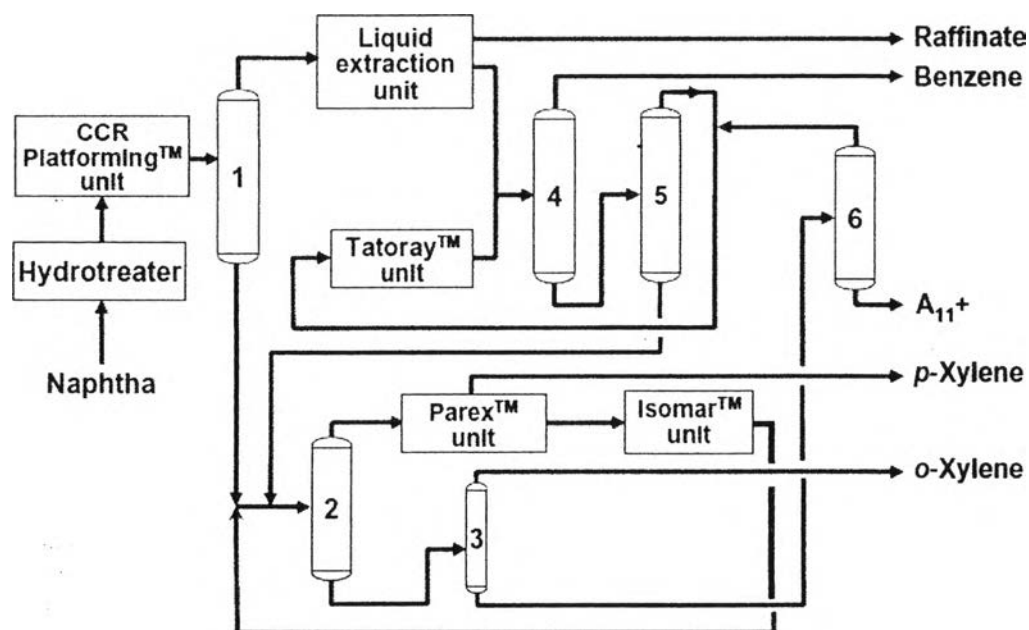


Figure 2.5 Typical aromatics complex with UOP technology.

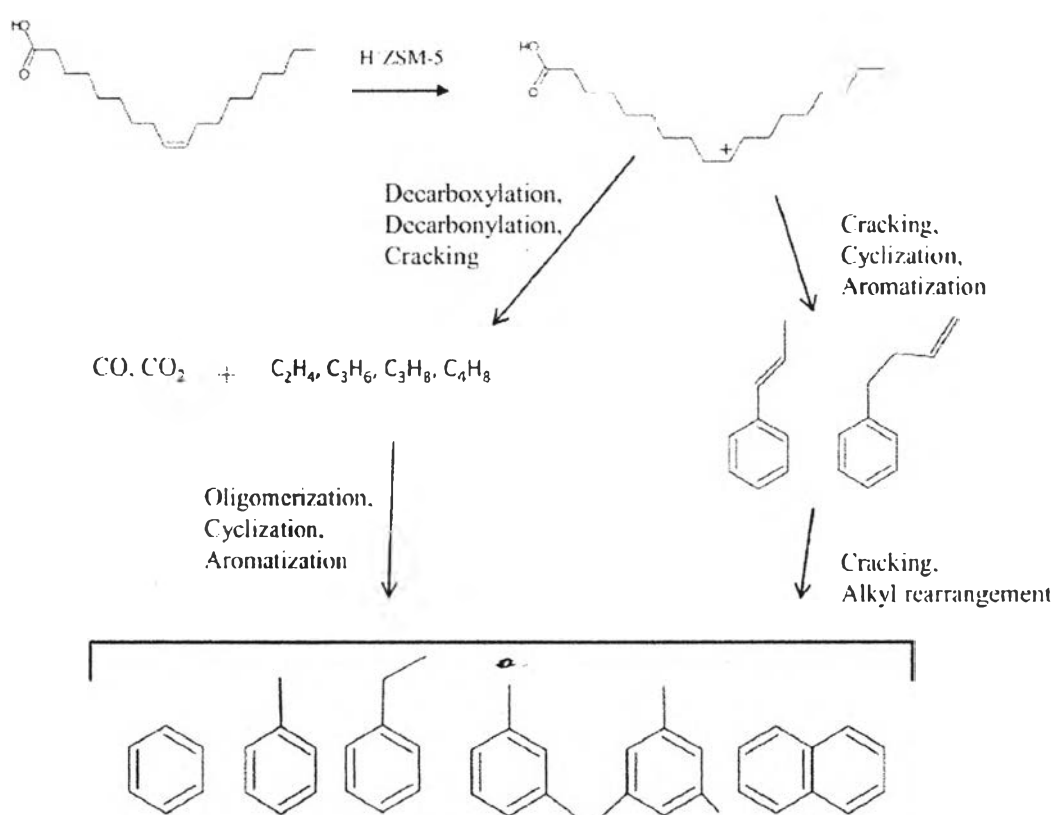
Naphtha enters the aromatics complex and is hydrotreated to remove sulfur, oxygen and nitrogen-containing organic compounds. The naphthenes and

paraffins in the treated naphtha are then reformed to aromatics in the UOP CCR Platforming™ process unit, producing a C<sub>5+</sub> stream referred to as reformat. The reformat is then sent to Column 1 where toluene and lighter boilers (A<sub>7-</sub>) are split from mixed xylene and heavier components (A<sub>8+</sub>). The A<sub>8+</sub> components go to Column 2 where they are sent along with an A<sub>8</sub> recycle stream from the UOP Isomar™ process unit and an A<sub>8+</sub> stream from the UOP Tatoray™ process unit. A portion of the *o*-xylene and all the A<sub>9+</sub> leaves the bottom of Column 2. The mixed xylenes go overhead and on to the UOP Parex™ process unit. The Parex unit extracts the *p*-xylene in the stream at 99.7 – 99.9% purity at a recovery in excess of 97%. The other stream exiting the Parex unit contains the unextracted mixed xylene components. This Parex raffinate stream is sent to the Isomar unit where the mixed xylenes are reacted in the presence of hydrogen over a zeolitic catalyst to an equilibrium mixture of mixed xylenes containing about 22% *p*-xylene. The equilibrated xylenes are recycled to Column 2 to remove trace A<sub>9+</sub> by-product formed in the xylene isomerization reaction. Some *o*-xylene is recovered in Column 3 from the bottoms stream of Column 2 to produce a > 98.5% purity *o*-xylene product. The A<sub>9+</sub> from Column 3 is rerun in Column 4 so that the A<sub>11+</sub> components are removed before sending the A<sub>9</sub> – A<sub>10</sub> components to the Tatoray unit. Meanwhile, the A<sub>7-</sub> aromatics from the Column 1 overhead are extracted by extractive distillation using Sulfolane solvent in the UOP Sulfolane™ process unit.

The non-aromatics in the C<sub>5</sub> – C<sub>8</sub> range are rejected as raffinate for use as gasoline or feed to naphtha steam cracker for ethylene and propylene production. The extracted benzene and toluene are sent to Column 4 along with A<sub>6+</sub> produced in the Tatoray unit. A > 99.9% benzene product is produced from the overhead of Column 4. The bottoms of Column 4 are sent to Column 5 where the toluene is taken overhead and returned to the Tatoray unit to be transalkylated over a zeolitic catalyst in the presence of hydrogen with the A<sub>9</sub> – A<sub>10</sub> material from Column 6, to produce more benzene and mixed xylenes. The A<sub>8+</sub> material from the bottom of Column 5 is sent to Column 2 for recovery of the mixed xylenes produced in the Tatoray unit.

### 2.3 Reaction Pathway of Fatty Acid to Aromatics

Benson and his co-worker investigated heterogeneous cracking of an unsaturated fatty acid and reaction intermediates on H-ZSM-5 catalyst in 2008. The oleic acid was reacted at 400 °C on H-ZSM-5 catalyst to determine the reaction steps involved in the catalytic transformation of an unsaturated fatty acid into aromatics.



**Figure 2.6** Proposed cracking chemistry for the transformation of oleic acid to aromatics (Tracy, J, B., 2008)

### 2.4 Zeolites

Zeolites are water-containing crystalline aluminosilicates of natural or synthetic origin with highly ordered structures. They consist of  $\text{SiO}_4$  and  $\text{AlO}_4^-$  tetrahedral, which are interlinked through common oxygen atoms to give a three-

dimensional network through which long channels run.

In the interior of these channels, which are characteristic of zeolites, are water molecules and mobile alkali metal ions, which can be exchanged with other cations. These compensate for the excess negative charge in the anionic framework resulting from the aluminum content. The interior of the pore system, with its atomic-scale dimensions, is the catalytically active surface of the zeolites. The inner pore structure depends on the composition, the zeolite type, and the cations.

#### 2.4.1 Catalytic Properties of the Zeolites (Hagen, 2006)

At the end of the 1960s, the concept of shape-selective catalysis with zeolites was introduced to petrochemistry (Selectoforming process), and the zeolites became of increasing importance in catalysis research and applied catalysis.

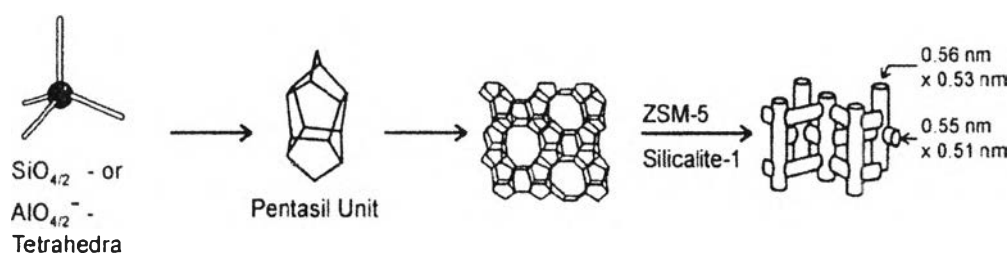
Advantages of zeolite over conventional catalysts as follow:

- Crystalline and therefore precisely defined arrangement of  $\text{SiO}_4$  and  $\text{AlO}_4^-$  tetrahedra. This results in good reproducibility in production.
- Shape selectivity: only molecules that are smaller than the pore diameter of the zeolite undergo reaction.
- Controlled incorporation of acid centers in the intracrystalline surface is possible during synthesis or by subsequent ion exchange.
- Catalytically active metal ions can be uniformly applied to the catalyst by ion exchange or impregnation. Subsequent reduction to the metal is also possible.
- Zeolite catalysts are thermally stable up to  $600^\circ\text{C}$  and can be regenerated by combustion of carbon deposits.

#### 2.4.2 Zeolite Socony Mobil-5 (ZSM-5)

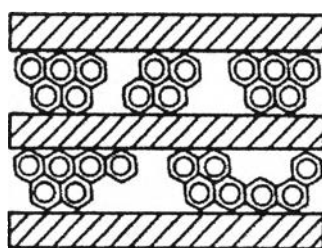
ZSM-5 zeolite or MFI (mordenite framework inverted) is a microporous crystalline material. It is one of the most important zeolite used in petroleum and petrochemical industry as a heterogeneous catalyst for dewaxing, fluid catalytic cracking (FCC) and hydrocarbon isomerization. The structure of ZSM-5 zeolite, show in Figure 2.7, has 10-membered oxygen ring which compose of 5-rings

as secondary building unit. It contains sinusoidal channels with pore mouth dimensions of  $5.4 \times 5.6 \text{ \AA}$  and straight channels with pore mouth dimensions  $5.1 \times 5.4 \text{ \AA}$ . These two channels are perpendicular to each other and generate intersections with diameters of  $8.9 \text{ \AA}$ . The shape-selectivity of ZSM-5 will not allow large molecules produced from the reaction to diffuse out the pores (Wan *et al.*, 2011).



**Figure 2.7** Structure of ZSM-5 zeolite.

For any molecules with carbon number  $> 12$  will be left in the pores and result in coking. Coking not only renders the accessibility of active sites, it also blocks the entrance of pores, and diminishes the catalytic activity of ZSM-5.



**Figure 2.8** Coke formation in zeolites (Hagen, 2006).

HZSM-5 is the protonic type of ZSM-5 zeolite which has been used in acid catalyzed reaction. Typically, HZSM-5 zeolite can be derived by following steps:

- i) Calcination to decompose the organic amine template
- ii) Ion exchange of zeolite in sodium form with  $\text{NH}_4\text{NO}_3$  solution to be  $\text{NH}_4^+$  form
- iii) Calcination of  $\text{NH}_4^+$  form into protonic form

Mo and Savage investigated the hydrothermal catalytic cracking of fatty acids with HZSM-5 in 2014. They found that hydrocarbon molecules such as aromatics, alkanes, and fuel gases can be produced from palmitic acid via hydrothermal catalytic cracking over HZSM-5. Reactions were conducted in 4 mL stainless steel Swagelok batch reactors. The highest yield of liquid phase products (73 wt%) occurred at 400 °C, 180 min, and absence of H<sub>2</sub>.

### 2.4.3 Acidity of Zeolites

The acidity and acid strength are the important properties of zeolites, which play an important role in the selectivity, and activity of zeolites.

Commonly, ZSM-5 zeolite crystal has different Si/Al molar ratios in the range of 10 – 50 (Shirazi *et al.*, 2008). It is widely observed that higher in acidity of ZSM-5, the better in catalytic activity. Generally, the acidity of ZSM-5 is proportional to the Al content that is adjacent to a silanol group. Table 2.4 shows that for higher Si/Al ratio, lower acidity and lower catalytic activity as well (Wan *et al.*, 2011).

**Table 2.4** TPD-NH<sub>3</sub> adsorption for ZSM-5 with different molar ratios of Si/Al (Shirazi *et al.*, 2008)

Sample	Total Acidity (mmole NH <sub>3</sub> /g catalyst)
ZSM-5(10)	27.02
ZSM-5(20)	23.03
ZSM-5(25)	21.38
ZSM-5(30)	20.76
ZSM-5(40)	19.93
ZSM-5(50)	19.93

The acid properties of zeolites can be characterized by using alkane cracking, temperature programmed desorption (TPD), micro-calorimetry, IR spectroscopy and MAS NMR observations. Two different type of acid site are Brønsted and Lewis acid sites. Typically, IR spectroscopy of pyridine adsorption can

be used to differentiate and measure ratio of Brønsted per Lewis acid sites. Brønsted acid sites are related to aluminum located in the framework of zeolites. However, Lewis acid sites are related to the extra-framework aluminum (EFAL) or distorted aluminum in the framework. EFAL is usually generated during the synthesis, calcination or/and ion exchange process (Farneth and Gort., 1995).

The concentration of the acid sites located on the external surface and in the pore mouth region of zeolites can be determined by using probe molecules with larger kinetic diameters compared with the pore of the zeolites. These molecules only interact with the acid sites located on the external surface and in the pore mouth region.

In 1998, Weber *et al.* measured the concentration of the acid sites of silylated HZSM-5 zeolites using TPD of 4-methyl-quinoline. The kinetic diameter of 4-methyl-quinoline (7.3 Å) is larger than the pore openings of HZSM-5 zeolites (5.6 × 5.3 Å), this molecule cannot enter into the pores. Consequently, the acid sites on the external surface of HZSM-5 can be determined quantitatively.

#### 2.4.4 Shape Selectivity

The accessibility of the pores for molecules is subject to define geometric. The shape selectivity of zeolites is based on interaction of reactants with the well-defined pore system.

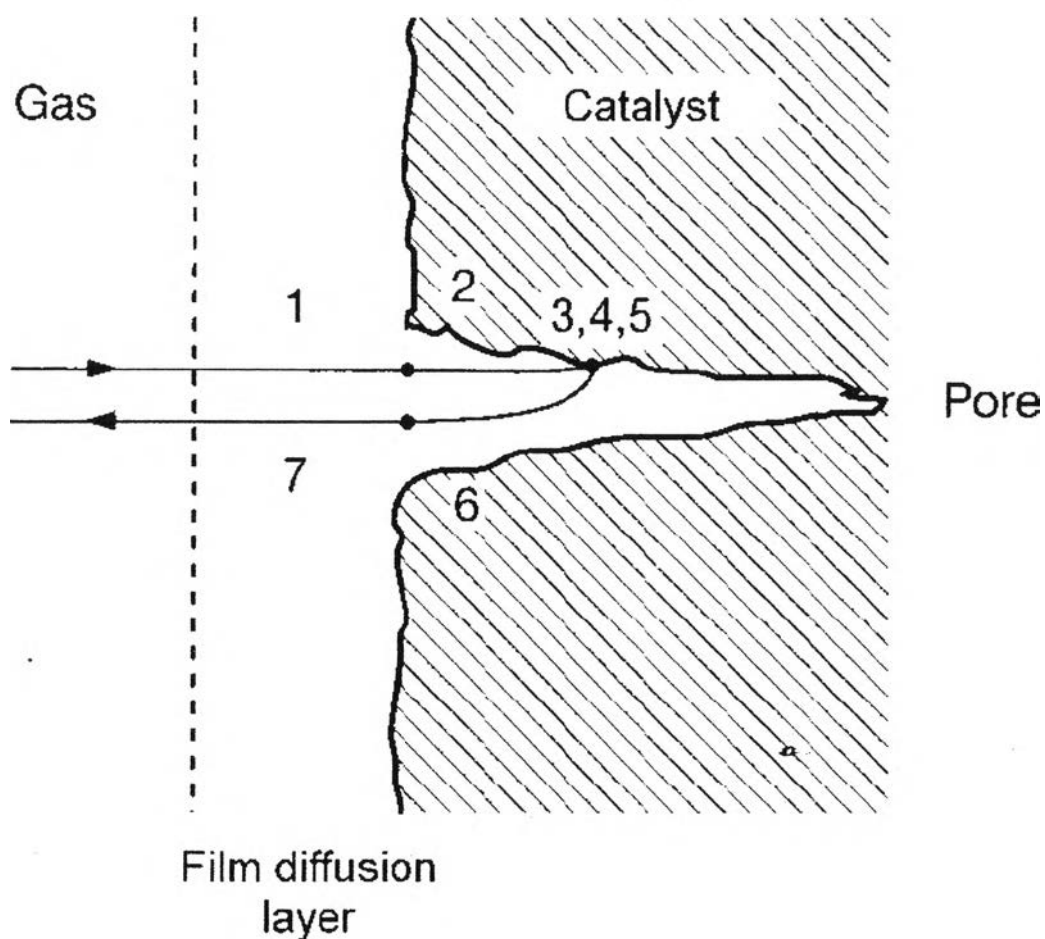
##### 2.4.4.1 Mechanisms of Adsorption in Heterogeneous Catalysis

(Hagen, 2006)

Heterogeneously catalyzed reactions are composed of purely chemical and physical steps. The following seven steps are simple case of catalytic gas reaction on zeolites (Figure 2.9):

- 1) Diffusion of the starting materials through the boundary layer to the catalyst surface.
- 2) Diffusion of the starting materials into the pores (pore diffusion).
- 3) Adsorption of the reactants on the inner surface of the pores.

- 4) Chemical reaction on the catalyst surface.
- 5) Desorption of the products from the catalyst surface.
- 6) Diffusion of the products out of the pores.
- 7) Diffusion of the products away from the catalyst through the boundary layer and into the gas phase.



**Figure 2.9** Individual steps of a heterogeneously catalyzed gas-phased reaction (Hagen, 2006).

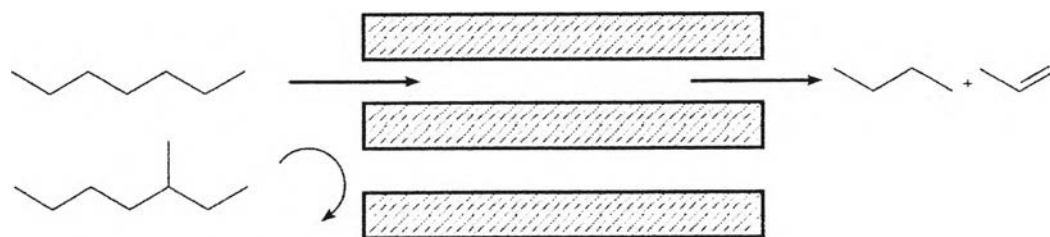
The shape selectivity of zeolites relate to step 2, 4 and/or 6. A distinction can be classified in three variants:

- Reactant selectivity
- Product selectivity
- Restricted transition state selectivity



#### 2.4.4.2 Reactant Selectivity

Reactant selectivity is the case that starting materials can diffuse into the interior of the zeolite pores and then attach to the active sites located inside the pores. In the case of the reactant molecule with a smaller kinetic diameter than the pore size of zeolite can penetrate into the pore.



**Figure 2.10** Reactant selectivity: cleavage of hydrocarbons (Hagen, 2006).

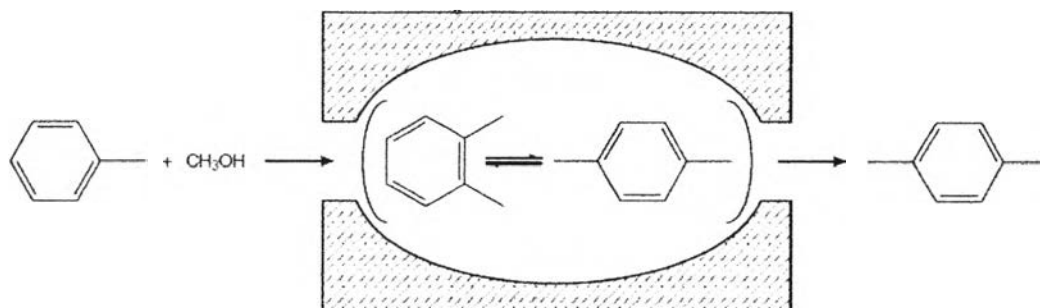
**Table 2.5** Molecular diameters and pore sizes of zeolites (Hagen, 2006)

He	0.25	KA	0.3
NH <sub>3</sub>	0.26	LiA	0.40
H <sub>2</sub> O	0.28	NaA	0.41
N <sub>2</sub> , SO <sub>2</sub>	0.36	CaA	0.50
Propane	0.43	Erionite	0.38 × 0.52
<i>n</i> -Hexane	0.49	ZSM-5	0.54 × 0.56/0.51 × 0.55
Isobutane	0.50	ZSM-12	0.57 × 0.69
Benzene	0.53	CaX	0.69
<i>p</i> -Xylene	0.57	Mordenite	0.67–0.70
CCl <sub>4</sub>	0.59	NaX	0.74
Cyclohexane	0.62	AlPO-5	0.80
<i>o</i> -, <i>m</i> -Xylene	0.63	VPI-5	1.20
Mesitylene	0.77		
(C <sub>4</sub> H <sub>9</sub> ) <sub>3</sub> N	0.81		

#### 2.4.4.3 Product Selectivity

Product selectivity associate to the cavity size of a zeolite, only products of a certain size and shape that can exit from the pore system are formed. This can be explained by the fact that smaller kinetic diameter molecule has a rate of diffusion faster than the larger molecule. This form of shape selectivity can

also have disadvantages. Large molecules that are unable to leave the pores can be converted to undesired side products or undergo coking, deactivating the catalyst (Hagen, 2006).

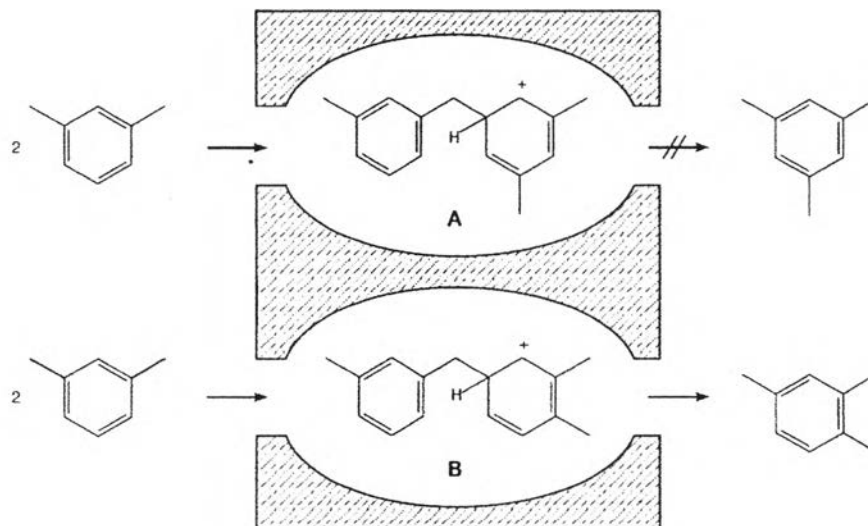


**Figure 2.11** Product selectivity: methylation of toluene (Hagen, 2006).

#### 2.4.4.4 Restricted Transition State Selectivity

Transition state selectivity depends on the fact that the chemical reactions usually undergo via intermediates. Due to the pore system, only those intermediates which have a suitable geometrical fit in the cage of zeolite can be formed during catalysis reaction.

For example, disproportionation of *m*-xylene to toluene and trimethyl-benzenes in the wide-pored zeolite Y. In the zeolite cavity, bulky diphenylmethane carbenium ion transition states can be formed as precursors for methyl group rearrangement, whereby the less bulky carbenium ion B is favored. Thus the reaction product consists mainly of the unsymmetrical 1,2,4-trimethylbenzene rather than mesitylene (case A).



**Figure 2.12** Transition state selectivity of disproportionation of *m*-xylene (Hagen, 2006).

#### 2.4.5 Modification of Zeolites

Aromatization of Dimethyl Ether (DME) over Zn/H-ZSM-5 catalyst was studied in 2010 by Yiwen and co-worker. The result shown that loading small amount of Zn on H-ZSM-5 catalyst, DME can be effectively converted into aromatics and a high selectivity for C<sub>8</sub> aromatics.

Conversion of alcohols to aromatics on ZSM-5 zeolite was studied in 1984 by Vasant and co-worker. They found that, as Si/Al ratio is decreased, the conversions of ethanol and methanol to aromatics are increased due to an increase in acid sites, which are involved in the aromatization reactions. For the aromatics products distribution, in case of methanol conversion, the concentration of xylene in aromatics passes through a minimum at Si/Al ratio of 17.2, benzene and A<sub>9+</sub> are increased, ethylbenzene is decreased and toluene is not significantly affected. In case of ethanol conversion, there is not significant variation in concentrations of benzene and xylenes but the concentration of ethylbenzene and A<sub>9+</sub> are decreased and that of toluene is increased.

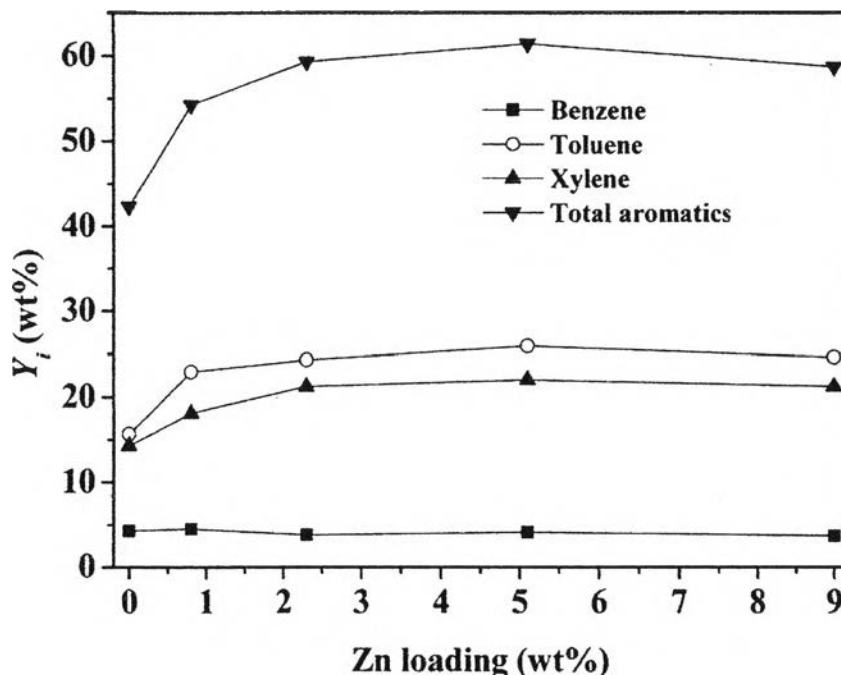
The influence of degree of cation exchange was also studied, when the degree of H<sup>+</sup> exchange is increased from 0.5 to 1.0 in both the methanol and ethanol conversions, the concentration of xylenes in the total aromatics passes through

maximum, the concentrations of benzene and toluene increase, and that of ethyl benzene and C<sub>9+</sub> aromatics decrease. These results indicated that the distribution of aromatics is controlled to some extent by secondary reactions, particularly by dealkylation reaction. The concentrations of benzene and toluene in aromatics increase and that of ethyl benzene and C<sub>9+</sub> aromatics decrease due to an increase in the rate of dealkylation because of the increase in the strong acid sites accompanying the increase in the degree of H<sup>+</sup> exchange.

In 1998, Vasant and his co-worker investigated the influence of zeolite factors affecting zeolitic acidity on the propane aromatization activity and selectivity of Ga/H-ZSM-5. They found that the acidity of Ga/H-ZSM-5 catalyst is strongly influenced by its Si/Al ratio and degree of H<sup>+</sup> exchange and calcination temperature. When Si/Al was decreased, the acidity was increased. For the zeolite catalyst with higher Ga loading, but lower in acidity, the propane conversion/aromatization activity was higher. Concisely, for optimum performance in the propane aromatization there should be a proper balance between the acidity and Ga loading.

In 1992, Saha and Sivasanker investigate the influence of Zn and Ga doping on the conversion of ethanol to hydrocarbons over ZSM-5 (82). The result indicated that incorporation of Zn and Ga not only increases the yield of the liquid products, but also increases the life of catalyst. Moreover, H-transfer reaction increase when Zn and Ga are incorporated in H-ZSM-5 due to the lower olefin product of Zn and Ga doping catalysts.

Lili and co-worker investigated transformation of isobutyl alcohol to aromatics over zeolite-based catalysts in 2012. To convert isobutyl alcohol, ZSM-5 zeolites gave higher aromatics yields (~42 wt%) than other zeolites catalyst. The aromatization could be enhance by supported several metal species (Zn, Ga, Mo, La, Ni, Ag, and Pt) on the ZSM-5. The aromatics yield was improved (~60 wt%) only on the Zn/ZSM-5 (5.1%) catalysts (Figure 2.13). The incorporation of Zn species preferentially decreased the strong-strength Brønsted acidity and suppressed the cracking to C<sub>3</sub> fragments. Thus, the Zn/ZSM-5 catalysts promote the formation of toluene and xylene and inhibit the generation of undesired propane and butane isomers.



**Figure 2.13** Product distributions as a function of Zn loading. Reaction conditions: 0.1 MPa, 450 °C, WHSV 3.88 h<sup>-1</sup>, time on stream = 3 h.

Trung and co-worker studied the conversion of glycerol to alkyl-aromatics over zeolites in 2010. They found that the pore structure of the zeolite plays an important role on the final product distribution. The major products over one-dimensional zeolites Mordenite and HZSM-22 were oxygenates (propenal, acetol, and heavy oxygenates) without formation of aromatic. HZSM-22 was suitable for the production of acrolein with 86% yield at 100% glycerol conversion. However, Trung also found that HY and HZSM-5 could convert glycerol to alkyl-aromatics with high yields, mainly C<sub>8</sub> – C<sub>10</sub>. For long contact time, higher temperatures, and higher pressures were the conditions that favor the formation of aromatics, with maximum yield of 60% over HZSM-5.

In 2002, Louis and Mike investigated the light alkanes aromatization to BTX over Zn-ZSM-5 catalysts enhancements in BTX selectivity by means of a second transition metal ion. The result shown that the selectivity obtain in the aromatization of propane over Zn-ZSM-5 based catalysts (Si/Al = 35) increased from 75-80% to over 91% where iron ions has been introduced by solid state ion exchange

(SSIE) method.

Dung and co-worker studied selective formation of *para*-xylene over H-ZSM-5 (70) coated with polycrystalline silicalite crystals in 2006. They used H-ZSM-5 (70) coat with polycrystalline silicalite-1 layers by a repeated hydrothermal synthesis. For this technique inhibiting the isomerization from *p*-xylene to the other xylene isomers near the external surface of ZSM-5. The silicalite coating significantly enhanced *para*-xylene selectivity up to 99.9% and also prevented catalyst deactivation too.

**Table 2.6** The alkylation of toluene with methanol over H-ZSM-5 (70) and silicalite/H-ZSM-5 (70)

	Silicalite/H-ZSM-5(70)	H-ZSM-5(70)
Conversion of toluene (%)	49.9	53.7
Product composition (%)		
Benzene	D.L.	0.2
<i>p</i> -Xylene	46.1	23.9
<i>m</i> -Xylene	D.L.	16.3
<i>o</i> -Xylene	D.L.	7.5
Ethyl toluenes	3.7	0.6
Trimethyl benzenes	0.1	4.1
Fraction of xylenes (%)		
<i>p</i> -Xylene	99.9	50.1
<i>m</i> -Xylene	<0.05	34.2
<i>o</i> -Xylene	<0.05	15.7