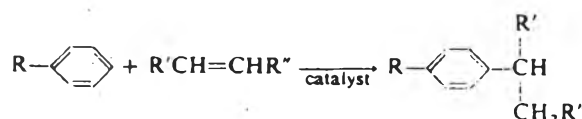# CHAPTER II
LITERATURE REVIEW

2.1 Alkylation of aromatics

The catalytic alkylation of aromatic hydrocarbon is a substitution reaction wherein one or more of the hydrogen atoms on the ring or side chain is replaced by an alkyl group. Both substituted and unsubstituted aromatic structures may be so call alkylated. In general, the following reaction occurs :


Figure 2.1 Alkylation of aromatic reaction. (Mcketta, 1993)

These reactions can occur through electrophilic (acid-catalyzed), nucleophilic (base-catalyzed), or free radical mechanism. The catalyst used dictates the mechanism by which the reactions occur (Mcketta, 1993).
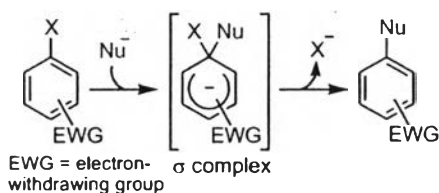
2.1.1 Electrophilic Substitutions

The most common reaction of benzene is electrophilic substitution. The typical benzene reaction has the benzene ring serving as a source of electrons, as nucleophiles. The reaction mechanism is two steps. The first step is the attack of an electrophile, E+, forming a carbocation intermediate with the aromatic ring and simultaneously destroying the aromaticity of the ring. In this structure, the positive charge is delocalized over the molecule by resonance, making this ion more stable than an ion with a localized positive charge. During the second step a proton leaves, aromaticity is regained, and the final product is formed. The rate limiting step for an electrophilic aromatic substitution is the addition of the electrophile to the aromatic ring.
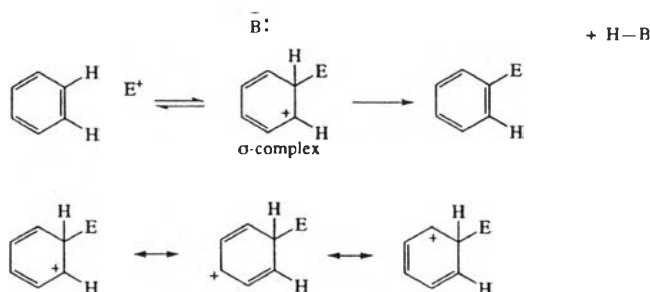
Figure 2.2 The electrophilic aromatic substitution reaction.
(http://classes.uleth.ca/200201/chem2600a/notesch12.pdf)

2.1.2 Nucleophilic Substitutions

Benzene usually undergoes substitution by electrophilic attack. However in some cases, nucleophilic attack is possible. The mechanism involves an electron rich nucleophile attack on the aromatic ring to give a resonance stabilized carbanion. The leaving group, such as a halide (X) on an aromatic ring, then departs to restore the aromaticity. Strong resonance electron withdrawing groups usually must be present in the ortho or para positions to stabilize the carbanion intermediate.


EWG = electron-withdrawing group   σ complex

Figure 2.3 The example of nucleophilic substitution.
(http://en.wikipedia.org/wiki/Nucleophilic_aromatic_substitution)

2.2 Alkylation catalysts

In former days the processes of aromatics alkylation have been mainly carried out in the presence of homogeneous Lewis acid catalysts such as $AlCl_3$, $FeCl_3$, and BF_3. The well-known drawbacks of such homogeneously catalyzed processes have to be overcome by applying heterogeneous catalysis. In this respect, the discov-

ery of the shape selective acidic ZSM-5 zeolite and the development of the Mobil-Badger process for the production of ethylbenzene from benzene and ethylene have been the base for breakthrough technology in the field of aromatic alkylation reactions using solid acid catalysts (Tanabe *et al.*, 1999).

Homogeneous alkylation catalysts may be Brönsted acids such as HF and H_2SO_4. Using alkenes as alkylating agents, a proton is donated by the acid to substrate.

$$H_2C{=}CH{-}CH_3 \xrightleftharpoons{HF} H_3C{-}\overset{+}{C}H{-}CH_3 \quad F^-$$
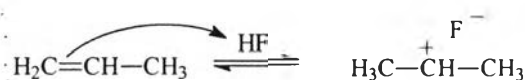
Figure 2.4 The formation of carbocation by using alkenes. (Wade, 2009)

When alkenes are treated with a Lewis acid such as $AlCl_3$, a small amount of a proton acid is normally added as a co-catalyst to promote the formation of carbocation.

If alcohols are the alkylating agents in the presence of Brönsted acids, they are protonated and carbocations may be formed.

$$ROH + H^+ \leftrightarrow \left[RO^+H_2\right] \leftrightarrow R^+ + H_2O$$
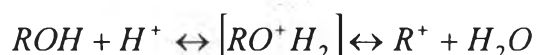
In presence of Lewid acids, such as $AlCl_3$, a complex is first formed with the alcohol and HCl is released. The complex then donates the carbocations.

$$ROH + AlCl_3 \rightarrow ROAlCl_2 + HCl$$

$$ROAlCl_2 \leftrightarrow R^+ + {}^-OAlCl_2$$
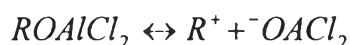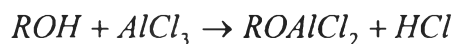
Sridevi *et al.* (2001) studied the alkylation of benzene with ethanol on $AlCl_3$ impregnated 13X zeolite to determine the kinetics of benzene alkylation, to develop a kinetic model, and to estimate the unknown parameters of the kinetic model so as to obtain an intrinsic rate expression. The experiments carried out with different amounts of $AlCl_3$ gave maximum benzene conversion with catalyst con-

taining 15% $AlCl_3$. Moreover, the results indicated no deactivation of $AlCl_3$ by hydrolysis with water generated by the reaction.

Alkyl halide has been extensively used to alkylate aromatic compounds. When $AlCl_3$ is used as the catalyst, the reaction is normally referred to as Friedel-Crafts reaction.
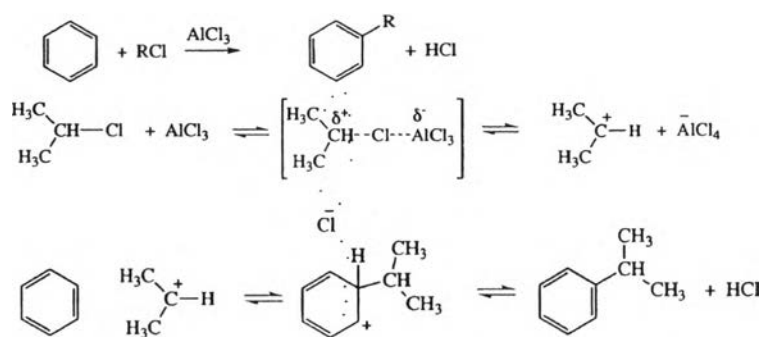
Figure 2.5 The Friedel-Crafts reaction.
(http://classes.uleth.ca/200201/chem2600a/notesch12.pdf)

In this mechanism an alkyl halide with aluminum chloride formed the intermediate carbocation, an activated electrophile, which subsequently attacked the aromatic ring. Other sources of carbocations are alcohols, esters, ethers and olefins (Mcketta, 1993).

However, The Friedel-Crafts alkylation has some limitations. The product of this alkylation is more reactive than benzene, so polyalkylation can occur. Moreover, Carbocation rearrangement can occur. Thus primary alkyl chlorides typically give secondary alkylbenzenes as the major product. The Friedel-Crafts alkylation is not a suitable way to make primary alkyl-substituted benzene derivatives.

Alkylation with heterogeneous catalysts has been carried out using a variety of acidic oxides such as Al_2O_3 and Al_2O_3/SiO_2. These catalysts also promote carbonium ion typed reactions. Depending the method of preparation, silica/alumina catalysts may be amorphous or crystalline. These compounds have both Brönsted and Lewis acid sites. When alkylating benzene with ethylene, on a zeolite catalyst for

example, adsorbed ethylene is protonated at a Brönsted acid site on the catalyst surface forming an ethylcarbonium ion.

$$Zeol - O^- H^+ + CH_2 = CH_2 \rightarrow CH_3 - CH_2^+ + Zeol - O^- \quad (4)$$
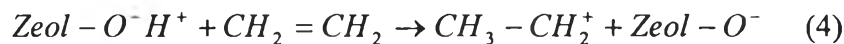
The carbocation then attacks the benzene ring giving ethylbenzene and the proton is regained by zeolite.
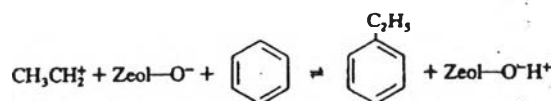
Figure 2.6 The carbocation attacks the benzene ring. (Matar *et al.*, 1989)

Zeolites were found to be more suitable alkylation catalysts than the amorphous types because of their activities and selectivity toward certain reactions. (Matar *et al.*, 1989)

Zeolites and related microporous molecular sieves consist of a three-dimensional network of metal–oxygen tetrahedra (in a few cases also octahedra) which provide the periodically sized microporous structure. Zeolites can be synthesis by using sodium aluminate, sodium silicate, or sodium hydroxide solutions. Reactants and synthesis parameters, such as temperature, time, and pH, determine the particular zeolite formed. The templating ion is especially critical. Usually an organic cation surrounded by an aluminosilicate lattice forms the templating ion. The main zeolite formula is $M_{x/n}[(AlO_2)_x(SiO_2)_y].zH_2O$, where M represents the metal cation and n is the oxidation number of the cation, and a general structure of tetrahedral building units form ring structures and polyhedral. Zeolite catalysts are strongly desired because of their high density of active acid sites, hydrothermal stability, and high size selectivity.

Acid sites result from the imbalance of the metal and the oxygen formal charge in the primary building unit. This can easily be recognized in the case of zeolites, which consist of a three-dimensional network of Si–O tetrahedral. A lattice

comprising of only Si–O tetrahedral is neutral (the 4^+ charge at the silicon is balanced by four oxygen atoms with each 2^- charge, however, belonging to two tetrahedral). Replacing one Si^{4+} atom by Al^{3+} causes a formal charge on the tetrahedron of 1^-. This negative charge is then balanced by a proton or metal cation forming an acid site. The bare, negatively charged tetrahedron is then the corresponding base.

In $AlPO_4$ type microporous materials the framework structure consists of a strictly alternating Al–O–P sequence (Al^{3+} and P^{5+}, balanced by four oxygen atoms with each 2^-charge, however, belonging to two tetrahedral), resulting in a completely neutral lattice as well, like in the case of pure silica zeolites. Depending on the combinations of the metal cation in the lattice, frameworks with positive or negative charges are in principal possible; however, so far only cation exchanged microporous materials are known. Vijayaraghavan *et al.* (2004) studied the activity of large pore $AlPO_4$-5 molecular sieves substituted with Mg, Mn and Zn in the vapor-phase ethylation of benzene with ethanol. They found that MAPO-5, ZAPO-5 and MnAPO-5 give higher conversion than $AlPO_4$-5 due to isomorphous substitution of metal in the frame work of the catalyst. Among the catalyst, MnAPO-5 is more active than others because of the presence of unpaired electrons in the d-subshell.

An important property relating to the activity of zeolites is their acidity. The activity requested is based on the formation of Brönsted acid sites arising from the creation of "bridging hydroxyl groups" within the pore structure of the zeolites. These "bridging hydroxyl groups" are usually formed either by ammonium or polyvalent cation exchange followed by a calcinations step. The "bridging hydroxyl groups", which are protons associated with negatively charged framework oxygens linked into alumina tetrahedra, are the Brönsted acid sites, as shown in Figure 2.7.
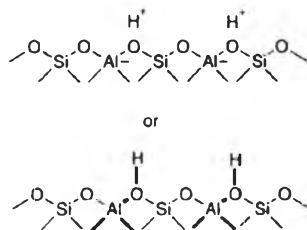
Figure 2.7 Brönsted acid sites ("bridging hydroxyl groups") in zeolites. (Stocker, 2005)

The protons are quite mobile at higher temperatures, and at 550°C they are lost as water molecules followed by the formation of Lewis acid sites, as shown in Figure 2.8. For zeolites, it can be stated that the concentration of aluminum in the lattice is directly proportional to the concentration of acid sites (Stocker, 2005).
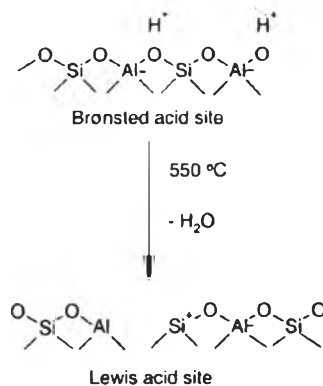
Figure 2.8 Formation of Lewis acid sites in zeolites. (Stocker, 2005)

2.2.1 ZSM-5

ZSM-5, Zeolite Sieve of Molecular porosity – 5 developed by Mobil oil, is an aluminosilicate zeolite which chemical formula is $Na_nAl_nSi_{96-n}O_{192} \cdot 16H_2O$ ($0<n<27$). In ZSM-5, the tetrahedral are linked to form the chain type building block. The chain can be connected to form a layer (Gates, 1992). ZSM-5 is composed of several pentasil units linked together by oxygen bridges to form pentasil chains. A pentasil unit consists of five oxygen atom in this structure. The

pentasil chains are interconnected by oxygen bridges to form 10-membered oxygen ring. These are importance because they provide openings in the structure large enough for passage of even rather large molecules (Gates, 1992). ZSM-5 is a highly porous material and throughout its structure it has an intersecting two-dimensional pore structure. The pore structure is shown in figure 2.9. There is a set of straight, parallel pores intersected by a set of perpendicular zigzag pore (Gates, 1992).
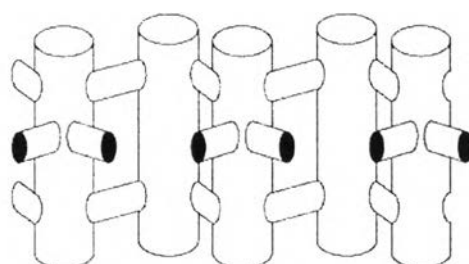
Figure 2.9 The pore structure of ZSM-5

(http://chemelab.ucsd.edu/methanol/memos/ZSM-5.html)

The aluminium sites in ZSM-5 are very acidic. The substitution of Al_3^+ in the place of the tetrahedral Si_4^+ silica requires the addition of positive charge. When H^+ is the positive charge, the acidity of the zeolite is very high. The reaction and catalysis chemistry of the ZSM-5 is due to this acidity. It is a shape-selective catalyst with remarkable catalytic properties and high thermal stability. The ZSM-5 zeolite catalyst is wildly used in the petroleum and petrochemical industry for hydrocarbon isomerization and alkylation of hydrocarbon.

Li *et al.* (2009) studied the catalytic synthesis of ethylbenzene by alkylation of benzene with diethyl carbonate over HZSM-5 with Si/Al ratios from 50 to 250. The results showed that the selectivity for p-DEB increases when the Si/Al ⬚ electives. They concluded that the isomerization of p-DEB is suppresses due to the absence of strong acid sites. Moreover, toluene obtained by the cracking of ethylbenzene decreases when Si/Al increases. They suggested that acidic sites that cata-

lyze the EB cracking reaction are stronger than those that catalyze benzene mono-alkylation reactions.

Sun *et al.* (2009) studied some post-treatment effects, including hydrothermal treatment, calcination and La_2O_3 modification, on the catalytic performance of a nanoscale HZSM-5 zeolite for ethylation of coking benzene with ethylene and ethanol. This study indicates that these post-treatments of the catalyst reduce both the total number of acid sites and the B/L ratio due to dealumination and transformation of framework Al, and change pore structure from the single micropores to the coexistence of micropores and large micropores. The decrease in the acidity, especial the Brönsted acidity, suppress the carbon deposit formation resulting in the improvement of catalytic stability. The results showed that La-C-HT-HZSM-5 exhibited higher stability in the ethylation of coking benzene under industrial reaction conditions with the coking benzene conversion of 14.5% and the total ethylbenzene selectivity of 98.8%.

Some zeolites are highly selective catalysts, and this has been correlated with the ability of the molecules to diffuse into, and the ability of the product molecules to diffuse out of the supercage, where is the locus of the catalytic activity of zeolite catalysts (Matar *et al.*, 1989). Raj *et al.* (2006) studied the para selectivity compared to meta and ortho in the vapor and liquid phase alkylation of various reactions over MnAPO-5 and MnAPO-11. They indicated the distribution of the reaction products for para, meta and ortho isomers is strongly influenced by the channel geometry and the transport of individual isomers into channel structure. From the results, the para isomer shows the greatest selectivity. The critical diameter of para isomer is smaller than meta so the para isomer diffuse out of the pore faster.

Another factor that affects the catalytic activity of zeolites is the type of cations on zeolites. The metal exchange into the HZSM-5 catalysts, using NaZSM-5, CoZSM-5, and CuZSM-5, for the methylation of benzene with methanol was observed by Adebajo *et al.* (2000). The results showed that the conversion and selectivity to toluene are higher when these catalysts were used at low temperature (250-350°C). Gao *et al.* (2009) investigated the catalytic activity in the vapor phase alkylation of benzene with ethanol by using ZSM-5 prepared by adding zinc salt into

the gel precursor. They indicated that zinc salt had great effect on ZSM-5 catalyst and the zinc containing catalysts showed higher ethylbenzene selectivity.

Romannicov *et al.* (1994) indicated that ZSM-5, small pore zeolite, promotes the formation mainly of para isomer products while wide-pore beta zeolite contains all three isomer products (para, meta and ortho). The ratios among them depend on the ratios of partial substitution rates.

Raimondo *et al.* (1997) studied the influence of the acidity and the pore dimension of a range of mid-pore zeolites using H-ZSM-5, mordenite, USY, Theta-1, BP-PILC and ATOS on the yield and selectivity of the products of benzene alkylation using methanol, ethanol, butanol, isopropanol and octanol as akylating agents. They stated that the catalytic reactivity and selectivity of a solid acid depends not only on the physicochemical properties of the active sites but also on the dimensions and shape of the pores. From the experiments, the pore dimension plays an important role than acidity. Thus, H-ZSM-5 shows the higher activity because its small pore size allows formation of a bulky intermediate which would result from the electrophilic attack of this charged species at the benzene ring.

2.3 Production of benzene derivatives

Benzene is not only the most important aromatic raw material in term of quantity, but it is also the most versatile from the viewpoint of its uses.

The major industrial products from benzene are alkylated derivatives such as ethylbenzene and cumene, which are used as basic materials for the production of styrene and phenol, and long-chain alkyl benzenes which are used as feedstock in the manufacture of surfactants (Frank H.G. and Stadelhofer J.W., 1988).

2.3.1 Ethylbenzene

Ethylbenzene is used almost exclusively as an intermediate in the production of styrene monomer. Almost all ethylbenzene is produced by liquid phase or vapor phase alkylation of benzene with ethylene. Lukyanov *et al.* (2008) study the alkylation of benzene with ethane into ethylbenzene over PtH-MFI bifunctional catalyst. They reported that the side reactions took place to compete ethylben-

zene formation. The main side reactions included ethylbenzene hydrogenolysis to toluene, further alkylation of ethylbenzene into diethylbenzene, and cyclization of alkylbenzene to naphthalene.

2.3.1.1 Traditional process

In the traditional process, developed in the 1930s, the alkylation is performed reacting benzene and ethylene in the presence of a Friedel–Crafts catalyst ,including $AlCl_3$–HCl, $AlBr_3$ and $FeCl_3$, at mild conditions (T = 160°C). Several companies have developed variations of this technology. Processes currently in use include those of Dow chemical, BASF, shell chemical, Monsanto, *societe chimique des cahrbonnages*, and union carbide/ badger. The Monsanto process is currently the most modern commercially licensed aluminum chloride alkylation technology. The ethylbenzene produced by benzene alkylation, may undergo polyalkylation to di- and other polyethylbenzenes, according to the reactions depicted in figure 2.10. The reaction is highly exothermic with a reaction enthalpy of -114 kJ/mol. The kinetic studied of benzene ethylation with ethanol over ZSM-5 catalysts in a fluidized-bed reactor was investigated by Odedairo *et al.* (2010). They observed that alkylation of benzene is the primary reaction that produced ethylbenzene. While, the secondary ethylation reaction produced diethylbenzene. The apparent activation energy of benzene ethylation was found to be higher than the value of ehylbenzene ethylation.
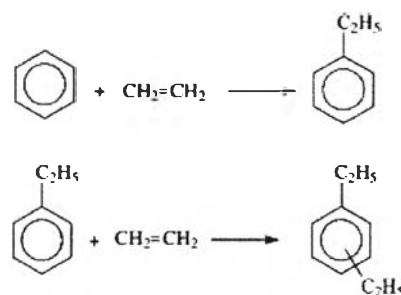
Figure 2.10 The benzene alkylation and poly alkylation. (Perego *et al.,* 2002)

After the product separation, the polyethylbenzenes are recycled back to the alkylation reactor. Here, polyethylbenzenes transalkylation takes place till the thermodynamic equilibrium is reached as shown in figure 2.11.
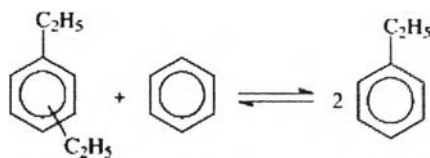
**Figure 2.11** The polyethylbenzenes transalkylation. (Perego *et al.*, 2002)

The final composition depends on the overall ethylene/benzene molar ratio. The reaction is performed in the liquid phase and the process is carried out in enameled or glass lined reactors because of the corrosive effect of the catalyst. As a possible solution to the corrosion problems, supported catalysts have been proposed in the 1960s by UOP for liquid phase (BF_3/Al_2O_3 in the Alkar^{TM} process) and gas-phase (Kieselguhr supported phosphoric acid (SPA)) operations. However, due to partial release of the acids, corrosion problems were not completely avoided. Besides, these catalysts are not active in the polyethylbenzenes transalkylation and cannot be regenerated. For these reasons such processes did not obtain large industrial interest (Perego *et al.*, 2002).

2.3.1.2 Mobil–Badger ethylbenzene process

First introduced in 1980, the Mobil–Badger vapor phase process is still the most widely used zeolite catalyzed ethylbenzene manufacturing process. Since its initial commercial application in 1981, over 35 units have been licensed with a total annual capacity of nearly 8 million metric tons. In the Mobil–Badger process, benzene is alkylated in a fixed-bed reactor with ethylene in the gas phase using a ZSM-5 based catalyst. Figure 2.12 is a simplified process flow diagram of the first generation Mobil–Badger process. Fresh and recycled benzene is combined with a diethylbenzene-rich recycle stream and fed, together with fresh ethylene, to an alkylation reactor. The process operates with a B:E ratio of 5-20 (M) at temperatures ranging from 370 to 420°C and pressures ranging from 0.69 to 2.76MPa (6.8–27.2 bar). WHSV, based on fresh feed, range from 300 to 400 hr^{-1}. The process has an overall ethylbenzene yield of at least 99.0%. Together with the Badger Technology Center of Raytheon Engineers & Constructors, Mobil introduced second and third generation processes in 1986 and 1991. These next genera-

tion processes provided improved cycle lengths and higher yields. Cycle lengths improved from 60 days to more than 1 year, and yields improved to greater than 99.5%. Selectivity losses to both heavy aromatics and xylenes dropped by more than 50%. The energy efficiency of the Mobil–Badger process is reported to be high. Essentially, all of the exothermic heat of reaction is recovered.

The Mobil–Badger process has also been modified to use dilute ethylene from FCC off-gas streams as a feedstock. The dilute ethylene process was first commercialized at Shell's Stanlow UK refinery in 1991 and has been in continuous use ever since.
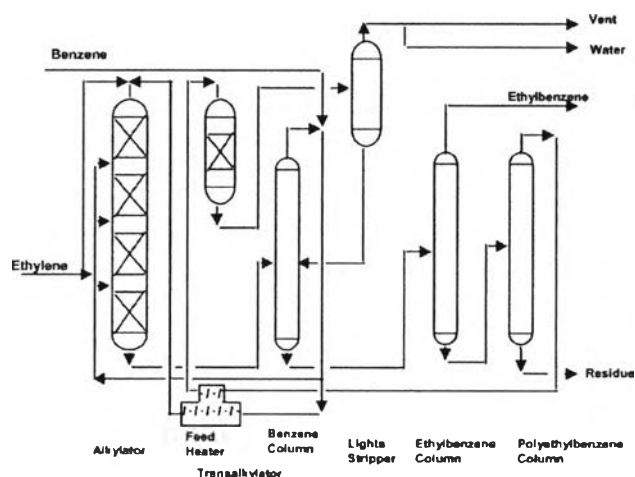
Figure 2.12 The Mobil–Badger vapor-phase ethylbenzene process. (Degnan Jr. *et al.*, 2001).

2.3.1.3 Mobil–Badger EBMax process

EBMax is a liquid phase ethylbenzene process that uses Mobil's proprietary MCM-22 zeolite as the catalyst. This process was first commercialized at the Chiba Styrene Monomer Co., Chiba, Japan in 1995. The MCM-22-based catalyst is very stable. Cycle lengths in excess of 3 years have been achieved commercially. The MCM-22 zeolite catalyst is more monoalkylate selective than large pore zeolites including zeolites beta and Y. This allows the process to use low feed ratios of benzene to ethylene. Typical benzene to ethylene ratios are in the range of 3

to 5. The lower benzene to ethylene ratios reduces the benzene circulation rate which improves the efficiency and reduces the throughput of the benzene recovery column. Because the process operates with a reduced benzene circulation rate, plant capacity can be improved without adding distillation capacity. This is an important consideration, since distillation column capacity is a bottleneck in most ethylbenzene process units. The EBMax process operates at low temperatures, and therefore the level of xylenes in the ethylbenzene product is very low, typically less than 10 ppm.

In the EBMax process, benzene is fed to the bottom of the liquid-filled multi-bed reactor. Ethylene is co-fed with the benzene and also between the catalyst beds. Polyethylbenzenes, which are almost exclusively diethylbenzenes, undergo transalkylation with benzene in a second reactor. Mobil–Badger offers both liquid phase and vapor phase transalkylation processes. The vapor phase process removes benzene feed co-boilers such as cyclohexane and methylcyclopentane as well as propyl and butylbenzenes. Because the EBMax process produces very low levels of propyl and butylbenzenes, for most applications, the more energy efficient liquid phase process is preferred. Worldwide, there are currently 10 licensed EBMax units with a cumulative ethylbenzene production capacity of 5 million metric tons per year.

2.3.1.4 Lummus–UOP process

In 1989, Unocal–ABB Lummus Crest introduced a liquid-phase process based on a modified zeolite Y catalyst. The process design is very similar to the Mobil–Badger EBMax process, and uses two reactors, one for benzene alkylation and the other for diethylbenzene transalkylation. The reactors operate at close to the critical temperatures of the reaction mixtures in order to maximize the yield. Reaction temperatures are typically less than 270°C. Operating pressure is approximately 3.8MPa (37 bar). UOP acquired the right to the Unocal patents in this area when it purchased the technology rights in 1997. ABB Lummus Global and UOP now license the process. It is believed that the Lummus–UOP liquid phase ethylbenzene technology has recently shifted to the use of catalysts based on zeolite beta. In 1994, Lummus also acquired worldwide licensing rights to a dilute ethylene-based process developed in China by SINOPEC and the Dalian Institute of Chemical Physics. The process, which is based on a ZSM-5 type zeolite, is currently operating

in a 30,000 metric ton per year unit in China. UOP and Lummus have continued to improve the process, and in 1996 commercialized the new, highly selective EBZ-500™ alkylation catalyst. The performance of the catalyst has been excellent, and its high selectivity has resulted in a significant improvement in yield via a reduction in both alkylation flux oil by-products and amount of transalkylation required. The catalyst is currently being used in 12 commercial units worldwide.

2.3.1.5 CDTech process

The CDTech process uses the company's proprietary catalytic distillation (CD) technology. CDTech is a partnership between ABB Lummus Global and Chemical Research & Licensing. Catalyst Recovery Inc. (CRI), an affiliate of Shell, acquired the right to CDTech's technology when it purchased the company in 1997. CDTech's CD column consists of two sections. The upper section is packed with the required catalysts and the lower section is equipped with distillation trays. Ethylene is fed into the CD column at the bottom of the catalyst bed and benzene is introduced to the top of the column via the reflux drum. The counter-current flow reduces coke formation and limits the production of unwanted byproducts. The catalyst is packed in specially designed bales of steel mesh and fiberglass fabric. These bales are placed in a column similar to structured packings. The CDTech process uses zeolite Y as a catalyst. Figure 2.13 is a schematic description of the reactive distillation unit. Operating temperatures are reportedly lower than the Lummus–UOP process. The product removed from the bottom of the column is a mixture of ethylbenzene and polyethylbenzene. Ethylbenzene is removed in a separate column and the polyethylbenzene is sent to a separate transalkylation reactor. The principal attributes of the CDTech process reportedly are its long catalyst life and high product selectivity. The CDTech technology can process polymer grade ethylene feedstock, FCC offgas, or other dilute ethylene streams with purity as low as 10 mol%. Three world-scale plants based on CDTech technology are currently in operation, with another unit in design.

Vent

Benzene

Catalyst

Bales

Ethylene

Produkt
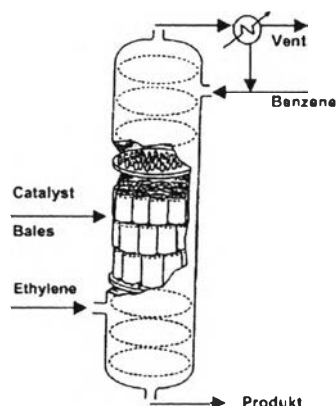
Figure 2.13 Schematic representation of the reactor/distillation column used in the CDTech ethylbenzene process. (Degnan Jr. *et al.,* 2001).

2.3.1.6 Albene process

In 1992, the Indian Petrochemicals Corporation (IPCL) introduced a process that uses dilute ethanol rather than ethylene as the alkylating agent. Ethanol has no distinct advantage over ethylene except that it can be derived from waste streams or from biomass. The process reportedly uses [Fe]ZSM-5 which contains iron instead of aluminium in its framework as the catalyst. The Albene process is operated at 623-673 K, with benzene to ethanol ratio of 4 and WHSV of 6 h^{-1}. Any diethylbenzene formed, was reacted with benzene in a separate reactor to form more ethylbenzene. (Degnan Jr. *et al.,* 2001).