

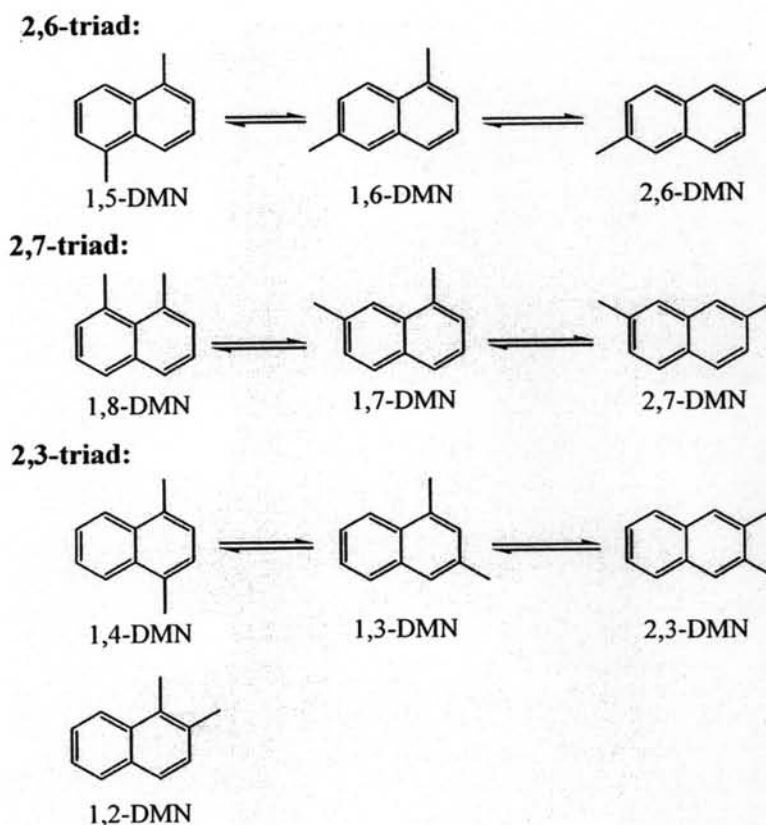
## CHARTER II

### BACKGROUND AND LITERATURE SURVEY

Background information and a literature survey related to 2,6-triad isomerization and purification of dimethylnaphthalene isomers are provided in this part. In addition, the principle of adsorption and the details of zeolite are described. After that, some information about aromatic properties is given. Finally, the details of reactive separation technology are provided.

#### 2.1 2,6-Dimethylnaphthalene Production

Dimethylnaphthalene (DMN) has 10 isomers that can be divided into three groups, each called a triad, with an additional isomer, as shown in Figure 2.1. It is known that the isomerization *within* any one of the triads can readily take place, but that *between* triads is very difficult. This is because of the migrational barriers between the adjacent beta positions, as well as between the two rings of the naphthalene nucleus. These migrational barriers can be described in terms of the stability of the intermediate complexes (Figure 2.2). In both cases the migrations result in a decrease of energy stabilization of the aromatic ring. This knowledge gives us advantages for manufacturing since one high purity isomer is often commercially required (Lillwitz, 2001).



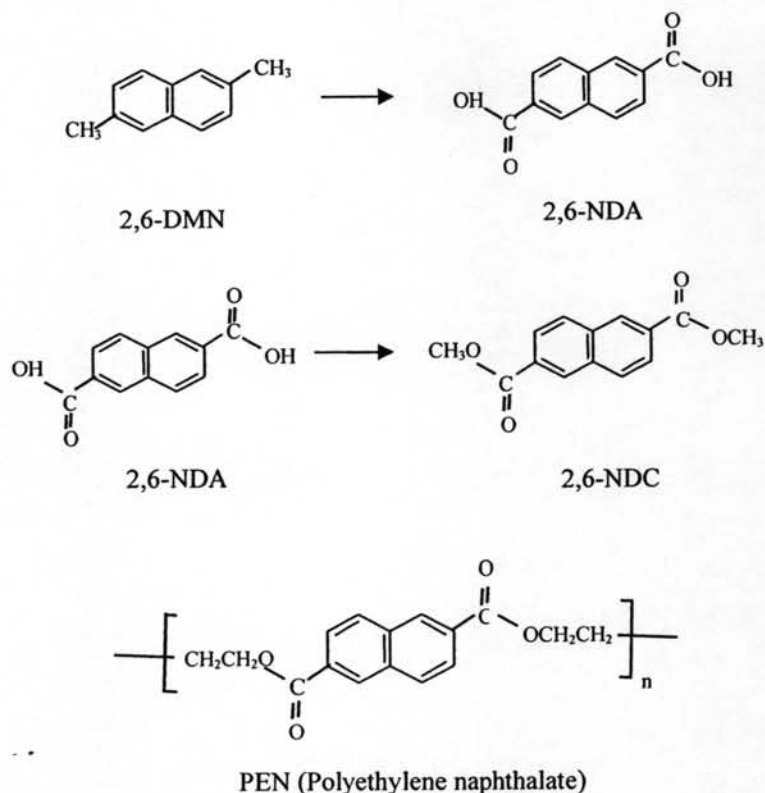
**Figure 2.1** Schematic representing isomerizations among 10 isomers (Lillwitz, 2001).



**Figure 2.2** Schematic representing the intermediate complexes for the isomerization across the triads (Lillwitz, 2001).

One of the most important isomers is 2,6-DMN. It can be further oxidized and esterified to 2,6-naphthalene dicarboxylate (NDC), which co-polymerizes with ethylene glycol to produce polyethylene naphthalate (PEN) and liquid crystal polymer (Figure 2.3). PEN is a high performance polyester with good physical properties in its strength, elasticity, thermal resistance, chemical stability, and its ability to act as a gas barrier. Many expected applications for PEN include film and bottle uses, long-lasting recording-type video film, hot fill containers, refillable bottles, and tire

cords. 2,6-DMN is more favorably used as a PEN monomer than other dialkyl-naphthalenes, such as 2,6 – diethyl- (2,6-DEN) or 2,6-diisopropyl-naphthalene (2,6-DIPN), because no carbon atoms are lost in the oxidation step, and the methyl group is more susceptible to oxidation than the other alkyl groups (Park *et al.*, 2005).

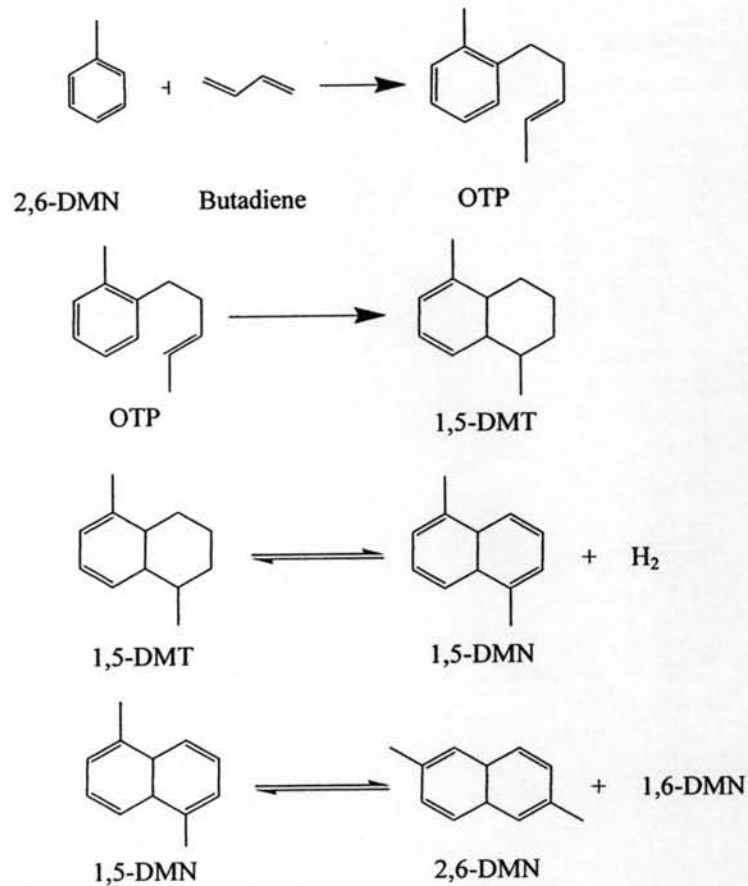


**Figure 2.3** Schematic representing production of polyethylene naphthalate (PEN) (Lillwitz, 2001).

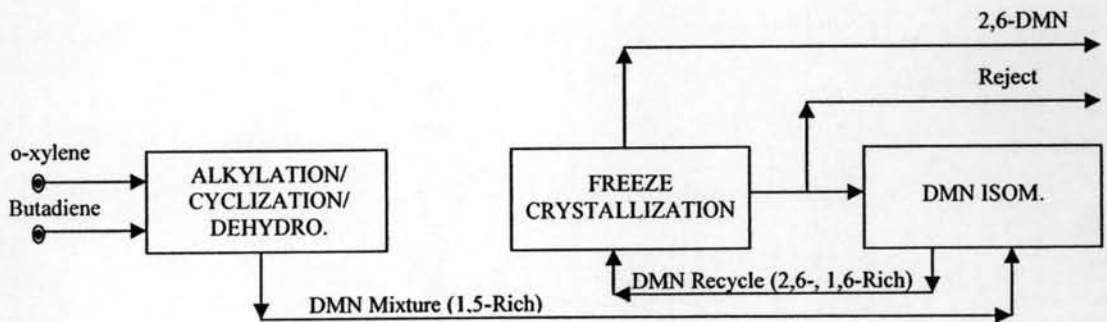
2,6-DMN can be obtained by isolation from tar fraction or petroleum fraction, by alkylation of naphthalene or xylene and by the cyclization of aromatics, i.e. o-xylene, p-xylene with butadiene (Lillwitz, 2001). However, the product stream contains almost all DMN isomers. Typical separation techniques cannot accomplish the high purity requirement because the DMN isomers have properties in common. It is required that 2,6-DMN have very high purity since the other nine isomers reduce PEN physical properties, i.e. thermal resistance and strength. PEN then degrades (Nakao *et al.*, 2004). The main limitation of PEN production comes from the avail-

ability of the 2,6-isomer. In order to avoid this limitation, methods for producing mixtures of isomers consisting essentially of 1,5-, 1,6- and 2,6-DMN, with as little as possible of the other triad isomers, are highly desirable.

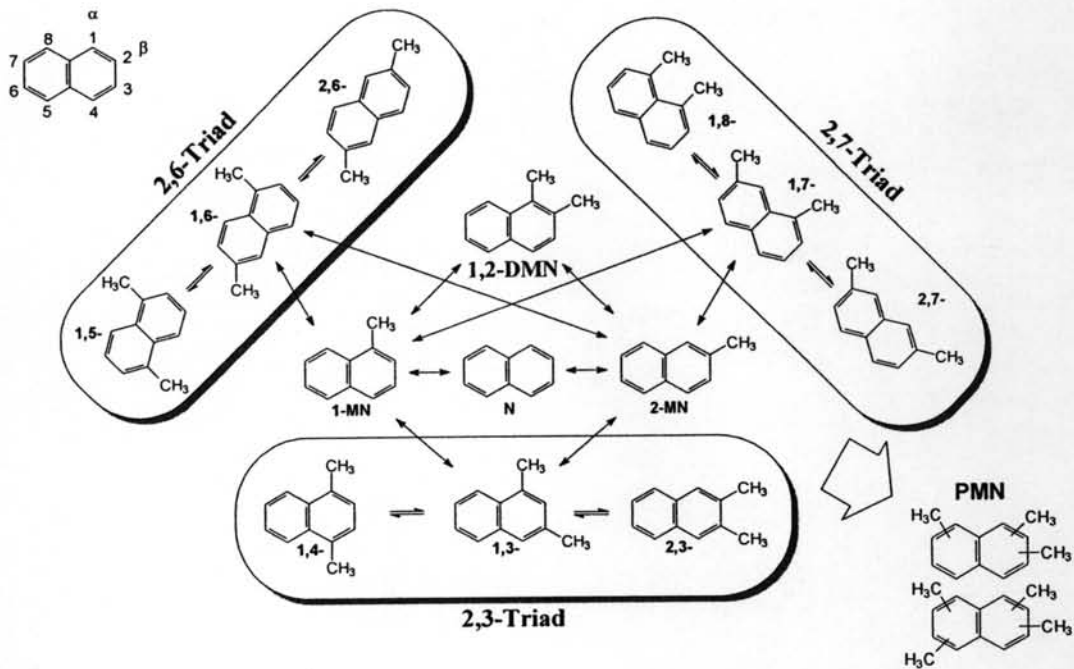
One such method is a multi-step synthesis used by BP Amoco. The company currently has the highest 2,6-NDC production capacity. Its technology is based on the alkenylation of *o*-xylene and butadiene, as shown in Figure 2.4. First, *o*-xylene and butadiene undergo alkenylation in the presence of an alkali metal catalyst to give 5-(*ortho*-tolyl)-pentene-2 (OTP). Then, OTP goes through cyclization over a platinum-and-copper-on-zeolite catalyst to give 1,5-dimethyltetralin (1,5-DMT). 1,5-DMT is dehydrogenated to produce a mixture of 1,5- and 1,6-DMN with the selectivity and conversion percentage as high as 90 or more. Finally, the DMN mixtures are isomerized to achieve a higher 2,6-DMN fraction. Nevertheless, BP Amoco encounters complexities due to the low yield of 2,6-DMN production from the isomerization step. As illustrated in Figure 2.5, another isomerization unit and purification unit are connected downstream in order to increase the production yield. The reason is that this reaction is thermodynamically limited; only 48% 2,6-DMN can be achieved. Also, some side reactions, such as non-2,6-triad isomerization and disproportionation, unavoidably take place, leading to the formation of seven other isomers and undesired hydrocarbons such as monomethylnaphthalene (MMN) and trimethylnaphthalene (TMN) (Figure 2.6). Then, high efficiency purification is still required. For BP Amoco, crystallization is employed (ChemSystems, 2000).



**Figure 2.4** Schematic representing production of 2,6-DMN from o-xylene and butadiene (Lillwitz, 2001).



**Figure 2.5** BP Amoco production route and block diagram (Lillwitz, 2001).



**Figure 2.6** Schematic representing the DMNs isomerizations and side reactions (Kraikul *et al.*, 2005).

Typically, commercial 2,6-DMN production processes have at least the following two-stage design: the isomerization reactor design and the separation unit design, in addition to the synthesis or isolation processes. Isomerization is used for converting DMN isomers into 2,6-DMN. After that, separation is used for recovering 2,6-DMN from unreacted reactants and undesired products. The unconverted reactants are recycled back to the isomerization and utilized to further increase the yield. The isomerization in the 2,6-triad will be explained in this part, and then the separation techniques will follow.

### 2.1.1 2,6-Triad Isomerization

Until now, only a few studies have been conducted on 2,6-triad isomerization; most of them have been distributed as patents. It has been claimed that the reaction can be carried out by means of a batch-wise or flow process either in a liquid or gaseous phase. However, a flow process is usually preferred from the indus-

trial point of view. A liquid phase is also known to be superior to a gaseous phase with regard to the service life of a catalyst, even though the operation in a gaseous phase offers a higher mass transfer (Sikkenga *et al.*, 1990). Takagawa *et al.* (1996a) found that the gaseous phase isomerization of DMN co-fed with a solvent sufficiently proceeded at much lower temperature than the liquid phase isomerization, especially when that solvent has a low boiling point (less than 150°C). It was also found that under a gaseous condition, after only 100 hours, the temperature was required to be increased. This meant that the catalyst performance was rapidly deteriorated. The result substantiated the hypothesis of longer service life of the catalyst when operated in a liquid phase.

To operate under a liquid phase condition, a solvent is sometimes used for enhancing the fluidity of the solid reactant (1,5-DMN). This solvent should be able to dissolve a large quantity of DMN and be stable at the isomerization conditions. Examples of these solvents are n-decane (Virdujin *et al.*, 1992), toluene (Hussmann and McMahon, 1988; Kraikul *et al.*, 2005), and benzene (Maki *et al.*, 1985; Takagawa *et al.*, 1996a). Even so, the preferred condition is suggested to be a solvent-free condition because, with the solvent being fed, the reactor would without a doubt be larger; the load of the downstream process would increase.

Recently, a solvent was found to have another benefit besides increasing the fluidity. Takagawa *et al.* (1996a) found that utilizing a low boiling point hydrocarbon (less than 150°C) as a solvent can bring the system to a gaseous phase isomerization at a lower temperature. There were an aromatic hydrocarbon, a saturated aliphatic hydrocarbon and a saturated alicyclic hydrocarbon employed for testing. A saturated aliphatic hydrocarbon and a saturated alicyclic hydrocarbon were found to promote disproportionation. Accordingly, an aromatic hydrocarbon is preferred. Interestingly, an aromatic hydrocarbon having an alkyl group on its side chain, such as toluene and xylene, was found apt to promote disproportionation. Hence, the most preferred solvent suggested by this work was benzene. The isomerization temperature was 100°C to 200°C, and the 2,6-DMN reached its equilibrium limit with the conversion of 1,5-DMN and yield of 2,6-DMN around 90 and 50, respectively. Nevertheless, when a liquid isomerization was tested with benzene co-fed, in the continuing work of Takagawa *et al.* (1996b), the solvent neither lowered

the reaction temperature nor suppressed the side reactions. The temperature was higher at about 250°C or close to the 2,6-DMN boiling point (260°C), to achieve the same conversion and yield. Moreover, since the solvent is a low boiling point hydrocarbon, the system needed to be pressurized. Then, the inventor claimed the use of a solvent-free condition instead. To avoid pressurization, it was also disclosed that the solvent should boil above 270°C, which can be normal paraffin, such as tetradecane, or an aromatic hydrocarbon, such as anthracene, in order to avoid pressurization (Sikkenga *et al.*, 1990). The reasonable explanation for this result is that a liquid phase has much higher mass transfer resistance. Then, some basic conclusion is that, to improve the liquid phase isomerization process, a higher activity catalyst is considered necessary to account for lower mass transfer in the liquid phase, otherwise the system would be inevitably pressurized and not suitable for the operation.

It is well known that various solid acids are useful as catalysts for the isomerization of aromatic hydrocarbon. The catalysts that have been used for studying 2,6-DMN production from isomerization are supported crystalline borosilicate (Hussmann and McMahon, 1988), MCM-22 (Motoyuki *et al.*, 2000) and ZSM (Maki *et al.*, 1985). For 2,6-triad isomerization, the most widely claimed catalyst is hydrogen-form mordenite (Bakas and Barger, 1988; Barger *et al.*, 1991; Ferino *et al.*, 1996). The effect of the molar ratio of silica to alumina ( $\text{SiO}_2/\text{Al}_2\text{O}_3$ ) has also been tested and found that the increase in the  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio lowered the isomerization temperature. The suitable  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio was claimed to be at least 100 (Takagawa *et al.*, 1996a). Nevertheless, this result shows the opposite when tested with H-BEA. Chen *et al.* (2004) found that the lower  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio provided the higher yield of 2,6-DMN. In any case, the dependency of the acid catalyst to the isomerization can be ensured.

For the liquid phase solvent-free system, there was also a claim for a modified zeolite beta catalyst by BP Amoco (Sikkenga *et al.*, 1990). Recently, work was done to compare the effect from the zeolite framework between H-beta and H-mordenite to the isomerization (Kraikul *et al.*, 2005). It was found that the reaction catalyzed by the H-beta catalyst reached the thermodynamic equilibrium at a temperature around 260°C. Because of the three-dimensional pore structure of \*BEA,



1,5-DMN reactant can diffuse through more rapidly than the one-dimensional pore structure of \*MOR. Then, H-beta is suitable for the reaction.

In the continuing research of Kraikul *et al.* (2006a), toluene was used for studying the effect of solvent on the isomerization catalyzed by H-beta. The result showed that using toluene can lower the temperature needed for the system to reach equilibrium and suppress side product formation under the studied conditions. The isomerization temperature was as low as 180°C for 10 wt% 1,5-DMN. It was also found that major side products were only generated when the temperature was higher than that required for the reaction to reach its equilibrium. Furthermore, the thermodynamics of the isomerization were modified by the presence of toluene, particularly for the first isomerization step from 1,5-DMN to 1,6-DMN. When using the solvent, the endothermicity of the first isomerization step was reduced and the isomerization was driven more toward the formation of 1,6-DMN than to 1,5-DMN. For the second step of isomerization, it appeared that toluene did not significantly affect the reaction thermodynamics. The yield of 2,6-DMN from the reaction was found to slightly increase, compared with that of the solvent-free system. It was believed that the very close dipole moment of 1,6-DMN and toluene resulted in a strong interaction between the two species. The solvation energy releasing from the interaction was claimed to be the major effect in the reduction in the isomerization endothermicity. The author suggested employing the solvent having a dipole moment close to 2,6-DMN dipole moment. Therefore, the second isomerization can be driven to obtain higher 2,6-DMN yield.

### 2.1.2 Purification Technology

The reason for the problem found in DMN separation is their similar properties, as shown in Table 2.1. Obviously, distillation cannot be employed; typical separation techniques for 2,6-DMN recovery are adsorption, crystallization, and adsorption followed by crystallization. Among these methods, crystallization is the simplest one, as utilized in many commercial processes. For instance, BP Amoco and OPTATECH employ freeze crystallization; EXXON MOBIL/KOBE employs pressure crystallization. Nevertheless, because the separation relies on heat removal, the process is very energy intensive. On the contrary, adsorption, a separation that uses

the difference in the affinity of each component toward the adsorbent, has drawn the attention of researchers to find an effective way for utilizing adsorption for 2,6-DMN production. The kinetic diameters shown in Table 2.1 imply the possibility for successful adsorption if the suitable coupling of an adsorbent and desorbent is found (ChemSystems, 2000).

**Table 2.1** Properties of 2,6-triad DMNs (Takagawa *et al.*, 1996b)

	1,5-DMN	1,6-DMN	2,6-DMN
Boiling point (°C)	269	266	262
Melting point (°C)	82	-16	112
Kinetic diameter (Å)	7.7	7.7	7.2

Up to now, adsorption alone has not been practical, since there are no known materials that preferentially adsorb 2,6-DMN over the other isomers. These limitations often necessitate the use of expensive materials (ChemSystems, 2000). So far, the most suggested adsorbent is the ion-exchanged faujusite zeolites (Maki *et al.*, 1988; Hobbs and Barder, 1989; Rota *et al.*, 1996; Munson *et al.*, 2000; Nakao *et al.*, 2004). Unless a large quantity of adsorbent and desorbent is used, the adsorption is not sufficient, such that multiple stages or other separation units, i.e. fractionation, crystallization, have to be added (Motoyuki *et al.*, 2000; Barger *et al.*, 1991; Yokoyama *et al.*, 1976; Munson *et al.*, 2000). For example, two-stage adsorptive separation was used to separate 2,6-DMN from DMN mixtures. The first stage operated at 2,6-DMN rejective conditions by using a potassium-exchanged type X zeolite adsorbent. Then, the 2,6-DMN enriched stream entered the second stage operating at 2,6-DMN adsorptive conditions with a carbonaceous adsorbent (Barger *et al.*, 1991). The rejective operation of a potassium-exchanged type X zeolite adsorbent may result in lower 2,6-DMN recovery and necessitate the use of another adsorbent. Nevertheless, all ion-exchanged faujasite zeolites seem to provide only rejective systems for 2,6-DMN. Among them, potassium-exchanged type Y zeolite has been found by many studies to be the most effective, under their testing conditions (Rota *et al.*, 1996; Munson *et al.*, 2000; Nakao *et al.*, 2004).

It is known that, besides its major function as a desorbent, the desorbent itself has an effect on adsorption capacity and selectivity. For instance, ion-exchanged faujasite zeolite adsorbents, which are always found to give the 2,6-DMN rejective system, enable the adsorptive system with selecting normal paraffin as the desorbent (Rota *et al.*, 1996). Usually, when adsorption is carried out in the liquid phase, a solvent would be used for dissolving the solid reactants. This solvent is always selected to be the same type as the desorbent. Along with various types of desorbent used, an aromatic hydrocarbon is the most broadly selected because a large amount of DMN is capable of dissolving in it. A suitable desorbent depends on a number of variables: the system condition, feed composition, etc. In order to achieve effective adsorption, the desorbent is usually circumspectly selected. For example, monochlorobenzene was suggested instead of toluene for its unknown effect to a better two-stage adsorptive separation performance (Hobbs and Barder, 1989). *p*-Xylene can increase the composition of 2,6-DMN from 13.4% to 70%, while toluene cannot purify the same feed stream; meaning that there was a considerable amount of 2,7-DMN in the product stream (Maki *et al.*, 1988). To date, the most suggested solvent is xylene (Maki *et al.*, 1988; Rota *et al.*, 1996; Munson *et al.*, 2000; Nakao *et al.*, 2004).

## 2.2 Adsorption

Liquid phase adsorption consists of two main pathways: adsorption and desorption. Adsorption of a liquid adsorbate onto an adsorbent is dictated by the characteristics of the adsorbate-adsorbent interaction. Desorption depends on the addition of a desorbent and its specific interactions with both the adsorbate and adsorbent. Liquid phase adsorption mechanisms are highly complex. This is due to the interaction of solid adsorbents, liquid adsorbates, and liquid desorbents during the separation process. By contrast, other conventional separation process mechanisms are based primarily on the differences in the physical properties of the components. In the liquid phase adsorption matrix, virtually infinite variability can be achieved as a result of the number of ways available for adsorbent and desorbent modification. Adsorbent variables include the framework structure, the counter exchange ion, and wa-

ter content. To achieve the liquid phase adsorption separation, one has to balance two opposing forces: the adsorptive force of the adsorbent to a component and the desorptive force of the desorbent (Kulprathipanja *et al.*, 2002).

The primary requirement for an economical separation process is an adsorbent with sufficiently high selectivity, capacity, and service life. The selectivity of most adsorption processes depends on equilibrium selectivity. A separation factor is defined as in the following equation:

$$\alpha_{AB} = \frac{X_A / X_B}{Y_A / Y_B}, \quad (2.1)$$

where  $X_A$  and  $Y_A$  are, respectively, the mole fractions of component A in adsorbed and fluid phases at equilibrium. Since the separation factor generally varies with temperature and often also with composition, the choice of suitable conditions to maximize the separation factor is a major consideration in process design. Commonly, it is necessary to screen a range of possible adsorbents, which may be conveniently accomplished by the measurement of chromatographic retention times. In addition to providing a quick and reliable method of estimating separation factors, the chromatographic method has the advantage that it also provides information on the adsorption kinetics (Ruthven, 1998).

Selectivity for an extract component with respect to a raffinate component may be characterized by the ratio of the distance between the center of the extract component peak envelope and the tracer peak envelope (or other reference point) to the corresponding distance between the center of the raffinate component peak envelope and the tracer peak envelope. Relative selectivity can be expressed not only for one feed compound as compared to another but can also be expressed between any feed mixture component and the desorbent material. If the selectivity of two components approaches 1.0, there is no preferential adsorption of one component by the adsorbent with respect to the other; they are both adsorbed to about the same degree with respect to each other. When the selectivity of one component over the other is larger than 1.0, this indicates preferential adsorption of that component within the adsorbent (Kulprathipanja, 1998).

For a desorbent, there are many general criteria for selecting the suitable desorbent. First, the desorbent material should displace an extract component, a more selectively adsorbed compound, from the adsorbent with reasonable mass flow rates. If the desorbent has a stronger interaction with the adsorbent than every adsorbate, all adsorbates will be rejected from the adsorbent at almost the same time; so the separation is poor. On the contrary, if the desorbent has a weaker interaction, the adsorbates will not be desorbed out. The large amount of the desorbent then has to be used, and this is not suitable from an economic point of view. In order to achieve a good separation, the desorbent should have appropriate interaction with the adsorbent. For a binary mixture, the desorbent should exhibit the adsorptivity between the two adsorbate species. In other words, it should be more selectively adsorbed than one component but less than the other (Kulprathipanja, 1998; Morbidelli *et al.*, 1985).

Secondly, desorbent materials must be compatible with the particular adsorbent and the particular feed mixture. More specifically, they must not reduce or destroy the capacity of the adsorbent or the selectivity of the adsorbent for an extract component with respect to a raffinate component. Additionally, desorbent materials should not chemically react with or cause a chemical reaction of any component in the feed. Both the extract stream and the raffinate stream are typically removed from the adsorbent. Any chemical reaction evolving from a desorbent material would complicate or prevent product recovery. Finally, desorbent materials should be readily available and reasonable in cost (Kulprathipanja, 1998).

The rate of exchange of an extract component with the desorbent can generally be characterized by the width of the peak envelopes at half intensity obtained from plotting the composition of various species in the adsorption zone effluent during a pulse test versus time. The narrower the peak width, the faster the desorption rate. The rate of exchange of various components can be expressed as "stage time" which is calculated from the net retention volume and the half width peaks of the components. The desorption rate can also be characterized by the distance between the center of a tracer peak envelope and the disappearance of an extract component which has just been desorbed (Kulprathipanja, 1998).

The "speed" of the adsorption steps at various conditions or for different adsorbent/desorbent combinations can be measured and compared as stage times. Stage times are normally inversely correlated with temperature. A higher temperature is normally desired since low stage times mean a smaller, less expensive plant is required to separate a given quantity of feed material. On the other hand, selectivity is normally negatively impacted by higher temperatures. That is, selectivity normally decreases as the temperature goes up. In designing a commercial scale separation unit of this type, it is therefore necessary to choose operating conditions based upon a balance or trade-off of stage times versus selectivity (Kulprathipanja, 1998).

An important characteristic of an adsorbent is the rate of exchange of the desorbent for the extract component of the feed mixture materials or, in other words, the relative rate of desorption of the extract component. This characteristic relates directly to the amount of desorbent material that must be employed in the process to recover the extract component from the adsorbent. Faster rates of exchange reduce the amount of desorbent material needed to remove the extract component and, therefore, permit a reduction in the operating cost of the process. With faster rates of exchange, less desorbent material has to be pumped through the process and separated from the extract stream for reuse in the process (Kulprathipanja, 1998).

### 2.3 Zeolite

A zeolite is a porous crystalline aluminosilicate. All zeolite frameworks can be built by linking in a periodic pattern a basic building unit (BBU), the tetrahedron. It is an assemblage of  $\text{SiO}_4$  and  $\text{AlO}_4$  tetrahedra, joined together in various regular arrangements through shared oxygen atoms, to form an open crystal lattice containing pores of molecular dimensions into which guest molecules can penetrate. More complex composite building units (CBUs) can be formed linking together groups of BBUs. Since the micropore structure is determined by the crystal lattice, it is precisely uniform with no distribution of pore size (Ruthven, 1998).

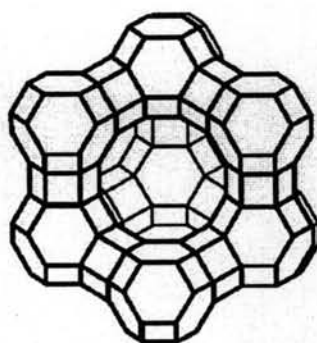
Each aluminum atom introduces one negative charge on the framework that must be balanced by an exchangeable cation. The exchangeable cations are located at preferred sites within the framework and play a very important role in determining

the adsorptive properties. By the appropriate choice of framework structure, Si/Al ratio, and cationic form, zeolites with widely different adsorptive properties may be prepared (Ruthven, 1998).

The intracrystalline diffusivity, and hence the kinetic selectivity, is determined mainly by the free diameters of the windows in the intracrystalline channel structure. The reduction in the free diameter of the window by the blocking of cations causes a dramatic reduction in the diffusivity of the guest molecules. By the appropriate choice of cationic form, it is sometimes possible to develop kinetic selectivity and even, in certain cases, to obtain a molecular sieve separation between two species, which can both diffuse easily in an unobstructed sieve (Ruthven, 1998). In the following part, examples of some zeolites are described.

### 2.3.1 Zeolites X, Y, and USY (FAU)

The synthetic zeolites X and Y and the natural faujusite zeolite all have the same framework structure, which is sketched in Figure 2.7. The channel structure is very open through the twelve-membered oxygen rings of free diameter  $\sim 7.4 \text{ \AA}$ . The difference between the X and Y sieves lies in the Si/Al ratio, which is within the range of 1-1.5 for X and 1.5-3.0 for Y.



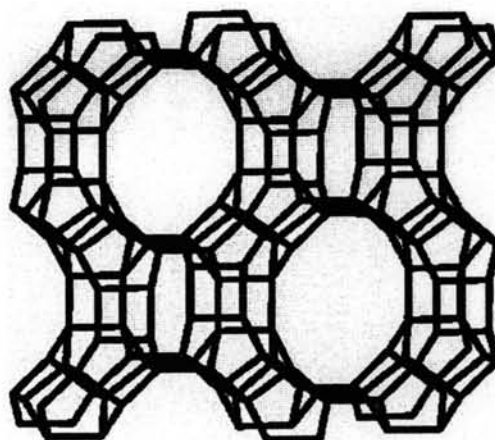
**Figure 2.7** Framework of zeolite Y (<http://www.iza-structure.org/databases>).

There is a corresponding difference in the number of exchangeable univalent cations, which varies from about 10-12 per cage for X to as low as 6 for high silica Y. The adsorptive properties of X and Y sieves may be greatly modified

by ion exchange and improvements in selectivity can sometimes be obtained by using mixed cationic forms. Presently, zeolite X is used primarily as an adsorbent and in gas drying. Zeolite Y and USY are the most widely used solid-acid catalysts in the world (Ruthven, 1998; Auerbach *et al.*, 2003).

### 2.3.2 Mordenite (MOR)

Mordenite is another important industrial solid acid catalyst (shown in Figure 2.8). It is used to upgrade the octane number of gasoline in the Isosiv process, and is used for the alkylation of biphenyl with propene. The Si/Al ratio in both natural and synthetic forms is generally close to 5.0 but the aluminum may be decreased substantially by acid leaching without significant loss of crystallinity. The main channel is one dimensional twelve-membered oxygen rings. This is a crucial characteristic with several important implications. First, diffusion in one dimension is inherently a slower process than diffusion in two or three dimensions. This is even more so when molecules are about the same size as the pore diameter. Second, one-dimensional zeolites are also highly prone to fouling (pore blockage) because it is easy to completely block access to one micropore by blocking the pores near their entrances. It is not possible to do so in multidimensional pore zeolites (Ruthven, 1998; Auerbach *et al.*, 2003).

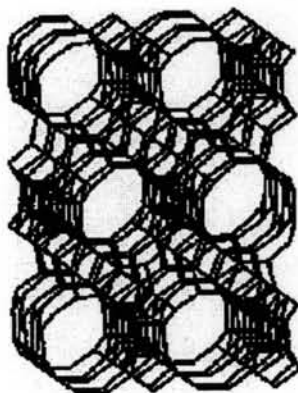


**Figure 2.8** Framework of mordenite (<http://www.iza-structure.org/databases>).



### 2.3.3 Zeolite Beta (BEA)

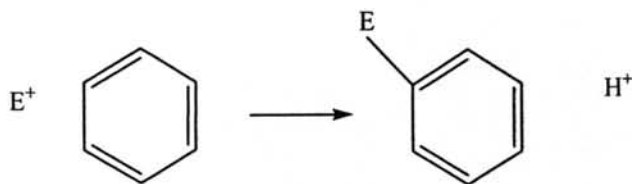
A zeolite of substantial industrial importance is zeolite beta (Figure 2.9). Beta zeolite was first synthesized by Mobil Oil Corporation. The structure of zeolite beta was only recently determined because the structure is very complex and interest was not high until the material became important for some dewaxing operations. In comparison to the previous two zeolites, beta zeolite is the most structurally defective. Zeolite beta consists of an intergrowth of two distinct structures termed Polymorphs A and B. The polymorphs grow as two-dimensional sheets and the sheets randomly alternate between the two. Both polymorphs have a three dimensional network of 12-ring pores. The Si/Al ratio is at least 10 (Auerbach *et al.*, 2003).



**Figure 2.9** Framework of zeolite beta (<http://www.iza-structure.org/databases>).

## 2.4 Aromatic Compounds

Benzene is the first aromatic compound discovered, in 1834 (Solomons and Fryhle, 2000). The important characteristic of an aromatic compound is its  $\pi$  electrons that are delocalized over the entire ring. It is these  $\pi$  electrons that create the stabilization of the compounds. Generally, aromatic hydrocarbons are known as arenes. An aryl group is one derived from an arene by removal of a hydrogen atom, and its symbol is Ar-. Thus, arenes are designated ArH. The most characteristic reactions of benzene or benzenoid arenes are the substitution reactions that occur when they react with electrophilic reagents, as shown in Figure 2.10.

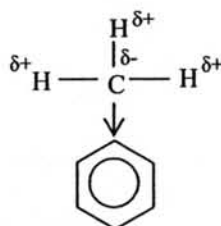


**Figure 2.10** Electrophilic aromatic substitution (EAS) of benzene (<http://www.chem.ucalgary.ca/courses/351/Carey/Ch12/ch12-1.html>).

The electrophiles are either a positive ion ( $E^+$ ) or some other electron-deficient species with a large partial charge. For example, benzene can be brominated when it reacts with bromine in the presence of  $FeBr_3$ . Bromine and  $FeBr_3$  react to produce positive bromine ions,  $Br^+$ , that acts as an electrophile and attacks the benzene ring. This reaction is called as an electrophilic aromatic substitution (EAS). When the substituted benzenes undergo further electrophilic attack, the substituent groups can affect the rate of the electrophilic substitution reaction. The substituents that cause the ring to have higher reactivity than benzene are called activating groups, such as a methyl group. These result from a combination of inductive and resonance effects (Solomons and Fryhle, 2000).

#### 2.4.1 Inductive Effect

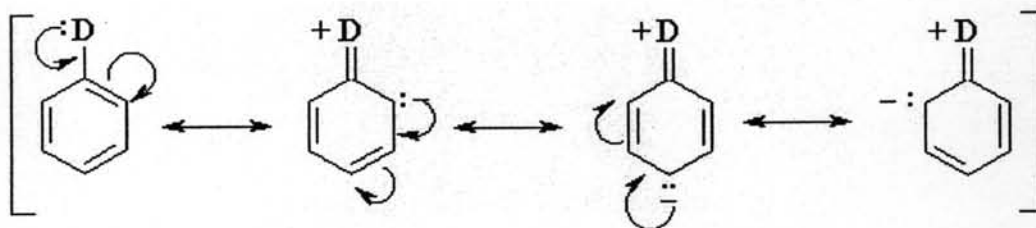
Inductive effects are due to the intrinsic electronegativity of atoms and thus to the bond polarity in functional groups. These effects operate by donating or withdrawing electrons through  $\sigma$  bonds. Alkyl groups are weakly electron-donating, and therefore activate the aromatic ring, as shown in Figure 2.11 (McMurry, 1990).



**Figure 2.11** Alkyl groups: inductively electron-donating.

### 2.4.2 Resonance Effect

Resonance effects operate via donating or withdrawing electrons through  $\pi$  bonds by overlap of an orbital on the substituent with a p orbital of the aromatic ring (McMurry, 1990).



**Figure 2.12** Resonance-electron donating group

(<http://www.chem.ucalgary.ca/courses/351/Carey/Ch12/ch12-8c.html>).

In order to determine the reaction, the net activating influence between both effects has to be experimentally proved.

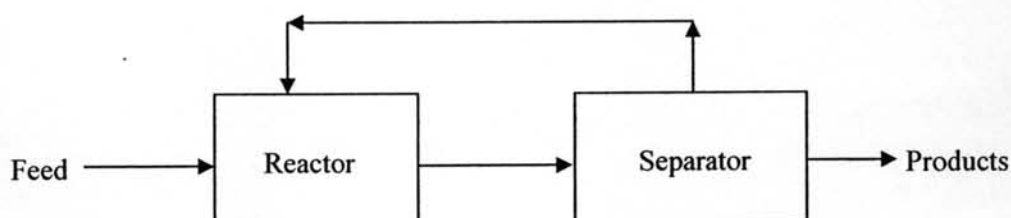
### 2.5 Reactive Separation

Process intensification (PI) is a term used to describe the strategy of making dramatic reductions in the physical size of a chemical plant while achieving a given production objective (Dautzenberg and Mukherjee, 2001). This trend has captured the interest of many researchers for many years. One of the basic components of PI are multifunctional reactors, which are reactors combining at least two functions that are conventionally performed in separate pieces of equipment. The integration of reaction and separation presents the most significant type of multifunctional reactors. In the simplest case, the integration of reaction and separation is on the equipment level; this means that the combination does not introduce any new functional interrelations between the operations involved. In most cases, however, the reaction and separation are integrated in order to benefit from the interaction effect between those two operations, such as a shift of the reaction product composition beyond the equilibrium by an in-situ separation/removal, or an enhancement of the separation effi-

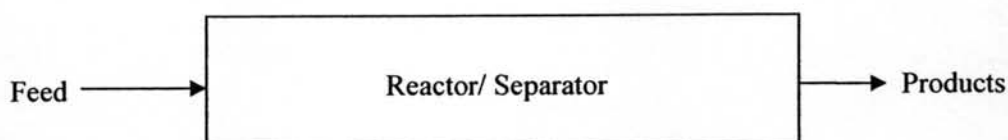
ciency by a chemical reaction. In these cases, multifunctional reactors are called reactive separations or separative reactors (Stankiewicz, 2003).

The concept of reactive separation is schematically shown in Figure 2.13. In conventional process design, a chemical reactor is typically sequenced with a downstream separator. The recycled stream is normally incorporated to reprocess unconverted feeds or intermediate products. The operating conditions of the reactor and separator have to be adjusted for optimization. In contrast, for the reactive separator, the design focuses on integrating the reactor and separator. With the proper design, the reactive separator has an advantage over the conventional design such that the reaction can be driven forward due to the removal of desired products away from the catalyst surface. The thermodynamic equilibrium, then, is no longer a limitation of the reaction. Side reactions are suppressed. Furthermore, conducting separation in zones where chemical reactions are taking place provides higher driving forces for separation (Kulprathipanja, 2002).

(a) Sequential Reaction/ Separation Process



(b) Integrated Reaction/ Separation Process

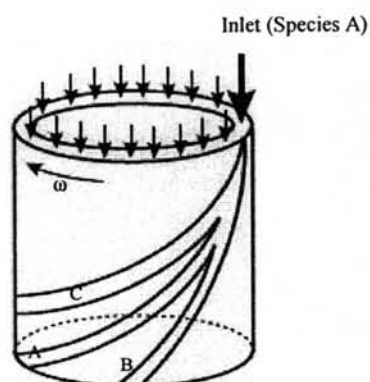


**Figure 2.13** Schematic of the concept of the reactive separation process (Kulprathipanja, 2002).

Reactive chromatography has been known for almost 40 years as a method for simultaneous reaction and adsorption. The drawback of this method is that the process operates in a batch mode leading to low efficiency of utilizing the stationary phase (adsorbent and catalyst) and large desorbent consumption (Kulprathipanja, 2002). Much research has been done to improve the reactive chromatography for a continuous mode by inventing the following three configurations:

### 2.5.1 Rotating Cylindrical Annulus Chromatographic Reactor

In this reactor, the stationary phase is contained between two concentrically arranged cylinders, rotating about their common axis. While an inert carrier is fed into the unit from the top, distributed uniformly along the annular area, a feed stream is introduced to the annulus at a stationary inlet. The reacting species thus introduced to the reactor are conveyed along the longitudinal axis of the column due to the carrier flow. The species are separated depending on their affinity towards the stationary phase, and then leave the reactor at different angles as compared to the stationary feed port. It has been found that its performance is fully equivalent to that of a batch chromatographic system; this implies an inefficient utilization of the solid phase. The sliding friction from the seals also has to be overcome (Lode *et al.*, 2001).



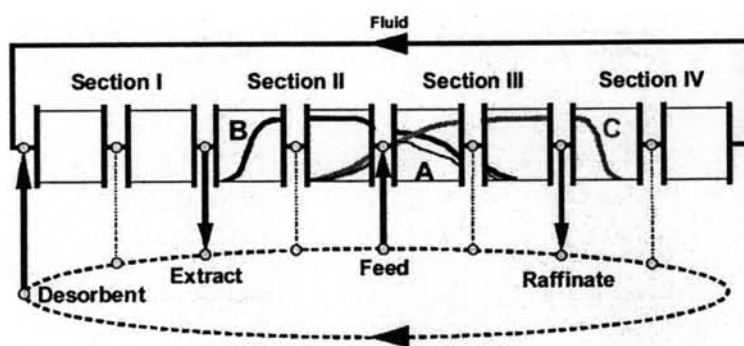
**Figure 2.14** Rotating cylindrical annulus chromatographic reactor (Stankiewicz, 2003).

### 2.5.2 Countercurrent Moving-Bed Chromatographic Reactor (CMCR)

In a CMCR, the solid enters at the top and flows by gravity as the carrier fluid is fed at the bottom and flows upward, counter to the solids, whereas the feed is introduced at a position along the column. The separation occurs when the more strongly adsorbed species have contact with the solid flowing downward and the more weakly adsorbed species are carried by the carrier fluid to the top. The problem with this reactor is the difficult handling of the solids flow in addition to the necessity to return the solids to the top of the reactor. Scale-up for commercialization requires either large diameter columns or multiple columns (Kulprathipanja, 2002).

### 2.5.3 Simulated Countercurrent Moving-Bed Chromatographic Reactor (SCMCR)

In an SCMCR, the solid bed does not move, but is held stationary in a fixed phase and the locations at which the various streams enter and leave the bed are periodically moved, as shown in Figure 2.15. Thus, the solid-handling disadvantages of a CMCR can be avoided while the advantages of countercurrency can be preserved. The carrier enters one end of the bed and flows through it. A number of ports, serving as inlets and outlets, are equally spaced along the length of the bed. The feed enters the inlet at one end, for a specified time interval, then is advanced to the next, and to the next, and so forth until the end is reached. The SCMCR is illustrated in Figure 2.15. The more strongly adsorbed species are removed from an outlet at a specified distance ahead of the feed while the more weakly adsorbed species are removed at the same distance behind the feed. Usually, the bed itself is a series of fixed sub-beds. The number of sub-beds depends on reaction and separation. The most commonly used range is from about four sub-beds to about 24 sub-beds for isomerization reactions (Kulprathipanja, 2002).



**Figure 2.15** Simulated countercurrent moving-bed chromatographic reactor (SCMCR) (Kulprathipanja, 2002).

Despite the potential advantages already mentioned, the major drawback of reactive adsorption is the reducing of the degrees of freedom used for designing process conditions. The technology cannot be applied to all processes; that process has to have compatible reaction and separation conditions. Often the temperature of reaction is high, resulting in poor adsorption capacity and selectivity. Up to now, a lot of reactive adsorption processes have been studied. For example, alkane isomerization to convert normal alkane to branched alkane was studied by using simulated moving bed technology in reactive chromatography. The catalyst was used for isomerizing some of the reactants while the adsorbent worked in the rejective condition of the desired products: the branched alkane. The isomerized products, which were less strongly adsorbed than the alkane reactants, were carried out with the fluid flow and removed when the unconverted reactants were adsorbed by the solid adsorbent which flowed countercurrently with the fluid. Then, the unconverted reactants were desorbed, and maybe catalytically isomerized to form additional isomerized products. The thermodynamic equilibrium constraint of the static system was no longer a limiting factor and a much greater conversion was obtained.