

CHAPTER II

LITERATURE SURVEY

2.1 Importance of 2,6-Dimethylnaphthalene (2,6-DMN)

2,6-Dimethylnaphthalene (2,6-DMN) is the most valuable isomer among the 10 isomers of DMN because it can be effectively used as a precursor for the production of high performance engineering plastic called polyethylene naphthalene (PEN) that has better mechanical properties than other thermoplastic polyesters, e.g. polyethylene terephthalate (PET) (Chem Systems, 2000; Lillwitz, 2001). Moreover, the chemical also provides the most economical impact for the PEN commercialization by affording the highest theoretical weight percentage yield of 2,6-naphthalene dicarboxylic (2,6-NDA) than that of the other higher chain-substituted dialkyl naphthalenes, e.g. 2,6-diethyl- (2,6-DEN) or 2,6-diisopropylnaphthalene (2,6-DIPN), during the oxidation process in the polymer synthesis (Lillwitz, 2001) as listed in Table 1.

Table 2.1 Theoretical weight percentage yield of 2,6-naphthalene dicarboxylic (2,6-NDA) from the oxidation of different dialkylnaphthalenes

Precursor of the Oxidation	Theoretical weight percentage yield of 2,6-NDA (%)
2,6-Dimethylnaphthalene (2,6-DMN)	138
2,6-Diethylnaphthalene (2,6-DEN)	117
2,6-Diisopropylnaphthalene (2,6-DIPN)	102

Many considerations have been paid on both feedstocks and processing options to optimize the process scheme to which the production cost of 2,6-DMN can offer a price that PEN can breakthrough the volume market of polyesters. Some of the various options have been outlined by Chem Systems (2000) as illustrated in Figure 2.1. Figure 2.2 exhibits some examples of the claimed process scheme from

four different companies with their production cost of 2,6-DMN. It can be observed that the production cost of 2,6-DMN are in order of Exxon Mobil / Kobe steel < BP Amoco < Optatech. However, it was remarked by Chem Systems (2000) that the price from Exxon Mobil / Kobe Steel process is calculated based on the adequate quantity and purity of naphthalene at an attractive price, and is more sensitive to the price of naphthalene than that of BP Amoco to the price of xylene. Therefore, the BP Amoco's process appears more applicable for the 2,6-DMN manufacturing.

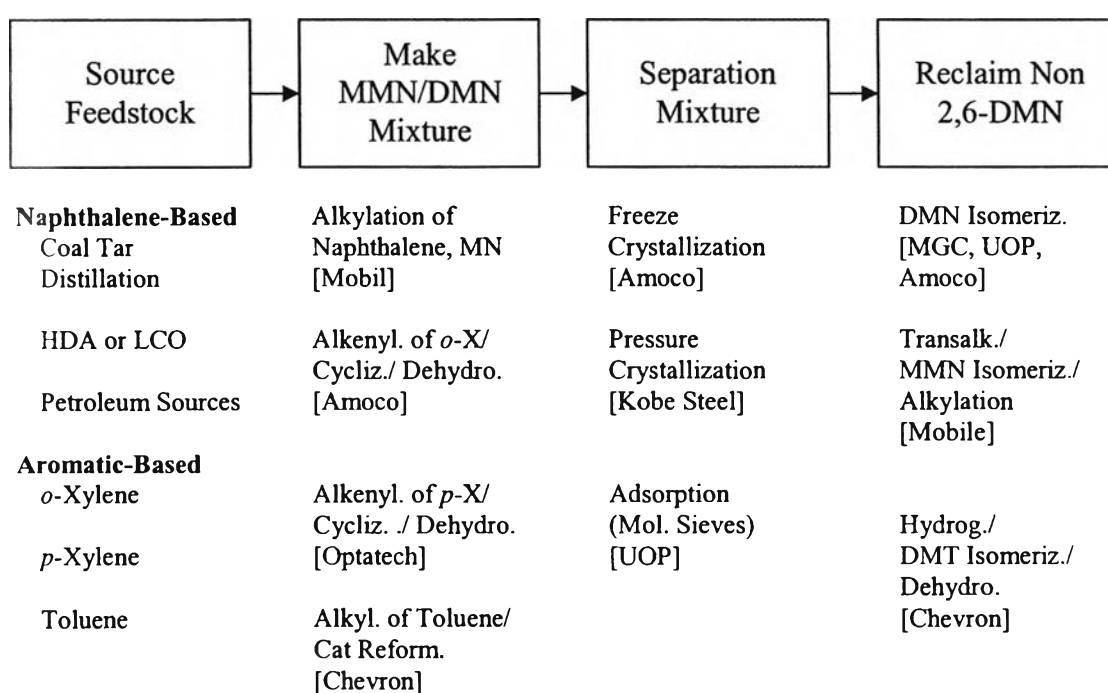


Figure 2.1 Overview of 2,6-DMN production process options (Chem Systems, 2000).

2.2 The BP Amoco Process for 2,6-DMN Production

The process licensed by BP Amoco is based on the aromatic/olefin cyclization using *o*-xylene and butadiene as feedstock. The chemistry of the process is shown in Figure 2.3. In this process, synthesis of 2,6-DMN is started from an alkylation between the two reactants into 5-(*o*-tolyl)-pentene-2 (5-OTP) using a

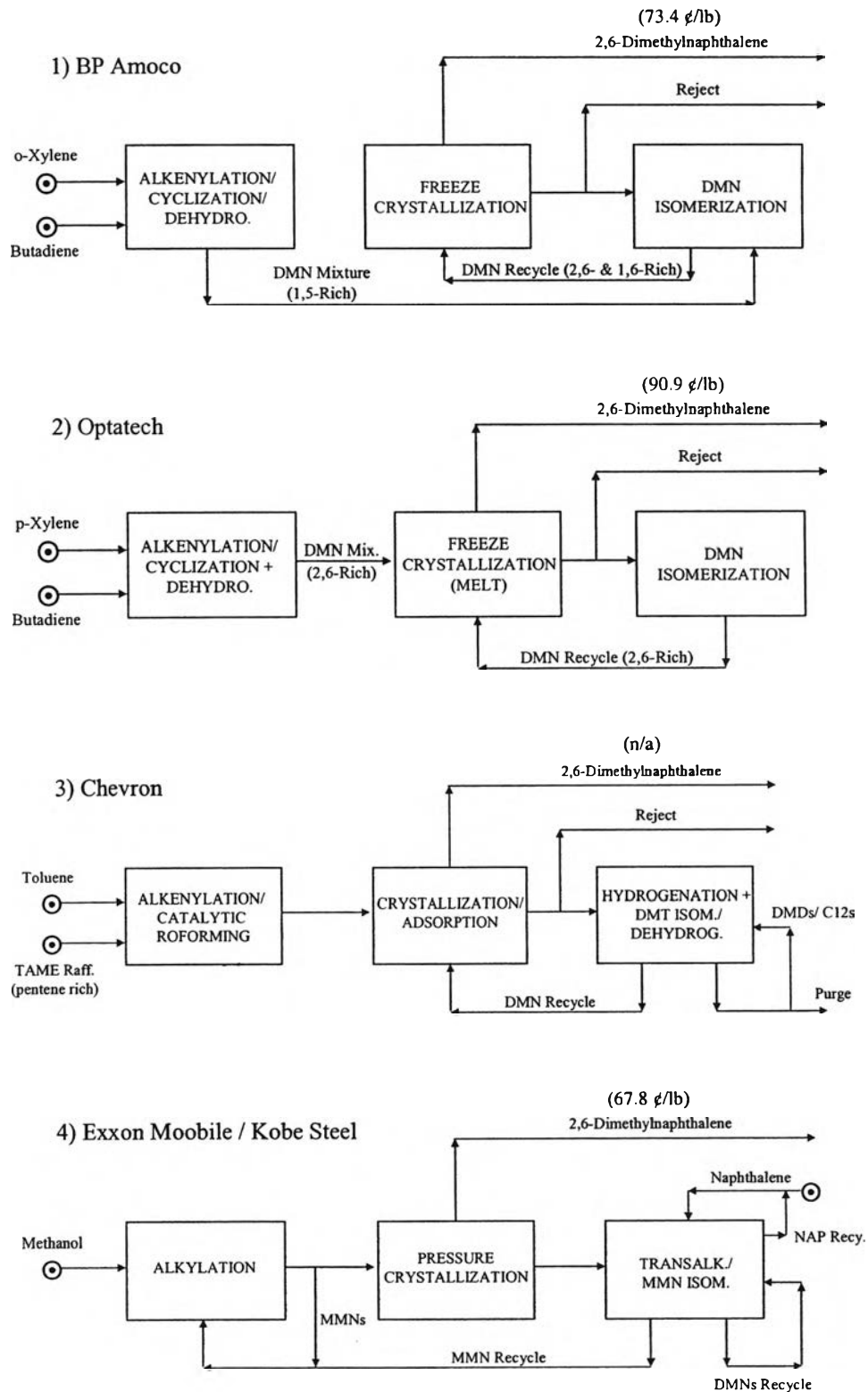


Figure 2.2 Company-specific block diagram for 2,6-DMN production (Chem Systems, 2000).

series of stirred-tank reactors with a strong base catalyst, e.g. liquid NaK, and ultrasonic sonicator to improve the catalyst dispersion and also 5-OTP selectivity (Lillwitz and Karachewski, 1993, 1994; Lillwitz, 2001). Subsequently, 5-OTP is cyclized to 1,5-dimethyltetralin (1,5-DMT) in liquid phase over an acidic zeolite with a complete conversion and 98% selectivity (Chem Systems, 2000). This reaction provides a high yield of 1,5-DMT because the heavy byproducts (mostly DMT-OTP dimmer) can be cracked back to the reactant in an equilibrium system (Sikkenga *et al.*, 1994; Lillwitz, 2001). Afterwards, liquid phase dehydrogenation of 1,5-DMT to 1,5-DMN is carried out at elevated temperature over a Pt-Ru/ γ -Al₂O₃ catalyst with conversion and selectivity to 1,5- and 1,6-DMN in the high 90s (Amelse, 1993; Chem Systems, 2000). Finally, the DMN mixture mainly contains 1,5-DMN is liquid phase isomerized to 2,6-DMN over a modified H-beta catalyst using either batch or fixed bed flow reactor (Sikkenga *et al.*, 1990). Since the isomerization is equilibrium controlled, the maximum yield of about 48% of the desired 2,6-DMN can be accomplished only when the reaction reaches its equilibrium (Chem Systems, 2000; Lillwitz, 2001). Freeze crystallization is then used for the purification of 2,6-DMN from its isomeric raffinate, which will be sent back to the isomerization unit afterwards. Figures 2.4 and 2.5 illustrate the schematic flow diagram of the BP Amoco process.

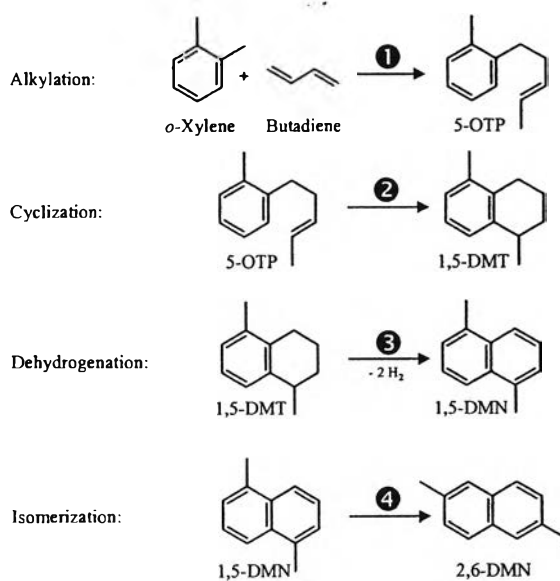


Figure 2.3 Chemistry of the BP Amoco's 2,6-DMN synthesis process (Chem Systems, 2000; Lillwitz, 2001).

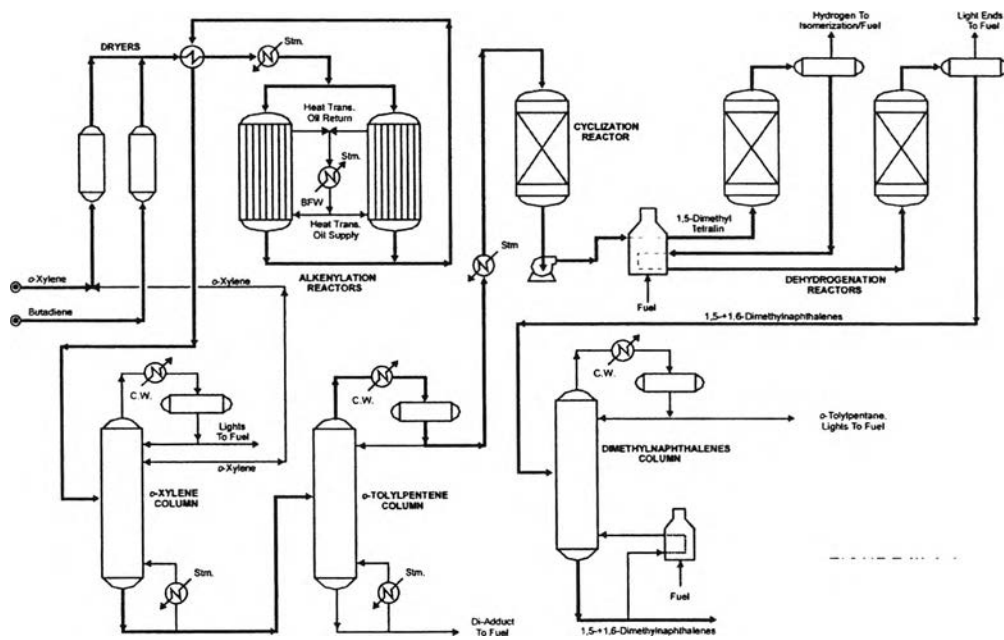


Figure 2.4 2,6-Dimethylnaphthalene by BP Amoco process: reaction and recovery (Chem Systems, 2000).

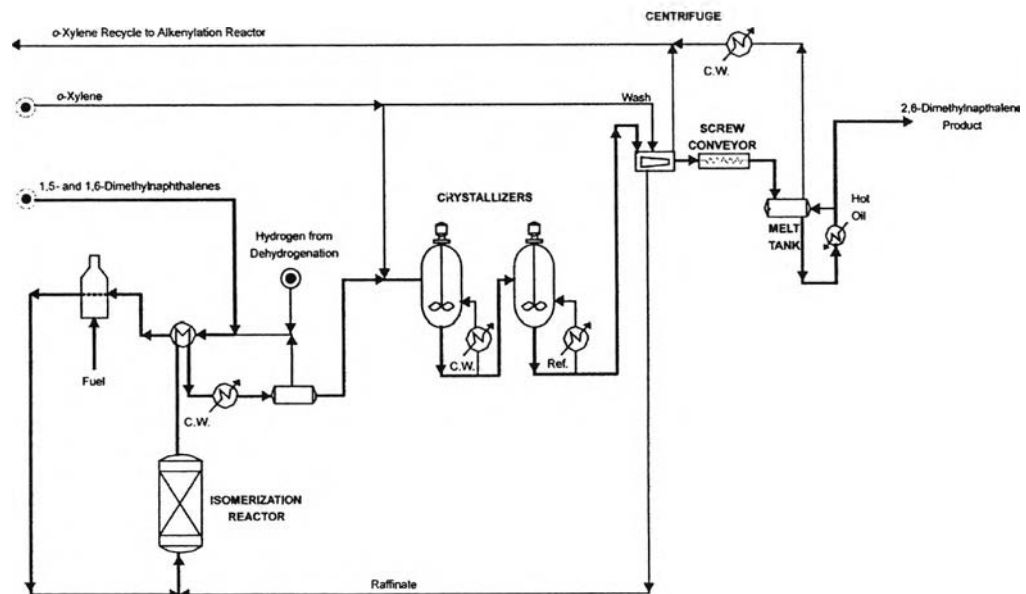


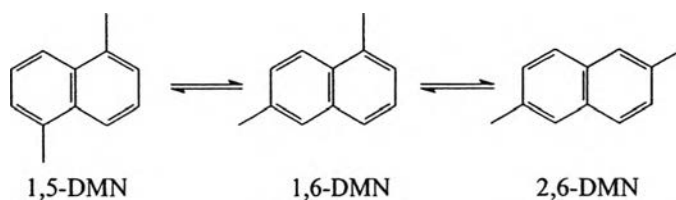
Figure 2.5 2,6-Dimethylnaphthalene by BP Amoco process: isomerization and crystallization (Chem Systems, 2000).

2.3 Isomerization of Dimethylnaphthalene

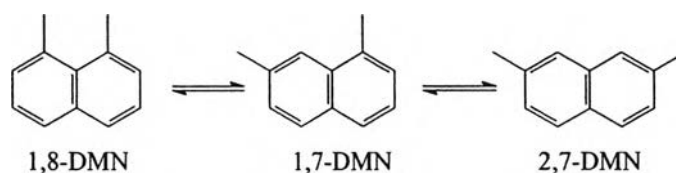
There are ten possible positional isomers of DMN, which can be divided into three groups of three (triads) and additional single isomer as shown in Figure 2.6. It is known that the isomerization within any one of the triad is relatively easy than those between the triads (Chem Systems, 2000). In other words, the shift of the methyl group from the α -position of naphthalene to the β -position in the same ring is relatively easy, whereas from the β -position to the β -position or from one ring to the other is difficult (Hara and Takahashi, 1975; Pu and Inui, 1996). This phenomenon has been reasoned with the migrational barrier and stability of the intermediate complexes by Suld and Stuart (1964). The formation of the intermediates from the migration between the adjacent β -position (Figure 2.7a), as well as between the two rings of naphthalene nucleuses (Figure 2.7b), would result in the loss of aromaticity and energy stabilization of aromatic ring, entailing the high barrier for such migrations. As the results, the possible DMN isomerization pathway can be exhibited as Figure 2.8. It is remarked that only two DMN isomers (1,5- and 1,6-DMN) are beneficial for the production of 2,6-DMN since they can be effectively isomerized to the profitable isomer while the others cannot. So, the loss of DMNs from the 2,6-triad by inter-triad isomerization means the loss of profit.

Catalytic isomerization of DMN within the 2,6-triad is of interest. The catalyst that can rapidly drive only the reaction in the 2,6-triad by taking the advantage on the migration barrier as beforehand mentioned would diminish the formation of byproduct, reduce the loss of the valuable DMNs from inter-triad isomerization and increase the ease for the subsequent purification. Few studies have been investigated for the catalytic isomerization within the 2,6-triad with little attention on the understanding of the thermodynamic limitation and the effect of reaction media, e.g. type of solvent (Ferino *et al.*, 1996; Millini *et al.*, 2003). The most intensively claimed catalyst is mordenite (Barger *et al.*, 1991; Ferino *et al.*, 1996; Takagawa *et al.*, 1996; Allen and Bertolaini, 1997; Millini *et al.*, 2003). However, the high energy requirement, the usage of noble metals as active sites for

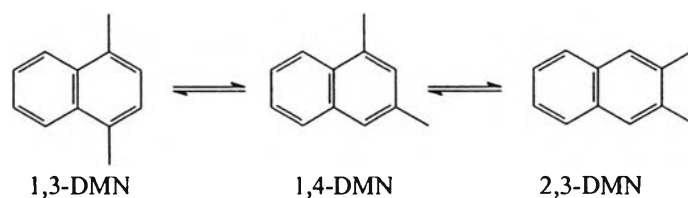
I) 2,6-triad:



II) 2,7-triad:



III) 2,3-triad:



IV)

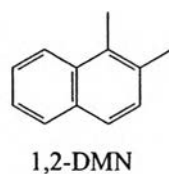


Figure 2.6 Schemes of dimethylnaphthalene isomers and their classifications.

the isomerization, as well as the formation of by-products are generally encountered. Other zeolites have also been investigated for their isomerization activity, e.g. ultrastable Y-type (Ferino *et al.*, 1996), 2%Cu/ultrastable Y-zeolite (Sikkenga *et al.*, 1992), ZSM-5 (Pu and Inui, 1996), X-zeolites (Yokayama *et al.*, 1974), A-zeolite (Yokayama *et al.*, 1974), L-zeolite (Yokayama *et al.*, 1974). However, Sikkenga *et al.* (1992) recently claimed that the using of H-beta zeolite as a catalyst for the isomerization provides more advantages on the reduction of byproducts formation, reduction of the loss of valuable DMNs from the 2,6-triad, and facilitation the formation of 2,6-DMN at lower reaction temperatures.

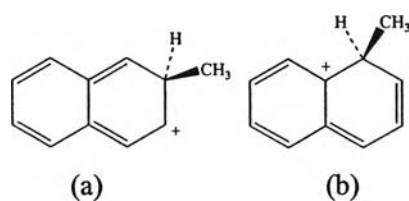


Figure 2.7 Proposed intermediate from the migration between (a) the adjacent beta positions and (b) the naphthalene nucleuses (Suld and Stuart, 1964).

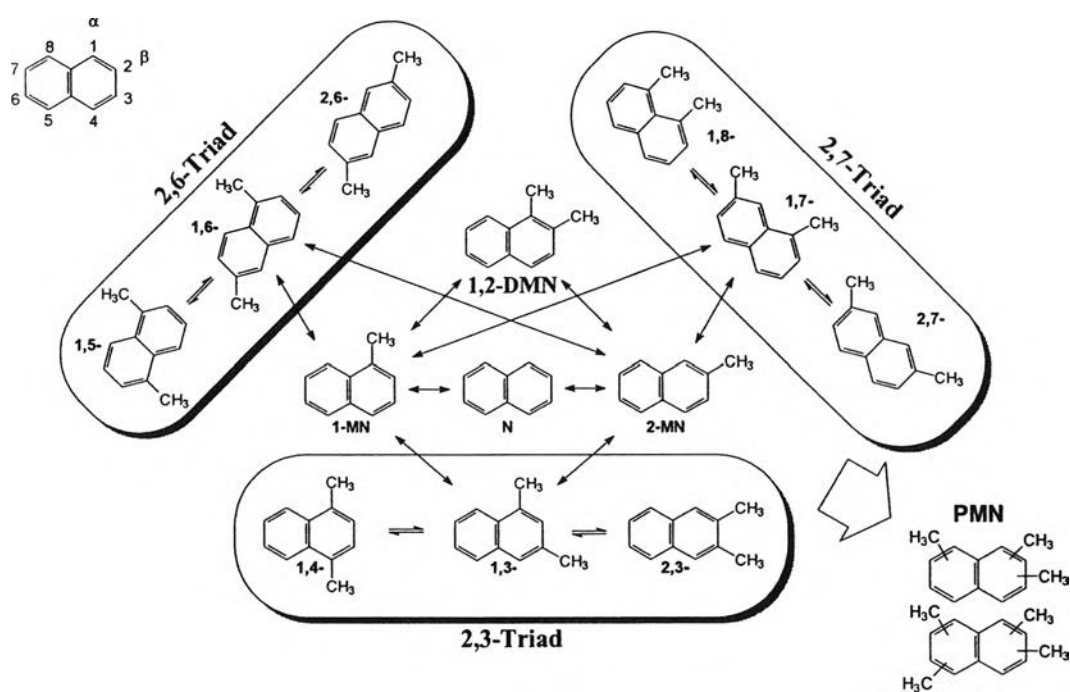


Figure 2.8 Schematic diagram representing isomerizations among 10 DMN isomers (Modified from Millini, 2004).

2.4 Purification of 2,6-Dimethylnaphthalene

Since the production of 2,6-DMN through its isomerization is controlled by thermodynamics, the isomerized product is generally comprised of 1,5-, 1,6- and 2,6-DMN with their equilibrium composition. These DMN isomers have very close physical properties and molecular size (Table 2.2); thus, typical separation techniques cannot successfully recover 2,6-DMN from the equilibrium mixture with high purity as industrial requirements (Chem Systems, 2000). In the process of BP Amoco, freeze crystallization was employed as a means for the 2,6-DMN purification (Smith *et al.*, 1999). However, energy intensive of the process entails the high production cost (Chem Systems, 2000) and draws many attentions to an adsorptive separation approach.

Table 2.2 Kinetic diameters and physical properties of the DMNs in the 2,6-triad (Pu *et al.*, 1996; Takagawa and Shigematsu, 2000)

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

Selective adsorption of 2,6-DMN has been conducted over a wide range of adsorbent. L-zeolite (Verduijn *et al.*, 1992), activated carbon (Barger *et al.*, 1991) and ion-exchanged faujasite zeolites (Maki *et al.*, 1988; Barger *et al.*, 1991; Inui and Pu, 1995; Rota *et al.*, 1996; Nakao *et al.*, 2004) have been utilized as adsorbents in literatures. Most processes encounter the problem of 2,6-DMN purity; thus, a crystallization process is usually combined downstream to increase the product purity (Chem Systems, 2000; Maki *et al.*, 1988). For ion-exchanged faujasite zeolites, some adsorptive systems for 2,6-DMN have been reported using paraffins as a solvent. For example, Inui and Pu (1995) investigated the adsorption of 2,6-DMN and its isomers on NaY and LiY zeolites using cyclohexane as a solvent and reported

that the different in kinetic diameters between 2,6-DMN and other isomers creates the selective adsorption of 2,6-DMN. However, the study only investigated the binary DMN isomers system and the selectivity of 2,6-DMN respected to the other isomers in the 2,6-triad are still not effective for the separation purpose. Rota *et al.* (1996) also claimed the potential adsorptive system for 2,6-DMN using KX zeolite. However, the adsorption from the binary system was accomplished in n-octane with the total concentration of DMN at 8 wt%, which is not adequate for commercial applications.

Performing the adsorption in aromatic solvents seems to pronounce applicability due to a high solubility of the DMNs. However, only rejective systems can be demonstrated for 2,6-DMN (Barger *et al.*, 1991; Maki *et al.*, 1988; Nakao *et al.*, 2004) and the lower purity than the adsorptive system has been observed. For example, the 2,6-DMN rejective process patented by Barger *et al.* (1991) can produce only 69% of 2,6-DMN using KX zeolite as an adsorbent. Consequently, the raffinate needs to be processed through the 2nd adsorptive stage using activated carbon to enhance the 2,6-DMN purity up to 95.8%.

2.5 Reactive Separation

Reactive separation is a hybrid process integrating the normally disjunct unit operations of reaction and separation into a single unit with simultaneous operation (Leet and Kulprathipanja, 2002). In the case that the reaction does not play role on the separation, nor has not been affected upon the separation, the integration generally provides the smaller inventory, compacter plant layout and/or better energy management without any interrelation between the operations involved (Stankiewicz, 2003). However, most cases of the integration aim to get the additional benefits from the interaction effect between the reaction and separation, including the enhancement of the separation efficiency by a chemical reaction and the enhancement of the process throughput by a shift of the reaction product composition beyond the equilibrium by *in situ* separation/removal (Krishna, 2002; Stankiewicz, 2003).

A variety of the separation principles and concepts can be incorporated into a reactor as shown in Figure 2.9. Since the integration forces both two processes to

be operated at a similar condition, a narrow operating window with the difficulties in process optimization is normally a major difficulty of the design (Stankiewicz, 2003; Ströhlein *et al.*, 2004). Obviously, the nature of reaction itself (phases present, type of catalyst, temperature, pressure) becomes the primary selection criterion of the separation technologies that could be potentially integrated in a reactive separation unit (Stankiewicz, 2003). However, the industrial practice as well as the maturity of the given technology and past experiences within the company often play nearly important role in the decision making as well.

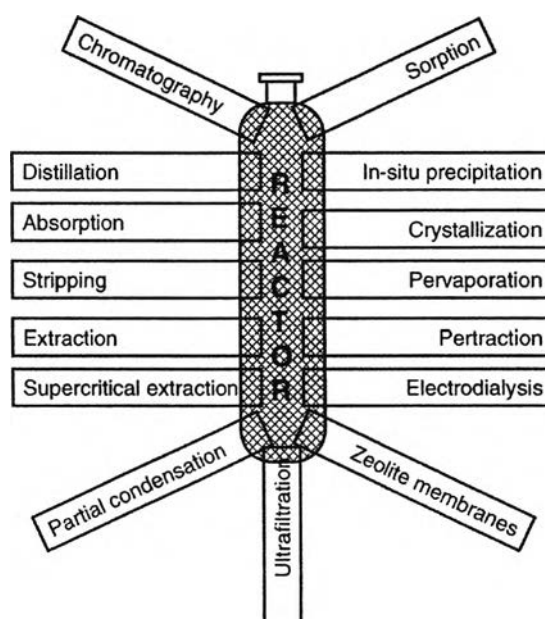


Figure 2.9 Various *in situ* separation functions integrated into the reactor (Krishna, 2002).

2.5.1 Reactive Adsorption

Reactive adsorption is unique in its combination of reaction and adsorption to be simultaneously carried out at the same time in a single unit. The combination is mostly suitable for (i) the equilibrium or selectivity limited reactions, (ii) reactions in which products can be separated by adsorption, (iii) compatible reaction and adsorption conditions and (iv) reactions in which other separation means do not work for products separation (Carr and Dandekar, 2002). Quite often, reactive

adsorption reactor is called as “chromatographic reactor” since the reactor is comprised of a chromatographic column that can simultaneously convert the solutes to products during their residence in the column (Fricke and Schmidt-Traub, 2003). There are three major types of chromatographic reactor; batch chromatographic reactor, true moving bed chromatographic reactor and simulated moving bed chromatographic reactor.

2.5.1.1 Batch Chromatographic Reactor (BCR)

Batch chromatographic reactor (BCR) is a simplest mode for operating reactive adsorption. Figure 2.10 illustrates the operating principle of the BCR for a reversible decomposition reaction. By injecting the feed A into the column, the formation of B and C are propagated along the movement. At the same time, the differences in adsorption affinity of the species create the separation, providing the chance for the reactant to be further converted before being eluted from the column. As a result, conversion exceeding the equilibrium limitation can be achieved. Performing the reactive adsorption using BCR has already been successfully conducted for many reactions, for instance, esterification of acetic acid and ethyl alcohol (Sardin *et al.*, 1992), oxidation of cyclohexene to cyclohexanol (Lertrodjanapanya, 2002), and phenol hydroxylation (Rangsunvigit and Kulprathipanja, 2004).

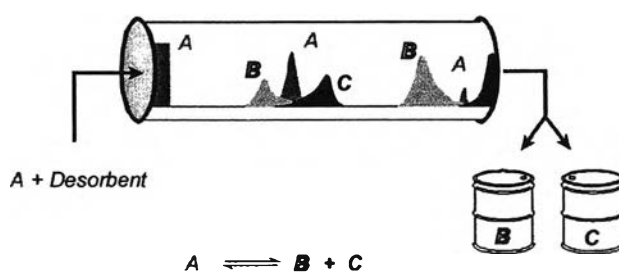


Figure 2.10 Operating principle of the batch chromatographic reactor (Fricke and Schmidt-Traub, 2003).

The main drawbacks of the BCR are that the process operates discontinuously with a requirement of catalyst and adsorbent in a large volume with the dilute product in the eluant (Carr and Dandekar, 2002). Therefore, the process is

solely appropriate for the production of low-volume high cost chemical, e.g. for the pharmaceutical, perfumery and fragrance industries (Krishna, 2002). The information from BCR also provides very important information for the further industrial developments of the process.

2.5.1.2 *True Moving Bed Chromatographic Reactor (TMBCR)*

For the true moving bed chromatographic reactor (TMBCR), the operation is based on the countercurrent moving of the solid particle and the feed stream. The position of in- and outlet is generally used to define the specific sections in the column (Figure 2.11) as the followings (Fricke and Schmidt-Traub, 2003);

- Section 1: located between the desorbent and the extract port. The flow rate is higher than in all the other sections in order to remove the more strongly adsorbed product from the adsorbent, for instance, molecule B from the same reaction over the same adsorbent as previously exhibited in BCR,

- Section 2: located between the extract and feed port in which the product B and C are formed. The less strongly adsorbed product (component C) is desorbed whereas B is still held on the adsorbent. Therefore, the extract stream contains more strongly adsorbed product,

- Section 3: located between the feed and raffinate port. In this section, the feed is converted into products while the strongly adsorbed molecule (component B) being adsorb. Thus, the raffinate contains the less strongly adsorbed product (component C) in very high concentration,

- Section 4: located between the raffinate and desorbent port. This section is allow the fluid to be cleaned before being recycled, for instance, provide a complete adsorption of component C and move it back to the section 3 with desorbent.

In practice, operation of TMBCR encounters many problems, such as, difficulty in the movement of the solid bed, process efficiency reduction by an unavoidable backmixing of the solid, and abrasion of the particle by the movement (Fricke and Schmidt-Traub, 2003).

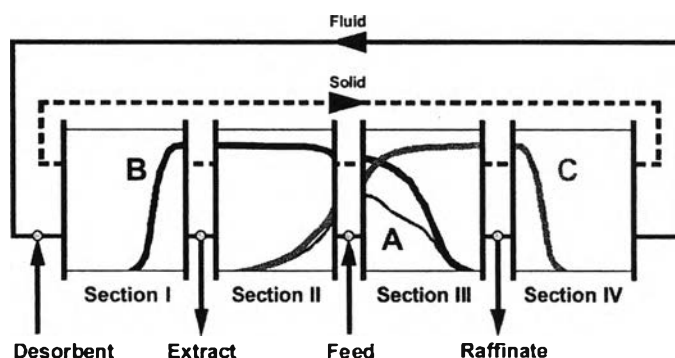


Figure 2.11 Schematic represents for the TMB chromatographic reactor (Fricke and Schmidt-Traub, 2003).

2.5.1.3 Simulated Moving Bed Chromatographic Reactor (SMBCR)

In stead of moving the solid bed, the countercurrent movement of the phases is simulated by sequentially switching the valves of interconnected columns in the direction of the liquid (Figure 2.12). This inventory can overcome the difficulties of the TMBCR and can be operated as identical as, however, the TMB-process. The SMBCR has been demonstrated for its successful to several reactions, for examples, production of bisphenol A (Kawase *et al.*, 1999), esterification of acetic acid with β -phenethyl alcohol (Kawase *et al.*, 1996), esterification of acetic acid with ethanol (Mazzotti *et al.*, 1996), the MTBE synthesis (Zhang *et al.*, 2001), enzyme-catalyzed production of lactosucrose (Pilgrim *et al.*, 2006), hydrogenation of ethylbenzene (Ray and Carr, 1995), oxidative coupling of methane (Kruglov *et al.*, 1996), partial oxidation of methane to methanol (Bjorklund and Carr, 2002). Moreover, it was proven both experimentally (Ray and Carr, 1995; Kawase *et al.*, 1996, 1999) and numerically (Ray *et al.*, 1994; Kawase *et al.*, 1996, 1999; Fricke *et al.*, 1999) that the simultaneous reaction and separation in a SMBCR can overcome the equilibrium yield in reversible reaction systems.

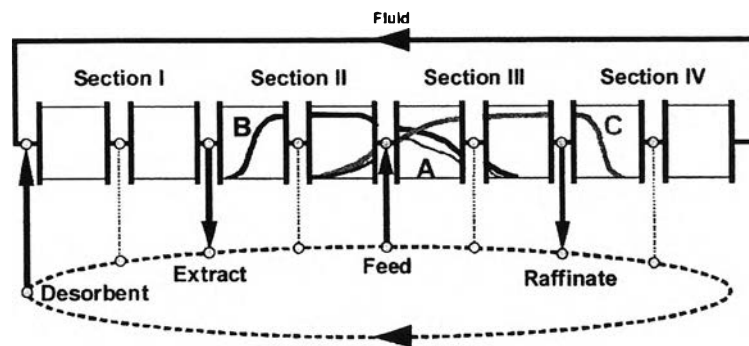


Figure 2.12 Schematic represents for the SMB chromatographic reactor (Fricke and Schmidt-Traub, 2003).