



## CHAPTER II

### BACKGROUND AND LITERATURE SURVEY

This research relates to the separation of normal paraffins from hydrocarbon mixture having 10 to 20 carbon atoms per molecule and containing normal paraffins and non-normal hydrocarbons by selective adsorption of the normal paraffins in adsorbent which is a crystalline zeolitic molecular sieve material. The feed may contain either or both kerosene or gas oil.

Kerosene may be broadly defined as a hydrocarbon mixture having an initial boiling point according to the American Society of Testing Materials (ASTM) of about 275° F and an ASTM final boiling point below 600° F. Kerosene contains between about 10 to 40 mol percent normal paraffins having 10 to 15 carbon atoms per molecule; these particular normal paraffins are used as raw materials for detergent manufacture.

Gas oil may be broadly defined as a hydrocarbon mixture having an initial boiling point according to the ASTM of above 400° F and an ASTM final boiling point below 700° F. Gas oil contains between about 10 to 40 mol percent normal paraffins having 13 to 20 carbon atoms per molecule.

It is known that crystalline zeolitic molecular sieves may be used for selective adsorption of normal paraffins from admixture with non-normal. The details of zeolite molecular sieve will be described below. Some techniques and previous work related to this research will also be described in this chapter as well.

#### 2.1 Zeolite (molecular sieve)

Zeolites are three-dimensional crystalline metal aluminosilicates having the basic formula:



Where M represent an exchangeable cation and n its valence. In general, a particular crystalline zeolite will have values for x and y that fall within a definite range (Avery, 1969).

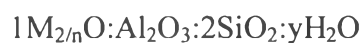
Zeolitic molecular sieves have pore openings of uniform dimensions as contrasted with conventional adsorbents. For normal paraffin extraction the molecular sieve must have pore size large enough to allow normal paraffin molecules but too small for the non-straight chain hydrocarbons to pass into the inner cagework for adsorption. Thus the molecular sieve selectively adsorbs normal paraffins from the hydrocarbon feed and rejects the larger non-straight chain hydrocarbon component of feed.

The approximate maximum dimension in Angstrom units of the minimum projected cross-section for several molecules is as follows: benzene-5.5, propane-4.9, ethane-4.0, and isobutane-5.6. These are calculated from bond lengths, bond angles and van der Waals radii. The corresponding maximum dimensions for larger normal saturated hydrocarbons such as normal tetradecane are substantially the same as for propane, as the length of the molecule is not a determining factor (Milton, 1963). This means the zeolite molecular sieves must have a pore size of from about 4.9 to about 5.5 angstrom.

Silva and Rodrigues (1999) indicated the increasing heat of adsorption with number of carbon atoms per molecule of normal paraffins.

Among the naturally occurring molecular sieves suitable for practicing this separation are eronite calcium rich chabazite and certain forms of mordenite. Suitable synthetic zeolitic molecular sieves include zeolite D, R, S, T and divalent metal cation-exchanged forms of zeolite A (Benazzi *et al.*, 1994).

Zeolite A is a crystalline molecular sieve which may be represented by the formula:



In this formula M represents a metal, n is a valence of M and y may be any value up to 6 depending on the identity of the metal and the degree of dehydration of the crystals (Avery, 1969).

Zeolite A consists basically of a three dimensional framework of  $SiO_4$  and  $AlO_4$  tetrahedra. The tetrahedra are cross-linked by the sharing of oxygen atoms so that the ratio of oxygen atoms to the total of the aluminum and silicon atoms is equal

to two. The electrovalence of the tetrahedra containing aluminum is balanced by the inclusion in crystal of a cation, for example, an alkali or alkaline earth metal ion. This balance may be expressed by the formula  $Al_2/Ca, Sr, Ba, Na_2, K_2$ .

Although there are a number of cations that may be present in zeolite A it is preferred to formulate or synthesize the sodium form of the crystal (zeolite 4A or zeolite NaA) since the reactants are readily available and water soluble. Anyway this zeolite NaA are not suitable for this research due to small pore size of about 4 angstrom which will not adsorb normal paraffins having more than four carbon atoms per molecule, nor any branched chain and cyclic hydrocarbons.

The NaA can be replaced by various other cations or by hydrogen ion. The commercial type 3A zeolite is formed by exchanging  $Na^+$  with  $K^+$ , resulting in a smaller effective aperture size due to the large  $K^+$ . The aperture size of the sodium form can also be increased by exchanging  $Na^+$  with  $Ca^+$  or  $Mg^+$ , since  $2Na^+$  are replaced by one divalent cation. The form of the exchanged  $Ca^{2+}$  or  $Mg^{2+}$  is type 5A with rather unobstructed and larger apertures (Yang, 1997).

As already indicated, a suitable form of zeolite A is divalent metal cation-exchanged forms such as calcium, strontium, and magnesium. These divalent cationic metal forms have larger pores than those in sodium zeolite A and can adsorb larger molecules of normal paraffins but still exclude other non-normal hydrocarbons. These forms of zeolite A can be prepared by ion exchange techniques.

Ion exchange of the sodium form of zeolite A or other forms of zeolite A may be accomplished by conventional ion exchange methods. A preferred continuous method is to pack zeolite A into a series of vertical columns with suitable supports at the bottom; and change the flow from the first bed to the second bed as the zeolite in the first bed becomes ion exchanged to desired extent.

Milton (1963) disclosed that at least 40% of sodium cation in zeolite A need to be replaced by divalent cations such as calcium and magnesium for effective separation of normal paraffins from other non-normal hydrocarbon.

Babich (2001) found that, usually, only a limited part of the packed bed is used effectively. In his experiment, only 60% of the sorbent can be used to reach

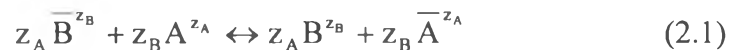
sufficient separation of n- and i-paraffins (purity of the effluent gas above 95%). Then, the separation process has to be stopped, and the sorbent must be regenerated.

## 2.2 Ion Exchange in Zeolites (Breck, 1984)

The cation exchange behavior of zeolites depends upon (1) the nature of the cation species, the cation size, both anhydrous and hydrated, and cation charge; (2) the temperature; (3) the concentration of the cation species in solution; (4) the anion species associated with the cation solution; (5) the solvent (most exchange has been carried out in aqueous solutions); and (6) the structural characteristics of the particular zeolite. Cation selectivities in zeolites do not follow the typical rules that are evidenced by other inorganic and organic exchanges. Zeolite structures have unique features that lead to unusual types of cation selectivity and sieving.

### 2.2.1 Ion Exchange Theory (Karge and Weitkamp, 2002)

Considering as an example a binary exchange involving cation A and B, the reaction equation is usually written as:



where  $z_A$ ,  $z_B$  are the charge of the exchange cations A and B and the overbars denote the zeolite phase. The preference displayed by the zeolite for one ion over another is then described by a selectivity coefficient.

$$k_{A/B} = \frac{c_A^{z_B} c_B^{z_A}}{c_A^{z_A} c_B^{z_B}} \neq k_{A/B}^x = \frac{\overline{x}_A^{z_B} c_B^{z_A}}{\overline{x}_B^{z_A} c_A^{z_B}} \neq k_{A/B}^E = \frac{\overline{E}_A^{z_B} c_B^{z_A}}{\overline{E}_B^{z_A} c_A^{z_B}} \quad (2.2)$$

where  $c_A$ ,  $c_B$  are the cation concentrations in solution ( $\text{mol dm}^{-3}$ ) and the corresponding concentrations in the molecular sieve are indicated with an overbar (equiv  $\text{kg}^{-1}$  dry exchanger). The definition of  $k_{A/B}$  is consistent with IUPAC recommendations but is not very convenient for zeolites because of the significant

water content.  $k_{A/B}^x$  and  $k_{A/B}^E$  are selectivity coefficients in which the zeolite phase cation concentrations are defined in terms of the mole fraction and equivalent fraction E, respectively:

$$\bar{x}_A = \bar{c}_A / \sum_i \bar{c}_i \quad (2.3)$$

$$\bar{E}_A = z_A \bar{c}_A / \sum_i \bar{c}_i \quad (2.4)$$

When  $z_A = z_B = z_i$ , then equivalent and mole fractions are numerically identical and  $k_{A/B}^x = k_{A/B}^E$ . Otherwise, these functions are not numerically identical. In practice,  $k_{A/B}^E$  has been used most extensively for studies on zeolites.

### 2.2.2 Exchange Capacity (Breck, 1984)

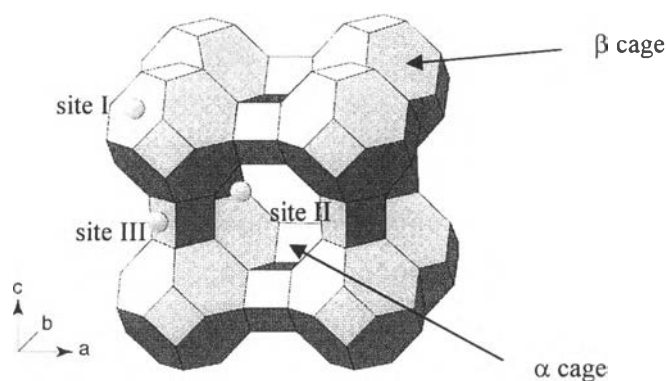
The ultimate base exchange capacity of a zeolite depends on the chemical composition; a higher exchange capacity is observed with zeolites of low SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio. In aqueous solution, the relevant capacity is that of the hydrated zeolite. In many cases the measured exchange capacities deviate from these values due to impurities (as in mineral zeolites) or variation in chemical composition. The specific exchange capacities vary with the exchange cation. The exchange capacity has been measured as part of characterization procedure in determining ion exchange equilibria. Exchange capacity of some zeolites are shown in Table 2.1.

**Table 2.1** Exchange capacity of various zeolites

Zeolite	Si/Al	Milliequiv/g Anhydrous		Milliequiv/g Hydrated	
		Powder	Pellet	Powder	Pellet
Zeolite A	1	7.0	5.6	5.5	4.4
Zeolite X	1.25	6.4	5.1	4.7	3.8
Zeolite Y	2	5.0	4.0	3.7	3.0

### 2.2.3 Ion Exchange of Zeolite A

Zeolite A displays a double ion-sieve action. Only small cations can penetrate the single 6-rings into  $\beta$ -cages. Large organic cations cannot penetrate the 8-rings into the  $\alpha$ -cages. In the typical zeolite A, 12 univalent ions are located in each pseudo-cubic unit cell of  $24(\text{Al}, \text{Si})\text{O}_4$  tetrahedra.



**Figure 2.1** Pseudo unit cell and cationic sites of zeolite A.

Ion exchange equilibria in zeolite A involved mostly univalent and divalent counter ions. Attempts to exchange with trivalent cerium ions were unsuccessful (Wiers *et al.*, 1982).

The order of decreasing selectivity for univalent ions is:



For divalent ions, the order of decreasing selectivity is:



While the order of divalent cation size is:



Barium ion exchange in zeolite A is possible without disruption of the structure if the zeolite is not dehydration (Sherry and Walton, 1966).

## 2.3 Normal Paraffins Extraction Conditions

Separating normal paraffins in a hydrocarbon mixture in the vapor phase has many advantages over liquid phase separation (Brodbeck, 1966). Working with

the vapor phase permits increased mass transfer rates and ease of movement of materials.

Vapor phase operation also help reducing nonselective component hold-up between adsorbent particles (Mazzotti, 1996).

Young *et al.* (1967) discovered that even when operating at adsorption and desorption temperature above the dew point of the hydrocarbon feed mixture is employed, relatively poor adsorption and desorption rates are obtained unless the temperature is maintained at least 40° C and more preferably at 50° C above the dew point temperature of the feed. Although the importance of maintaining the temperature above this minimum was not entirely understood at that time, it was believed that it was at least partially attributable to capillary condensation occurring in the sieve which may exist at lower temperature.

Later on this hypothesis was confirmed. Fuderer (1983) disclosed that the separation process should be carried out at temperature above the dew point of hydrocarbon feed and sufficiently high to avoid capillary condensation. However, too high temperature result in excessive cracking of the vapor feed and deactivation of molecular sieve.

Concerning the pressure, it is well known that increasing pressure results in increasing capacity of molecular sieve. In that aspect an increase in pressure is desirable. However, pressure above atmospheric require special equipment as well as higher temperature to maintain the system in vapor phase and, to that degree, are undesirable (Brodbeck, 1966).

#### **2.4 Displacement Purge Adsorption (DPA)**

Adsorbates can be removed from the adsorbent surface by replacing them with a more preferentially adsorbed species. This displacement fluid should adsorb about as strongly as the components which are to be desorbed. If the displacement fluid is adsorbed too strongly then there may be subsequent difficulties in removing it from the adsorbent.

One advantage of the displacement fluid method of regeneration is that the net heat generated or consumed in the adsorbent will be close to zero because the

heat of adsorption of the displacement fluid is likely to be close to that of the original adsorbate. Thus the temperature of the adsorbent should remain more or less constant throughout the cycle. With neither pressure nor temperature change from adsorption to desorption, regeneration by displacement purge depends solely on the ability of the displacement fluid to cleanse the bed in readiness for the next adsorption step.

In effect the original mixture of (A and B), which would have been difficult to separate by PSA or TSA, is separated by the "intervention" of another strongly adsorbed component D. The ease of separation of A from D, and B from D, in the additional distillation stages, is crucial in determining the economies of displacement purge cycle operation.

Usually, desorption stage of normal paraffins (regeneration stage) is slower than adsorption stage under the same experimental conditions (Babich, 2001). To reach the same cycle time, the flow rate of the regeneration stage should be greater than that of the adsorption stage.