CHAPTER II

LITERATURE SURVEY

2.1 Isobutane Separation Processes

A survey of the literature reveals that the possible processes of the isobutane separation are distillation, adsorption and combined processes of distillation and adsorption. A brief description of the processes is as followed.

2.1.1 Distillation Process

Vora and Vickers (1981) patented an isobutane separation process of an alkylation reaction zone for the hydrocarbon effluent stream comprising isobutane, normal butane, propane and alkylate. The hydrocarbon effluent stream was charged to an isostripper column. An isobutane vapor stream from the top of the column was condensed by indirect heat exchange with the lower liquid stream comprising n-butane. The lower liquid stream was flashed by indirect heat exchange with the vapor stream to provide a vapor phase, which was compressed and recycled to the column at a temperature to promote vapor formation therein.

Schorre *et al.* (1982) patented a C_4 separation process concerning to the energy conservation by the use of an open heat pump and heat portion to an n-butane/isobutane splitter as the compression fluid in the heat pump. The unusual characteristics of n-butane/isobutane on compression producing liquid-vapor phase could cause damage to the compressor. This problem was overcome by passing the vaporized n-butane prior to compression, through an apparatus that removed any entrained liquids and heated the vapors to a temperature sufficient to prevent the formation of the liquid phase under compression. A feed used for this process contained 5 to

95% by mole of isobutane, 5 to 95% by mole of n-butane, 0 to 20% by mole of butenes, 0 to 20% by mole of butadiene, 0 to 5% by mole of propane and lighter hydrocarbons, and 0 to 5% by mole of pentane and heavier hydrocarbons.

O'Connell and Nye (1988) patented an n-butane/isobutane splitter which separated isobutane from the feed mixture of n-butane/isobutane by compressing the isobutane overhead to increase its condensing temperature, using the compressed overhead to heat bottoms in a reboiler, which was operated to condense the overhead and cool the condensed overhead to a temperature no lower than the top tray temperature and no higher than $20^{\circ}F$ above the top tray temperature, whereby the throughput of the splitter was increased by 10 to 20%. A feed mixture used for this procedure contained 5 to 95% by mole of isobutane, 5 to 95% by mole of n-butane, 0 to 20% by mole of butene, 0 to 5% by mole of propane and lighter hydrocarbons, and 0 to 5% by mole of pentane and heavier hydrocarbons.

2.1.2 Adsorption Process

Holcombe (1979) patented a normal paraffin/isoparaffin separation process. Normal paraffins were isolated from a feedstock mixture of normal and non-normal paraffins in the vapor phase at super atmospheric pressure. The adsorption system comprising at least four fixed adsorption beds contained a 5 Angstrom molecular sieve adsorbent, each of which cyclically undergone the stages of adsorption-fill, adsorption, void space purging, and purge desorption. The improvement of the present process comprises recycling in the vapor phase in the combination with feedstock. The mixture of isoparaffins and normal paraffins purged from one bed of the system during the stage of void space purging to another bed of the system undergoing the stage of adsorption. In conventional practice the void space contained hydrocarbons purged from each bed during the stage of void space purging

was cooled, separated from the purging gas, pumped to a holding tank in the liquid phase and thereafter reheated to form the vapor phase before being admixed with fresh feedstock for further treatment.

Volles and Cusher (1986) patented an n-butane/isobutane separation process. Isobutane was separated from normal butane in a pressure swing adsorption system of at least three adsorbent beds and each adsorbent bed was adapted to selectively adsorb normal butane from a mixture thereof with isobutane. The adsorption front of normal butane formed in each adsorbent bed upon the passage of the feed gas mixture was moved through the bed to an extent enhancing the utilization of the adsorptive capacity. By the combination of depressurization and repressurization together with purge, desirable product purity levels were obtained, while the cost of adsorbent equipment and operation was reduced to the extent possible consistent with the purity requirements of a given application.

Cho *et al.* (2000) patented an adsorption separation and purification apparatus and process for obtaining high purity isobutane by removing paraffins and olefins from light hydrocarbon mixtures containing isobutane with zeolite 5A and carbon molecular sieve adsorbents. This invention provided high purity isobutane producing apparatus and it comprised a pressure regulator which regulated feed gas pressure; a plurality of adsorption beds packed with zeolite 5A and carbon molecular sieve through which the mixed gas flow passed. A flow rate control valve was located between the pressure regulator and the adsorption beds where impurities were removed. Isobutane from the adsorption beds flowed to a surge tank. A vacuum pump was located for removing the impurities from the adsorption beds and some valves were arranged between the pressure regulator and the adsorption beds, between the adsorption beds and the tank, and between the adsorption beds and the vacuum pump.

2.1.3 Combined Processes of Distillation, Adsorption and Isomeri-

sation

For producing isoparaffins from a mixture of 4C hydrocarbons, Minkkinen *et al.* (1994) patented a process which comprised of deisobutanization, adsorption, desorption, isomerization and separation. Deisobutanisation was carried out by distillation of a 4C mixture and effluent from a desorber below with part condensation of distillate for recycle as reflux liquid. Adsorption of the other part of the distillate was achieved by upward flow through a bed of molecular sieve whilst in vapor phase to give essentially pure isobutane product. Desorption, alternating with adsorption step, was done by lowering pressure in the adsorber and passing through a portion of the isobutane product from adsorber, with desorption effluent being passed to the column in deisobutanizer. Isomerisation of residue from deisobutanizer was in the vapor phase and Separation of isomerisation product into recycled vapor phase and liquid crude effluent. This patent gave high purity of isobutane, which was produced with minimized energy use.

2.2 Shortcut Distillation Methods

Shortcut distillation calculation methods are used to determine column conditions such as separations, minimum number of trays, and minimum reflux ratios. The shortcut method assumes that an average relative volatility is defined for the column. These methods consist of four methods; Fenske, Underwood, Gilliland and Kirkbride methods. The Fenske method is used to compute the separations and minimum number of trays required. The minimum reflux ratio is determined by the Underwood method. The Gilliland method is used to calculate the number of theoretical trays required, the actual reflux rates and condenser and reboiler duties for a given set of actual to minimum reflux ratios. Finally, the Kirkbride method is used to determine the

optimum feed location. (Henley and Seader, 1981; Simulation Sciences Inc., 1994; Kister, 1992)

2.2.1 Fenske Method

The relative volatility between components i and j at each tray in the column, is equal to the ratio of their K-values at that tray, as shown in the equation below.

$$\alpha_{ij}^N = \frac{y_i^N / x_i^N}{y_j^N / x_j^N} = \frac{K_i^N}{K_j^N} \tag{2.1}$$

where

y = mole fraction in the vapor phase

x = mole fraction in the liquid phase

subscripts i, j refer to components i and j respectively

superscript N refers to tray N

For small variations in volatility throughout the column, an average volatility is defined. This is taken as the geometric average of the values for the overhead and bottoms products:

$$\alpha_{ij}^{av} = \sqrt{\alpha_{ij}^1 \, \alpha_{ij}^N} \tag{2.2}$$

The minimum number of theoretical stages is then given by:

$$N_{min} = \frac{\log \dfrac{x_{i,D} \; x_{j,B}}{x_{j,D} \; x_{i,B}}}{\log \alpha_{ij}^{av}} \tag{2.3}$$

where subscripts B, D refer to the bottoms and distillate respectively.

2.2.2 Underwood Method

The values of the relative volatilities of the feed components determine which components are the light and heavy key components. The light key component for a feed of equivalent component concentrations is usually the most volatile component. The heavy key component is similarly found to be the least volatile component, or the least volatile component found at significant concentrations.

The relative volatility of each component can therefore be expressed in terms of the volatility of the heavy key, i.e.,

$$\alpha_J = \frac{K_J}{K_{hk}} \qquad (2.4)$$

where J refers to any components and hk refers to the heavy key component For components lighter than the heavy key, $\alpha_J > 1$, and for components heavier than the heavy key, $\alpha_J < 1$. For the heavy key component itself, $\alpha_J = 1$.

The Underwood method is used to determine the reflux ratio required an infinite numbers of trays to separate the key components. For a column with infinite trays, the distillate will exclude all components heavier than the heavy key component. Similarly, the bottom products will exclude all components lighter than the light key. Components whose volatilities lie between the heavy and light keys will distribute between the distillate and bottoms products. At minimum reflux ratio:

$$\frac{x_{J,D}\,D}{x_{J,F}\,F} = \frac{\alpha_J - 1}{\alpha_{lk} - 1}\frac{x_{lk,D}\,D}{x_{lk,F}\,F} + \frac{\alpha_{lk} - \alpha_J}{\alpha_{lk} - 1}\frac{x_{hk,D}\,D}{x_{hk,F}\,F} \qquad (2.5)$$

If the value of the ratio given by equation 2.5 is less than -0.01 or greater than 1.01 for any component J, then that component will likely not distribute between both products. Therefore to test if the correct key components are selected, equation 2.5 should be applied to those components

lighter than the light key, and heavier than the heavy key. If they fail the test described above, then new key components should be selected.

It should be noted that an exact value of R_{min} is not needed. This value is necessary only to provide an estimate of the product composition, and to determine if the specified reflux ratio is reasonable. The Underwood equations assume a constant relative volatility, as well as a constant liquid/vapor rate ratio throughout the column. The first equation to be solved is

$$(1 - q) = \sum_{i=1}^{N} \frac{\alpha_J x_{J,F}}{\alpha_J - \phi} \tag{2.6}$$

$$q = \frac{H_G - H_F}{H_V} \tag{2.7}$$

where

q   = thermal condition of feed

= heat to convert to saturated vapor/heat of vaporization

H_G = molar enthalpy of feed as a saturated vapor

H_F = molar enthalpy of feed

H_V = molar latent heat of vaporization

$x_{J,F}$ = mole fraction of component J in feed

ϕ = a value between the relative volatilities of the light and heavy

keys, i.e., α_{hk} (=1) < ϕ < α_{lk}

The second equation to be solved is:

$$(R_{min} + 1) = \sum_{i=1}^{N} \frac{\alpha_J x_{J,D}}{\alpha_J - \phi} \tag{2.8}$$

where

R_{min} = minimum reflux ratio = (L/D)min

$x_{J,D}$ = mole fraction of component J in distillate

2.2.3 Kirkbride Method

The optimum feed tray location is obtained from the Kirkbride equation;

$$\log\left[\frac{m}{p}\right] = 0.206 \ \log\left\{\frac{B}{D}\frac{x_{hk,F}}{x_{lk,F}}\left(\frac{x_{lk,B}}{x_{hk,D}}\right)^2\right\} \qquad (2.9)$$

where

    m = number of theoretical stages above the feed tray

    p = number of theoretical stages below the feed tray

2.2.4 Gilliland Correlation

The Gilliland correlation is used to predict the relationship of minimum trays and minimum reflux to actual reflux and corresponding theoretical trays. The operating point (expressed as either fraction of minimum reflux or fraction of minimum trays) is selected as the mid-point for a table of trays and reflux. Based on the corresponding reflux ratio, the column top conditions are calculated and the associated condenser duty determined. The reboiler load is computed from a heat balance.

2.3 Distillation Column Sequencing

2.3.1 Synthesis of Separation Sequences

The synthesis of distillation sequences is based on separation methods and arrangement of separators. A recursion formula for the number of sequences, S, is corresponding to the separation of a mixture of R components into R products. For the first separator in the sequence, (R-1) separation points are possible. Let j be the number of components appearing in the overhead product; then (R-j) equals the number of components appearing in the bottom products. If S_j is the number of possible sequences for i components, then, for

a given split in the first separator, the number of sequences is the product $S_j S_{Rj}$. But in the first separator, (R-1) different splits are possible. Therefore, the total number of sequences (S_{ij}) for R components is shown in equation 2.10 (Douglas, 1988).

$$S_{ij} = S_j S_{R-j} = \frac{[2(R-1)]!}{R!(R-1)!}$$ (2.10)

2.3.2 Shortcut Evaluation of Distillation Sequence

A boiling capacity variable, K, had been developed as a cost indicator for vapor-liquid equilibrium separation processes. This variable is associated with a stream; all streams leaving the same equilibrium stage have the same value of the capacity variable. For a product leaving a single equilibrium stage, K is defined as (Jobson et al., 1996; Jobson, 1997):

$$K - K_{feed} = \frac{molar\ rate\ of\ vaporization}{molar\ feed\ flow\ rate} = \frac{V}{F}$$ (2.11)

The overall capacity variable of a process, K_{ov}, is defined as the weighted average of the capacity variables of the product streams. For a general sequence of columns, K_{ov} is defined as:

$$K_{ov} - K_{feed} = \frac{N_R V_R + (N_S + 1)V_S + \varphi D}{F}$$ (2.12)

where

F   =   molar feed flow rate

D   =   molar distillate flow rate

N   =   number of stages

V_R =   vapor flow rate in the rectification sections

   =   (R+1)/D

V_S =   vapor flow rate in the stripping sections

   =   (R+1)/D - φF

φ = vapor fraction of the distillate

2.4 Column Sizing

Methods developed by Glitsch (Simulation Sciences Inc., 1994) are used to compute the capacity or flood point, and the pressure drop for valve trays. For sieve or bubble cap trays, the capacity is computed by using 95 and 85% of the valve capacities respectively. The tray pressure drop is calculated by the Fair method for sieve trays, and by the method of Bolles for bubble cap trays. The capacity of a tray column is defined in terms of a vapor flood capacity factor, at zero liquid loads, CAF0. Nomographs are used to obtain the capacity factors based on tray spacing and vapor density. Foaming on trays is taken into account by using a so-called system factor.

For sizing an existing tray column, or for calculating the percent of flood for a given column diameter, the column vapor load is used. The vapor load may be determined by using:

$$V_{load} = ACFS\left(\rho_G/\left(\rho_L - \rho_G\right)\right)^{0.5} \qquad (2.13)$$

where

V_{load} = vapor load capacity

ACFS = actual vapor volumetric flow rate

ρ_G = vapor density

ρ_L = liquid density

The total tray pressure drop for valve, sieve, or bubble cap trays is a sum of the dry tray pressure drop, and the pressure drop due to the liquid holdup on the trays:

$$\Delta P = \Delta P_{dry} + \Delta P_l \qquad (2.14)$$

where

ΔP = total pressure drop, inches liquid

ΔP_{dry} = dry tray pressure drop, inches liquid

ΔP_l = pressure drop through the liquid on the trays, inches liquid

The dry tray pressure drop is obtained from nomographs relating the pressure drop to the weight of the valves at low vapor flow rates, and to the square of the vapor velocity at high vapor flow rates. For valve trays, the pressure drop through the liquid is given by:

$$\Delta P_l = 0.4\left(\left(L/l_W\right)^{2/3} + h_W\right) \qquad (2.15)$$

where

L = total liquid flow rate, gpm

l_W = weir length, inches

h_W = weir height, inches

2.5 Economic Analysis

2.5.1 Capital Investment

Before an industrial plant can be put into operation, a large sum of money must be supplied to purchase and install the necessary machinery and equipment. Land and service facilities must be obtained, and the plant must be erected complete with all piping, control and services. In addition, it is necessary to have money available for the payment of expenses involved in the plant operation. The capital need to supply the necessary manufacturing and plant facilities is called the fixed-capital investment, while that necessary for the operation of the plant is termed the working capital. The sum of the fixed-capital investment and the working capital is known as the total capital investment.

Peters and Timmerhaus (1991) introduced a method for estimating capital investment called the percentage of delivered-equipment cost method. This method requires determination of the delivered equipment

cost. The other items included in the total direct plant cost were then estimated as percentages of the delivered-equipment cost. The additional components of the capital investment are based on average percentages of the total direct plant cost, total direct and indirect plant cost or total capital investment. The average values of the various percentages were shown in Table 2.1

2.5.2 Return on Investment

Return on investment (ROI) is ordinarily expressed on an annual percentage basis. The yearly profit divided by the total initial investment necessary represents the fractional return, and this fraction times 100 is the standard percent return on investment (Douglas, 1988):

$$\%ROI = \frac{Annual\ profit}{Total\ investment} \times 100 \tag{2.16}$$

where the annual profit is defined as the difference between annual income and annual expense.

Therefore, annual profit is a function of the quantity of goods or services produced and the selling price. The return on investment often is used for preliminary design calculations and the recommended process should have a return on investment greater than 20 percent.

2.5.3 Net Present Value

The net present value is the difference between the total present value of the annual cash flows to the project and the initial required investment. The present value of the annual cash flows to the project is obtained by summing the individual present values for each year of operation including the present value of the working capital and savage-value recovery at the end of the service life. The equation of the net present value is shown below (Peters and Timmerhaus, 1991).

$$NPV = \sum_{j=1}^{N} \left\{ \left(B_j - C_j \right) \left(\frac{1}{(1+i)^N} \right) \right\} - C_{invest} \qquad (2.17)$$

where

    B_j = benefits at the end of period j, $

    C_j = cost at the end of period j, $

    C_{invest} = cost for investment, $

    j   = period of time, year

    i   = a discount rate

    N = service life of equipment, year

For alternative investments, the greatest advantage alternative is the investment, which gives the highest net present value (NPV).

Table 2.1 Ratio factors for estimating capital investment items based on delivered-equipment cost (Peters and Timmerhaus, 1991)

Item	Percent of delivered-equipment cost
Direct costs	
Purchased equipment-delivered	100
Purchased-equipment installation	47
Instrumentation and control (installed)	18
Piping (installed)	66
Electrical (installed)	11
Buildings (including services)	18
Yard improvements	10
Service facilities (installed)	70
Total direct plant cost	340
Indirect costs	
Engineering and supervision	33
Construction expenses	41
Total direct and indirect plant costs	414
Contactor's fee	21
Contingency	41
Fixed capital investment	476
Working capital	84
Total capital investment	560