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Hollow Fibers as Structured Packing for Olefin/Paraffin Separation

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Abstract:

In this study, the hollow fibers replace conventional trays and/or structured packing. Using a column less than 40 cm long, an ~ 8% enrichment of propylene from a 30% propane/70%propylene mixture was achieved. An HTU as low as 8.8 cm was obtained. Such a low HTU has not been previously reported for propane/propylene separations. The mass transfer time was less than one second.

Introduction:

Ethylene and propylene are two of the largest commodity chemicals in the U.S. and are major building blocks for the petrochemicals industry. These olefins are currently separated by cryogenic distillation, which demands extremely low temperatures and high pressures. Over 75 billion pounds of ethylene and propylene are distilled annually in the U.S. at an estimated energy requirement of 400 trillion BTU's[1]. Many petroleum companies have been aggressively pursuing non-cryogenic alternatives to light gas separations. The largest potential area for energy reduction is the cryogenic isolation of the product hydrocarbons from the reaction by-products, methane and hydrogen. This separation requires temperatures as low as -150 °F and pressures exceeding 450 psig. This report will focus on developing a new type of packing structure - parallel hollow tubes made from plastic materials which are light weight and less costly than metal. This material will replace conventional packing materials (such as tray or structured packing) by separating olefinic and/or paraffinic mixtures from light gas byproducts with greater efficiency.

Over the past few decades many researchers have investigated the use of membranes as contactors in distillation processes.[2,3] The main focus has been in desalinization, food industry and biological/medical applications. As material science advances, more and more polymeric materials with different geometries and morphologies are becoming commercially available. Although appreciable progress has been made during the past decade, fouling of the membrane remains the primary obstacle for many of these applications. There have also been many reports on the use of reactive or selective membranes for olefin and paraffin separations.[4-9] However, the difficulty of long term stability associated with these facilitated transport membranes has been a major obstacle. Recently, Devlin et. al. explored the possibility on separating olefin and/or paraffin gases from light gas by-products using hollow fibers, and obtained promising results.[7] Coincidently, Cussler's group reported their work on the use of non-selective membranes as structured packing to replace distillation columns for the water-isopropanol separation. They also indicated the possibility of using this technology for light hydrocarbon mixture separation.[10,11] In this report, we investigate the use of non-selective polymeric membranes as structured packing for the propane/propylene separation. The height of transfer unit (HTU) for our system is as low as 8.8 cm., which is at least 5 to 10 times better than the most efficient structured packing (Sulzer 250 Y). The mass transfer coefficient is > 0.01 cm/sec. This result demonstrates the possibility of using hollow fibers or tubes as an alternate packing for olefin and paraffin separation. We have also shown that hollow fibers can help overcome flooding or loading problems offering a wider range of operating conditions. The large mass transfer area should result in increased efficiency and may ultimately reduce the operating and capital cost compared to the conventional distillation tower.

Theory

Figure 1 (a) presents a distillation column. In a typical distillation process, the feed solution is fed to the middle of the column, the high boiling point component is concentrated and removed from the reboiler while the low boiling point component is collected after the condenser. In order to increase the separation efficiency, a partial amount of condensed material is returned back to the column. To evaluate a distillation process it is convenient to operate under the condition of total reflux (all the condensed liquid is returned to the column) illustrated in figure 1 (b). This simplifies the analysis and allows us to determine the minimum number of stages and height of a transfer unit HTU for the separation.

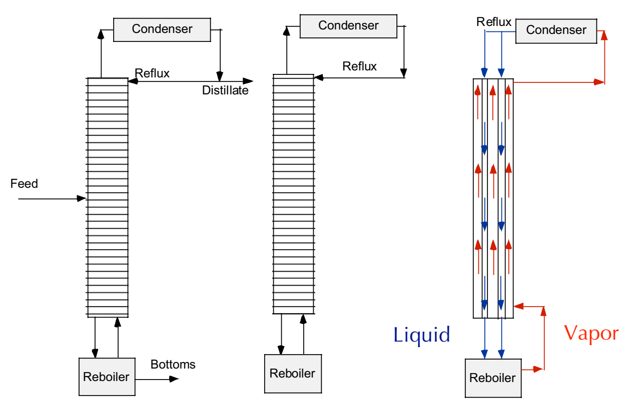

Figure 1. Flowcharts of a typical distillation process (a), a distillation process under total reflux condition (b), and a hollow fiber distillation column under total reflux condition (c).

In our hollow fiber distillation column (see Figure 1 (c)), the gas flows up the outside of fiber (shell) while the liquid counter-currently flows down inside the lumen of the hollow fiber. Using this approach we can decouple the liquid and vapor flows allowing operations above the normal flooding limit. Under total reflux conditions, the mass balance between the gas and liquid phase is simply:

$$G' = L', \qquad \text{Eq. 1}$$

where G′ and L′ are the molar gas and liquid flowrate in the column. In a continuous flow condition, we can assume a constant molar flow at different sections along the length of the column. For the total reflux, the operating line is simply:

$$x = y, \qquad \text{Eq. 2}$$

where x and y are the mole fraction of the more volatile species in the vapor and the liquid phase, respectively. For the mass balance on a vapor phase alone, we have the following equation:

$$0 = -G\frac{dy}{dz} + K_y a(y^* - y) \quad \text{Eq. 3}$$

where K_y is the overall gas phase mass transfer coefficient, a is the mass transfer area (cm^2/cm^3), z is the distance measured from the bottom of the column, y is the mole fraction of the most volatile species in the vapor, y^* is the mole fraction in equilibrium with the liquid, and G is the gas molar flux in the shell side. This is a rate equation and the integrated form of Eq. 3 is Eq. 4:

$$l = \int_0^l dz = \frac{G}{K_y a}\int_{y_0}^{y_l}\frac{dy}{y^* - y} \quad \text{Eq. 4}$$

Eq. 4 can be written as:

$$l = HTU \bullet NTU \quad \text{Eq. 5}$$

where HTU is the height of a transfer unit defined as:

$$HTU = \frac{G}{K_y a} = \frac{v_G}{K_G a} \qquad \text{Eq. 6}$$

and NTU is the number of a transfer unit given by:

$$NTU = \int_{y_0}^{y_l}\frac{dy}{y^* - y} \qquad \text{Eq. 7}$$

Both HTU and NTU are important parameters. The HTU is an indication of the efficiency of the equipment while the NTU is a measure of the difficulty of the separation. A large NTU suggests a difficult separation while the small HTU is a sign of an efficient tower. Since the HTU is directly related to the mass transfer coefficient (K_G) which in turn depends on the velocity (v_G), this number changes for different operating conditions. However, typically the HTU is between 0.3 and 2.7 meters.[12,13] The NTU depends on the intrinsic properties of the materials to be separated. The propane and propylene separation is a very difficult separation due to their low relative volatility (<1.2 within a wide temperature range).

Experimental

The apparatus is shown schematically in Figure 2. There are three major components for this system: reboiler, condenser, and membrane module. There are four sampling stations for monitoring the gas composition at different sections during operation. Two heater/chiller systems are used to precisely control operating temperature. A view port mounted between the condenser and module is used to ensure the hollow fibers are filled with liquid during the experiment. A ~30% propane and propylene mixture is used in this study. All gases were 99.999% purity (Tri-gas Inc).

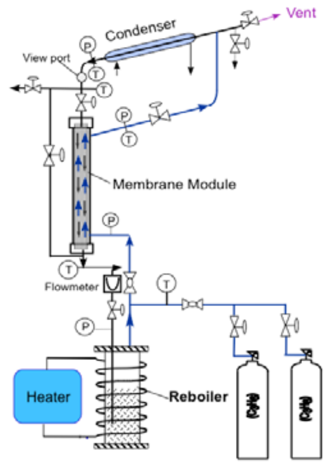

Figure 2. The flowchart of the distillation system for the olefin and paraffin separation.

An HP M series micro gas chromatograph (GC) (Model number G2762A) was used to characterize gas compositions. A RHEONIK coriolis meter (Liquid controls, LLC) with RHM 03 sensor and RHE08-transmitter was used for measuring the liquid flow. The vapor flow rate at total reflux was back calculated from the liquid flow based on the mass balance between the vapor and liquid flow. PX880 – 300 Electronic pressure transmitters (Omega) are mounted at four different sections for monitoring the pressure change in the system. T and K type thermocouples are used for monitoring the temperature. Stanford Research System model SR630 thermocouple readout with 16 channel scanner was used to acquire and digitize a 0 – 5 V voltage signal from the temperature and pressure transducers.

Several hollow fiber modules have been investigated in this study. Each module was packed with polymeric hollow fibers. Table 1 contains a summary of the module characteristics based on our own measurements.

Table 1. Summary of several modules' parameters*.

	BP - module	LANL – 3 module	LANL - 6 module	PM - module
Fiber ID (mm)	1.5	0.626	0.240	0.612
Fiber OD (mm)	2.7	1.20	0.300	0.914
Number of fiber	19	20	198	104
Mass transfer area per volume (cm^2/cm^3)	6.23	2.98	14.1	15.1

*:Active length of these modules is 36.8 cm. All of these fibers were potted inside plastic tube with 1.27 cm ID. The Celgard® hollow fibers were used in LANL - 6 module.

Results and Discussion

In general a fresh module typically required several hours to adapt to the working environment in order to reach steady state. Once it was conditioned the system needed less time to reach a steady state. Figure 3 presents the temperature and pressure profile of a typical trial conducted near 25 °C. For this particular run, the system temperature and pressure reached steady state within 5 hours, at which point the gas samples were withdrawn and analyzed by GC.

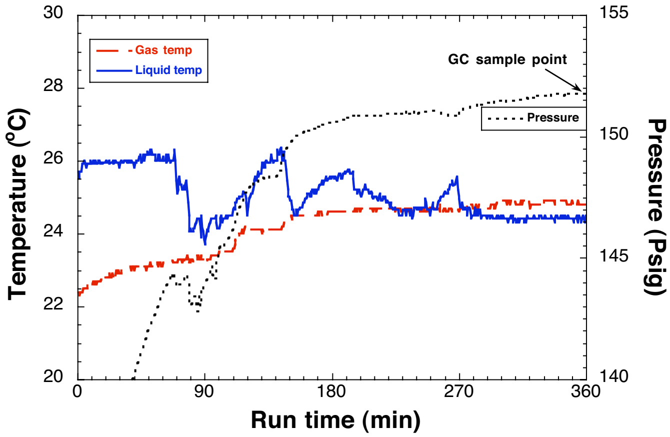

Figure 3. Temperature and pressure profiles for a typical run.

By controlling the temperature difference between the reboiler and the chiller, we are able to control the fluid velocity inside and outside of the hollow fibers. Since both liquid and vapor have their own channels for flow, the operational problems associated with loading and flooding encountered with conventional packing in a tower can be minimized. A plot of flow parameter vs. the capacity of packing materials is commonly used to indicate the operation range for different packing materials. Figure 4 presents the correlation between the flow parameter ($L/G*(\rho_G/\rho_L)^{0.5}$– where ρ is density, the subscript of L and G indicating liquid and vapor phase, respectively) and the capacity of the modules at different operation conditions. Most of the experimental points are above the flooding line where the conventional packing materials experience flooding.

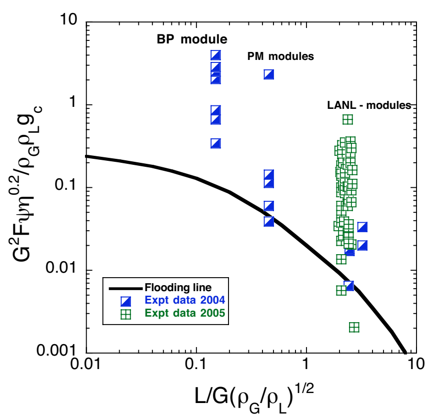

Figure 4. The correlation between flow parameter (on the abscissa) and the capacity factor of our modules (on the ordinate).

Using measured gas compositions, Eq. 7, and V-L equilibrium data the NTU is calculated. From equation 5, we can determine the HTU for the hollow fiber modules. Figure 5 shows a plot of the experimentally obtained HTU vs. gas velocity. As is expected the HTU increases with increasing gas velocity. For the BP module, when the gas velocity is lower than 25 cm/sec, the HTU is as low as 8.8 cm, the best result reported for the propane/propylene separation.

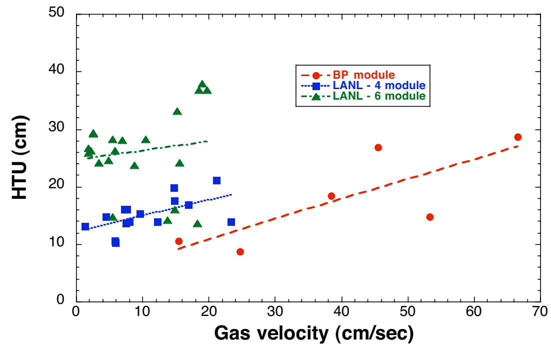

Figure 5. HTUs of BP and LANL modules as functions of vapor velocity.

Conclusion

In this report, we demonstrated the possibility of using hollow fibers as structured packing for olefin/paraffin separations. Due to its large surface area, a low HTU (<10 cm) as compared to conventional packing is achieved. Furthermore, the hollow fibers, allow the liquid and vapor to flow counter-currently and separately on the inside and outside of hollow fiber. The flooding and loading problems common for the conventional packing materials are minimized. Using low cost and lightweight polymeric materials to replace metal as structured packing can significantlydecrease capital cost.

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