

MEMBRANE SEPARATION OF A MIXTURE OF CLOSE BOILING HYDROCARBON COMPONENTS

BACKGROUND

[0001] Olefins, particularly ethylene and propylene, are important chemical feedstocks. Typically they are found in nature or are produced as primary products or byproducts in mixtures that contain saturated hydrocarbons and other components. Before the raw olefins can be used, they usually must be purified from these mixtures. Numerous difficulties have been experienced in this type of separation. Due to their similar relative volatilities, energy-intensive, capital-intensive, multi-trayed distillation columns typically have been used to purify light olefins.

[0002] An example of a prior art distillation column for the separation of propylene and propane is illustrated in **FIG. 1**. In an exemplary method of operation, a raw feedstock of Refinery Grade Propylene (RGP) comprising 70% propylene and 30% propane is introduced to distillation column **105** along feed pipe or pipes **100**. Distillation column **105** generally comprises multiple trays, or levels (not shown). In an embodiment, distillation column **105** comprises 135 trays. Operation of a distillation column **105** is primarily determined by a combination of the number of trays and the reflux ratio. In general, the more trays in a distillation column **105**, the greater the separation at a constant reflux ratio, but also the greater the capital cost. Conversely, fewer trays can be used if reflux is increased, but operating cost also increases. In the distillation column **105**, the lighter components tend to rise and the heavier components tend to sink. The lighter components are extracted along piping **135** and directed to condenser **145** for cooling. Some of the condensed lighter components may be injected back into distillation column **105**. Some of the condensed lighter components may be utilized as a propylene product stream **130**, such as Commercial Grade Propylene (CGP nominally 93% propylene).

[0003] A second stream comprising propane and other heavier components may be extracted from column **105** along piping **115**, re-vaporized in vaporizer **125**, and injected

back into column **105** along piping **110**. Some of the second stream may be utilized as a propane product **120** having typically greater than 95% propane.

[0004] Column **105** is merely one example of a propylene and propane distillation column. One of ordinary skill in the art would readily understand that many variations are possible.

[0005] Typical results from a single distillation column, with a 70% propylene feed, produces a propylene product of 93% purity and a propane product of 95% purity. Accordingly, an improved system would produce results at least as good as a typical prior art distillation column.

[0006] The field of art has proposed the use a membrane-based system. U.S. Pat. No. 3,758,603 and U.S. Pat. No. 3,864,418 in the names of Robert D. Hughes and Edward F. Steigelmann describe membranes used in conjunction with metal complexing techniques to facilitate the separation of ethylene from ethane and methane. Similar metal complex and membrane hybrid processes, called facilitated transport membranes, have been described in U.S. Pat. No. 4,060,566 in the name of Robert L. Yahnke and in U.S. Pat. No. 4,614,524 in the name of Menahem A. Kraus.

[0007] Further membranes have been considered for the separation of olefins from paraffins as an alternative to distillation. However, the separation is difficult largely because of the similar molecular sizes and condensability of the components desired to be separated. The membrane must operate in a hydrocarbon environment under conditions of high pressure and temperature, often resulting in plasticization that may result in a loss of selectivity and/or permeation rate. Such harsh conditions tend to adversely affect the durability and stability of the separation performance of many membrane materials. A membrane system with sufficiently high olefin/paraffin selectivity, high productivity, and sufficient durability in long-term contact with hydrocarbon streams under high pressure and temperature is highly desired.

[0008] The art is replete with processes said to fabricate membranes possessing both high selectivity and high fluxes. Without sufficiently high fluxes the required membrane areas required would be so large as to make the technique uneconomical. It is now well

known that numerous polymer membranes are much more permeable to polar gases (examples include H_2O , CO_2 , H_2S , and SO_2) than to nonpolar gases (N_2 , O_2 , and CH_4), and that gases of small molecular size (He , H_2) permeate more readily through polymer membranes than large molecules (CH_4 , C_2H_6).

[0009] However, even considering these difficulties, utilization of membrane separation has taken an important place in chemical technology for use in a broad range of applications. Gas separation has become a major industrial application of membrane technology in the last 15 years. Membrane based technology for the production of nitrogen from air, removal of carbon dioxide from natural gas, and purification of hydrogen now occupy significant shares of the markets for these processes.

[0010] Membrane materials and systems for separating olefinic hydrocarbons from a mixture of olefinic and saturated hydrocarbons have been reported, but are not easily or economically fabricated into membranes that offer the unique combination of high selectivity and durability under industrial process conditions to provide economic viability.

[0011] For example, several inorganic and polymer/inorganic membrane materials with good propylene/propane selectivity have been studied. However, fabrication of these membranes into practical industrial membranes has proven difficult. Likewise, liquid facilitated-transport membranes have been demonstrated to have attractive separation performance in the lab, but have been difficult to scale up, and have exhibited declining performance in environments typical of an industrial propylene/propane stream.

[0012] Solid polymer-electrolyte facilitated-transport membranes have shown to be capable of fabrication into more stable thin film membranes for ethylene/ethane separation. See Ingo Pinnau and L. G. Toy, Solid polymer electrolyte composite membranes for olefin/paraffin separation, J. Membrane Science, 184 (2001) 39-48. However, these membranes are severely limited by their chemical stability in the olefin/paraffin industrial environment.

[0013] Carbon hollow-fiber membranes have shown promise in laboratory tests ("Propylene/Propane Separation", Product Information from Carbon Membranes, Ltd.,

Israel), but are vulnerable to degradation caused by condensable organics or water present in industrial streams. Moreover, carbon membranes are brittle and difficult to form into membrane modules of commercial relevance.

[0014] Membranes based on rubbery polymers typically have olefin/paraffin selectivity too low for an economically useful separation. For example, Tanaka et al. report that the single-gas propylene/propane selectivity is only 1.7 for a polybutadiene membrane at 50°C (K. Tanaka, A. Taguchi, Jianquiang Hao, H. Kita, K. Okamoto, J. Membrane Science 121 (1996) 197-207) and Ito and Hwang report a propylene/propane selectivity only slightly over 1.0 in silicone rubber at 40°C (Akira Ito and Sun-Tak Hwang, J. Applied Polymer Science, 38 (1989) 483-490).

[0015] Membranes based on glassy polymers have the potential for providing usefully high olefin/paraffin selectivity because of the preferential diffusivity of the olefin, which has a smaller molecular size than the paraffin.

[0016] Membrane films of poly(2,6-dimethyl-1,4-phenylene oxide) exhibited pure gas propylene/propane selectivity of 9.1 (Ito and Hwang, Ibid.) Higher selectivity has been reported by Ilinitch et al. (J. Membrane Science 98 (1995) 287-290, J. Membrane Science 82 (1993) 149-155, and J. Membrane Science 66 (1992) 1-8). However, the membrane exhibited plasticization, most likely due to the presence of hydrocarbons.

[0017] Polyimide membranes have been studied extensively for the separation of gases. An article by Lee and Hwang discloses a hollow fiber membrane of a polyimide that exhibits a mixed-gas propylene/propane selectivity in the range of 5-8 with low feed pressure (2-4 bar). Kwang-Rae Lee and Sun-Tak Hwang, Separation of propylene and propane by polyimide hollow-fiber membrane module, J. Membrane Science 73 (1992) 37-45.

[0018] Krol et al. report a hollow fiber membrane of a polyimide composed of biphenyltetracarboxylic dianhydride and diaminophenylindane which exhibited a pure-gas propylene/propane selectivity of 12. J.J. Krol, M. Boerrigter, G.H. Koops, Polyimide hollow fiber gas separation membranes: preparation and the suppression of

plasticization in propane/propylene environments, J. Membrane Science. 184 (2001) 275-286. However, this membrane was plasticized at even low pressures.

[0019] Matrimid and P84/Matrimid blend hollow fiber membranes have been shown to plasticize and lose selectivity when exposed to a propane/propylene stream. T. Visser and M. Wessling, Auto and Mutual Plasticization In Single and Mixed Gas C3 Transport Through Matrimid-Based Hollow Fiber Membranes, J. Membrane Science, 312 (2008) pp. 84-96.

[0020] Many of these prior art membrane-based techniques of propane/propylene separation utilize a pervaporation mode (liquid feed, gaseous permeate) or gas separation mode (gaseous feed, gaseous permeate). In the pervaporation mode of operation, the liquid feed is "evaporated" to the permeate stream. The latent heat of vaporization is large and a large temperature decrease accompanies the separation. Pervaporation based separation has similarities to propane refrigeration. The high pressure feed permeates the membrane to low pressure. This process is similar to the expansion of propane across an expansion valve in a propylene refrigeration system, resulting in cooling of the permeate stream.

[0021] A convenient mathematical method of describing pervaporation is to divide the separation into two steps. The first is evaporation of the feed liquid to form a hypothetical saturated vapor phase on the feed side of the membrane. The second is permeation of this vapor through the membrane to the low pressure permeate side of the membrane. Although no evaporation actually takes place on the feed side of the membrane during pervaporation, this approach is mathematically simple and is thermodynamically equivalent to the physical process.

[0022] In pervaporation, transmembrane permeation is typically induced by maintaining the pressure on the permeate side lower than the vapor pressure of the feed liquid. The permeate side pressure can be reduced, for example, by drawing a vacuum on the permeate side of the membrane, by sweeping the permeate side to continuously remove permeating vapor, or by cooling the permeate vapor stream to induce

condensation. The feed may also be heated to raise the vapor pressure on the feed side or to at least partially compensate for the temperature drop on permeation.

[0023] Certain issues accompany the use of pervaporation, namely, and typically regarded as most important, the temperature decrease causes membrane productivity to decrease and further increase membrane selectivity. This is an inherent problem for pervaporation. It is very difficult to supply sufficient heat at the correct location (face of the membrane) to maintain constant temperature. As a result, productivity decreases exponentially and the number of modules necessary to achieve a desired productivity becomes unacceptably large. Further, the large temperature drop of the feed to the membrane due to the pressure drop often condenses the feed.

[0024] At least one prior art patent has identified that temperature has an effect on membrane performance. U.S. Pat. No. 5,679,133 discloses a glassy polymer membrane that is operated at temperatures of less than about 5°C for separation of gas components. The patent claims a permeation method comprising contacting a first side of a gas separation membrane having a glassy polymer discriminating layer or region with a gas mixture. The polymer cellulose triacetate is expressly excluded. A difference in chemical potential is maintained from the first side of the membrane to a second side of the membrane. At a minimum, one component of the gas mixture relative to a second component selectively permeates from the first side of the membrane through the membrane to the second side of the membrane. The gas mixture contacts the membrane at a temperature of 5°C or lower. The membrane having a glassy region is selected so that, when using a mixture of 80 mole percent nitrogen and 20 mole percent oxygen as a feed at 30°C with a pressure of 30 psia on the first side of the membrane and a vacuum of less than 1 mm Hg on the second side of the membrane, the permeability of oxygen in barrers is less than 2000. This patent illustrated that temperatures below ambient could be utilized in permeation procedures.

[0025] U.S. Pat. App. Pub. No. 2004/0000513 discloses a plurality of membrane modules disposed in a first product group, a second product group, and optionally one or more intermediate groups used for simultaneous recovery of a very pure permeate

product and a desired non-permeate product from a mixture containing organic compounds. Examples of propylene/propane separation are given as simulated by a computer model. The preferred embodiment is a system of three membranes with propylene selectivity over propane. The embodiments disclosed pump feed stock (about 70% propylene/30% propane) in liquid form to a vaporizer and then to a first membrane. The permeate flows through, is compressed, cooled to 200°F and passed through a second membrane. The permeate is collected as a stream comprising greater than 95% propylene. The non-permeate from the first membrane is passed to a third membrane. Permeate from the third membrane is compressed and passed back through the second membrane. Non-permeate from the third membrane is collected as a propane product.

[0026] U.S. Pat. No. 6,986,802 discloses a membrane device comprising multiple perm-selective membranes that are capable of effecting separation of a mixture of two or more compounds in a feed stock which when subjected to appropriately altered conditions of temperature and/or pressure exhibit a bubble point. The enthalpy of the feed stock is adjusted by a heat exchanger. Membrane Efficiency Index of the non-permeate fluid, when withdrawn, is within a range from about 0.5 to about 1.5. The Membrane Efficiency Index is defined as a ratio of the difference between the specific enthalpy of the feed stream entering the membrane device and specific enthalpy of the non-permeate fluid effluent to the difference between the specific enthalpy of the feed stream and the bubble point specific enthalpy of the non-permeate fluid at the non-permeate product pressure and composition. At an MEI of one, the non-permeate is disclosed as being a liquid at its bubblepoint.

[0027] U.S. Pat. No. 7,070,694 discloses an apparatus comprising a fractional distillation column and one or more membrane devices utilizing solid perm-selective membranes. The processes are stated as capable of use in simultaneous recovery of a very pure permeate product, a desired non-permeate stream, and one or more distillate products from a fluid mixture containing at least two compounds of different boiling point temperatures. The patent discloses that the cooling effect produced by a membrane when a low pressure permeate is produced from a high pressure feed stock is due to

the Joule-Thompson effect. The patent further expresses the need for the incorporation of heat integrated membrane apparatuses with pressure driven membrane separations. [0028] However, these various prior art approaches require excessive capital costs and a multitude of membrane modules.

[0029] U.S. Pat. App. Pub. No. 2008/0167512 improves upon the cited prior art. The '512 publication discloses membrane-based systems and methods for separation of propylene and propane that overcome certain issues associated with prior devices and take advantage of a temperature drop across the associated separation membrane. However, the systems and methods still require use of a recycle compressor, which has an associated capital cost as well as operating cost component.

[0030] Accordingly, there is a need in the art field for an improved membrane and/or membrane system for the separation of olefins and paraffins that uses fewer membrane modules and requires less capital and operating cost.

SUMMARY

[0031] Disclosed is a process for the membrane-based separation of a mixture of close-boiling hydrocarbon components. A feed stream comprising the mixture of close-boiling hydrocarbon components is fed to a first membrane stage at a temperature and a pressure above a critical point of the mixture. A first permeate stream and a first non-permeate stream are extracted from the first membrane stage. The process may include one or more of the following aspects:

- cooling the first permeate stream to produce a liquid product.
- the feed stream and the first non-permeate stream each having a viscosity and the ratio of the viscosity of the first non-permeate stream to that of the feed stream being less than 5.
- the feed stream and the first non-permeate stream each having a density and the ratio of the density of the first non-permeate stream to that of the feed stream being less than 5.
- the feed stream comprising a mixture of propane and propylene.

- the first membrane stage having a selectivity for propylene over propane of at least 5.0.
- the first membrane stage having a selectivity for propylene over propane of at least 6.5.
- the pressure of the feed stream being 700 psi or higher.
- the pressure of the feed stream ranging from about 900 psi to about 1100 psi.
- the temperature of the feed stream being 96°C or higher.
- feeding the first non-permeate stream to a second membrane stage at a temperature and pressure above the critical point of the first non-permeate stream, extracting a second non-permeate stream, extracting a second permeate stream, and combining the second permeate stream with the feed stream.
- the second membrane stage having a selectivity for propylene over propane of at least 3.0.
- the second membrane stage having a selectivity for propylene over propane of at least 5.0.
- the second non-permeate stream being collected as a liquid or as a two-phase gas/liquid stream having a purity of at least about 95% propane.

[0032] Also disclosed is a system for the membrane-based separation of a mixture of close boiling hydrocarbon components. In the system, a feed stream comprising a mixture of close boiling hydrocarbon components is fed to the inlet of a pump. The pump is adapted and configured to pressurize the feed stream to a pressure above a critical pressure of the mixture. The pump's outlet is in fluid communication with the inlet of a first evaporator. The first evaporator is adapted and configured to raise the feed stream's temperature to a temperature above the critical temperature of the mixture. The first evaporator's outlet is in fluid communication with the feed port of the first membrane stage. The first membrane stage further comprises a permeate port and a non-permeate port. The first membrane stage exhibits a selectivity for propylene over

propane of at least 6.5. The first membrane stage's non-permeate port is in fluid communication with the feed port of the second membrane stage. The second membrane stage further comprises a permeate port and a non-permeate port. The second membrane stage exhibits a selectivity for propylene over propane of at least 3.0.

[0033] The system may further include a second evaporator having an inlet and outlet. The inlet of the second evaporator may be in fluid communication with the non-permeate port of the first membrane stage and the outlet of the second evaporator may be in fluid communication with the feed port of the second membrane stage. The second evaporator is adapted and configured to raise a temperature of a non-permeate stream from the first membrane stage to a temperature above a critical temperature of the non-permeate stream.

BRIEF DESCRIPTION OF THE FIGURES

[0034] For a further understanding of the nature and objects of the disclosed systems and methods, reference should be made to the following detailed description, taken in conjunction with the accompanying drawings, in which like elements are given the same or analogous reference numbers and wherein:

[0035] **FIG 1** is a flow diagram showing a prior art distillation column for the separation of propylene and propane.

[0036] **FIG 2** is a flow diagram showing an embodiment of the current system and method using a membrane separation approach applied to a propylene/propane separation.

[0037] **FIG 3** is a flow diagram showing an alternate embodiment of the current system and method applied to a propylene/propane separation.

[0038] **FIG 4** is a flow diagram showing a second alternate embodiment of the current system and method applied to a propylene/propane separation.

DETAILED DESCRIPTION

[0039] The following definitions and explanations are meant and intended to be controlling in any future construction unless clearly and unambiguously modified in the following Description or when application of the meaning renders any construction meaningless or essentially meaningless. In cases where the construction of the term would render it meaningless or essentially meaningless, the definition should be taken from Webster's Dictionary, 3rd Edition. Definitions and/or interpretations should not be incorporated from other patent applications, patents, or publications, related or not, unless specifically stated in this specification or if the incorporation is necessary for maintaining validity.

[0040] As used herein, a "fluid" is a continuous, amorphous substance whose molecules move freely past one another and that has the tendency to assume the shape of its container, for example, a liquid or a gas.

[0041] As used herein, "membrane apparatus" means and refers to flat sheet membranes, spiral wound flat sheet membranes, tubular tube membranes, hollow fiber membranes, and/or other membranes commonly used in industry.

[0042] As used herein, "evaporator" means and refers to a heater or an evaporator. In other words, the evaporators utilized herein may be used to raise the temperature and/or change the phase of the stream being processed from liquid to gas or supercritical.

[0043] As used herein, "condenser" means and refers to a cooler or a condenser. In other words, the condensers utilized herein may be used to reduce the temperature and/or change the phase of the stream being processed from gas to liquid.

[0044] The present disclosure has wide applicability across the art field for systems and methods for the separation of streams containing a mixture of close-boiling hydrocarbon components. The system may operate with either counter current or cross flow membrane bundles. The method relates primarily to a membrane-based system for the

separation of streams containing a mixture of close-boiling components that are condensable at ambient conditions by utilizing a feed fluid in its supercritical state.

[0045] The details herein were discovered when improving upon the two step process disclosed in U.S. Pat. App. Pub. No. 2008/0167512 by obviating the need for the recycle compressor. Operating the process at a temperature and pressure such that the feed stream fed to the membranes is above the critical point of the feed stream enables the permeate/low pressure side of the membrane to be set at conditions such that the permeate gas phase may be condensed to a liquid by merely lowering the temperature. The resulting liquid permeate may either be available for downstream processing or recycled back to the membrane feed without the need for additional compression. Operation at pressures and temperatures above the critical point also ensures a continuum of densities and viscosities and as a result there are no sharp phase demarcations within the membrane module.

[0046] The disclosure therefore provides a method of separating streams containing close-boiling hydrocarbon mixtures, including, but not limited to, mixtures of ethane and ethylene; propane and propene; 1-butene and butane; and 1-butene, butane, and propane. For the purposes of this application, close-boiling hydrocarbon mixtures are defined as mixtures that contain two or more hydrocarbon compounds with at least one of the compounds having a boiling point close to that of at least a second of the compounds at the pressure at which the disclosed system is operated. Close boiling points are usually within about 45°F (25°C) or less, preferably within about 27°F (15°C) or less, or more preferably within about 9°F (5 °C) or less.

[0047] The disclosure further provides a method of separating nonideal organic streams. For purposes of this application, nonideality is defined by the inability of the ideal gas law to describe the PVT (pressure volume temperature) behavior of the gas. Non ideality for organic gases increases with molecular weight: methane is more ideal than ethane, ethane is more ideal than propane, propane is more ideal than butane, and the like. In most cases, membrane-based separation of nonideal organic gases leads to a temperature decrease on separation. The temperature change increases with

increasing non-ideality of the stream. The temperature change arises due to the reduction in pressure experienced by the permeated gas from the initial feed pressure to the final permeate pressure. This temperature change can be approximated by a Joule-Thompson expansion $(dT/dP)_H$.

[0048] In general, the disclosed system comprises, at a minimum, a membrane apparatus, a pump, and an evaporator. A supercritical feed containing a mixture of close-boiling compounds is introduced into the disclosed system.

[0049] Many of the negative aspects of membrane-based separation of a nonideal fluid stream are minimized in the present disclosure. In the disclosed process, the feed is initially pumped or compressed to a pressure above the critical pressure of the mixture. The pressurized feed stream is then heated in a vaporizer to a temperature higher than the critical temperature of the feed stream. Vaporization of the stream after pressurization reduces the heat required for vaporization relative to that for vaporization prior to pressurization. This is due to the fact that the heat of vaporization decreases with increasing pressure. Pressurization of the feed has additional benefits. Higher pressure reduces total membrane count (i.e., the number of membranes required). Higher pressure increases the pressure-ratio (i.e., feed pressure to the membrane divided by permeate pressure from the membrane). Higher pressure ratio improves separation performance, in various embodiments. Preferably, the pressure difference between the permeate stream and the feed stream is less than about 2,000 psig, more preferably less than about 1,500 psig, and even more preferably less than about 1,300 psig.

[0050] The final pressure and temperature of the feed mixture are selected so as to place the feed mixture into its supercritical region, and preferably well into its supercritical region. As a result, the supercritical mixture exhibits properties of both a gas and a liquid. It exhibits the diffusivity of a gas and the solvent properties of a liquid. Initial test results for supercritical mixtures of propane and propylene indicate that the mixture permeates through the membrane like a gas. The supercritical mixture does not exhibit surface tension because the liquid/gas phase boundary no longer exists.

Therefore, although the non-permeate or residue stream may exhibit a temperature below its critical temperature, thereby technically forming a liquid, the pressure of the non-permeate remains above its critical pressure, which results in a slight density and viscosity difference between the supercritical feed and the remaining non-permeate stream. In other words, it is believed that utilizing a supercritical feed stream benefits both the membrane and process because the viscosities and densities of the feed and non-permeate streams remain close. To further benefit the membrane and process, the ratio of the viscosity of the non-permeate stream to that of the feed stream should preferably be less than 5, and more preferably less than 2. Additionally, the ratio of the density of the non-permeate stream to that of the feed stream is preferably less than 5, and more preferably less than 3.

[0051] Table 1 lists the critical temperature and critical pressure above which the specific exemplary and non-limiting mixtures of close-boiling compounds A, B, and C must be raised to be placed into the supercritical phase, as well as the density and viscosity of the mixture at that temperature and pressure. One of ordinary skill in the art would be capable of calculating the critical temperature and pressure of other mixtures that may also be separated according to the disclosed method.

Table 1

<u>% (v/v) A</u>	<u>% (v/v) B</u>	<u>% (v/v) C</u>	<u>Temp</u> <u>(°C)</u>	<u>Press</u> <u>(psig)</u>	<u>Density</u> <u>(g/cm³)</u>	<u>Viscosity</u> <u>(cp)</u>
50% Ethylene	50% Ethane	0%	21	722	0.1	0.02
20% Ethylene	80% Ethane	0%	28	709	0.1	0.02
90% Ethylene	10% Ethane	0%	12	719	0.1	0.02
81% Propylene	19% Propane	0%	93	649	0.1	0.02
60% Propylene	40% Propane	0%	93	636	0.1	0.02
20% Propylene	80% Propane	0%	95	613	0.1	0.02
5% Propylene	95% Propane	0%	96	604	0.1	0.02
10% Propylene	80% 1-Butene	10% Butane	142	584	0.2	0.03
10% Propylene	80% t2Butane	10% Butane	149	582	0.2	0.03
50% 1-Butene	50% Butane	0%	149	571	0.2	0.03
10% 1-Butene	80% Butane	10% Isobutane		150	546	0.1 0.02
10% 1-Butene	80% C2 Butene	10% Isobutane		158	596	0.2 0.03
30% 1-Butene	60% Butane	10% Propane	146	574	0.2	0.02

[0052] Raising the feed pressure of the mixture above and into the supercritical region significantly mitigates concerns of phase change as the mixture undergoes changes in

composition, temperature, and pressure as it emerges as the non-permeate stream. In addition, raising the permeate pressure provides additional advantages. For example, the permeate stream may undergo a phase change from gas to liquid with only modest cooling. Therefore, the compressors 365 and 395 disclosed in FIG 3 and 465 in FIG 4 of U.S. Pat. App. No. 2008/0167512 are not needed. Also the pressure of the permeate stream remains low enough to provide a reasonable pressure ratio across the membrane without effecting the fluid separation. Finally as a liquid pump is used to provide additional compression, the energy requirements may be reduced as much as by 75% when compared to systems that require compressors.

[0053] The permeation process causes the temperature of the permeate and non-permeate streams to drop. However, as stated previously, the pressure of the non-permeate stream remains above its critical pressure. Therefore, the density and viscosity of the non-permeate stream remain similar to that of the feed stream. Through optimization of the feed pressure, non-permeate staging, and interstage heating, the temperature difference between the feed stream, the permeate stream, and the non-permeate stream may remain within 30°C, preferably within 20°C, and more preferably within 10°C.

[0054] The disclosure contemplates a process for the separation of a mixture containing close-boiling hydrocarbon compounds. The feed stream is at an initial temperature, preferably so that the feed stream is in liquid form. The pressure of the stream is increased to a pressure above the critical pressure of the mixture. The liquid stream is then vaporized and heated to a temperature above the critical temperature of the mixture. The resultant supercritical stream enters the membrane separator. The olefin preferentially permeates through the membrane and the remaining stream (primarily paraffin) is removed as a non-permeate stream. The olefin-enriched permeate may be cooled to form a liquid product. The non-permeate stream may then be reheated to its supercritical phase and passed through another membrane separator wherein the second non-permeate stream is collected as a paraffin product and the second permeate olefin-rich stream is recycled back to the feed stream to increase recovery of

the olefin in the olefin product. The second permeate stream requires no further recompression, but simply cooling to be condensed to a liquid and readily mix with the feed stream of the process.

[0055] Accordingly, the disclosed process generally comprises the steps of feeding a feed stream comprising a mixture of close-boiling hydrocarbon compounds to a first membrane at a temperature and pressure above the critical point for the mixture, said membrane having a selectivity for olefin as compared to the paraffin of at least 5.0; extracting a permeate olefin enriched stream; cooling the permeate stream; and, recovering the permeate stream as a liquid olefin product stream.

[0056] Now referring to **FIG 2**, an illustration of a system for the separation of a mixture of close boiling hydrocarbon components is disclosed. System **200** comprises various elements, such as, but not limited to, pump **205**, evaporator **215**, and membrane stage **225**. These elements are interconnected by any means for connection common in the art, such as, but not limited to line(s), piping, valves, and/or the like. For example, in **FIG 2**, a line introduces feed fluid **201** to pump **205**, a line conveys the pressurized feed fluid **210** to evaporator **215**, a line conveys the supercritical feed **220** to membrane stage **225**. From membrane stage **225**, a line conveys an olefin enriched stream **230** and/or a line conveys a paraffin enriched stream **240**.

[0057] In a preferred embodiment, during operation of system **200**, a feed stock or feed stream **201** comprising at least propylene and propane is introduced or injected into system **200**. In this embodiment, the feed stream may be refinery grade propylene (RGP) comprising between about 60% and about 80% propylene, preferably at least about 70% propylene. However, RGP comprising other concentrations of propylene is possible and acceptable. In general, any feed stock comprising any concentration propane and propylene can be utilized in the teachings herein. One of ordinary skill in the art will recognize that this system may also be used to separate different mixtures of close boiling hydrocarbon components.

[0058] As disclosed, feed stream **201** is pumped to pressure in pump **205**. To separate a mixture comprising at least propylene and propane, the pressure of feed stream **201**

is pumped to a pressure of 700 psia or higher prior to introduction to membrane stage **225**. Preferably, the pressure of feed stream **201** is pumped to a pressure of about 900 psia to about 1,100 psia prior to introduction to membrane stage **225**. In this embodiment, the pressurized feed stream **210** is then vaporized at vaporizer **215** to 96°C or higher. As a result, the feed stream **220** is fed in its supercritical state to membrane stage **225**. One of ordinary skill in the art will recognize that different target temperatures and pressures may be necessary to adapt the system **200** to separate different mixtures of close boiling hydrocarbon components.

[0059] Membrane stage **225** may utilize one or more gas separation modules (not shown). In a preferred embodiment, membrane stage **225** is selective for propylene over propane. In this embodiment, any membrane capable of effecting a propylene/propane separation can be used. Membranes capable of operating in a supercritical hydrocarbon environment and effecting a propylene/propane separation are preferred. An example of a membrane capable of operating in a hydrocarbon supercritical environment is a polyimide membrane, and particularly a polyimide membrane made of polymers sold under the tradenames P84 or P84HT from HP Polymers GmbH. Preferred membranes of P84 or P84HT are disclosed in U.S. Pat. No. 7,018,445, titled POLYIMIDE BLENDS FOR GAS SEPARATION MEMBRANES, and U.S. Pat. No. 7,422,623 titled SEPARATION MEMBRANE BY CONTROLLED ANNEALING OF POLYIMIDE POLYMERS. The entire disclosures of these applications are incorporated herein by this reference.

[0060] Additional exemplary, non-limiting embodiments and/or disclosures of propane/propylene separation membranes that may be used with the systems and methods disclosed herein are detailed in U.S. Pat. No. 4,374,657; U.S. Pat. No. 4,444,571; U.S. Pat. No. 4,857,078; U.S. Pat. No. 4,952,751; U.S. Pat. Nos. 4,978,430; 5,057,641; U.S. Pat. No. 5,273,572; U.S. Pat. No. 5,326,385; U.S. Pat. No. 5,679,133; U.S. Pat. No. 6,187,196; U.S. Pat. No. 6,187,987; U.S. Pat. No. 6,517,611; U.S. Pat. No. 6,986,802; U.S. Pat. No. 7,025,804; and, U.S. Pat. No. 7,070,694, the contents of which are hereby incorporated by reference, as if they were presented herein in their

entirety. In general, any membrane apparatus for use in the separation of propylene and propane is capable of use with the present disclosure with varying degrees of performance, as would be readily apparent to one of ordinary skill in the art.

[0061] In a preferred embodiment, the selectivity of the propylene/propane membrane for propylene may range from at least about 3.0 to about 20.0. Preferably, the selectivity for propylene ranges from about 5.0 to about 15.0. More preferably, the selectivity for propylene ranges from about 6.5 to about 13.0. Even more preferably, the selectivity for propylene ranges from about 8.0 to about 12.0.

[0062] Due to the cooling effect in membrane stage **225**, non-permeate stream **230** and permeate stream **240** may be expected to be cooler than feed stream **220**. However, it is expected that the temperature and pressure of permeate stream **240** will be such that it remains in its gaseous state. Either or both of stream **230** and/or stream **240** may be further processed as is desired.

[0063] The permeate stream **240** may pass from membrane stage **225** and be collected as a gaseous product or cooled to produce a liquid product. In the preferred embodiment, the permeate stream may be used as a chemical-grade propylene product. In this embodiment, the system **200** may be adapted to yield a permeate stream **240** having at least about 93% propylene purity. The percentage recovery of propylene may range from about 50% to about 99%, preferably from about 75% to about 99%, and more preferably from about 85% to about 99%. In the preferred embodiment, the system **200** may be adapted to yield a non-permeate stream **230** having at most about 5% propylene. The percentage recovery of propane from non-permeate stream **230** may range from about 75% to about 99%, preferably from about 80% to about 92%. However, one of ordinary skill in the art will recognize that the percent purity and recovery may vary by design and by composition of the feed stream **201**.

[0064] Now referring to **FIG 3**, an illustration of an alternate embodiment of a system **300** for the separation of a mixture of close boiling hydrocarbon components is disclosed. System **300** comprises various elements, such as, but not limited to, pump

305, first and second evaporators **315**, **335**, first and optional second condensers **365**, **385** (optional), first membrane stage **325**, and second membrane stage **345**.

[0065] These elements are interconnected by any means for connection common in the art, such as, but not limited to line(s), piping, valves, and/or the like. For example, in **FIG 3**, a line introduces feed fluid **301** to pump **305**, a line conveys the pressurized feed fluid **310** to first evaporator **315**, a line conveys the supercritical feed **320** to first membrane stage **325**, etc. In a preferred embodiment, during operation of system **300**, a feed stock or feed stream **301** comprising at least propylene and propane is introduced or injected into system **300**. In this embodiment, the feed stream may be refinery grade propylene (RGP) comprising between about 60% and about 80% propylene, preferably at least about 70% propylene. However, RGP comprising other concentrations of propylene is possible and acceptable. In general, any feed stock comprising any concentration propane and propylene can be utilized in the teachings herein. One of ordinary skill in the art will recognize that this system may also be used to separate different mixtures of close boiling hydrocarbon components.

[0066] Feed stream **301** is pumped to pressure in pump **305**. The pressure of feed stream **301** is pumped to a pressure above its critical pressure so that, after vaporization, the pressure of the supercritical feed stream **320** remains within its supercritical state. To separate a mixture comprising at least propylene and propane, the feed stream **301** is pumped to a pressure of 700 psia or higher, and more preferably to between about 900 psia and about 1,100 psia. The pressurized feed stream **310** is then vaporized at first evaporator **315** to a temperature of 96°C or higher, preferably from about 100°C to about 105°C. As a result, the feed stream **320** is fed in its supercritical state to first membrane stage **325**. One of ordinary skill in the art will recognize that different target temperatures and pressures may be necessary to adapt the system **300** to separate different mixtures of close boiling hydrocarbon components.

[0067] First membrane stage **325** may utilize one or more gas separation modules (not shown). In a preferred embodiment, the first membrane stage **325** may use membranes similar to those listed above with reference to the membrane stage **225** of

FIG 2 having selectivity for propylene over propane as described above. From first membrane stage **325**, a line conveys non-permeate stream **330** and a line conveys permeate stream **340**. Permeate stream **340** will exit the first membrane stage **325** at a lower temperature than that at which stream **320** entered first membrane stage **325**. However, in a preferred embodiment, it is expected that the temperature and pressure of permeate stream **340** will be such that it remains in its gaseous state. Permeate stream **340** is conveyed to optional second condenser **385** for cooling and conveyed as a hydrocarbon stream **390**. In a preferred embodiment, hydrocarbon stream **390** contains substantial quantities of propylene, preferably greater than about 90% propylene, more preferably greater than about 92% propylene, and even more preferably greater than about 93% propylene. Stream **390** may be collected as a product, sent for further processing, used elsewhere in the process, and/or the like.

[0068] Non-permeate stream **330** is typically depleted in the olefin component as compared to permeate stream **340** or feed stream **320**. However, non-permeate stream **330** is capable of containing some olefin component. Although the percentage of olefin and paraffin has changed in non-permeate stream **330**, in a preferred embodiment, the critical temperature and critical pressure for the non-permeate stream **330** remain close to that of feed stream **320**. The critical temperature and critical pressure for propylene/propane mixtures only range approximately 4°C and approximately 60 psig, respectively. As is well known, the pressure of non-permeate stream **330** remains close to that of feed stream **320**. Therefore, when the pressure of stream **320** is sufficiently above its critical pressure, additional compression is not required to raise the pressure of non-permeate stream **330** above its supercritical pressure before sending to second membrane **345**.

[0069] Due to the cooling effect in first membrane stage **325**, non-permeate stream **330** may be expected to be cooler than stream **320**. In **FIG 3**, non-permeate stream **330** is conveyed to a second evaporator **335** to heat stream **330** above its supercritical temperature prior to being fed to second membrane stage **345**. In a preferred embodiment, second evaporator **335** heats stream **330** to 96°C or higher, preferably

from about 100°C to about 105°C. As a result, the non-permeate stream **330** is fed in it supercritical state to second membrane stage **345**.

[0070] Like the first membrane stage **325**, second membrane stage **345** may utilize one or more gas separation modules (not shown). Furthermore, to minimize the temperature change between the non-permeate stream **330**, the second non-permeate stream **350**, and the second permeate stream **360**, one or more combinations of second evaporator **335** and second stage membrane **345** may be utilized in series. For example, a third evaporator (not shown) and a third membrane stage (not shown) may be placed in series with second membrane stage **345** such that they are fed by second non-permeate stream **350** with the resulting permeate stream being mixed with second permeate stream **360** and the resulting non-permeate stream being collected as product. If necessary, to further minimize temperature change, additional evaporator and membrane stage combinations may be utilized in series to process the non-permeate stream.

[0071] Second membrane stage **345** is selective for the olefin component over the paraffin component, such that a paraffin-enriched stream **350** is extracted and an olefin-enriched stream **360** is extracted. In a preferred embodiment, second membrane stage **345** may use membranes similar to those listed above for the membrane stage **225** of **FIG 2** having selectivity for propylene over propane as described above. One of ordinary skill in the art will recognize that first and second membrane stages **325** and **345** may utilize the same or different membranes, which may have the same or different selectivities, depending ultimately on the intended purpose of the system **300**.

[0072] The second permeate stream **360** may pass from second membrane stage **345** and into first condenser **365** for cooling, forming a liquid olefin-enriched stream **370** to be added to stream **301** to form a combined, well-mixed stream **380**. One of ordinary skill in the art will recognize how to effectively mix streams **301** and **370**. The combination of stream **370** with stream **301** may further improve recovery of olefin in stream **340**. As a result, the olefin content of stream **380** may be higher, and the paraffin content lower, than that of stream **301**. In a preferred embodiment, the system **300** may

be adapted to yield a second permeate stream **360** having less than about 93% propylene purity. The percentage recovery of propylene may range from about 50% to about 99%, preferably from about 75% to about 99%, and more preferably from about 85% to about 99%. However, one of ordinary skill in the art will recognize that the percent purity and recovery may vary by design and by composition of the feed stream **301**.

[0073] In a preferred embodiment, the system **300** may be adapted to yield a second non-permeate stream **350** having at most about 5% propylene. If the propylene composition of second non-permeate stream **350** is less than 5%, it may be collected as a liquefied petroleum gas (LPG) product. Alternatively, as discussed above, it may be sent to another membrane stage (not shown), set up with components similar to evaporator **335** and second membrane stage **345**. The percentage recovery of propane from second non-permeate stream **350** may range from about 50% to about 99%, preferably from about 75% to about 99%, and more preferably from about 80% to about 95%. However, one of ordinary skill in the art will recognize that the percent purity and recovery may vary by design and by composition of the feed stream **301**.

[0074] Now referring to **FIG 4**, an illustration of an alternate embodiment of a system **400** for the separation of a mixture of close boiling hydrocarbon components is disclosed. System **400** discloses a feed stream **401**, pump **405**, first heat exchanger **505**, second heat exchanger **510**, third heat exchanger **515**, first evaporator **415**, first membrane stage **425**, fourth heat exchanger **520**, second evaporator **435**, second membrane stage **445**, first condenser **465**, second condenser **485**, and third condenser **525**. In order to maximize heat recovery and minimize operating costs for the system **400**, heat exchangers **505**, **510**, **515**, and **520** have been added. One of ordinary skill in the art will recognize that more or fewer heat exchangers may be used without departing from the teachings herein.

[0075] These elements are interconnected by any means for connection common in the art, such as, but not limited to line(s), piping, valves, and/or the like. For example, in **FIG 4**, a line introduces feed fluid **401** to pump **405**; lines convey the pressurized feed fluid

410 through first heat exchanger 505, second heat exchanger 510, third heat exchanger 515, and first evaporator 415; a line conveys the supercritical feed 420 to first membrane stage 425, etc. As in the previous figures, in a preferred embodiment, during operation of system 400, a feed stock or feed stream 401 comprising at least propylene and propane is introduced or injected into system 400. In this embodiment, the feed stream may be refinery grade propylene (RGP) comprising between about 60% and about 80% propylene, preferably at least about 70% propylene. However, RGP comprising other concentrations of propylene is possible and acceptable. In general, any feed stock comprising any concentration propane and propylene can be utilized in the teachings herein. One of ordinary skill in the art will recognize that this system may also be used to separate different mixtures of close boiling hydrocarbon components. [0076] Stream 401 is typically introduced to system 400 as a liquid and pumped to a pressure sufficiently above the critical pressure of stream 401 in pump 405, producing some heat, so that the supercritical feed stream 420 remains within its supercritical range when fed to first membrane stage 425. In a preferred embodiment, the pressure of feed stream 401 is pumped to a pressure so that the pressure of supercritical feed stream 420 is at a pressure of 700 psia or higher prior to introduction to first membrane stage 425. Preferably, the pressure of supercritical feed stream 420 is at a pressure between about 900 psia and about 1,100 psia prior to introduction to first membrane stage 425. One of ordinary skill in the art will recognize that different target pressures may be necessary to adapt the system 400 to separate different mixtures of close boiling hydrocarbon components.

[0077] Pressurized feed stream 410 is passed through various heat exchangers for heating by and to provide cooling to other streams. For example, stream 410 may be heated by and provide cooling to streams 450, 440, and/or 460. However, any one or combination of streams 450, 440, and/or 460 may also serve to be cooled by and to heat stream 410.

[0078] In a preferred embodiment, first evaporator 415 heats pressurized feed stream 410 to a temperature of 96°C or higher, preferably from about 100°C to about 105°C,

resulting in supercritical stream **420**. One of ordinary skill in the art will recognize that different target temperatures may be necessary to adapt the system **400** to separate different mixtures of close boiling hydrocarbon components. Stream **420** is conveyed to first membrane stage **425**. As discussed with respect to **FIGS 2 and 3**, first membrane stage **425** may utilize one or more gas separation membrane modules (not shown). In a preferred embodiment, first membrane stage **425** may use membranes similar to those listed above for the membrane stage **225** of **FIG 2** having selectivity for propylene over propane as described above.

[0079] Permeate stream **440** will exit the first membrane stage **425** at a lower temperature than that at which stream **420** entered first membrane stage **425**. However, it is expected that the temperature and pressure of permeate stream **440** will be such that it remains in its gaseous state. Permeate stream **440** is conveyed to fourth heat exchanger **520**, second heat exchanger **510**, and second condenser **485** for cooling and conveyed as a liquid hydrocarbon stream **490**. In a preferred embodiment, liquid hydrocarbon stream **490** contains substantial quantities of propylene, preferably greater than about 90% propylene, more preferably greater than about 92% propylene, and even more preferably greater than about 93% propylene. Stream **490** may be collected as a product, sent for further processing, used elsewhere in the process, and/or the like.

[0080] Non-permeate stream **430** is typically depleted in olefin as compared to permeate stream **440**. However, non-permeate stream **430** is capable of containing olefin. As stated with reference to **FIG 3**, although the percentage of paraffin and olefin have changed in non-permeate stream **430**, in a preferred embodiment, the critical temperature and critical pressure for the non-permeate stream **430** remain close to that of feed stream **420**. Therefore, when the pressure of stream **420** is sufficiently above its critical pressure, additional compression is not required to raise the pressure of non-permeate stream **430** above its supercritical pressure before sending to second membrane stage **445**.

[0081] Due to the cooling effect in first membrane stage **425**, however, non-permeate stream **430** may be expected to be cooler than stream **420**. The non-permeate stream

430 is passed across fourth heat exchanger **520** with permeate stream **440**. Fourth heat exchanger **520** acts to heat stream **430** and cool stream **440**. However, little heating of stream **430** may occur due to the volume of the non-permeate stream **430** being greater than that of the permeate stream **440**. Alternatively, heating of the non-permeate stream **430** in fourth heat exchanger **520** may range from none at all to more than a minimal amount. If necessary, additional heat may be provided to non-permeate stream **430** by second evaporator **435** to raise the temperature of stream **430** above its supercritical temperature.

[0082] Non-permeate stream **430** is conveyed to second membrane stage **445** to produce paraffin-enriched, second non-permeate stream **450** and olefin-enriched, second permeate stream **460**. Like first membrane stage **425**, second membrane stage **445** may utilize one or more gas separation membrane modules (not shown).

Furthermore, to minimize the temperature change between the non-permeate stream **430**, the second non-permeate stream **450**, and the second permeate stream **460**, one or more combinations of second evaporator **435** and second stage membrane **445** may be utilized in series. For example, a third evaporator (not shown) and a third membrane stage (not shown) may be placed in series with second membrane stage **445** such that they are fed by non-permeate stream **450** with the resulting permeate stream being mixed with second permeate stream **460** and the resulting non-permeate stream being collected as product. If necessary, to further minimize temperature change, additional evaporator and membrane stage combinations may be utilized in series to process the non-permeate stream.

[0083] Second membrane stage **445** is selective for olefin over paraffin, such that a paraffin-enriched stream **450** is extracted and an olefin-enriched stream **460** is extracted. In a preferred embodiment, second membrane stage **445** may use membranes similar to those listed above for the membrane stage **225** of **FIG 2** having selectivity for propylene over propane as described above. One of ordinary skill in the art will recognize that first and second membrane stages **425** and **445** may utilize the

same or different membranes, which may have the same or different selectivities, depending ultimately on the intended purpose of the system **400**.

[0084] Second non-permeate stream **450** may be at or near supercritical temperature and therefore act to heat stream **410** in first heat exchanger **505**. Second non-permeate stream **450** may also be cooled in third condenser **525** and collected as a paraffin-enriched liquid product **530**. In a preferred embodiment, the system **400** may be adapted to yield a second non-permeate stream **450** having at most about 5% propylene. If the propylene composition of second non-permeate stream **450** is less than 5%, a LPG product may be collected as stream **530** after cooling in first heat exchanger **505** and third condenser **525**. Alternatively, second non-permeate stream **450** may be sent to another membrane stage (not shown), set up in the same manner with components similar to fourth heat exchanger **520**, second evaporator **435**, and second membrane stage **445**. The percentage recovery of propane from second non-permeate stream **450** may range from about 75% to about 99%, preferably from about 80% to about 92%. However, one of ordinary skill in the art will recognize that the percent purity and recovery may vary by design and by composition of the feed stream **401**.

[0085] Second permeate stream **460** will be pressure depleted and olefin-enriched. At least a portion of stream **460** may act to be cooled by and to provide heat to stream **410** in third heat exchanger **515** and may be cooled in first condenser **465**. The resulting liquid olefin-enriched stream **470** may be mixed with feed stream **401** to provide for the additional recovery of olefin. As a result, the olefin content of stream **480** may be higher, and the paraffin content may be lower, than that of stream **401**. The combined liquid olefin-enriched stream **470** and feed stream **401** form well-mixed stream **480**. One of ordinary skill in the art will recognize how to effectively mix streams **401** and **470**. In a preferred embodiment, the system **400** may be adapted to yield a second permeate stream **460** having less than about 93% propylene purity. The percentage recovery of propylene may range from about 50% to about 99%, preferably from about 75% to about 99%, and more preferably from about 85% to about 99%. However, one

of ordinary skill in the art will recognize that the percent purity and recovery may vary by design and by composition of the feed stream 401.

[0086] Further embodiments may comprise additional membranes as desired. For example, a further membrane may be added to separate olefin from streams 390 and 490, such as to produce, in a preferred embodiment, a Polymer Grade Propylene Product (PGP) product. Alternatively, streams 390 and 490 may be fed to a distillation column for further processing. Further, a different arrangement of heat exchangers, evaporators, compressors, and condensers can be used within the general inventive guidelines of the present invention. The addition of another membrane allows improving olefin purity without the necessity of improving or modifying membrane structure, i.e., membrane selectivity and/or the like. In a preferred embodiment, adding at least one additional membrane increases the purity of propylene to at 99%.

EXAMPLES

[0087] Higher pressure reduces the module count and the higher pressure-ratio (feed pressure to the membrane divided by permeate pressure from the membrane) improves separation performance. Further maintaining the feed in a supercritical state allows operation of the permeate stream at a high enough pressure to achieve its phase change by a simple temperature change.

[0088] It has been found that traditional gas separation systems require 12% more overall horsepower and 9.5% more energy for processing RGP than embodiments of the current inventive process. The current inventive process uses 1/3 more pump horsepower than the traditional gas separation approach.

[0089] Application of these concepts is illustrated in the following examples. For each of these examples, membrane stages having propylene permeance of 2 and a selectivity of propylene to propane of 8 is assumed.

[0090] Example

[0091] Three simulations were performed based upon the system illustrated in **FIG 3**, without the optional **385** heat exchanger. In the range of operation, the fugacity coefficient of the feed and non-permeate streams below is estimated to be on the order of approximately 0.5. For an ideal gas, fugacity equals pressure and the fugacity coefficient equals 1. Due to the low fugacity coefficient of the feed stream, the actual driving force across the membrane is roughly half of the pressure-based driving force calculated below. To compensate for this, the bundle counts calculated below should be multiplied by approximately 2 to provide the estimated bundle counts actually needed to practice the disclosed system and method.

[0092] The system incorporates membranes **325** and **345** having a propylene permeance of 2 and a propylene to propane selectivity of 8. One of ordinary skill in the art will recognize that membranes **325** and **345** having different selectivities may also be utilized, depending ultimately on the intended purpose of the apparatus. For example, one of ordinary skill in the art will recognize that an increase in the membrane selectivity will result in the need for more membrane modules and that a decrease in the membrane selectivity will result in the need for a larger pump **305**.

[0093] In each of the three simulations, a feed **301** containing 70.0% (v/v) propylene, 29.8% (v/v) propane, and 0.2% (v/v) iso-butane at a flow of 5326 Nm³/hr, 198.7 psig, and 15.0°C is fed to pump **305**. Pump **305** pressurizes the stream to 1099.0, 899.0, or 699.0 psig respectively. Evaporator **315** vaporizes the pressurized stream **310** to a temperature of 105.0, 100.0, or 100.0°C, respectively. First membrane stage **325** is used to separate the feed into a propylene enriched stream **340** containing approximately 93% propylene and a propane enriched stream **330**. The propane enriched stream **330** is reheated by evaporator **335** to 105.0, 100.0, or 100.0°C, respectively, and further processed by second membrane stage **345** into a 95% propane product **350** and a lower pressure propylene-enriched stream **360**. Stream **360** is cooled by condenser **365**. The resulting propylene-enriched stream **370** is comingled with the feed **301** to produce stream **380**. The combined stream **380** is fed to the pump **305**. As stated previously, as a result of the addition of liquid propylene-enriched stream

370, the propylene content of the stream **380** fed to the pump **305** may be higher than or equal to, and the propane content lower than or equal to, that of feed stream **301**.

[0094] Table 2 lists the various properties of the 1099.0 psig pressurization simulation.

Table 3 lists the various properties of the 899.0 psig pressurization simulation. Table 4 lists the various properties of the 699.0 psig pressurization simulation.

Table 2: Stream Properties for 1099.0 psig pressurization

		Feed	Residue	Permeate	Feed	Residue	Permeate
Total Bundle Count							182
Stream #	301	320	330	340	330	350	360
Flow [Nm ³ /hr]	5326	14954	11051	3903	11051	1391	9660
Pressure [psig]	198.7	1099.0	1099.0	200.0	1096	1092	200
Temp [C]	15.0	105.0	85.8	97.9	105	67	82
% Propylene	70.0	72.3	65.0	93.0	65.0	4.4	73.7
%Propane	29.8	27.5	34.8	6.9	34.8	95.2	26.1
% iso-Butane	0.2	0.2	0.2	0.1	0.2	0.4	0.2
Density [g/cm ³]	0.518	0.350	0.408	0.023	0.408	0.447	0.025
Viscosity [cp]	0.105	0.045	0.059	0.011	0.059	0.074	0.011
Flow [lb/hr]	22374	62754	46542	16212	46542	6028	40515
Total Pump + Recycle Energy [KW]							131
Total Heating Energy [KW]							3104
Total Cooling Energy [KW]							3016

Table 3: Stream Properties for 899.0 psig pressurization

		Feed	Residue	Permeate	Feed	Residue	Permeate
Total Bundle Count							291
Stream #	301	320	330	340	330	350	360
Flow [Nm ³ /hr]	5326	17926	14035	3891	14035	1397	12638
Pressure [psig]	198.7	899.0	898.5	200.0	896	891	200
Temp [C]	15.0	100.0	87.0	97.2	100	68	75
% Propylene	70.0	72.9	67.3	93.0	67.3	4.6	76.3
%Propane	29.8	26.9	32.5	6.9	32.5	95.0	23.5
% iso-Butane	0.2	0.2	0.2	0.1	0.2	0.4	0.2
Density [g/cm ³]	0.518	0.337	0.390	0.023	0.390	0.437	0.025
Viscosity [cp]	0.105	0.043	0.054	0.011	0.054	0.070	0.010

Flow [lb/hr]	22374	75208	59045	16163	59045	6053	52992
Total Pump + Recycle Energy [KW]							123
Total Heating Energy [KW]							3655
Total Cooling Energy [KW]							3573

Table 4: Stream Properties for 699.0 psig pressurization

	Feed			Residue			Permeate		
	Feed	Residue	Permeate	Feed	Residue	Permeate	Feed	Residue	Permeate
Total Bundle Count									657
Stream #	301	320	330	340	330	350	360		
Flow [Nm ³ /hr]	5326	27393	23510	3884	23510	1413	22097		
Pressure [psig]	198.7	699.0	697.9	200.0	695	691	200		
Temp [C]	15.0	100.0	98.4	99.9	100	52	95		
% Propylene	70.0	74.1	70.9	93.1	70.9	4.5	80.5		
%Propane	29.8	25.7	28.9	6.8	28.9	95.1	19.3		
% iso-Butane	0.2	0.2	0.2	0.1	0.2	0.4	0.2		
Density [g/cm ³]	0.518	0.167	0.199	0.023	0.199	0.461	0.023		
Viscosity [cp]	0.105	0.020	0.023	0.011	0.023	0.080	0.011		
Flow [lb/hr]	22374	114860	98729	16131	98729	6123	92606		
Total Pump + Recycle Energy [KW]									135
Total Heating Energy [KW]									6084
Total Cooling Energy [KW]									6029

[0095] As discussed previously, although the non-permeate stream exhibits a temperature below its critical temperature, thereby forming a liquid, the density and viscosity of the non-permeate stream remain close to that of the supercritical feed stream, providing less concern about phase change. The system and method disclosed operate most efficiently when the ratios of the viscosity and the density of the non-permeate stream to that of the feed stream approach 1.

[0096] At the first membrane stage of the 1099.0 psig pressurization system, the viscosity ratio between the residue and feed stream is 1.3 and the density ratio between the same is 1.16. The viscosity ratio between the residue and feed stream at the first membrane stage of the 899.0 psig pressurization system is 1.2 and its density ratio for the same is 1.16. Similarly, the viscosity ratio between the residue and feed stream at the first membrane stage of the 699.0 psig pressurization system is 1.2 and its density ratio for the same is 1.19.

[0097] At the second membrane stage of the 1099.0 psig pressurization system, the viscosity ratio between the residue and feed stream is 1.2 and the density ratio between the same is 1.10. The viscosity ratio between the residue and feed stream at the first

membrane stage of the 899.0 psig pressurization system is 1.3 and its density ratio for the same is 1.12. In contrast, the viscosity ratio between the residue and feed stream at the first membrane stage of the 699.0 psig pressurization system is 3.5 and its density ratio for the same is 2.32.

[0098] As can be seen, the 1099.0 psig pressurization provides the best results. The 1099.0 psig pressurization apparatus utilizes less membrane modules than the 899.0 and 699.0 examples (see total bundle count). It also utilizes less heating and cooling energy. Finally, the 1099.0 psig pressurization exhibits a smaller viscosity and density ratio between the residue and feed streams of the second membrane stage, which is beneficial to operation of the disclosed membranes and process.

[0099] It will be understood that many additional changes in the details, materials, steps, and arrangement of parts, which have been herein described and illustrated in order to explain the nature of the invention, may be made by those skilled in the art within the principle and scope of the invention as expressed in the appended claims. Thus, the present invention is not intended to be limited to the specific embodiments in the examples given above and/or the attached drawings.

CLAIMS

What is claimed is:

1. A process for the membrane-based separation of a mixture of close-boiling hydrocarbon components, said process comprising the steps of:
 - pumping and vaporizing a feed stream of refinery grade propylene comprising propane and 60-80% propylene to a pressure between 900 psia and 1,100 psia and a temperature of 96°C or higher so that the pumped and heated refinery grade propylene is in a supercritical state;
 - feeding the supercritical refinery grade propylene to a first membrane stage at a temperature and a pressure above a critical point of the mixture, the first membrane stage containing one or more gas separation modules selective for propylene over propane;
 - extracting a first gaseous permeate stream from the first membrane stage;
 - cooling the first gaseous permeate stream at a condenser to produce a liquid product, the liquid product being chemical-grade propylene product;
 - extracting a first non-permeate stream from the first membrane stage;
 - heating the first non-permeate stream to above its critical temperature so that it is in a supercritical state;
 - feeding the first supercritical non-permeate stream to a second membrane stage at a temperature and pressure above the critical point of the first non-permeate stream, the second membrane stage containing one or more gas separation modules selective for propylene over propane;
 - extracting a second non-permeate stream having less than 5% propylene, the second non-permeate stream being liquefied petroleum gas (LPG) product;
 - cooling the second non-permeate stream to produce a liquid olefin-enriched stream;
 - extracting a second permeate stream; and
 - combining the liquid olefin-enriched stream with the feed stream upstream of where the feed stream is pumped and heated to improve recovery of propylene.
2. The process of claim 1, wherein the feed stream and the first non-permeate stream each has a density and the ratio of the density of the first non-permeate stream to that of the feed stream is less than 5.
3. The process of claim 1, wherein the first membrane stage has a selectivity for propylene over propane of at least 5.0.

4. The process of claim 1, wherein the second membrane stage has a selectivity for propylene over propane of at least 3.0.