

(19) United States

(12) Patent Application Publication (10) Pub. No.: US 2017/0175014 A1 PREVOST et al.

Jun. 22, 2017 (43) **Pub. Date:**

(54) FRACTIONATION PROCESS FOR A PROCESS FOR OLIGOMERISING LIGHT **OLEFINS**

- (71) Applicant: AXENS, Rueil Malmaison Cedex (FR)
- (72) Inventors: Isabelle PREVOST, Rueil Malmaison (FR); Jerome PIGOURIER, Meudon (FR)
- (73) Assignee: AXENS, Rueil Malmaison Cedex (FR)
- Appl. No.: 15/388,232
- Filed: Dec. 22, 2016 (22)
- (30)Foreign Application Priority Data

Publication Classification

Int. Cl. (51)(2006.01)C10G 57/02

U.S. Cl. (52)CPC C10G 57/02 (2013.01); C10G 2300/1092 (2013.01); C10G 2400/06 (2013.01); C10G 2400/02 (2013.01)

(57)ABSTRACT

The invention relates to a process for oligomerising light olefins in which the effluent from the oligomerisation section is passed to a prefractionator that leads to at least one head fraction containing a mixture of liquefied petroleum gas and light gasoline and a bottom fraction containing a mixture of heavy gasoline and middle distillate, the said head fraction being passed to a debutaniser that leads to at least one liquefied petroleum gas cut and a light gasoline cut, the said bottom fraction and at least part of the said light gasoline cut being passed to a separator enabling at least a gaseous fraction, a gasoline fraction and a gasoil fraction to be obtained.

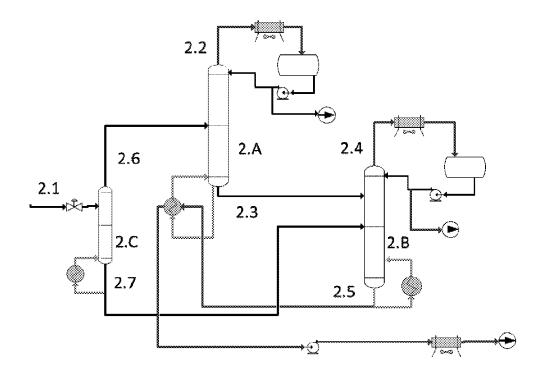


Fig. 1

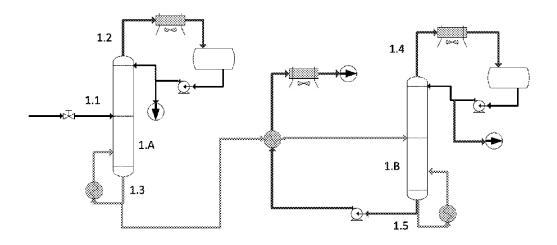


Fig. 2

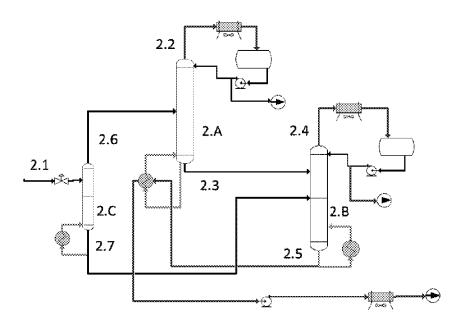
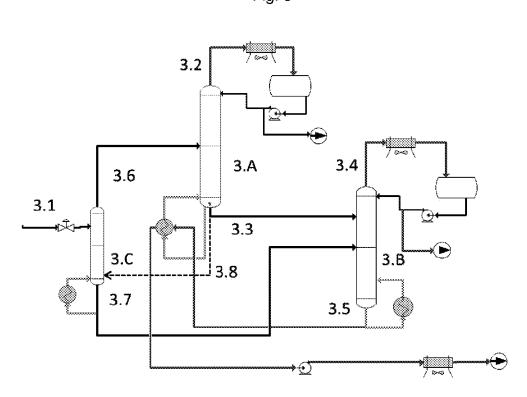


Fig. 3



FRACTIONATION PROCESS FOR A PROCESS FOR OLIGOMERISING LIGHT OLEFINS

FIELD OF THE INVENTION

[0001] The invention relates to the field of the production of oligomers from light olefins, and more particularly oligomers having more than 8 carbon atoms with boiling points in the range of gasolines, kerosene and gasoil. In particular the invention relates to the step of separating the products obtained in the course of an oligomerisation process.

PRIOR ART

[0002] Oligomerisation reactions lead to different products having different boiling points, and therefore downstream of the oligomerisation section a fractionation section is necessary in order to isolate the desired products such as liquefied petroleum gas (LPG), gasolines and middle distillates

[0003] In general the fractionation section of an oligomerisation process enabling LPG, gasolines and middle distillates to be obtained employs two fractionation columns. The effluent from the oligomerisation section is passed to a first distillation, the debutaniser, which enables the lightest components, mainly hydrocarbons containing 4 or fewer carbon atoms, to be separated, so as to produce a light gasoline cut whose vapour pressure is between 0.005 and 0.09 MPa. Thus, the debutaniser produces at the head a hydrocarbon-rich flow containing 4 or fewer carbon atoms, which is passed to a liquefied petroleum gas (LPG) store, and at the bottom a mixture of gasoline and distillate which is then fractionated in a second distillation, the separator (splitter according to English terminology), so as to produce the gasoline and distillate having the specifications required for refining. In order to minimise energy consumption in the fractionation stage, the operating pressures of the two columns are minimised without however lowering their condensation temperatures below the cooling conditions realisable by the available cold units. Thus, the temperatures of the condensers of the columns are typically between about 30° C. and about 50° C., and the pressures are of the order of 0.6 to 0.7 MPa for the debutaniser and generally of the order of atmospheric pressure (0.1 MPa) for the separator. [0004] U.S. Pat. No. 4,720,600 describes an oligomerisa-

[0004] U.S. Pat. No. 4,720,600 describes an oligomerisation process for light olefins in which olefins having a number of carbon atoms between 3 and 6 are oligomerised in a reaction section in the presence of a zeolitic catalyst. The effluent obtained is fractionated by means of three columns so as to obtain a distillate, which constitutes the desired product, a light fraction and a heavy fraction, which are at least partly recycled to the oligomerisation reaction section. The said distillate, which is in the kerosene range, includes in particular compounds having a boiling point between 165° C. and 290° C.

[0005] US Patent Application 2014/0134064 describes a fractionation device enabling an oligomerate to be upgraded according to two fractionation section variants containing a succession of three distillation columns in order to obtain three main products and a flow of C5 hydrocarbons, downstream of the oligomerisation reaction section. According to a first variant, the said fractionation section comprises a first fractionation column (debutaniser) separating the hydrocarbons containing 1 to 4 carbon atoms and the hydrocarbons

containing at least 5 carbon atoms. The fraction comprising the hydrocarbons containing at least 5 carbon atoms is added to a second fractionation column (depentaniser) which enables the hydrocarbons containing 5 carbon atoms to be recovered at the head of the column, which can be recycled to the reaction section, and the hydrocarbons containing at least 6 carbon atoms to be recovered at the bottom of the column, part of which may be upgraded as gasoline base and a second part may be passed to a third fractionation column (middle distillate recovery column), which enables a cut comprising hydrocarbons containing 6 to 9 carbon atoms and a diesel cut to be separated. According to a second variant, the second fractionation column (depentaniser) is replaced by a stripper adjacent to the debutaniser (sidestripper according to English terminology). This stripper is supplied by a side offtake situated on the debutaniser and sufficiently at the head of the column in order to be able to sample a hydrocarbon cut containing 5 carbon atoms. Part of this side offtake can be recycled to the oligomerisation reactor so as to maintain the oligomerisation reaction zone in the liquid phase, to control the exothermicity and to maximise the gasoline yield, while a second part is sent to the stripper to separate the hydrocarbons containing 4 or fewer carbon atoms, which are passed to the debutaniser and the hydrocarbons containing 5 carbon atoms.

[0006] The fractionation of the oligomerate required in order to separate the three desired products, namely the liquefied petroleum gas, the gasolines and the middle distillates, is a costly operation that typically represents more than 70% of the total energy consumption of an oligomerisation unit. The total consumption of hot utilities of the fractionation section corresponds to the sum total of the services, duties according to English terminology, associated with reboiling of the distillations. Since the oligomerate contains molecules with a large number of carbon atoms, the reboiling temperatures of the columns are therefore generally greater than 140° C. for the debutaniser (first column) and greater than 200° C. for the second gasoline/middle distillates separation column (separator). These reboiling temperatures depend on the composition of the oligomerate, as well as on the choice of the operating pressures. Furthermore, there are very few or even no hot fluids available in the unit with a thermal energy sufficient to permit a thermal

[0007] There is therefore a real need to improve the fractionation section so as to limit the energy consumption.

[0008] Surprisingly, the inclusion of a prefractionation column has enabled the applicant to greatly reduce the energy requirements of an oligomerate fractionation process.

DEFINITIONS

[0009] Hot fluid is understood to mean a fluid of the process that undergoes a recooling.

[0010] Cold fluid is understood to mean a fluid of the process that undergoes a reheating.

[0011] Hot utility is understood to mean a fluid external to the process that undergoes a cooling in order to deliver heat to a cold fluid.

[0012] Cold utility is understood to mean a fluid external to the process that undergoes a reheating in order to extract heat from a hot fluid.

[0013] Thus, the consumption of hot utilities of a process corresponds to the total amount of heat supplied by one or more hot utilities to the said process.

[0014] Service, duty according to English terminology, is understood to mean the amount of heat energy transferred between two fluids.

[0015] Thus, the reboiling service corresponds to the amount of heat energy supplied to a distillation column and the condensation service corresponds to the amount of heat energy extracted from a distillation column.

OBJECT OF THE INVENTION

[0016] The invention thus relates to a fractionation scheme for a process for oligomerising light olefins, comprising a prefractionation of the effluent from the reaction section.

[0017] The invention relates more particularly to a process for oligomerising light olefins in which the effluent from the oligomerisation section is passed to a prefractionator that provides at least one head fraction containing a mixture of liquefied petroleum gas and light gasoline and a bottom fraction containing a mixture of heavy gasoline and middle distillate, the said head fraction being passed to a debutaniser that provides at least a liquefied petroleum gas cut and a light gasoline cut, the said bottom fraction and at least part of the said light petroleum cut being passed to a separator enabling at least a gaseous fraction, a petroleum fraction and a gasoil fraction to be obtained.

[0018] An advantage of the present invention is that it significantly reduces the consumption of hot utilities without adversely affecting the amounts and qualities of the obtained LPG, gasoline and gasoil.

[0019] Another advantage of the present invention is that it permits a thermal integration by using one or more hot fluids available in the process, such as the bottom products of the second column, the inter-reactor effluent and the effluent from the last reactor of the oligomerisation reaction section.

[0020] Another advantage of the present invention is that two gasoline cuts can be obtained, a heavy cut rich in middle distillates obtained from the bottom of the high-temperature prefractionation column and a light cut depleted in middle distillates obtained from the bottom of the lowest temperature debutaniser, which enable the separator to be supplied at two different levels, thereby facilitating the separation of a gasoline fraction and a middle distillate fraction.

DETAILED DESCRIPTION OF THE INVENTION

[0021] The oligomerisation reactions are exothermic, and the temperature of the reaction section is generally between 120° C. and 300° C.

[0022] In accordance with the invention an effluent produced by an oligomerisation section is passed to a fractionation section that comprises primarily a prefractionator enabling a prefractionation stage to be carried out.

[0023] At least part of the oligomerate obtained from the oligomerisation reaction section is therefore passed, without any treatment other than a possible heat exchange via a heat exchanger for example, to a distillation column, a so-called prefractionator, enabling a prefractionation of the said oligomerate to be carried out.

[0024] The said prefractionation leads to at least two fractions:

[0025] a head fraction containing a mixture of liquefied petroleum gas (LPG)/light gasoline, containing less than 15% by weight with respect to the hydrocarbons feedstock containing at least 8 carbon atoms, and preferably less than 10%.

[0026] a bottom fraction containing a heavy gasoline/middle distillate mixture containing less than 15% by weight with respect to the hydrocarbons feedstock containing at most 5 carbon atoms, and preferably less than 8%.

[0027] According to a preferred variant of the invention, the prefractionator contains between 5 and 20 theoretical trays and preferably between 8 and 18 theoretical trays and operates at a pressure between 0.1 and 2 MPa, preferably between 0.3 and 1.2 MPa, the feedstock is fed to a tray situated at the head of the column, preferably to trays 1 to 6, the trays being numbered starting from the head of the column, the head vapours are withdrawn at a temperature between 100° C. and 150° C., preferably between 110° C. and 140° C., and the bottom liquid is withdrawn at a temperature between 170° C. and 220° C., preferably between 185° C. and 205° C.

[0028] In accordance with the invention the said head fraction is passed to a second column, the so-called debutaniser, which leads to at least two cuts:

[0029] a head cut containing the LPG containing hydrocarbons having 4 or fewer carbon atoms,

[0030] a bottom cut containing the light gasoline containing hydrocarbons having at least 5 carbon atoms.

[0031] According to a preferred variant, the debutaniser contains between 15 and 35 theoretical trays and preferably between 18 and 30 theoretical trays, and operates at the same pressure as the prefractionator, the feedstock is fed between the theoretical trays 8 and 25 and preferably between the theoretical trays 10 and 18, the trays being numbered starting from the head of the column, the head vapours are removed, condensed and subcooled to a temperature between 35° and 55° C., preferably between 40° and 50° C. in an air-cooled condenser, and the bottom liquid is withdrawn at a temperature between 100° C. and 130° C., preferably between 105° and 125° C.

[0032] In accordance with the invention the said bottom fraction and at least part of the said bottom cut are passed to a third distillation column, the so-called separator, in order to separate the various desired products from one another. The main products obtained are gasoline and middle distillate (kerosene and/or gasoil).

[0033] According to a preferred variant, the separator contains between 20 and 40 theoretical trays and preferably between 25 and 35 theoretical trays and operates at a lower pressure than the pressure of the said debutaniser, between 0.01 MPa and 0.6 MPa and preferably between 0.05 and 0.3 MPa. The said bottom fraction obtained from the prefractionator is fed between the trays 5 and 15 and preferably between the trays 7 and 12, the said bottom cut obtained from the debutaniser is fed between the theoretical trays 2 and 12 and preferably between the trays 2 and 6, the trays being numbered starting from the head of the column. The head vapours are removed, condensed and subcooled to a temperature between 40° C. and 80° C., preferably between 50° C. and 70° C. in the air-cooled condenser, the bottom liquid is removed at a temperature between 200° C. and 240° C., preferably between 210° C. and 230° C.

[0034] Preferably the said bottom fraction and the said bottom cut feed the separator at two different levels, in order to facilitate the gasoline/middle distillate separation. The separator generally contains between 20 and 40 theoretical trays.

[0035] In the case where the said bottom fraction and the said bottom cut feed the separator at two different levels, the said bottom fraction is preferably introduced between the theoretical trays 7 and 15 and the said bottom cut is introduced above the latter, preferably between the trays 2 and 12, the trays being numbered starting from the head of the column.

[0036] Advantageously the said bottom cut is also in part passed to the gasoline pool, in part purged, in part returned to the oligomerisation reaction section, or preferably in part recycled to the prefractionation column.

[0037] In the case where the said bottom cut is in part recycled to the prefractionation column, the said bottom cut is preferably introduced to several trays above the reboiler. Preferably the degree of recycling of the said bottom cut is between 5% by weight and 20% by weight and more preferably between 7% by weight and 15% by weight.

[0038] Without increasing the amount of energy to be supplied to the reboilers, the prefractionator arranged upstream of the debutaniser leads to a reduction of at least 30° C. of the reboiling temperature required for the functioning of the debutaniser, which allows a thermal integration in particular thanks to a hot fluid of the process that is available at a temperature greater than or equal to 130° C. or thanks to a hot utility that is available at a relatively low temperature. Furthermore, the partial recycling of the said bottom cut to the said prefractionation column also leads to a reduction of the reboiling temperature of the said prefractionator of between 5° C. and 15° C.

[0039] The different hot fluids of the process enable several forms of implementation of the said thermal integration to be envisaged.

[0040] In a first preferred embodiment, the bottom effluent of the said separator is used for a heat exchange with the reboiler of the said debutaniser.

[0041] In a second embodiment the effluent obtained from the first reactor is cooled before its pressure is reduced and it is introduced into the prefractionator, which enables heat to be recovered and the reboiler of the said debutaniser to be reheated.

[0042] These two embodiments may be combined so as to ensure a larger part of the reboiling of the debutaniser via thermal integration.

BRIEF DESCRIPTION OF THE FIGURES

[0043] FIG. 1 shows a conventional fractionation process scheme according to the prior art for obtaining a LPG fraction, a gasoline fraction and a middle distillate fraction. The oligomerate (1.1) is passed to a debutaniser (1.A), which separates at least two fractions, namely a column head fraction (1.2) and a column bottom fraction (1.3). The said column bottom fraction (1.3) is then passed to a separator (1.B) that separates in turn two fractions (1.4 and 1.5).

[0044] FIG. 2 shows an embodiment of the process according to the invention in which a prefractionation column (2.C) is installed upstream of the process shown in FIG. 1. The head fraction containing a mixture of liquefied petroleum gas and light gasoline (2.6) from the prefractionator (2.C) is passed to the debutaniser (2.A), while the

bottom fraction containing a mixture of heavy gasoline and the middle distillate (2.7) is passed directly to the separator (2.B).

[0045] FIG. 3 shows an embodiment similar to that shown in FIG. 2 of the process according to the invention in which, in addition, a part of the bottom fraction containing a mixture of heavy gasoline and middle distillate (3.7) from the debutaniser (3.A) is recycled (3.8) to the said prefractionator (3.C).

[0046] Without further elaboration, it is believed that one skilled in the art can, using the preceding description, utilize the present invention to its fullest extent. The preceding preferred specific embodiments are, therefore, to be construed as merely illustrative, and not limitative of the remainder of the disclosure in any way whatsoever.

[0047] In the foregoing and in the examples, all temperatures are set forth uncorrected in degrees Celsius and, all parts and percentages are by weight, unless otherwise indicated.

[0048] The entire disclosures of all applications, patents and publications, cited herein and of corresponding application No. FR 1563036, filed Dec. 22, 2015 are incorporated by reference herein.

EXAMPLES

[0049] All the examples 1 to 3, 21 t/hr. of oligomerate obtained from an oligomerisation section consisted of 28% by weight of hydrocarbons containing 4 or fewer carbon atoms, 14% by weight of hydrocarbons containing 5 carbon atoms, 10% by weight of hydrocarbons containing 6 carbon atoms, 2% by weight of hydrocarbons containing 7 carbon atoms, 12% by weight of hydrocarbons containing 8 carbon atoms and 34% by weight of hydrocarbons containing at least 9 carbon atoms.

[0050] The operating conditions are adjusted so as to fractionate the said oligomerate into 3 products, the amounts of which are given in the table below:

Product	Flow rate (t/hr.)
Liquefied petroleum gas	5.8
Gasoline	7.8
Middle distillate	7.4

[0051] The liquefied petroleum gas contains 2% by weight of hydrocarbons containing 5 or more carbon atoms.

[0052] The gasoline is characterised by an initial boiling point D 86 of 13° C. and a final boiling point D 86 of 140° C., and a content of hydrocarbons containing 4 or fewer carbon atoms of only 1.9% by weight.

[0053] The middle distillate is characterised by an initial boiling point D 86 of 164° C. and a flash point determined by the Nelson method of 43.9° C.

Example 1 (Comparative)

[0054] The process of Example 1 is shown in FIG. 1. The oligomerate (1.1) is passed to a debutaniser (1.A) which separates it into at least two fractions, namely a column head fraction (1.2) and a column bottom fraction (1.3). The said column bottom fraction (1.3) is then passed to a separator (1.B) that separates in turn two fractions (1.4 and 1.5). The bottom product from the debutaniser (1.4) exchanges its heat with the effluent feeding it (1.3). The debutaniser and the

separator operate with 23 theoretical trays, their feed positions being optimised so as to minimise the heat dispensed to the reboilers. Accordingly the feed of the debutaniser (1.A) is located at tray 13 and the feed of the separator (1.B) is located at tray 8, the trays being numbered starting from the head of the column. The debutaniser (1.A) operates at 0.65 MPa and the separator (1.B) operates at 0.2 MPa.

Example 2 (According to the Invention)

[0055] The process of Example 2 is shown in FIG. 2. In Example 2, a prefractionation column (2.C) is installed upstream of the process of Example 1. The head fraction from the prefractionator (2.6) is passed to the debutaniser (2.A) while the bottom fraction (2.7) is passed directly to the separator (2.B).

[0056] The prefractionator (2.C) comprises 14 theoretical trays and operates at 0.65 MPa. The bottom effluent from the separator (2.5) is used for a heat exchange with the reboiler of the debutaniser (2.A) before it is cooled and stored. The bottom cut of the debutaniser (2.3) and the bottom fraction (2.7) obtained from the prefractionation are passed in whole to the separator (2.B), respectively to tray 4 and to tray 10, the trays being numbered starting from the head of the column.

Example 3 (According to the Invention)

[0057] The process of Example 3 is shown in FIG. 3. In Example 3 the same process as in Example 2 (FIG. 2) is implemented, with in addition the recycling (3.8) of 0.5 t/hour of the said bottom cut (3.3) from the debutaniser (3.A) to the prefractionator (3.c) at the level of tray 12, the trays being numbered starting from the head of the column and the column containing 14 trays.

	Example 1	Example 2	Example 3
	Prefractionator		
Flow rate (tons/hour) Reboiler service (MW) Reboiler temperature (° C.)	First column	11.9 0.63 197.6	11.9 0.58 187.1
Reflux rate (tons/hour) Side reboiler service (MW) Side reboiler temperature (° C.)	13.9	12.8	12.8
Reboiler service (MW) Reboiler temperature (° C.) Condenser service (MW) Condenser temperature	1.0 145.0 1.9 45.0	0.53 116.7 1.75 45.0	0.52 116.4 1.75 45.0
(° C.)	Second column		
Reflux rate (tons/hour) Reboiler service (MW) Reboiler temperature (° C.) Condenser service (MW) Condenser temperature (° C.) Total reboiler services Total hot utilities (MW)	5.4 1.20 224 1.7 45.0 2.2 2.2 Not in accordance	4.2 1.08 224 1.4 61.0 2.24 1.71 In	4.1 1.13 224 1.4 61.0 2.23 1.71 In accordance

[0058] The process according to the invention enables, for the same amounts and specifications of obtained products, the consumption of hot utilities to be reduced in the fractionation stage of the oligomerate by 22% compared to a simple fractionation carried out by means of two successive distillations without a prefractionation section.

[0059] Furthermore, by a simple partial recycling of the light gasoline cut depleted in middle distillate to the prefractionation column, it is possible to adjust the proportion of the heavy and light gasoline cuts, so as to regulate the temperature of the reboiler of the prefractionation column. [0060] The preceding examples can be repeated with similar success by substituting the generically or specifically described reactants and/or operating conditions of this invention for those used in the preceding examples.

[0061] From the foregoing description, one skilled in the art can easily ascertain the essential characteristics of this invention and, without departing from the spirit and scope thereof, can make various changes and modifications of the invention to adapt it to various usages and conditions.

- 1. Process for the oligomerisation of light olefins in which the effluent from the oligomerisation section is passed to a prefractionator, which leads to at least one head fraction containing a mixture of liquefied petroleum gas and light gasoline and a bottom fraction containing a mixture of heavy gasoline and middle distillate, the said head fraction being passed to a debutaniser that leads to at least one liquefied petroleum gas cut and a light gasoline cut, the said bottom fraction and at least part of the said light gasoline cut being passed to a separator enabling at least a gaseous fraction, a gasoline fraction and a gasoil fraction to be obtained.
- 2. Process according to claim 1, in which the said head fraction contains a liquefied petroleum gas (LPG)/light gasoline mixture, containing less than 15% by weight with respect to the hydrocarbon feedstock containing at least 8 carbon atoms, and the said bottom fraction containing a heavy gasoline/middle distillate mixture containing less than 15% by weight with respect to the hydrocarbon feedstock containing at most 5 carbon atoms.
- 3. Process according to claim 1, in which the said prefractionator contains between 5 and 20 theoretical trays, operates at a pressure between 0.1 and 2 MPa, the feedstock being supplied to a tray situated at the head of the column, the head vapours being withdrawn at a temperature between 100° and 150° C. and the bottom liquid being withdrawn at a temperature between 170° C. and 220° C.
- **4.** Process according to claim **1**, in which the said liquefied petroleum gas cut contains hydrocarbons containing 4 or fewer carbon atoms and the said light gasoline cut contains hydrocarbons containing at least 5 carbon atoms.
- 5. Process according to claim 1, in which the said debutaniser contains between 15 and 35 theoretical trays and operates at the same pressure as the prefractionator, the feedstock being fed between the theoretical trays 8 and 25, the trays being numbered starting from the head of the column, the head vapours are removed, condensed and subcooled to a temperature between 35° and 55° C. in an air-cooled condenser, and the bottom liquid is removed at a temperature between 100° C. and 130° C.
- **6**. Process according to claim **1**, in which the said separator contains between 20 and 40 theoretical trays and operates at a lower pressure than the pressure of the said debutaniser, namely between 0.01 MPa and 0.6 MPa.
- 7. Process according to claim 1, in which the said bottom fraction obtained from the prefractionator is fed between the trays 5 and 15 of the said separator, the said bottom fraction

obtained from the debutaniser is fed between the theoretical trays 2 and 12 of the said separator, the trays being numbered starting from the head of the column, the head vapours being removed, condensed and subcooled to a temperature between 40° C. and 80° C. in an air-cooled condenser and the bottom liquid being removed at a temperature between 200° C. and 240° C.

- **8**. Process according to claim **1**, in which the said bottom fraction and the said bottom cut supply the said separator at two different levels.
- **9.** Process according to claim **1**, in which the said bottom cut is in part recycled to the prefractionation column.
- 10. Process according to claim 9, in which the said bottom cut is preferably introduced to several trays above the reboiler.
- 11. Process according to claim 9, in which the degree of recycling of the said bottom cut is between 5% by weight and 20% by weight.
- 12. Process according to claim 1, in which the bottom effluent from the said separator is used for a heat exchange with the reboiler of the said debutaniser.
- 13. Process according to claim 1, in which the effluent obtained from the last reactor is cooled before its pressure is released and it is introduced to the prefractionator, which enables heat to be recovered and the reboiler of the said debutaniser to be reheated.

* * * * *