May 16, 1967 HANS-WALTHER BRANDT ETAL 3,320,138

PROCESS FOR SEPARATING C_5-HYDROCARBON MIXTURES, CONTAINING PARAFFINIC, MONOOLEFINIC AND DIOLEFINIC C_5-HYDROCARBONS BY DISTILLATION WITH N-METHYLPYRROLIDONE

Filed Dec. 23, 1963 2 Sheets-Sheet 1

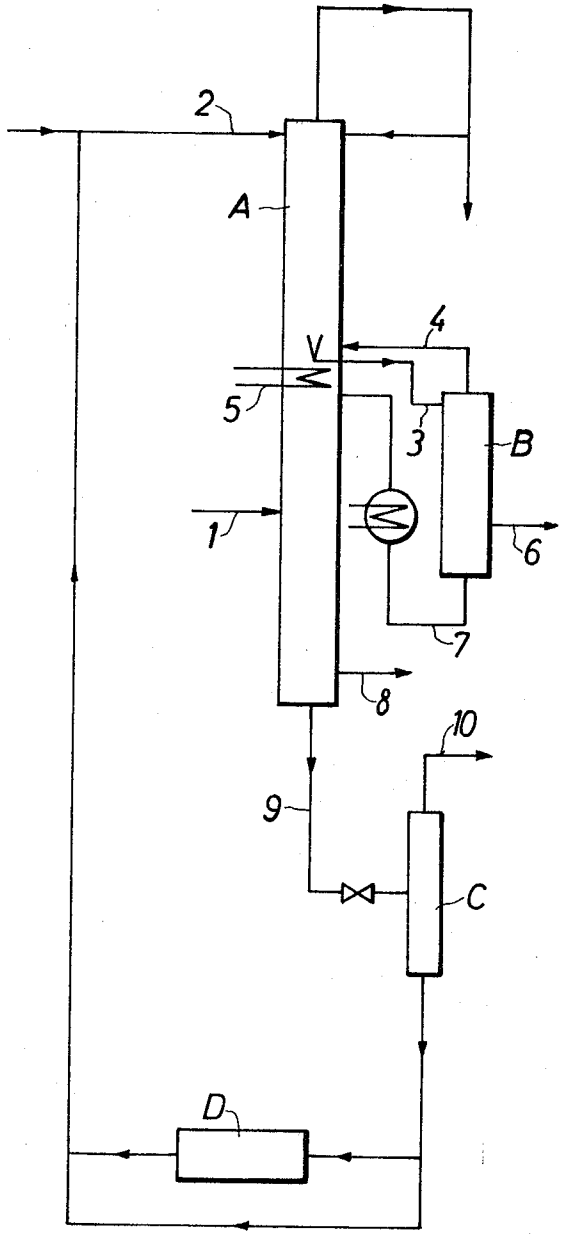


FIG. 1

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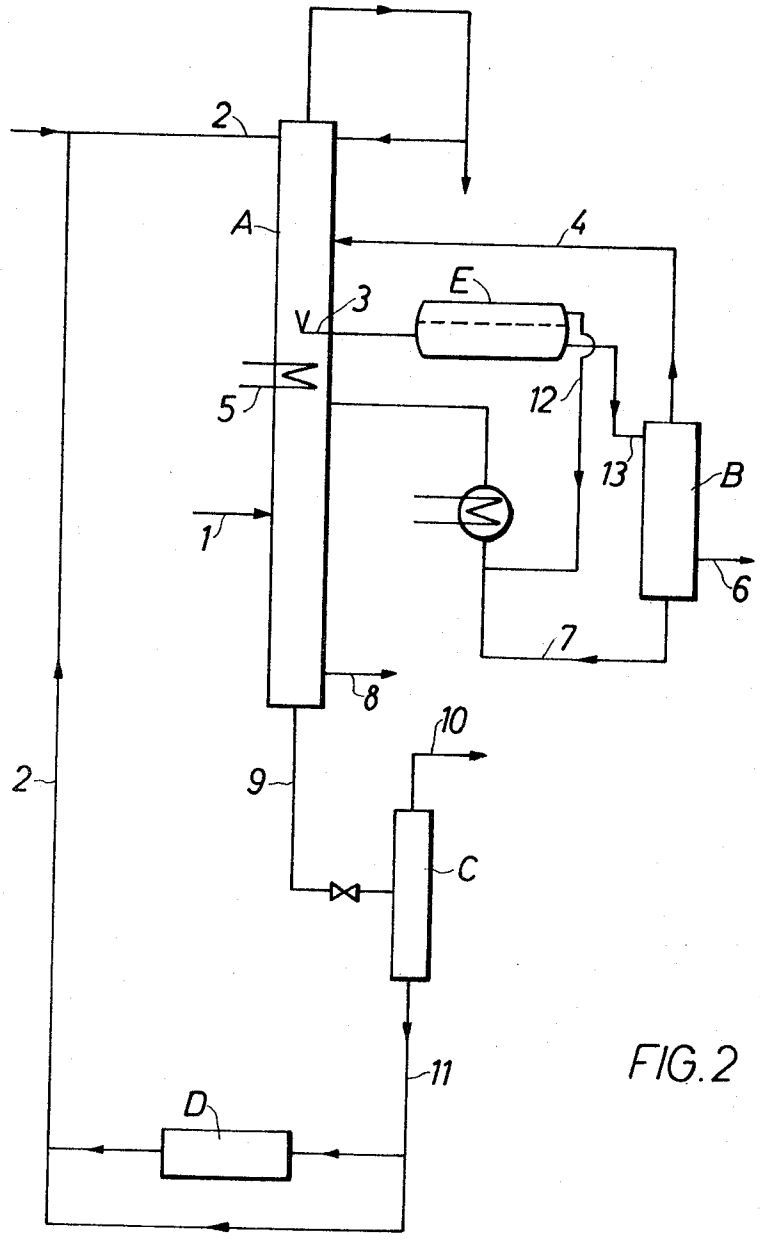


FIG. 2

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PROCESS FOR SEPARATING C_5-HYDROCARBON MIXTURES, CONTAINING PARAFFINIC, MONOOLEFINIC AND DIOLEFINIC C_5-HYDROCARBONS BY DISTILLATION WITH N-METHYLPYRROLIDONE

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In the pyrolysis of mineral oils, especially of crude oils or of their fractions at temperatures above 600° C., there is formed together with the gaseous cleavage products a benzene fraction as well, the so-called cracked benzine, which is rich in C_5-hydrocarbons of varying degree of saturation, i.e. pentanes, pentenes, and pentadienes. In general, these fractions contain the following compounds: Isopentane, n-pentane, cyclopentane, n-pentene-1, cispentene-2, trans-pentene-2, 2-methylbutene-1, 2-methylbutene-2, cyclopentene, isoprene, trans-1,3-pentadiene, cis-1,3-pentadiene, cyclopentadiene and acetylene.

It has now been found, that the aforementioned C_5-hydrocarbon mixtures, which contain paraffinic, monoolefinic and diolefinic C_5-hydrocarbons, can be separated into fractions consisting substantially only of paraffines or monoolefines or diolefines, by subjecting the C_5-hydrocarbon mixtures to an extractive distillation in the presence of N-methylpyrrolidone as selective solvent, the hydrocarbon mixture to be separated being introduced into the middle part of the extractive distillation column, the N-methylpyrrolidone being fed in at the top of the column, while a liquid side stream is withdrawn at the lower part of the upper half of the column, said stream containing, beside N-methylpyrrolidone, substantially only the C_5-monoolefines, returning the methylpyrrolidone to the column below the withdrawal point after freeing it from the C_5-monoolefines and effecting, in the region above this feedback point, a partial condensation of gaseous hydrocarbons in order to maintain the ratio of N-methylpyrrolidone to hydrocarbons approximately constant in the extractive distillation column, withdrawing from the lower portion of the extractive distillation column above the sump the C_5-diolefines and withdrawing at the head of the column the paraffines while the N-methylpyrrolidone collecting in the sump of the column is optionally returned to the head of the column after purification.

The process of the invention will now be explained with reference to FIG. 1.

A mixture of pentanes, pentenes and C_5-dienes is introduced into the middle portion of an extractive distillation column A, in the form of a vaporous mixture, through the conduit **1**. The N-methylpyrrolidone is fed in at the head of the column A through the pipe **2**. The pentane fraction is taken off at the head of column A, to be fed back partly to the head of said column after a condensation as reflux. The volume of the N-methylpyrrolidone fed in through the pipe **2** is approximately three times the volume of the reflux. In the upper half of column A, at a point located about three-quarters of the height of the column, a portion of the hydrocarbon-charged solvent is withdrawn over the pipe **3** and fed into an auxiliary column B, in liquid form. The head product of this column B is taken off in vapour form through the pipe **4** and is fed back to column A at approximately the same height. Below the withdrawal point **3** of the liquid product, a partial condensation of

the evaporated hydrocarbons takes place in column A on the condenser **5**, the setting of which is such that the ratio of hydrocarbons to N-methylpyrrolidone is maintained constant over the entire height of column A. In the lower half of the auxiliary column, for example five trays above the sump of this column, the pentene fraction is withdrawn in vapour form through the pipe **6**, with a pentene-content exceeding 95%. The hydrocarbon-free sump product of column B, which is taken off through the pipe **7**, consists of N-methylpyrrolidone and is fed back into the main column A below the condenser **5**. In the lower part of the extractive distillation column A, for example about five trays above the sump of this column, a fraction consisting substantially of C_5-diolefines is taken off in vapour form through the pipe **8**. The liquid sump product of the extractive distillation column A is fed through pipe **9** to a distillation column C, for removal of residual hydrocarbons through the conduit **10**. The hydrocarbon-free N-methylpyrrolidone is withdrawn at the sump of column C through the pipe **11** and fed back to the head of column A through the pipe **2**. A small portion of the solvent is processed in a regenerating installation D, which is not detailed because it is a conventional solvent regeneration system well known in the art.

It has furthermore been found that it is advantageous to feed the liquid side stream drawn, as mentioned above, from the lower portion of the upper half of the extractive distillation column, which contains substantially only the C_5-monoolefines in addition the N-methylpyrrolidone, possibly after cooling, to a separator vessel, in which a segregation into a pentene-poor hydrocarbon layer and a pentene-rich solvent layer takes place, returning the pentene-poor hydrocarbon layer to the extractive distillation column below the take-off point and processing the pentene-rich solvent layer in the conventional manner.

This embodiment of the invention will now be explained on hand of a special form of execution, with reference to FIG. 2.

A gaseous mixture of pentanes, pentenes and C_5-dienes is fed to the middle portion of an extractive distillation column A through the conduit **1**. The N-methylpyrrolidone is fed to the head of column A through the pipe **2**. The pentane fraction is drawn off at the head of column A in the gas phase and is fed back to the head of the column after a partial condensation, as reflux. The N-methylpyrrolidone supplied through the pipe **2** is advantageously fed in amounts three times the volume of the reflux. In the upper half of column A, at approximately three-quarters column height, the whole of the liquid produced is withdrawn from a plate and fed to a separating vessel E through the pipe **3**. Here, a separation takes place into an upper pentane-rich hydrocarbon layer and into a lower pentene-rich, hydrocarbon-saturated solvent layer. The lower solvent layer is fed to an auxiliary column B in the liquid phase, through the pipe **13**. The head product of this column B is taken off in the vapour phase through the conduit **4** and is returned to the column A at approximately the height of the take-off pipe **3**. Below the liquid-product take-off **3**, there occurs a partial condensation in column A of the evaporated hydrocarbons on the condenser **5**, which is so set that a constant hydrocarbon-N-methylpyrrolidone ratio is maintained over the entire height of the column. The hydrocarbon layer is withdrawn from the separating vessel E through the pipe **12** and is fed back to the main column A below the condenser **5**. In the lower part of the secondary column B, for example five plates above the sump, the pentene fraction is taken off in the vapour phase through the pipe **6**. The pentene content exceeds 92%. The hydrocarbon-free sump product of column B, which is drawn off through the pipe **7**, consists of N-

methylpyrrolidone and is recycled to the main column below the condenser **5** combined with pipe **12**. In the lower part of the extractive distillation column A, for example five plates above the sump of the column, a fraction consisting essentially of C_5-diolefines is drawn off in the vapour phase through the pipe **8**. The liquid sump product of column A is fed to the distillation column C through the pipe **9**, for the purpose of removing residual hydrocarbons through the pipe **10**. The hydrocarbon-free N-methylpyrrolidone is drawn off at the sump of column C through the pipe **11** and fed through the pipe **2** back to the head of column A. A small portion of the solvent is processed in a regenerating installation D which is not detailed because it is a conventional solvent regeneration system well known in the art.

Example 1

In a laboratory apparatus corresponding to FIG. 1, there was charged a mixture of C_5-hydrocarbons having the following composition:

	Weight percent
Isopentane	15.45
n-Pentane	24.65
Cyclopentane	2.20
n-Pentene-1	5.21
Cis-pentene-2	2.74
Trans-pentene-2	12.63
2-methylbutene-1	12.63
Cyclopentene	2.41
Isoprene	13.25
Trans-1,3-pentadiene	5.34
Cis-1,3-pentadiene	2.50
Cyclopentadiene	8.51
Acetylene	0.05
C_4-hydrocarbons	0.15
2-methylbutene-2	4.91

This product stream is fed after evaporation into a laboratory column equipped with trays. The column had a diameter of 50 mm. and had 135 trays. The product was fed in at the 65th tray. At the head of this column, N-methylpyrrolidone with 5% water serving as selective solvent was fed in in such amounts, that the stream returning to the column consisted of 75% solvent and 25% hydrocarbons. The reflux ratio R/F was 7. The head temperature was 45° C., the pressure 1000 torrs.

At the head of the column, a pentane fraction of the following composition was taken off:

	Weight percent
Isopentane	35.31
n-Pentane	56.20
Cyclopentane	0.20
n-Pentene-1	3.24
Cis-pentene-2	1.50
Trans-pentene-2	2.85
2-methylbutene-2	0.57
C_4-hydrocarbons	0.13

At the 100th tray, about one-third of the N-methylpyrrolidone charged at the head of the column was withdrawn in liquid form and fed to the head of a second column (column B of FIG. 1); this column had 70 trays and a diameter of 40 mm. A gaseous pentene fraction was withdrawn above the 5th tray, having the following composition:

	Weight percent
Isopentane	2.08
n-Pentane	3.47
Cyclopentane	5.30
n-Pentene-1	15.50
Cis-pentene-2	8.30
Trans-pentene-2 / 2-methylbutene-1	46.30
2-methylbutene-2	18.70
Isoprene	0.35

The head temperature of this second column was 45° C., the sump temperature 165° C. The sump product of the second column was cooled to 45° C. and fed back to the main column A at a point located below the aforedescribed liquid take-off point. At this point, a partial condensation takes place in column A by indirect cooling, to produce a constant solvent/hydrocarbon ratio. Five trays above the sump of the main column A, a diolefine fraction was withdrawn in vapour form, having the following composition:

	Weight percent
Cyclopentane	2.36
Cis-pentene-2	0.10
n-Methylbutene-2	0.10
Cyclopentene	7.03
Isoprene	38.73
Trans-1,3-pentadiene	15.62
Cis-1,3-pentadiene	7.33
Cyclopentadiene	24.92
Acetylene	1.05
Higher hydrocarbons	3.66

The sump temperature was 165° C.

Example 2

Into an apparatus corresponding to FIG. 2, there is charged a mixture of C_5-hydrocarbons, having the following composition:

	Weight percent
Isopentane	15.45
n-Pentane	24.65
Cyclopentane	2.20
n-Pentene-1	5.21
Cis-pentene-2	12.63
2-methylbutene-1	12.63
2-methylbutene-2	4.91
Cyclopentene	2.41
Isoprene	13.25
Trans-1,3-pentadiene	5.34
Cis-1,3-pentadiene	2.50
Cyclopentadiene	8.51
Acetylene	0.05
C_4-hydrocarbons	0.15

After evaporation, this product stream is fed to a column equipped with 135 plates and having a diameter of 50 mm. The input point is at the 65th plate. N-methylpyrrolidone containing 5% water is fed as selective solvent to the head of this column, in such amounts that the stream returning to the column consists of 75% solvent and 25% hydrocarbons. The reflux ratio R/F is 7. The head temperature is at 45° C., the pressure 1000 torrs.

A pentane fraction is drawn off at the head of the column, which has the following compositions:

	Weight percent
Isopentane	35.31
n-Pentane	56.20
Cyclopentane	0.20
n-Pentene-1	3.24
Cis-pentene-2	1.50
Trans-pentene-2	2.85
2-methylbutene-2	0.57
C_4-hydrocarbons	0.13

The whole of the liquid present is withdrawn at the 100th plate and fed to a separator vessel E of FIG. 2. The upper hydrocarbon phase then separating consists of 81.3 weight percent hydrocarbons and 18.7 weight percent solvent. The lower, solvent phase consists of 11.1 weight percent hydrocarbons and 88.9 weight percent solvent. The pentane-content of the hydrocarbon phase is of 78 weight percent, while the pentane-content of the solvent phase is of 55 weight percent. The solvent phase is fed to the head of a second column (column B of FIG. 2), which has 70 plates and has a diameter of 40 mm. A

gaseous pentene fraction is drawn from above the 5th plate, which has the following composition:

	Weight percent
Isopentane	0.52
n-pentane	1.00
Cyclopentane	5.55
n-Pentene-1	16.10
Cis-pentene-2	8.70
Trans-pentene-2 / 2-methylbutene-1	48.19
2-methylbutene-2	19.58
Isoprene	0.36

The head temperature of this second column is at 45° C.; the sump temperature is 165° C. The sump product of the second column is cooled to about 45° C. and is fed to the main column A together with the hydrocarbon phase at a point below the aforedescribed take-off point. At this point of the column A there occurs a partial condensation due to indirect cooling, in order to achieve a constant solvent/hydrocarbon ratio. A diolefine fraction is withdrawn five plates above the sump of the main column A, in the vapour phase, and has the following composition:

	Weight percent
Cyclopentane	2.36
Cis-pentene-2	0.10
n-Methylbutene-2	0.10
Cyclopentene	7.03
Isoprene	38.73
Trans-1,3-pentadiene	15.62
Cis-1,3-pentadiene	7.33
Cyclopentadiene	24.92
Acetylene	1.05
Higher hydrocarbons	3.66

The sump temperature is of 165° C.

We claim:

1. Process for separating C_5-hydrocarbon mixtures, containing paraffinic, monoolefinic and diolefinic C_5-hydrocarbon fractions, into hydrocarbon fractions each consisting substantially of only one of said fractions, which comprises feeding the C_5-hydrocarbon mixture to the middle portion of an extractive distillation column, feeding N-methylpyrrolidone to the head of said column to act as a selective solvent; withdrawing a liquid side-stream, which contains substantially only the C_5-monoolefines and N-methylpyrrolidone from the lower portion of the upper half of the column; returning the N-methylpyrrolidone, after freeing it from the C_5-monoolefines, to the extractive distillation column at a point below the withdrawal point; maintaining the N-methylpyrrolidone/hydrocarbon ratio approximately constant in the extractive distillation column by effecting a partial condensation of vaporous hydrocarbons above the feedback point; withdrawing the

C_5-diolefines in vapor form from the lower portion of the extractive distillation column above the sump; withdrawing the paraffines at the head of the extractive distillation column; and returning the N-methylpyrrolidone collected in the bottom of the extractive distillation column to the head of said column.

2. Process according to claim 1, which comprises maintaining a different liquid/vapour ratio in the upper and lower portion of the column.

3. Process as claimed in claim 1, including the further step of purifying said N-methylpyrrolidone prior to returning such to the head of said extractive distillation column.

4. Process as claimed in claim 1, wherein the liquid side stream drawn from the lower part of the upper half of the extraction distillation column is fed to a separator vessel in which a segregation into a pentene-poor hydrocarbon layer and a pentene-rich solvent layer is effected; returning the pentene-poor hydrocarbon layer to the extractive distillation column below the take-off point.

5. Process according to claim 4, which further comprises introducing the pentene-rich solvent layer into the middle to upper half of a stripping column, withdrawing the pentene from the lower part of the column; and returning the N-methylpyrrolidone collected in the bottom to the extractive distillation column.

6. Process as claimed in claim 2, wherein the liquid side stream drawn from the lower part of the upper half of the extractive distillation column is fed to a separator vessel in which a segregation into a pentene-poor hydrocarbon layer and a pentene-rich solvent layer is effected; returning the pentene-poor hydrocarbon layer to the extractive distillation column below the take-off point.

7. Process as claimed in claim 4, wherein the liquid side stream drawn from the lower part of the upper half of the extractive distillation column is cooled prior to feeding such to the separation vessel.

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UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,320,138 May 16, 1967

Hans-Walther Brandt et al.

It is certified that error appears in the above identified patent and that said Letters Patent are hereby corrected as shown below:

In the heading to the printed specification, lines 10 and 11, "Farbenfabriken Bayer Aktiengessellschaft, Leverkusen, Germany, a German corporation" should read -- Erdolchemie Gesellschaft mit beschrankter Haftung and Farbenfabriken Bayer Aktiengesellschaft, both of Leverkusen, Germany, a corporation of Germany --

Signed and sealed this 24th day of March 1970.

(SEAL)
Attest:

Edward M. Fletcher, Jr.
Attesting Officer

WILLIAM E. SCHUYLER, JR.
Commissioner of Patents