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FRACTIONATION OF HYDROCARBON MIXTURES

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4 Claims. (Cl. 208—364)

This invention relates to the fractionation of hydrocarbon mixtures, especially petroleum fractions, containing aromatic, naphthenic and paraffinic hydrocarbons. More particularly the invention relates to the treatment of such mixtures to obtain fractions richer in at least one of the above hydrocarbon types than the original mixture. The invention is particularly suitable for the fractionation of hydrocarbon mixtures having an ASTM initial boiling point (measured on the basis of atmospheric pressure) of at least 150° C. and especially petroleum fractions boiling above 350° C.

According to the present invention a hydrocarbon distillate fraction containing at least two types of hydrocarbons selected from aromatics, naphthenes and paraffins, and having an initial boiling point of at least 150° C., is vacuum redistilled at a pressure below that at which it was originally distilled so that, as respects aromatics, naphthenes and paraffins in the fraction having the same boiling point at the original distillation pressure, the said aromatics in the fraction distil at the redistillation pressure at lower temperatures than the said naphthenes and the said naphthenes distil at the redistillation pressure at a lower temperature than the said paraffins, so that the lower boiling fractions obtained are richer in aromatics. Preferably the refractionation is carried out at a pressure of not more than 100 mm. Hg and preferably this pressure less than $\frac{1}{10}$, desirably less than $\frac{1}{100}$, that of the original distillation.

It has been observed that, under vacuum conditions, the effect of reducing pressure on the rate of change of boiling point of hydrocarbons varies significantly with hydrocarbon type. This is illustrated, for example, in the following Table 1 which shows the boiling points over a range of pressures from 760 mm. to 0.001 mm. Hg for aromatic, naphthenic and paraffinc hydrocarbons having normal boiling points of 200, 300, 400, 500 and 600° C.

The difference in boiling point, over the same range of pressures, between aromatic, naphthenic and paraffinic hydrocarbons having identical boiling points at 760 mm. Hg is illustrated in the following Table 2.

TABLE 2

Pressure, mm. Hg	Average Boiling Point Difference Between Hydrocarbons Having Identical Boiling Points at 760 mm. Hg pressure, ° C.		
	A–N	N–P	A–P
760	0	0	0
100	2	3	5
10	4	4	9
1	7	7	14
0.1	9	9	17
0.01	10	10	20
0.001	12	12	23

Similar tables can be constructed showing the boiling point differences, at various pressures, between the different types of hydrocarbons having the same boiling points at pressures other than 760 mm. Hg.

It is seen from Table 2 that, under vacuum conditions, aromatic hydrocarbons become relatively lower boiling than naphthenic hydrocarbons and the naphthenic hydrocarbons become relatively lower boiling than the paraffinic hydrocarbons. The difference in boiling point between the different hydrocarbon types increases with increasing pressure differential between the two distillations. In practice the maximum average boiling point difference that may be expected with successive distillations at 760 mm. and 0.001 mm. Hg is seen from Table 2 to be 23° C. for aromatics/paraffins and 12° C. for both aromatics/naphthenes and naphthenes/paraffins.

These observations may be used in both laboratory and commercial operations. For example, the principle may be used to effect separation of hydrocarbons by type. In order to effect good separation by hydrocarbon type according to the method of the present invention by successive distillations, the second distillation being carried out at lower pressure, the second distillation should be carried out on narrow boiling fractions. Preferably the boiling range of these fractions should be of the order of the boiling point difference anticipated to occur between the various components of the feedstock due to the change in pressure.

TABLE 1

Pressure, mm. Hg	Boling Point, ° C.														
	A	N	P	A	N	P	A	N	P	A	N	P	A	N	P
760	200	200	200	300	300	300	400	400	400	500	500	500	600	600	600
100	129	131	133	218	221	223	312	314	317	404	407	409	503	504	508
10	74	78	81	156	160	164	240	244	249	327	332	337	416	421	425
1	31	38	45	107	113	119	186	192	199	267	274	282	355	362	371
0.1	--------	--------	--------	69	77	84	143	151	159	218	227	236	302	311	321
0.01	--------	--------	--------	38	47	56	107	116	126	178	189	198	256	267	278
0.001	--------	--------	--------	--------	--------	--------	78	88	99	146	158	169	219	232	245

A=Aromatics. N=Naphthenes. P=Paraffins.

i.e. in the case of the above example illustrated in Table 2 with distillations at 760 mm. and 0.01 mm. Hg, the boiling range should be of the order of 20° C. The use of wider-boiling fractions in the second distillation will result in a poorer separation, particularly in the middle of the boiling range.

If it is particularly desired to separate aromatics from the other hydrocarbon types this separation can be improved by conducting the second, lower pressure distillation as an extractive or azeotropic distillation, i.e. in the presence of a solvent which is selective for aromatics such as, for example,

If it is desired to increase the yield of aromatics, or if the yield of naphthenes is unimportant, improved yields and separation of aromatics may be obtained by first subjecting the feedstock to a mild dehydrogenation treatment in known manner to convert naphthenes to aromatics. This is illustrated by the following Example 1.

EXAMPLE 1

Hexa methyl cyclohexane, n-dodecane, and naphthalene have boiling points at 760 mm. Hg pressure of 212°, 216.3°, and 218.0° C. respectively, and they are difficult to separate by distillation. A mixture of these components was subjected to dehydrogenation conditions so that the hexa methyl cyclohexane was converted into hexa methyl benzene, which has a boiling point at 760 mm. Hg of 263.8° C., i.e. considerably higher than that of n-dodecane or naphthalene. The dehydrogenated material was then distilled under a vacuum of 10 mm. Hg. At this pressure, n-dodecane and naphthalene have boiling points of 91.6° and 87.6° C. respectively, the boiling point difference between the two being 4° C. which is considerably greater than the difference of 1.7° C. at 760 mm. Hg pressure. The boiling point of hexa methyl benzene at 10 mm. Hg pressure is approximately 129° C. On distillation at 10 mm. Hg pressure n-dodecane, naphthalene and hexa methyl benzene fractions of high purity were recovered. Following the distillation, the hexa methyl benzene fraction was converted back to hexa methyl cyclohexane by hydrogenation.

The process may be employed to separate aromatics from naphthenes or to separate each of the three types. As the aromatics, naphthenes and paraffins distil in that order, aromatics concentrate in the overheads fraction and paraffins in the residue, naphthenes being removable separately as a heart cut if required.

The principle of the present invention may also be used to adjust or improve the composition and properties of petroleum fractions, particularly gas oils and lubricating oil fractions.

The effect of redistillation at lower pressure according to the present invention is again illustrated in the following Example 2.

EXAMPLE 2

A distillate obtained by distilling a Kuwait crude oil under the industrial pressure of 40 mm. of mercury are redistalled under the absolute pressures of 13 mm., 1 mm. and 0.001 mm. of mercury.

This distillate possesses the following properties:

Density at 15° C. (NF.T. 60.101)	0.940
Kinematic viscosity at 210° F. (IP.71) centistokes	15.8
Pour point (NF.T. 60.105) ° C.	+39

The analysis of the different fractions obtained by distillation under these different vacuum levels is shown in Table 3, 4 and 5.

TABLE 3.—DISTILLATION UNDER A VACUUM OF 13 mm. Hg

Fractions	Distribution of hydrocarbons expressed as percentage of carbon atoms (1)		
	Aromatic	Naphthenic	Paraffinic
1	20.7	15.4	63.9
2	21.1	14.9	64
3	21.3	14.0	64.7
4	21.3	14.4	64.3
5	21.8	12.9	65.3
6	21.8	12.2	66.0
7	21.6	12.9	65.5
8	22.0	12.1	65.9
9	22.3	11.6	66.1
10	22.3	12.0	65.7
11	22.0	12.8	65.2
12	23.0	10.5	66.5
Residue	23.7	9.4	66.9

See footnotes at end of Table 10.

TABLE 4.—DISTILLATION UNDER A VACUUM OF 1 mm. Hg

Fractions	Distribution of hydrocarbons expressed as percentage of carbon atoms (1)		
	Aromatic	Naphthenic	Paraffinic
1	22.3	14.1	63.6
2	22.7	13.8	63.5
3	22.5	13.4	64.1
4	22.5	13.6	63.9
5	22.4	12.9	64.7
6	22.3	12.6	65.1
7	22.3	12.2	65.5
8	21.8	12.6	65.6
9	22.2	11.2	66.6
10	21.9	11.3	66.8
11	22.4	9.9	67.7
12	21.5	10.5	68.0
Residue	22.0	9.4	68.6

See footnotes at end of Table 10.

TABLE 5.—DISTILLATION UNDER A VACUUM OF 0.001 mm. Hg

Fractions	Distribution of hydrocarbons expressed as percentage of carbon atoms (1)		
	Aromatic	Naphthenic	Paraffinic
1	23.9	13.9	62.2
2	23.2	13.5	63.3
3	23.0	13.6	63.4
4	23.1	13.1	63.8
5	22.7	12.8	64.5
6	22.3	12.5	65.2
7	22.1	12.3	65.6
8	21.8	11.8	66.4
9	21.5	11.6	66.9
10	21.2	11.3	67.5
11	20.8	11.6	67.6
12	20.5	11.2	68.3
Residue	19.7	11.6	68.7

See footnotes at end of Table 10.

It is seen that as the pressure differential of the distillations increases the lighter fractions became progressively richer in aromatics.

The invention may therefore be applied with advantage to the production of lubricating oils because it is possible to produce, by simple distillation from a lubricating oil base stock, a variety of fractions having different hydrocarbon type distributions which can be blended as required to produce lubricating oils of desired characteristics.

According to a further features of the invention, the base stock is first of all fractionated into a number of fractions by distillation under a moderate vacuum, these fractions then being redistilled under a much higher vacuum. In this way the separation effect that is characteristic of the invention is greately enhanced. This mode of operation is illustrated by the following Example 3.

EXAMPLE 3

An atmospheric distillation residue was distilled under a vacuum of 1 mm. to produce fractions whose characteristics are shown in Table 6.

TABLE 6

	Viscous Gas Oil	Distillate A	Distillate B	Distillate C1	Distillate C2	Residue in vacuo	Methods
Density at 70° C./4° C		0.8670	0.8787	0.8910	0.9038	1.028	NF-T 60.101.
Kinematic viscosity:							
At 210° F. (in cSt)	1.87					1.180	IP 71.
At 170° F. (in cSt)		6.05	10.4	16.1	28.6		Do.
At 122° F. (in cSt)	4.45	12.8	24.7	44.5	92.6		Do.
Pour point, ° C	+3	+18	+30	+36	+42	+39	NF-T 60.105.
Inflammability, ° C	123	198	225	238	213		NF-T 60.103.
Penetration, 100g./5 sec./25° C						28	NF-T 66.004.
Softening point, ° C						35	NF-T 66.008.
Acidity, mg./KOH/g		0.20	0.23	0.21	0.08		NF-T 60.204.
Ramsbottom carbon		0.11	0.11	0.13	0.52		PN-T 60.117.
Sulphur, percent by wt	1.72	2.53	2.55	2.79	2.93		NF-M-07.005.
NPA colour		3.4	4.3	>7	>8		ASTM-D.155.
Refractive index (Ray D at 68° C.)	1.468	1.485	1.4922	1.4982	1.5058		NF-T 60.212.

Fractions A, B, C_1 and C_2 were then redistilled under a vacuum of 0.001 mm. of mercury. The analyses of the different fractions obtained from the above fractions are shown in Tables 7 to 10 respectively.

TABLE 7

Fractions	Kinematic viscosity in centistokes at 210° F.	Distribution of hydrocarbons expressed as percentage carbon atoms [1]		
		Aromatic	Naphthenic	Paraffinic
1		23.4	20.5	56.1
2	2.92	22.0	19.2	58.8
3		21.7	17.7	60.6
4		20.4	18.6	61.0
5		19.2	18.0	62.8
6	3.34	18.8	17.4	63.8
7		17.8	18.4	63.8
8	3.78	16.5	19.0	64.5
9	3.56	17.1	17.8	65.1
10		15.4	19.0	65.6
11		14.8	19.0	66.2
12	4.68	15.1	15.8	69.1
13		14.0	18.1	67.9
14		15.0	19.2	65.8
Distillate A		18.2	19.5	62.3

See footnote 1 at end of Table 10.

TABLE 8

Fractions	Kinematic viscosity in centistokes at 210° F.	Distribution of hydrocarbons expressed as percentage carbon atoms [1]		
		Aromatic	Naphthenic	Paraffinic
1		23.3	17.7	59.0
2	4.69	21.7	17.0	61.3
3	4.72	21.5	17.9	60.6
4		20.6	18.0	61.4
5		19.5	17.4	63.1
6	5.23	19.0	16.4	64.6
7		17.8	18.1	64.1
8		17.4	18.3	64.3
9	5.82	16.7	18.6	64.7
10		16.1	18.9	55.0
11		15.7	17.8	66.5
12		14.5	18.3	67.2
13	8.15	14.5	19.1	66.4
14		15.6	19.4	65.0
Distillate B		17.9	19.1	63.0

See footnote 1 at end of Table 10.

TABLE 9

Fractions	Kinematic viscosity in centistokes at 210° F.	Distribution of hydrocarbons expressed as percentage carbon atoms [1]		
		Aromatic	Naphthenic	Paraffinic
1		23.5	17.9	58.6
2		22.1	18.6	59.3
3	7.32	24.8	12.6	62.6
4		23.3	15.5	61.2
5	7.64	19.6	18.7	61.7
6		19.3	18.4	62.3
7		18.6	18.7	62.7
8	8.13	17.4	18.8	63.8
9		17.1	18.8	64.1
10		15.9	19.1	65.0
11	8.99	15.4	19.5	65.1
12		15.1	17.6	67.3
13	11.1	14.9	17.6	67.5
14		16.6	16.8	66.6
Distillate C1		18.4	18.2	63.4

See footnote 1 at end of Table 10.

TABLE 10

Fractions	Kinematic viscosity in centistokes at 210° F.	Distribution of hydrocarbons expressed as percentage carbon atoms [1]		
		Aromatic	Naphthenic	Paraffinic
1		21.1	16.3	62.6
2	10.2	18.5	20.7	60.8
3		22.0	16.0	62.0
4	12.0	21.5	16.0	62.5
5		20.7	16.4	62.9
6		20.8	15.1	64.1
7	13.8	19.9	15.6	64.5
8		19.7	14.8	65.5
9		19.2	14.5	64.3
10	16.7	18.3	15.2	66.5
11		17.9	15.0	67.1
12		18.3	13.1	68.6
13	24.1	17.6	13.4	68.0
14		20.7	11.9	67.4
Distillate C2		20.1	15.2	64.7

[1] Method described in "Aspects of the constitution of mineral oils" by Van Nes and Van Westen—Elsevier Publishing Company (1951).

The invention may also be employed to improve the properties of gas oils. Subjecting a gas oil to a second distillation at lower pressure according to the present invention yields distillate fractions having higher specific gravity and lower pour points, cloud points and wax contents, all of which are desirable. During the second distillation, the paraffins, which are responsible for poor cold test characteristics, tend to concentrate in the residue.

The invention may also be applied to advantage to the de-oiling of paraffin wax. For the purpose of this invention the expression "hydrocarbon distillate" includes a portion of such a distillate and particularly paraffin wax separated from such a distillate. For example a paraffin wax having an oil content (ASTM D. 721) of 3.35% by weight is distilled under a vacuum of 0.001 mm. of mercury. The results obtained are shown in Table 11.

TABLE 11

Fraction	Percent	Oil content, percent by weight ASTM Method D721
1	10	4.2
2	10	4.0
3	10	3.8
Residue	70	2.9
Charge		3.55

I claim:

1. In a process for the treatment of a hydrocarbon distillate mixture having an ASTM initial boiling point above 150° C. to concentrate a low boiling aromatic fraction as a recovered product from the distillate mixture containing said aromatic fraction and at least one other hydrocarbon fraction selected from the group consisting of naphthenes and paraffins, the said distillate mixture having been obtained from an initial distillation zone operated at substantially atmospheric pressure, and having aromatic and said other hydrocarbon fractions present therein which will have substantially the same boiling point at atmospheric pressure, the improvement comprising; subjecting the hydrocarbon mixture to a vacuum redistillation at a pressure of not more than 100 mm. Hg to increase the boiling point differential between the respective constituents so that the boiling point temperature of the aromatic fraction is below that of the naphthene fraction which is below that of the paraffin fraction, and recovering the low boiling fraction rich in said aromatic as a withdrawn product from the redistillation zone.

2. A process as claimed in claim 1 wherein the redistillation is carried out at a pressure less than 1/10 that of the original distillation.

3. A process as claimed in claim 1 wherein the hydrocarbon distillate mixture is a petroleum distillate having an initial boiling point above 350° C.

4. A process as claimed in claim 1 wherein the redistillation is carried out at a pressure less than 1/100 that of the original distillation.

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UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

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Jacques Demeester

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 1, line 44, for "paraffinc" read -- paraffinic --; column 2, line 47, for "pressure." read -- pressure, --; column 3, line 9, for "lower pressure" read -- lower pressure, --; line 64, for "redistalled" read -- redistilled --; column 4, line 69, for "greately" read -- greatly --.

Signed and sealed this 30th day of July 1968.

SEAL)

ttest:

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Commissioner of Patents