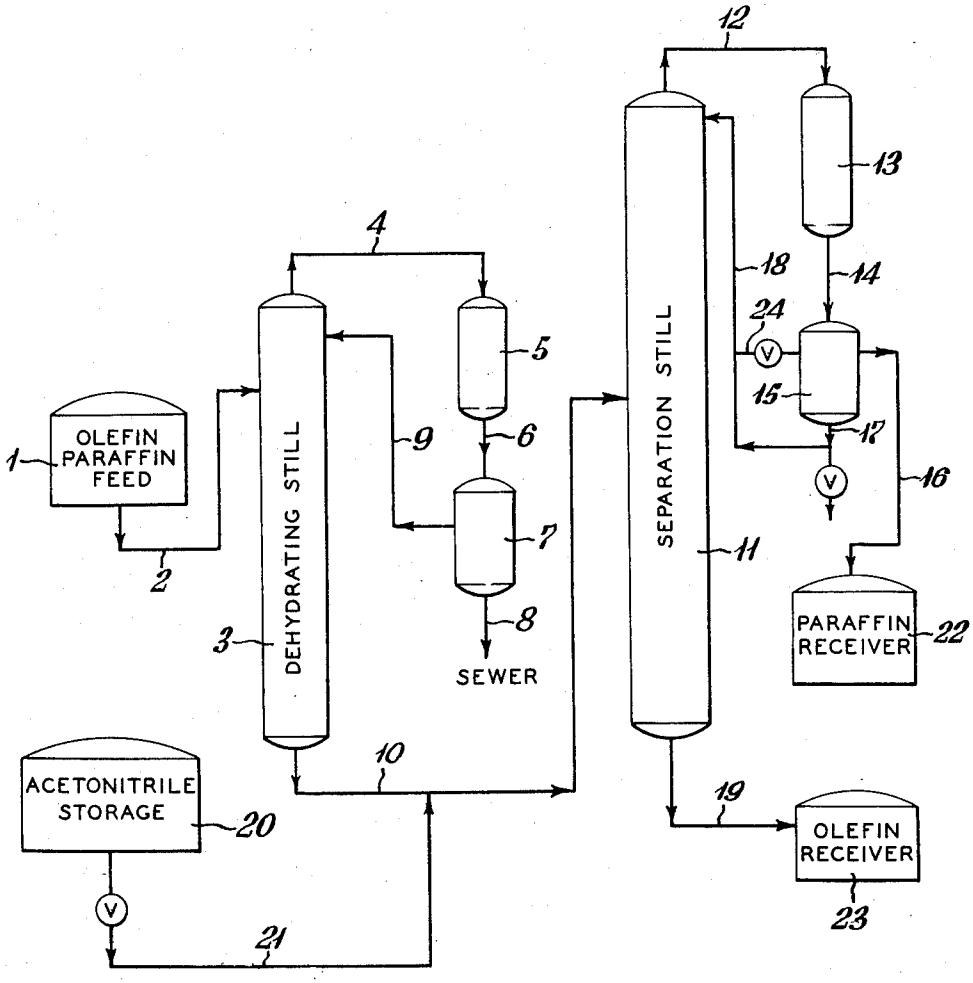
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RECOVERY OF OLEFINS FROM C_7 TO C_9 CORRESPONDING OLEFIN-PARAFFIN MIXTURES

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RECOVERY OF OLEFINS FROM C_7 TO C_9 CORRESPONDING OLEFIN-PARAFFIN MIXTURES

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This invention relates to the separation of olefin-paraffin mixtures wherein the constituents contain from seven to nine carbon atoms, and particularly to the recovery of olefin rich fractions from such hydrocarbon mixtures. Still more particularly, the invention relates to the separation and recovery of relatively high boiling isomeric olefins from mixtures of their corresponding isomeric paraffins by azeotropic distillation. While the process of the present invention is applicable to any mixture of an olefin and its corresponding paraffin, provided it contains from 7 to 9 carbon atoms, the mixtures herein shown are by-product hydrocarbon fractions of the well known Oxo Process. This is merely illustrative and not intended in any way to limit or restrict this invention. The present invention is applicable to any corresponding paraffin-olefin mixtures of hydrocarbons having from 7 to 9 carbon atoms, regardless of the source of the mixture.

Distillation of the products from the hydroformylation of olefins yields a head fraction containing a mixture of the olefin, its corresponding paraffin and aldehydes. This occurs in the well known Oxo Process wherein olefinic hydrocarbons are reacted with carbon monoxide and hydrogen to produce an aldehyde-alcohol mixture. A portion of the olefin raw material passes through the converter unreacted and is removed with the aldehyde-alcohol in the mixed product stream. Another portion of the olefin raw material is hydrogenated to the corresponding saturated hydrocarbon by a side reaction in the converter. The unreacted olefin and the by-product paraffin, some of the aldehyde and water are removed as a heads fraction on distillation of the converter product. This mixed hydrocarbon fraction generally contains 50 to 55 percent of the unreacted olefin, a concentration too low for economic recycling to the converter. Resolution between the olefinic and paraffinic hydrocarbons cannot be made by fractional distillation because each is a mixture of isomers of overlapping volatilities. The usual methods of separation employed, such as extractive distillation, solvent extraction and adsorption, are either inoperable, economically prohibitive or of poor efficiency when olefins of seven or more carbons are involved.

The present invention provides a means of separating the unreacted olefin from this mixture through the use of a relatively small quantity of a moderately priced entrainer, said entrainer being recycled with little make-up required, and is adaptable to simple conventional carbon steel equipment. The olefin fraction so obtained can be readmitted to the Oxo Process without further treatment.

The preferred form of the invention involves its application to a continuous process and the use of acetonitrile as the entrainer. The preferred form is illustrated in the FIGURE.

Referring to the figure, the olefinic-paraffinic hydrocarbon mixture is fed from storage tank **1** through line **2** to the side of the dehydrating still **3**. The base of this continuous column is heated conventionally, resulting in the removal of the hydrocarbon-water azeotropes through vapor line **4** and condenser **5** to decanter **7**. After phase separation, the water layer is removed through line **8** and the upper hydrocarbon layer is returned as reflux through line **9** to dehydrating still **3**. The dehydrated hydrocarbons are removed from the base of the still through line **10** and are fed through line **10** to separation still **11**. In this column, the hydrocarbon mixture is contacted with acetonitrile, which had previously been pumped into the column from acetonitrile storage tank **20** through lines **21** and **10**. The more volatile paraffin-acetonitrile azeotropes are removed from the top of the column through vapor line **12** and are condensed in condenser **13**. The condensate there flows through line **14** into decanter **15**, where it separates into an upper hydrocarbon-rich phase and a lower acetonitrile-rich phase. The upper layer is withdrawn from the system through line **16** to receiver tank **22** and the lower acetonitrile layer is returned as reflux to column **11** through line **18**. To maintain proper reflux on the column, a portion of the upper layer may also be returned to the column through line **24**.

The amount of acetonitrile in the column is limited to the extent that a separation between the acetonitrile-hydrocarbon azeotropes and the concentrated olefins is effected in the lower trays, and the concentrated olefins, containing little or no acetonitrile, are removed through line **19** from the base of the column and collected in receiver tank **23**. To compensate for minor losses of acetonitrile by partial solution in the upper layer of decanter **15**, acetonitrile may be added intermittently from storage tank **20** through lines **21** and **10**. In case of incomplete water removal in dehydrating still **3**, a slow bleed of acetonitrile-water mixture can be taken from the lower layer of decanter **15** through line **17** to maintain anhydrous conditions in column **11**.

The invention can also be applied to a batchwise technique. In this case, a mixture of the acetonitrile and the olefin-paraffin mixture is charged to the kettle of a batch still. The overhead product from the column is condensed and the liquid phases separated in a decanter. The lower acetonitrile layer is returned to the column as reflux, together with sufficient upper layer to maintain proper reflux on the system. A stream from the upper layer, consisting of a concentrate of the paraffinic hydrocarbons, is also withdrawn to the product tank. When separation of the paraffinic component by this method is essentially complete, the reflux and product system is changed so that all the upper layer is returned as reflux to the column and all of the lower layer is withdrawn to a second product tank. When the acetonitrile has been stripped from the system in this manner, the still can be shut down and the kettle liquid, consisting of enriched olefins suitable for recycling to the Oxo Process, can be pumped from the system. The acetonitrile solvent, in the second product tank, can then be returned to the system for reuse with the next batch.

Acetonitrile can also be used as the aqueous azeotrope, containing 81.5 percent acetonitrile at the expense of some of the separation efficiency. Usage of this azeotrope would obviate the need of dehydrating still **3** in the figure, and would permit the base of separation column **11** to operate at a lower temperature.

The following specific examples will serve to further illustrate the present invention and are not to be construed as limiting the present invention.

EXAMPLE 1

A mixture of 200 milliliters recovered C_9 hydrocarbon (41 percent nonane, 54 percent nonene and 5 percent decanal) and 90 milliliters of acetonitrile (containing 0.25 percent water) was fractionally distilled through a 30-tray Oldershaw column. The distillate was condensed and the lower (acetonitrile) layer was returned to the column. Distilled fractions and the residue were analyzed for the components, and the results are reported in Table I.

Table I

Fraction	Head temp., ° C.	Composition, vol. percent, CH_3CN free basis				Vol. percent nonenes, CH_3CN and aldehyde free basis
		Percent of total C_9 charge	Nonanes	Nonenes	Aldehyde as decanal	
1	65	7.5	77	18	4.9	19
2	65 -66	7.5	76	24	0.4	24
2A (lower layer)	66 -77	Nil				
3	77 -78	7.5	80	20	Nil	20
4	78	7.5	67	32	0.7	32
5	78	7.5	60	40	0.4	40
6	78 -78.5	7.5	64	34	1.9	35
7	78.5	7.5	45	55	0.4	55
8	78.5-79	7.0	40	59	0.7	60
9	79	7.0	31	67	1.9	68
Col. hold-up (calc.)		5.5	20	78	1.9	80
Residue		28.0	8	73	19.2	90

Considering fractions 1 through 6 as the waste nonane fraction and fractions 7 through 9 plus the column hold-up and residue as the recovered nonene fraction, a distribution of the components of the sample appears in Table II.

Table II

	Vol. of contained component, milliliters			Percent nonenes, aldehyde and CH_3CN free basis
	Nonanes	Nonenes	Aldehyde as decanal	
Waste nonane fraction	63.6	26.2	1.2	29
Recovered nonene fraction	23.4	75.4	11.4	76
Total	87.0	101.6	12.6	

A recovery of 74 percent of the contained nonenes, in a fraction of 76 percent purity (on an aldehyde and acetonitrile free basis), was achieved. The recovered nonene fraction also contained 91 percent of the aldehydes present in the original sample.

EXAMPLE 2

A mixture of 200 milliliters recovered C_9 hydrocarbon (41 percent nonane, 54 percent nonene and 5 percent decanal) and 90 milliliters wet acetonitrile (containing 20 percent water by weight) was fractionally distilled through a 30-tray Oldershaw column. The distillate was condensed and the lower (acetonitrile-water) layer was returned to the column. Distilled fractions and the residue were analyzed for the components and the results are reported in Table III.

Table III

Fraction	Head temp., ° C.	Composition, vol. percent, CH_3CN free basis				Vol. percent nonenes, CH_3CN and aldehyde free basis
		Percent of total C_9 charge	Nonanes	Nonenes	Aldehyde as decanal	
1	64.5-65	7.0	66	31.5	2.5	32
1A (lower layer)	65 -71					
2	71	7.0	62	38	Nil	38
3	71	7.5	59	41	Nil	41
4	71 -72	6.5	58	42	Nil	42
5	72	7.5	58	42	Nil	42
6	72 -72.5	7.5	53	47	Nil	47
7	72.5-73	7.5	54	46	Nil	46
8	73	7.5	54	46	Nil	46
9	73	7.5	45	55	0.4	55
Col. hold-up (calc.)		7.0	30	70	0.4	70
Residue		27.5	15	67	17.6	82

Considering fractions 1 through 8 as the waste nonane fraction and fraction 9 plus the column hold-up and residue as the recovered nonene fraction, a distribution of the components of the sample is provided in Table IV.

Table IV

	Vol. of contained component, milliliters			Percent nonenes, aldehyde and CH_3CN free basis
	Nonanes	Nonenes	Aldehyde as decanal	
Waste nonane fraction	67.2	48.5	0.3	42
Recovered nonene fraction	19.2	54.9	9.8	74
Total	86.4	103.4	10.1	

A recovery of 53 percent of the contained nonenes, in a fraction of 74 percent purity (on an aldehyde and acetonitrile free basis), was achieved. The recovered nonene fraction also contained 97 percent of the aldehydes present in the original sample.

EXAMPLE 3

A nonene-nonane mixture (48 percent nonane, 51 percent nonene and 1 percent decanal) was separated into nonene-rich and nonene-lean fractions by continuous azeotropic distillation with acetonitrile. The crude hydrocarbon mixture was introduced at the side of a continuous column at a point approximately equidistant from the top and bottom of the packed section. The column contained a limited amount of acetonitrile, so that there was a sharp temperature gradient in the lower sections of the column, and the product stream from the base of the column contained no acetonitrile. The overhead stream from the column was condensed, and the liquid layers separated. The lower (acetonitrile) layer and a portion of the upper (hydrocarbon) layer were returned to the column as reflux. The remainder of the upper layer was collected as overhead product. The column was operated so that the overhead product and the base product streams

were removed at the same rate. Make-up acetonitrile was added occasionally to the feed. Summarizing:

	Grams
Overhead product:	
Nonanes	2,166
Nonenes	1,071
Aldehydes, as decanal	22
Total	3,259
Base Product:	
Nonanes	887
Nonenes	2,547
Aldehyde, as decanal	53
Total	3,487
Total recovery	[1] 6,746

[1] 99 percent.

The base product stream contained 70.4 percent of the nonenes present in the original sample, and had a nonene purity of 73 percent, on an aldehyde-free basis. This stream also contained 71 percent of the aldehyde present in the original sample.

A total of 266 grams of acetonitrile was required in this separation of which 165 grams were recovered by stripping from the column at the end of the run. The remaining 101 grams of acetonitrile left the system with the overhead product, from which it can be recovered either by subsequent distillation of this stream or by extraction with water.

EXAMPLE 4

A mixture of 700 milliliters recovered C_9 hydrocarbon (41 percent nonane, 54 percent nonene and 5 percent decanal) and 50 milliliters acetonitrile (containing 0.25 percent water) was fractionally distilled through a 30-tray Oldershaw column. The distillate was condensed and the lower (acetonitrile) layer was returned to the column. Distilled fractions and the residue were analyzed for the components and the results are collected in Table V.

Table V

Fraction	Head temp., ° C.	Composition, vol. percent, CH_3CN free basis				Vol. percent nonenes, CH_3CN and aldehyde free basis
		Percent of total C_9 charge	Nonanes	Nonenes	Aldehyde as decanal	
1 (lower layer)	61 -62.5	0.3	80	----------	----------	20
2	62.5-65	13.7	72	26	2	27
3	65	14.0	69	31	Nil	31
4	65	14.0	65	35	Nil	35
5	65 -66.8	14.0	47	53	Nil	53
6	66.8-67.5	14.0	30	70	Nil	70
Col. hold-up (calc.)	----------	3.3	19	81	Nil	81
Residue	----------	26.7	8	74	17.6	90

Considering fractions 1 through 4 as waste nonene fraction and fractions 5 through 6 plus the column hold-up and residue as the recovered nonene fraction, a distribution of the components of the sample is collected in Table VI.

Table VI

	Vol. of contained component, milliliters			Percent nonenes, aldehyde and CH_3CN free basis
	Nonanes	Nonenes	Aldehyde as decanal	
Waste nonane fraction	202.1	90.0	1.9	31
Recovered nonene fraction	94.9	277.5	33.6	75
Total	297.0	367.5	35.5	----------

A 200 milliliter portion of the waste nonane fraction (69 percent nonane, 30.6 percent nonene and 0.4 percent dacanal) was then mixed with 50 milliliters of acetonitrile and distilled through the same column in the same manner as in the initial distillation. Analyses of the resulting fractions is collected in Table VII.

Table VII

Fraction	Head temp., ° C.	Composition, vol. percent, CH_3CN free basis				Vol. percent nonenes, CH_3CN and aldehyde free basis
		Percent of total C_9 charge	Nonanes	Nonenes	Aldehyde as decanal	
1	77.0-77.9	11.7	84	16	0.4	16
2	77.9-78.0	12.2	78	22	Nil	22
3	78.0	12.2	75	25	Nil	25
4	78.0	12.2	73	26	0.7	26
5	78.0-78.2	12.5	72	28	Nil	28
6	78.2	12.5	72	27	0.7	27
7	78.2	7.5	64	36	Nil	36
Col. hold-up (calc.)	----------	0.7	55	45	Nil	45
Residue	----------	18.5	45	54	0.9	55

Considering all the distilled fractions and the column hold-up as a waste nonane fraction and the residue as a recovered nonene fraction, a distribution of the components is collected in Table VIII, when calculated on the basis of the entire nonane fraction from the previous distillation (294 milliliters).

Table VIII

	Vol. of contained component, milliliters			Percent nonenes, aldehyde and CH_3CN free basis
	Nonanes	Nonenes	Aldehyde as decanal	
Waste nonane fraction	178.2	60.8	0.7	25
Recovered nonene fraction	24.5	29.4	0.5	55
Total	202.7	90.2	1.2	----------

The nonene recoveries and the purities of the nonene fractions are shown in Table IX for the initial distillation singly and for the combined initial distillaton and subsequent redistillation of the nonane fraction.

Table IX

	Initial distillation	Redistillation of nonane fraction	Combined distillation
Nonene recovery, vol. percent	75.5	8.0	83.5
Nonene purity, vol. percent of recovered nonene fraction, aldehyde and CH_3CN free basis	75	55	70
Aldehyde recovery, vol. percent	95	1	96

EXAMPLE 5

A heptene-heptane mixture (40 percent heptane and 51 percent heptene), simulating the recovered hydrocarbon fractions obtained as a by-product from the hydroformylation of heptenes to produce octyl alcohols, was prepared by the partial hydrogenation of a sample of heptenes. A mixture of 600 milliliters of the heptene-heptane mixture and 50 milliliters of acetonitrile was fractionally distilled through a packed column. The distillate was condensed and the lower, acetonitrile layer was returned to the column. Distilled fractions and the residue were analyzed for the components and the results are collected in Table X.

Table X

Fraction	Head temp., ° C.	Percent of total C_7 charge	Composition, vol. percent, CH_3CN free basis	
			Heptanes	Heptenes
1	62.5–64.5	16.0	74	26
2	64.5–65.5	15.7	78	22
3	65.5–66.0	16.3	75	25
Vol. Hold-up (calc.)		6.2	46	54
Residue		45.8	17	83

Considering fractions 1 through 3 as the waste heptane fraction and the column hold-up and residue as the recovered heptene fraction, a distribution of the components of the sample is presented in Table XI.

Table XI

	Vol. of contained components, milliliters		Percent heptenes CH_3CN free basis
	Heptanes	Heptenes	
Waste heptane fraction	217.9	70.1	24
Recovered heptene fraction	63.8	248.2	80
Total	281.7	318.3	

A recovery of 78 percent of the contained heptenes, in a fraction of 80 percent purity (on an acetonitrile-free basis) was achieved.

It is to be understood that the invention is not to be limited to the exact details of operation shown and described, as obvious modifications and equivalents will be apparent to one skilled in the art, and the invention is, therefore, to be limited only by the scope of the appended claims.

What is claimed is:

1. The method of separating corresponding paraffins and olefins from mixtures comprised of hydrocarbons containing from seven to nine carbon atoms by distilling said mixture with acetonitrile as an azeotrope entrainer and removing the paraffinic fraction as the heterogenous azeotrope from the entrainer.

2. The process of claim 1 where the admixture to be separated is composed of isomeric nonenes and their corresponding isomeric nonanes.

3. The process of claim 1 where the admixture to be separated is composed of isomeric heptenes and their corresponding heptanes.

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