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FRACTIONATION PROCESS CONTROL

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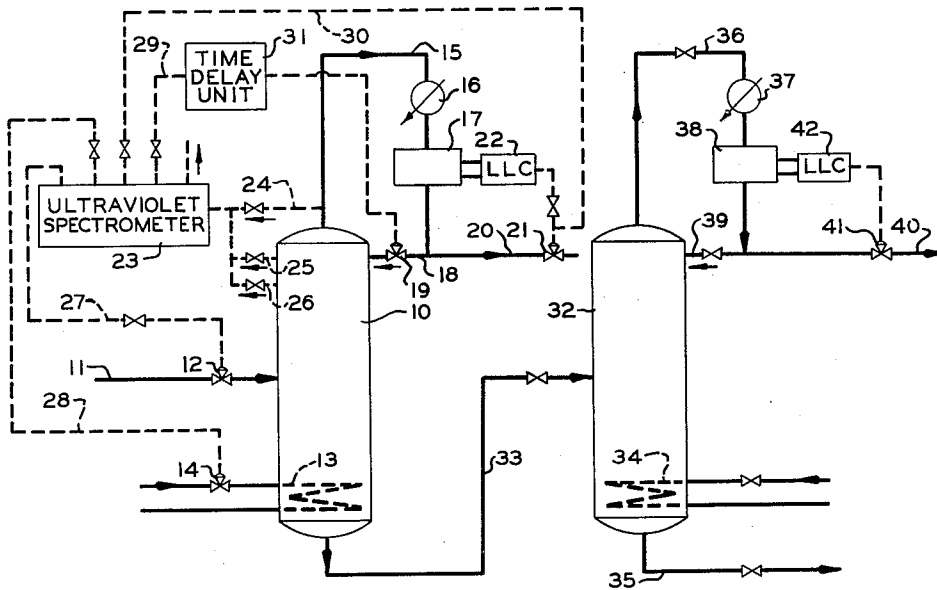


FIG. 1

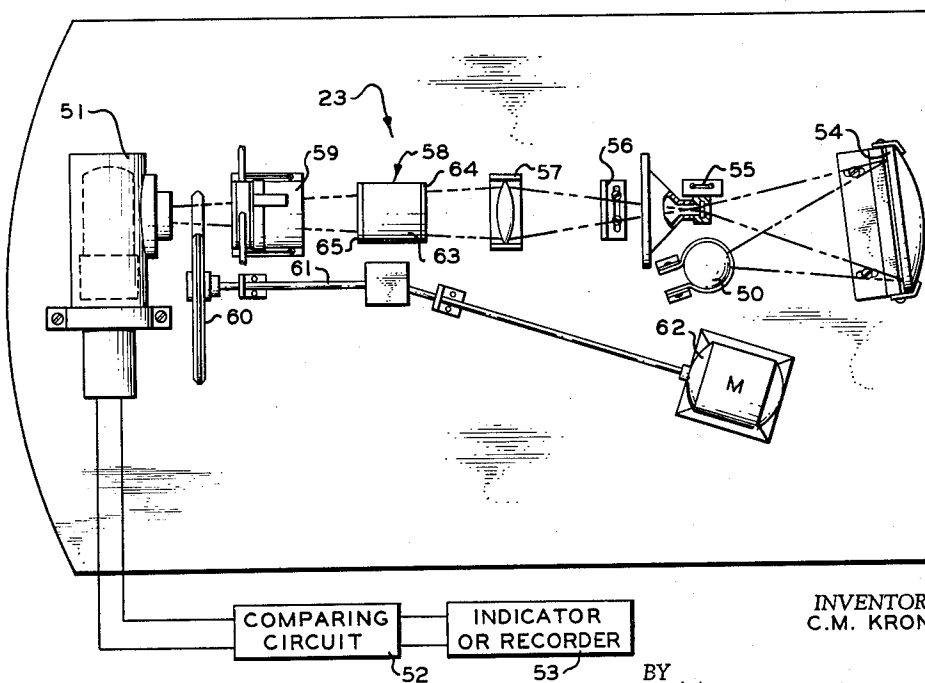


FIG. 2

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1

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FRACTIONATION PROCESS CONTROL

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This invention relates to a method of controlling a fractionation process.

In many commercially important fractionations involving paraffinic and naphthenic hydrocarbons having 6 to 8 carbon atoms, especially 6 or 7 carbon atoms, together with small quantities of an aromatic hydrocarbon having up to 8 carbon atoms, especially benzene or toluene, it is important to accurately control the conditions at which the separation takes place.

For example, in the fractionation of straight run gasolines, a light gasoline product is taken overhead and a bottom product is produced which is further fractionated to provide a heavy straight run gasoline suitable as feed to a platforming unit and a cyclohexane concentrate. The latter fraction can be processed in a hexane isomerization unit.

In the first fractionation above mentioned, it is desired that normal hexane and less volatile materials appear in the kettle product while isohexanes and more volatile materials are taken off in the overhead product. If normal hexane is taken overhead, it appears in the light gasoline fraction and thus is lost to the feed to the hexane isomerization unit. Conversely, "undercutting" in the column results in loss of desired isohexane materials in the light gasoline fraction. Close control of the operation of this particular fractionation permits an octane number improvement of 1.1 to 1.3 numbers or even more in the light gasoline product.

A similar problem exists in making analogous separations, for example, in fractionating mixed hexane fractions or cyclohexane concentrates. Direct analysis for normal hexane in the overhead product of such separations is difficult and unsatisfactory.

In accordance with this invention, a sample from the upper part of the column, or a sample of the overhead product, is analyzed to determine its benzene content. The benzene is present only in small amounts in the feed, and, surprisingly, it co-distills with the normal hexane despite a substantial difference in boiling point of the two materials. Thus, by controlling the process to keep the benzene concentration at a predetermined low value in the sample, normal hexane and less volatile materials do not appear in the overhead product. Yet, the column can be operated under conditions of the greatest efficiency and throughput short of permitting normal hexane to appear in the overhead product.

The analysis can be made, according to the invention, by an ultraviolet analyzer, and this instrument can be arranged to automatically control one or more of the process variables of the fractionation column, for ex-

2

ample, the rate of withdrawal of overhead product, the reflux rate, or the feed rate.

Such an ultraviolet analyzer can be utilized to control separations where the cut is made between paraffinic or naphthenic hydrocarbons having 7 carbon atoms where toluene co-distills with the most volatile paraffinic or naphthenic component of the kettle product to be obtained in the fractionation.

Accordingly, it is an object of the invention to provide an improved method of controlling the fractionation of streams containing 6 and 7 carbon atom paraffinic and naphthenic hydrocarbons.

It is a further object to provide an improved fractionation control process utilizing an ultraviolet analyzer.

It is a still further object to provide a close fractionation control yielding substantial economies in operation.

Various other objects, advantages and features of the invention will become apparent from the following detailed description taken in conjunction with the accompanying drawings in which:

Figure 1 is a flow diagram of a fractionation process utilizing the improved control system; and

Figure 2 is a top view of a suitable ultraviolet analyzer.

Referring now to Figure 1, I have shown a fractionation zone or column 10 to which feed is supplied by a line 11 under the control of an automatic valve 12. Heat can be supplied to the bottom of the column in various ways. In the example illustrated, steam is fed through a coil 13 under the control of an automatic valve 14.

Overhead product is withdrawn through a line 15 and passed through a condenser 16 to an accumulator 17. A portion of the condensed material is withdrawn through a line 18 and is passed back to the column as reflux in an amount controlled by an automatic valve 19. The remainder of the material from the accumulator 17 is passed through an overhead product withdrawal line 20 at a rate determined by an automatic valve 21 normally controlled by a liquid level controller 22 responsive to the material in the accumulator 17.

In accordance with the invention, an ultraviolet spectrometer 23 is connected to receive a sample from one of a plurality of valved sample lines 24, 25 or 26. The line 24 is connected directly to the overhead line 15, the line 25 is connected to the third tray below the top of the column and the line 26 is connected to the sixth tray below the top of the column. Thus, a sample can be withdrawn as desired from any of these three locations. Broadly speaking, a sample can be withdrawn from any tray in the top region of the column, i.e., one more than five trays above the feed tray with the usual fractionating devices for this type of service which have 30 to 100 trays.

The output of the spectrometer 23, which is shown as a pneumatic output, is selectively applied through the valved lines 27, 28, 29 and 30 to the control units of the respective valves 12, 14, 19 and 21. It will be noted that the valve in each of the lines 27 to 30 permits the control impulse to be applied to any desired one or combination of the valves 12, 14, 19 and 21. In this manner, one or more process variables of the system are controlled, the ones specifically illustrated being, of course, the rate at which heat is supplied to the bottom of the column, the feed rate, the reflux rate, and the rate of overhead product withdrawal. Where the latter

variable is controlled, the liquid level controller 22 is disconnected from the valve 21.

It is oftentimes desirable to incorporate a time delay in the correction made to the process variables corresponding to the time taken for the process to respond to the correction. For this purpose, I have shown a time delay unit 31 in the control line 29.

In many commercial embodiments of the invention, the bottom product from the column 10 is further fractionated. To this end, I have shown a fractionation column 32 to which the bottom product from the column 10 is fed by a line 33. The column 32 is provided with a suitable source of heat at the lower end thereof, this being a steam coil 34 in the example illustrated. The column 32 also has a bottom product withdrawal line 35, and an overhead product withdrawal line 36 which extends to a condenser 37 connected to an accumulator 38. A portion of the material from the accumulator 38 is passed back to the top of the column as reflux through a valved line 39 while the remainder of the material from the accumulator is passed to an overhead product withdrawal line 40 under the control of an automatic valve 41 and a liquid level controller 42 responsive to the level in the accumulator 38.

In operation, a stock to be fractionated containing 6 or 7 carbon atom paraffinic and naphthenic hydrocarbons together with a small amount of benzene or toluene is fed to the fractionator 10 through the line 11. The operating variables of the process are so controlled that the benzene or toluene co-distills with the most volatile paraffinic or naphthenic component of the kettle product to be obtained in the fractionation. For example, where the feed contains isohexanes, normal hexane and benzene, the normal hexane is the most volatile component of the bottom product, and this material distills with the benzene. As another example, where the separation is made between n-heptane and lower boiling branched chain C₇'s, in the presence of toluene, the toluene co-distills with the n-heptane, which is the more volatile component of the kettle product. Therefore, by analyzing for toluene in the overhead product or at a lower tray of the column, the amount of n-heptane at that part of the column can be controlled. Similarly, in the separation of n-octane from lower boiling branched chain C₈'s in the presence of ethyl benzene, analysis is made of the overhead product for ethyl benzene. As still another example, where the separation is made between n-octane and 2-methyl heptane in the presence of toluene, the latter compound co-distills with the toluene, and the analysis detects toluene in the kettle product or at a lower tray of the column.

Assuming that the sample is fed to the spectrometer through the line 24, the presence of aromatic material, as determined by the spectrometer, is indicative of the presence of the undesirable paraffinic or naphthenic component in the overhead product. Responsive to an output representative of aromatics, one of the variables of the column is adjusted to increase the efficiency of the separation to such an extent that the aromatic hydrocarbon, and thus the undesirable paraffinic or naphthenic component, is eliminated from the overhead product.

Where the analyzer sample is withdrawn through one of the lines 25 or 26, the analyzer is set to maintain a fixed predetermined concentration of aromatic hydrocarbon at the tray of the column from which the sample is withdrawn. This amount of aromatic, for example, 0.01 percent at the third tray from the top, produces an overhead product which is free from aromatic materials and thus of the undesired paraffinic or naphthenic component. Conversely, if the aromatic concentration falls below its pre-set value, the process is adjusted to increase the amount of material processed so that the efficiency of separation remains at its highest value. Even more accurate control can be obtained, in many cases, by providing a time delay unit 31 in the output of the analyzer

which produces a delay corresponding to the length of time taken by the process to react to the control impulse. This prevents "hunting" or oscillation of column operation.

In one specific example, the control system of the invention was applied to the fractionation of a straight run Panhandle crude fraction boiling at 50 to 400° F. A thirty tray fractionation column was employed with the feed entering at the sixteenth tray. The analyses of the feed, overhead product and kettle product prior to control by the method of the invention were as follows:

Composition, Liquid Volume Percent	Feed	Overhead Product	Kettle Product
Propane.....	0.8	3.6	-----
Isobutane.....	0.4	3.8	-----
n-Butane.....	2.0	15.4	-----
Isopentane.....	2.4	17.6	-----
n-Pentane.....	5.5	31.6	-----
Cyclopentane.....	0.6	3.1	-----
2,2-Dimethylbutane.....	Trace	0.6	-----
2,3-Dimethylbutane.....	0.3	1.8	0.1
2-Methylpentane.....	2.4	9.6	1.1
3-Methylpentane.....	1.7	4.5	1.1
n-Hexane.....	5.3	6.4	5.2
Methylcyclopentane.....	2.7	1.5	2.9
Benzene.....	0.5	0.5	0.5
2,2-Dimethylpentane.....	0.1	Trace	0.1
2,4-Dimethylpentane.....	0.1	Trace	0.2
Cyclohexane.....	2.5	-----	3.1
3,3-Dimethylpentane.....	Trace	-----	Trace
1,1-Dimethylcyclopentane.....	0.3	-----	0.5
2,3-Dimethylpentane.....	0.7	-----	0.4
2-Methylhexane.....	1.2	-----	1.7
Cis and trans 1,3-Dimethylcyclopentane.....	1.7	-----	2.0
Cis and trans 1,2-Dimethylcyclopentane.....	1.6	-----	2.1
3-Methylhexane.....	1.4	-----	2.8
3-Ethylpentane.....	0.2	-----	0.2
n-Heptane.....	5.7	-----	7.3
Heavier than heptane.....	59.9	-----	68.7

Typical operating conditions for the column charging Panhandle crude were as follows:

No. 1 tower (column 10):	
Charge, barrels/hour.....	900
Overhead, barrels/hour.....	168
Bottoms, barrels/hour.....	732
Reflux, barrels/hour.....	215
Charge, temperature, ° F.....	250
Top tower, temperature, ° F.....	165
Bottom tower, temperature, ° F.....	322
Accumulator, temperature, ° F.....	102
Top tower, pressure, p.s.i.g.....	48
No. 2 tower (column 32):	
Charge, barrels/hour.....	732
Overhead, barrels/hour.....	352
Bottoms, barrels/hour.....	380
Reflux, barrels/hour.....	150
Charge, temperature ° F.....	218
Top tower, temperature, ° F.....	205
Bottom tower, temperature, ° F.....	299
Accumulator, temperature, ° F.....	99
Top tower, pressure, p.s.i.g.....	4

On applying the control system of the present invention, with the sample taken from the line 15, the amount of benzene in the overhead product is reduced from 0.5 liquid volume percent to a trace with a consequent reduction in the amount of normal hexane appearing in the overhead product to 0.2 liquid volume percent.

By controlling the benzene content within the range of 0.00 to 0.10 liquid volume percent, the normal hexane content can be controlled within the range of 0.0 to 2.0 percent.

In the described system, the kettle product is further fractionated in the column 32 to provide a cyclohexane concentrate for feed to a hexane isomerization unit, and a feed to a heavy gasoline platforming unit. On applying the present invention, the normal hexane is substantially eliminated from the light gasoline overhead prod-

5

uct, and yet the isohexanes are effectively concentrated in this overhead product. This results in an octane number improvement of from 1.1 to 1.3 octane numbers in the light gasoline fraction. Also, since the benzene all goes to the kettle in the column 10, this material is available for conversion into the more valuable cyclohexane by hydrogenation in an ensuing step of the process.

Similar results are obtained on charging a Mex-Tex crude fraction of essentially the same boiling range.

A test was made to show how the normal hexane content of the overhead product of column 10 varies directly with the benzene concentration. The data obtained were as follows:

Volume Percent Distilled	Normal Hexane Liquid Volume Percent	Benzene Liquid Volume Percent
14.0	0.1	0.0
15.1	0.5	0.01
16.0	2.2	0.1
17.1	5.5	0.3
18.1	9.5	0.5
19.1	13.3	0.7
20.2	16.9	0.9
21.2	19.6	1.2
22.2	21.1	1.4

Thus, it is evident that the benzene and normal hexane co-distill in the above separation, so that the column can be effectively controlled by determination of the benzene content; direct analysis for the normal hexane in the above stream cannot at present be made with sufficient accuracy for successful control of a commercial operation.

In another specific example, a cyclohexane concentrate boiling at 130 to 176° F. is separated in a 70 tray fractionation column, the feed entering at the thirty-first tray, into an overhead fraction of isohexanes and more volatile materials together with a bottom product of normal hexane and less volatile materials. The operating conditions are as follows:

Stream	Feed	Over head Product	Kettle Product
Temperature, ° F.	228	200	242
Volume, Thousand Gallon per Day	392.7	148.9	243.8
Composition, Liquid Volume Percent:			
Isopentane	2.4	6.4	-----
n-Pentane	7.2	19.0	-----
Cyclopentane	1.9	5.1	-----
2,2-Dimethylbutane	0.4	1.1	-----
2,3-Dimethylbutane	1.4	3.6	-----
2-Methylpentane	20.6	42.1	7.6
3-Methylpentane	14.2	19.3	11.0
n-Hexane	31.1	1.9	49.0
Methylcyclopentane	10.9	1.7	16.5
2,2-Dimethylpentane	0.5	-----	0.7
Benzene	2.2	Trace	3.5
2,4-Dimethylpentane	0.4	-----	0.7
Cyclohexane	6.3	-----	10.2
3,3-Dimethylpentane	0.1	-----	0.1
1,1-Dimethylcyclopentane	0.1	-----	0.2
2,3-Dimethylpentane	0.1	-----	0.1
2-Methylhexane	0.2	-----	0.4
Pressure, p.s.i.g.:			
Top	-----	35	-----
Bottom	-----	44	-----
Reflux/Feed, Volume/volume	-----	1.53	-----

By maintaining the benzene percentage at the sixth tray below the top of the column at a preselected value, for example, 1.0 percent, the amount of normal hexane in the overhead product is reduced from 1.9 percent to less than 0.2 percent, thus effecting substantial economic in operation.

In still another specific embodiment, a mixed hexane stream boiling at 130 to 160° F. is fractionated in a fifty tray fractionation column, the feed entering at the twentieth tray, into an overhead product of isohexanes

6

and more volatile materials together with a bottom product of normal hexane and less volatile materials. The operating conditions are as follows:

Stream	Feed	Over-head Product	Kettle Product
Temperature, ° F.	210	230	256
Volume, Thousand Gallon per Day	111.2	42.3	68.9
Composition, Liquid Volume Percent:			
Isopentane	0.3	0.7	-----
n-Pentane	7.8	17.2	-----
Cyclopentane	4.3	9.3	-----
2,2-Dimethylbutane	1.5	3.3	-----
2,3-Dimethylbutane	3.2	6.8	0.1
2-Methylpentane	23.8	46.0	5.0
3-Methylpentane	13.6	14.3	13.0
n-Hexane	32.4	2.1	53.0
Methylcyclopentane	8.5	0.3	15.3
2,2-Dimethylpentane	0.2	-----	0.4
Benzene	1.6	Trace	3.0
2,4-Dimethylpentane	0.2	-----	0.4
Cyclohexane	2.6	-----	4.8
Pressure, p.s.i.g.:			
Top	-----	35	-----
Bottom	-----	42	-----
Reflux/Feed, Volume/volume	-----	3.90	-----

By maintaining the benzene concentration three trays below the top of the tower at 0.1 percent, the amount of normal hexane in the overhead product is reduced from 2.1 percent to less than 0.2 percent and the column is operated at maximum output.

The described analysis for benzene or toluene can be effectively made by an ultraviolet analyzer of the type shown by Figure 2. In this analyzer, a beam of ultraviolet radiation from a source, such as a hydrogen lamp 50, is trained upon a detector unit 51 which can be a photomultiplier tube. The tube 51, in turn, is connected to a comparing circuit 52 and an indicator or recorder 53 which can have an electrical or pneumatic output.

In its passage from the source to the detector, the ultraviolet energy is collected by a mirror 54 and focused on an aperture assembly 55 which serves as a point source of ultraviolet radiation for the rest of the apparatus. From the aperture 55, the ultraviolet radiation traverses a filter 56, and a lens 57 which focuses the radiation upon the detector 51. Disposed in the path of the beam between the lens 57 and the detector 51 are a gas filter 58, a sample cell 59, and a rotatable chopper 60 fixed on a shaft 61 which is driven by a motor 62.

The cell 59 is adapted to contain a liquid sample of the material to be analyzed which is fed thereto from one of the lines 24, 25, or 26, Figure 1, and it is of adjustable length.

The chopper 60 comprises a plurality of sector-shaped elements formed from filter material which alternate with sector-shaped sections of material transparent to ultraviolet radiation.

In one specific embodiment of the invention, the filter material attenuates radiation having a wavelength lower than about 250 to 260 millimicrons. Where the cut-off frequency is 250 millimicrons, the filter material can be a liquid thickness of 1/2 centimeter of carbon tetrachloride. Where a liquid filter material is used, it is incorporated within interior chambers, not shown, of the chopper disc which is formed from a radiation-transparent material such as quartz. Alternatively, the filter material can be a type 9700 filter manufactured by the Corning Glass Works having color specification 9-53, cut to a thickness of 1 millimeter.

Where the cut-off wavelength is 260 millimicrons, a thickness of 1/4 centimeter of carbon tetrachloride can be utilized or, alternatively, a 2-millimeter thickness of the aforementioned type 9700 filter having a color specification of 9-53.

The filter 56 is of the band pass type which passes wavelengths of about 230 millimicrons to an upper wavelength of greater than 275 millimicrons, for example, 420

millimicrons. Where a liquid-type filter is desired, a thickness of 5 centimeters of an aqueous solution containing 240 grams per liter nickel sulfate ($\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$) and 45 grams per liter cobalt sulfate ($\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$) can be utilized. The liquid is contained within a quartz liquid-containing cell transparent to ultraviolet radiation. Alternatively, the filter 56 can be a type 9863 filter produced by the Corning Glass Works having a color specification 7-54 and a thickness of 3 millimeters.

The auxiliary filter 58 which cuts off ultraviolet radiation of wavelength greater than 270 millimicrons, can be a 5 centimeter thickness of chlorine gas. As will become evident hereafter, this is an optional feature of the invention. Where used, the gas is contained within a cylindrical body 63 of opaque material having transparent end plates 64 and 65.

In the operation of one specific embodiment of the invention, Figure 2, the overhead product fed to the cell 59 contains a trace to 2.0 percent of benzene which is to be quantitatively analyzed. Benzene has strong absorption bands at wavelengths of 225 to 270 millimicrons. The filter 56 has a pass band extending from a lower wavelength of about 250 millimicrons to an upper wavelength of greater than 275 millimicrons. The filter 58 transmits wavelengths of less than 270 millimicrons and attenuates radiation of longer wavelength.

Accordingly, the filters 56, 58 in combination define a band pass filter extending from 250 to 270 millimicrons so that the ultraviolet radiation passing through the sample and the filter system varies in intensity in accordance with the amount of benzene in the sample.

The filters in the chopper disc 60 are formed from material which attenuates radiation having a wavelength lower than a value of about 250 millimicrons and which passes radiation of higher wavelengths. Therefore, when one of these filters is positioned in the path of the radiation beam, the amount of radiation incident upon the detector 51 is not responsive to the benzene concentration of the sample. However, when the transparent portions of the disc 60 are in the path of the beam, the output is responsive to the benzene concentration. Thus, by electrically comparing these two outputs in the circuit 52, a resultant signal is produced which is insensitive to absorption caused by miscellaneous components which may be in the sample and absorb at other wavelengths. The filter 58 aids by cutting out interference caused by absorption at ultraviolet wavelengths of greater than 270 millimicrons. Accordingly, the resultant output at unit 53 is responsive solely to the benzene concentration in the sample.

The described arrangement can also be used for analysis of toluene which has strong absorption bands at wavelengths of 225 to 275 millimicrons. However, when analyzing for small concentrations of toluene, somewhat greater sensitivity can be obtained by eliminating the chlorine gas filter 58, and changing the cut-off wavelength of the filter material in the chopper 60 to 260 millimicrons. In this manner, the absorption bands existing between the chlorine cut-off wavelength of 270 millimicrons and the upper wavelength limit of the toluene band, 275 millimicrons, contribute to the signal produced when the beam passes between the sectors of the chopper disc. By increasing the cut-off wavelength of the chopper disc material itself to 260 millimicrons, the toluene bands are

sufficiently screened out of the detector output so that adequate compensation for interfering components is made when the output produced with the filter sections of the disc 60 in the path of the beam is compared with the output produced when the transparent sections are in the path of the beam.

The present analyzer permits accurate and close control of the normal hexane or other key component concentration in the overhead product of the column 10, Figure 1, through analysis for benzene or toluene. The column is thus controlled to obtain significant advantages in commercial operation.

While the invention has been described in connection with a present, preferred embodiment thereof, it is to be understood that this description is illustrative only and is not intended to limit the invention.

I claim:

1. In the art of fractionating a stream containing isohexane, normal hexane and a small amount of benzene, the steps which comprise introducing said stream into a fractionation zone; controlling heat supplied to the bottom of said zone, heat withdrawn from the top of said zone, the feed rate, the rate of withdrawal of overhead product and bottom product and the reflux rate as operating variables to separate said stream into an overhead product containing isohexane and more volatile materials and a bottom product containing normal hexane and less volatile materials; withdrawing a sample from a region of said zone located substantially above the region of feed introduction; analyzing said sample to produce an output signal representative of the benzene content thereof by passing a beam of ultraviolet radiation through said sample and measuring the intensity of the beam after it has passed through said sample, the measured intensity being representative of said output signal; and controlling one of said operating variables in accordance with said output signal to maintain said benzene content at a predetermined value less than the benzene content of said stream so that substantially no normal hexane appears in said overhead product.

2. The process of claim 1 wherein the operating variable is the reflux rate.

3. The process of claim 1 wherein the operating variable is the product withdrawal rate.

4. The process of claim 1 wherein the operating variable is the feed rate.

5. The process of claim 1 wherein the operating variable is the supply of heat to the kettle of said fractionation zone.

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