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D. M. BOYD

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SYSTEM AND METHOD FOR FRACTIONATION

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Sheet 1 of 2

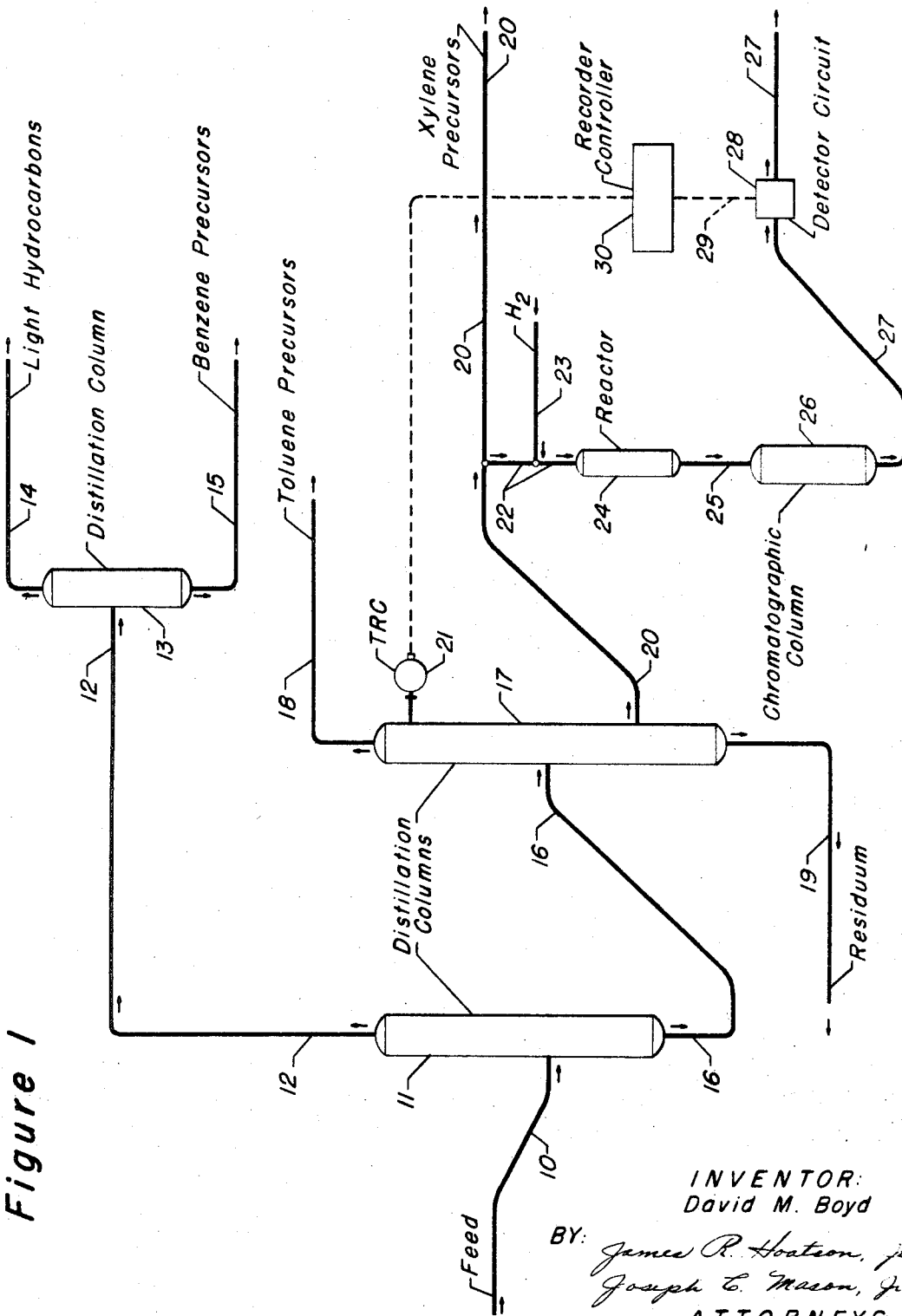


Figure 1

INVENTOR:
David M. Boyd

BY: *James R. Hoatson, Jr.*
Joseph C. Mason, Jr.
ATTORNEYS

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3,436,337

SYSTEM AND METHOD FOR FRACTIONATION
David M. Boyd, Clarendon Hills, Ill., assignor to Uni-
versal Oil Products Company, Des Plaines, Ill., a cor-
poration of Delaware

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13 Claims

ABSTRACT OF THE DISCLOSURE

System and method for fractionating a hydrocarbon feed mixture such as one containing toluene and xylene precursors. The distillation of this mixture is controlled by sampling one product stream, converting the precursors therein to the corresponding aromatic hydrocarbon via catalytic means, resolving the effluent from the conversion zone via chromatographic means and using a signal generated from the chromatographic means to vary at least one operating condition, such as temperature, on the distillation column.

BACKGROUND OF THE INVENTION

The present invention relates to a system and method for controlling fluid separation processes. It particularly relates to a method for preparing selected feedstocks for a catalytic reforming process unit. It specifically relates to a method for preparing selected feedstocks containing predetermined aromatic hydrocarbon precursors for charge to a catalytic reforming process unit utilizing distillation means having associated therewith analytical means for determining the presence of such aromatic hydrocarbon precursors.

In the production of petroleum and chemical products composed of a mixture of components the basic and fundamental unit operation is distillation. The petroleum refiner, for example, uses distillation to separate the components present in crude oil into selected fractions having desirable physical and chemical characteristics for further processing. For example, the fractions containing lubricating oil components are initially separated via distillation means. The fractions having desirable motor fuel blending characteristics are also separated by distillation means. In more recent times, the advent of catalytic reforming for both the production of gasoline motor fuel blending components and/or aromatic hydrocarbons, such as high purity benzene and toluene and xylene, has demanded the use of distillation means for segregating from crude oil selected naphtha fractions which contain the proper precursors for the aromatic hydrocarbons. As those skilled in the art well know, the catalytic reforming operation encompasses a wide variety of chemical reactions, such as dehydrogenation, aromatization, cyclization, hydrocracking, and the like, in order to convert the naphtha feedstock by proper and selective molecular rearrangement into proper aromatic hydrocarbons and/or motor fuel blending components. Traditionally, the naphtha fraction has been treated with hydrogen in order to remove such deleterious contaminants, such as sulfur, and then charged directly into the catalytic reforming unit. The effluent from the reforming unit is frequently separated by solvent extraction means in order to recover therefrom high purity benzene, toluene, and the xylenes.

However, the aromatic hydrocarbon market has been subjected to differing demands for specific aromatic hydrocarbons. In some instances there has been a relatively high demand for benzene which has resulted in the dealkylation of the toluene formed in order to maximize benzene production. In other instances the market for toluene has been depressed, thereby causing a relatively

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high inventory in the market place of toluene, particularly in the market situations where the demand for benzene has also stabilized.

Accordingly, it would be desirable to provide a method for preparing selected feedstocks for acatalytic reforming process unit which would have the flexibility of being adjustable according to market demand for the various aromatic hydrocarbons which are produced therefrom. One such method, of course, is the prefractionation of the traditional naphtha feed stock via distillation means roughly according to aromatic hydrocarbon precursor type. However, in utilizing the prefractionation means, it was discovered that the control thereof was extremely difficult since the efficiency of such a separation was not finally determinable until the effluent from the catalytic reforming process unit had been properly separated into its aromatic components. This enormous lag time between the operation of the prefractionation section and the separation of the catalytic reforming effluent into aromatic hydrocarbons has presented extreme difficulties to the petroleum industry. For example, in a toluene depressed and benzene stabilized market it would be desirable not to charge the toluene precursors to a catalytic reforming unit. However, if the catalytic reforming unit did produce an extraordinary large amount of toluene, the information necessary to correct the prefractionation section desirably is generally too late for proper control since variations in naphtha feedstock could easily have caused different results to be taking place in the catalytic reforming unit during this analytical determination. In other words, before an upset on the prefractionation section could be determined, a large volume of undesirable material had already been processed through the catalytic reforming process unit, thereby effecting considerable costs on the operation as a whole.

SUMMARY OF THE INVENTION

It is therefore an object of this invention to provide a system and method for controlling fluid separation processes, particularly the distillation process.

It is another object of this invention to provide a method for preparing selected feedstocks for a catalytic reforming process unit.

Therefore, according to the practice of this invention, there is provided a method for preparing selected feedstock for a catalytic reforming process unit which comprises: (a) introducing a hydrocarbon mixture comprising precursors for single ring aromatic hydrocarbons into a separation zone under conditions sufficient to separate said mixture into a relatively light precursor concentrate stream, a relatively intermediate precursor concentrate stream, and a relatively heavy precursor concentrate stream; (b) passing a portion of a selected precursor concentrate stream through a miniaturized conversion zone maintained under conditions sufficient to convert precursors in said selected concentrate stream into single ring aromatic hydrocarbons; (c) resolving the hydrocarbon effluent from said conversion zone into bands of identifiable aromatic hydrocarbons using chromatographic means; (d) obtaining from said chromatographic means a signal quantitatively correlatable to a predetermined single ring aromatic hydrocarbon; (e) employing said signal to vary said separation zone conditions in response to said quantitative measurement, thereby maintaining the amount of at least one precursor in said selective concentrate stream at a predetermined value; and (f) removing from said separation zone the remaining portion of the concrete stream of Step (b) as the selected feedstock for a catalytic reforming process unit.

Another embodiment of the invention includes the method hereinabove wherein said single ring aromatic

hydrocarbons comprise benzene, toluene, and xylene and wherein said light precursor is for benzene, said intermediate precursor is for toluene, and said heavy precursor is for the xylenes.

Still another embodiment of this invention includes the method hereinabove wherein said signal of Step (e) varies a temperature of the separation zone.

A still further embodiment of this invention provides a system for controlling a distillation column which comprises in combination a distillation column, means for introducing a feed mixture into said column, means for withdrawing an overhead product fraction from the top of the column, means for withdrawing a heavier product fraction from the column, means for controlling the temperature in an upper portion of said column, sampling means for at least one of said product fractions, means for converting a component in said sample fraction to a preselected identifiable compound, means for analyzing the product from said converting means for said identifiable compound, means for generating a signal from said analyzing means quantitatively correlatable to said identifiable compound, and means for employing said signal to vary said temperature control means responsive to said quantitative measurement.

Thus, one feature of the present invention involves the use of analytical means for controlling a prefabrication system which is preparing feedstock for a subsequent conversion operation. The analytical means in essence further involves the use of a miniaturized conversion zone which is substantially identical in function to the subsequent commercial conversion operation for which the selected feedstock is being prepared. The effluent from this miniature operation is characterized by chromatographic means which generate a proper signal which is utilized in varying the operating conditions in the prefractionation section according to the quantitative results obtained by the overall analytical means. It was found that by operating in this manner the lapsed time between sampling and adjustment of conditions was considerably lessened. Frequently, the practice of this invention enabled changes to be made in the prefractionation section in a shorter time as from 5 minutes to 30 minutes whereas previous operations would have required several hours or more for determining whether or not corrective measures were needed in the prefractionation system.

The selection of the proper precursor for use in controlling the distillation means for preparing the selected feedstock for catalytic reforming process units can, of course, be varied widely, depending upon the desires of the refiner. Preferably, however, for the situation of depressed toluene market, the analysis is performed on the xylene precursor stream and is correlated to the presence of toluene in such precursor stream. A convenient means of control is to adjust the operating conditions in the prefractionation zone to produce less than 10% by volume toluene in the xylene precursor stream. More preferably, less than 5% of toluene is an acceptable target. It is to be understood, however, that the quantitative measurement which is correlated to a particular precursor can be on xylene or any other measurement. From the teachings presented herein, it is equally feasible for the analytical technique to be performed on the toluene precursor stream, such that a proper xylene precursor stream is also produced. Any other variations obvious to those skilled in the art from the teachings presented herein is broadly encompassed in the concept of the present invention.

While this invention has been described with particular reference for the prefractionation of a benzene, toluene, and xylene precursor stream, it will be obvious to those skilled in the art that the concepts of the present invention are equally applicable to any other environment which is of the precursor type. In other words, the concepts of this invention can be utilized to prepare selected feedstocks for any conversion zone wherein the sample is actually

converted in a miniaturized conversion zone and the results of this sample conversion are more or less immediately translated into the control of the equipment preparing the feedstock for such conversion zone.

As previously indicated, the present invention is uniquely applicable to the preparation of a selected feedstock for a catalytic reforming process unit. Therefore, the miniaturized conversion zone as stated in the claims embodies a catalytic reforming reactor containing typically platinum catalyst and utilizing conventional operating conditions which are also used in the commercial unit which subsequently follows the prefractionation operation. One advantage in operating in this manner is that the hydrogen produced in this miniaturized reactor can also be used as the carrier gas in the subsequent chromatographic separation means. Another advantage, of course, is that the catalyst in the miniaturized reactor does not require regeneration. Since it is of such small scale, any deactivation of the catalyst can be corrected by the addition of fresh catalyst, or if desired a series of miniaturized reactors can be used in swing reactor fashion in order to process the proper sample.

The chromatographic separation means utilized in this analytical technique is well known to those skilled in the art. This subject is discussed in detail in the publication "Gas Chromatography," by A. I. M. Keulemans (Reinhold Publishing Corporation, 1957). Therefore, a detailed presentation of gas chromatography methods will not be incorporated herein. Those skilled in the art are referred to such notable publications for the details of this separation technique.

Briefly, chromatographic separation means includes introducing a gaseous sample into a column which is packed with suitable separatory material. The components of the sample are separated by sweeping the column with a carrier gas so that the components are eluded from the separatory material and emerge from the column in bands or slugs of materials having similar elution velocities roughly determined by their well known partition coefficients. A detecting device is used to sense the composition of the bands of components as they emerge from the column and a quantitative and qualitative determination of the sample may be obtained.

In the present invention, the detection device also generates a signal which is amplified and correlatable to the desirable aromatic precursor or actually the aromatic hydrocarbon, and which is passed into one integrator which is adaptable for the specific aromatic hydrocarbon. The signal is also passed into another integrator which is adaptable for the total aromatics produced in the miniaturized reactor. The signals from the integrators are passed into a suitable dividing circuit which calculates the percent of the specific aromatic hydrocarbon present in the sample stream. Since the chromatographic means is a batch operation and therefore any signal therefrom is intermittent, the information from the integrators and dividing circuits are stored in suitable memory blocks from which a combined signal is transmitted to a conventional recorder-controller which activates control valves for varying the selected operating conditions on the prefractionation zone.

All of the specific instruments which are utilized in this broad analytical device are conventional and well known to those skilled in the art. As non-limiting examples of this equipment the chromatography column may be a Beckman Model 320-C Process Gas Chromatograph, the integrators may be conventional analog electronic integrators which produce a current output proportional to the length of time and amplitude of the applied signal. At this point it should be noted that the purpose of the integrator is actually to record the cumulative area of the chromatogram at timed intervals, preferably, about every 10 to 15 seconds, or a similar digital system could be employed. The recorder-controller, of course, is conventional and is preferably a recording potentiometer. Fre-

quently, the signal from the detection unit must be amplified and preferably an amplifier is used. The actual amplifications developed will vary, of course, depending upon the type of recorder and/or integrator employed. However, some method is required for amplifying the millivolt signal from the chromatograph bridge in order to feed it to the integrators and recorder. Thus, the amplifier may be of any suitable type available commercially.

The packing material utilized in the chromatographic column can be any of the inert stationary type. Advantageously, crushed firebrick or diatomaceous earth is used as an inert solid support for a partitioning liquid, such as diethylene glycol succinate polymer which will resolve the various components in the feed to the chromatographic column into bands of its individual components for detection. Preferably, crushed firebrick of about 40 to 50 mesh is employed for most purposes.

The carrier gas employed in sweeping or eluting the components of the feedstock to the chromatographic column may be of any of the conventional carrier gases which are not reactive with the sample mixture or the materials of the apparatus and which do not produce a response in the detector device. Among the carrier gases generally suitable for this are hydrogen, helium, nitrogen, air, carbon dioxide, argon, etc., with, as previously mentioned, hydrogen being the preferred carrier gas for the practice of this invention.

Those skilled in the art are familiar with the difficulties of utilizing an intermittent signal for process control. Exemplary of solutions found by those skilled in the art may be understood with reference to U.S. Patent No. 2,994,646 to L. D. Kleiss and U.S. Patent No. 3,009,864 to R. D. Webb. Both of these patentees address themselves to the handling of the intermittent signal resulting from the detection device accompanying chromatographic separation means. These solutions and others known to those skilled in the art may be found useful for incorporation in the system and method of the present invention, although such devices it must be pointed out, are not absolutely necessary for the practice of this invention.

The invention may be more fully understood with reference to the accompanying drawings wherein:

FIGURE 1 is a schematic representation of prefractionation means for preparing a selected feedstock for a catalytic reforming process unit, and

FIGURE 2 is a more detailed schematic representation of the instrumentation involved in the system for controlling the distillation column.

DESCRIPTION OF THE DRAWINGS

Referring now to FIGURE 1, a suitable naphtha feedstock containing aromatic hydrocarbon precursors enters the system via line 10 and is passed into distillation column 11. Operating conditions are maintained in column 11 sufficient to produce a relatively light precursor concentrate stream which is withdrawn via line 12 and leaving behind an aromatic hydrocarbon precursor bottoms stream which subsequently will be separated into relatively intermediate concentrate streams and relatively heavier concentrate streams and which is withdrawn from column 11 via line 16.

The material in line 12 is passed into a further distillation column 13 wherein light hydrocarbons and normally gaseous hydrocarbons are withdrawn via line 14 and a relatively light precursor concentrate stream comprising, in this case, as an example, benzene precursors, is withdrawn via line 15 for charge to a catalytic reforming process unit, if desired. The material in line 16 contains among other things precursors for toluene and precursors for xylene. Illustrative of the operation of the present invention, this material is passed into distillation column 17 wherein it is desired to split from the feed the toluene precursors so that a concentrate of xylene precursors will be available as charge to the subsequent

catalytic reforming operation. Accordingly, suitable operating conditions are maintained in distillation column 17, preferably controlled by temperature, utilizing TRC 21, the control of which is more fully explained hereinafter. The toluene precursor stream is removed via line 18 and utilized, for example, as a motor fuel blending component. A residuum stream is withdrawn from distillation column 19 and may also be used in motor fuel blending.

The desired xylene precursor stream is withdrawn from column 17 via line 20 and passed preferably in conjunction with the material in line 15 into a subsequent catalytic reforming process unit operating in conventional manner.

According to this invention, a sample of the material in line 20 is passed via line 22 through suitable sample valve means (not shown), admixed with relatively pure hydrogen gas from line 23, and passed into reactor 24 which contains platinum on alumina catalyst. Proper operating conditions are maintained in reactor 24 to convert any aromatic hydrocarbon precursors in the sample into the respective aromatic hydrocarbon. The hydrocarbon effluent is removed from reactor 24 via line 25 and passed into chromatographic column 26 which operates in conventional manner under conventional conditions utilizing hydrogen as the carrier gas. Typically, chromatographic column 26 may be packed with a substrate of diethylene glycol succinate on 42-60 mesh crushed firebrick. As the bands of components are eluted from column 26, they are passed via line 27 through detector circuit 28 which contains sufficient devices for generating a proper signal quantitatively correlatable, for example, on the toluene content of the material in the sample obtained in line 22. This signal is passed via appropriate circuit 29 into recorder-controller 30 which activates TRC 21 according to the quantitative measurement obtained from the detector circuit 28. TRC 21 can, of course, activate control valves on the reflux stream (not shown) to column 17 or can activate control valves on the reboiler system, if any, (not shown) on column 17. It should also be noted at this point that recorder-controller 30 can, of course, vary other operating conditions in column 17, such as pressure and/or reflux ratio, etc. The function of the information of recorder-controller 30 is to properly adjust the operating conditions in distillation column 17 so that the predetermined value of xylene precursors is ultimately removed from the system in line 20. As those skilled in the art know, the initial portion of the detector circuit 28 contains a detection device, such as a thermal conductivity cell or an ionization detector or other devices well known to those skilled in the art. It may be advantageous in the practice of this invention to use a hydrogen flame ionization detector since hydrogen gas is already available in the analytical system.

Referring now to FIGURE 2, it should be noted that the same numerals have been utilized to denote the same items as was used in FIGURE 1 for ease of analysis. As previously mentioned, the feed in line 16 contains aromatic hydrocarbon precursors for both toluene and xylene. This material is passed into distillation column 17 which is maintained under distillation conditions and controlled by temperature, utilizing TRC 21. The toluene precursor stream or relatively intermediate precursor concentrate stream is removed from column 17 via line 18. A residuum stream is removed from column 17 via line 19. The material in lines 18 and 19 are preferably both utilized as gasoline blending components. A xylene precursor concentrate stream or relatively heavy precursor concentrate stream is withdrawn from column 17 via line 20 and passed preferably to catalytic reforming process units, not shown. A sample of the material in line 20 is obtained via line 22 through suitable sample valves, not shown, admixed with hydrogen from line 23, and passed into catalytic reforming reactor 24 which is

a miniaturized version of the previously mentioned subsequent catalytic reforming process unit. Reactor 24 contains platinum or alumina catalyst and is operated under conditions of temperature and pressure substantially the same as that of said subsequent process unit. The effluent

withdrawn at a temperature of about 306° F. Operating under these conditions, the following separation was made with TRC 21 being controlled by the inventive method of the present invention at a temperature of 240° F.

TABLE I

Line No.	10	12	16	14	15	18	19	20
Component:								
C ₃	47.04	47.04		47.04				
iC ₄	78.51	78.51		78.51				
nC ₄	290.24	290.24		290.24				
iC ₅	449.42	449.42		449.42				
nC ₅	480.08	480.08		480.08				
iC ₆	618.56	618.56		373.86	244.70			
nC ₆	488.59	488.59		4.84	483.75			
iC ₇	661.68	62.79	598.83		62.79	594.75		4.14
nC ₇	345.66		345.66			311.09		34.57
iC ₈	444.88		444.88			4.28	7.87	432.73
nC ₈	348.03		348.03				118.03	230.00
iC ₉	630.16		630.16				547.17	82.99
nC ₉	194.60		194.60				175.63	18.97
CP	39.43	39.43		39.43				
MCP	77.46	77.46		0.70	76.76			
CH	147.97	146.23	1.64		146.23	1.64		
C ₇ N	408.40	42.23	366.17		42.23	374.86		18.31
C ₈ N	394.33		394.33			1.85		322.25
C ₉ +N	328.61		328.61				70.23	290.26
B	177.03	177.03		1.77	175.26			
T	157.57		157.57			120.05		37.52
C ₈ A	208.39		208.39				141.31	67.08
C ₉ +A	74.78		74.78				70.18	4.60
Total	7,091.32	2,997.61	4,093.71	1,765.89	1,231.72	1,381.52	1,420.68	1,291.51

from reactor 24 is passed via line 25 into chromatographic column 26 wherein the aromatic hydrocarbon components in the feed are resolved into individual component bands and eluted with hydrogen gas. The bands as they are removed from column 26 are passed via line 27 into detecting device 28 which in particular contains detector 31 which may be of the thermal conductivity type. The sample having passed through detector 31 may be passed via line 43 back into the main stream of xylene precursor concentrate in line 20 or may be discarded. The signal generated by detector 31 is passed via lead 32 into amplifier 33. The signals are passed via lead 34 in at least two fashions. The signal containing the toluene component is passed into integrator 36 and subsequently via lead 37 into dividing circuit 38. Another signal which is correlatable to the total aromatic content of the sample is passed via lead 39 into integrator 40 from which this total integrated signal is passed via lead 41 into dividing circuit 38 for the calculation of the amount of, say, toluene in line 22. This information is stored in a suitable memory device 42 and subsequently passed via lead 29 into recorder-controller 30. Recorder-controller 30 then varies TRC 21 which in turn varies the operation of column 17 responsive to the quantitative measurement obtained from detecting circuit 28. It is to be noted that since the inventive device and method is responsive to the ratio of, say, toluene, to total aromatic hydrocarbons, the catalytic convertor does not have to be 100% efficient in converting precursors to aromatics.

The following example will illustrate the preferred embodiment of the invention.

Example

A commercial scale prefractionation zone arranged according to the configuration of FIGURE 1 was operated by charging a virgin naphtha stream into the system via line 10, as previously mentioned. Distillation column 11 was operated under a slightly superatmospheric pressure of approximately 10 to 15 pounds, an overhead temperature of 165° F., and a bottoms temperature of about 360° F. Distillation column 13 was operated under an imposed pressure of about 25 pounds, an overhead temperature of about 150° F., and a bottoms temperature of about 280° F. Distillation column 17 was operated under an imposed pressure of approximately 15 p.s.i.g., an overhead temperature of 241° F., a bottoms temperature of about 370° F., and the side-cut stream in line 20 was

The control feature of the present invention embodied in the system sampled the material in line 20 according to conventional chromatography techniques which included, preferably, the use of a sample charging valve although a serum cap and syringe, a bulb and crushing apparatus, or the like, could also be used. The sample was heated by suitable means, such as an electrical resistance heater, in order to vaporize the sample upon introduction into the chromatographic column. On the other hand, the material from the sample reactor 24 may be passed without condensation directly in its vapor state via line 25 into chromatographic column 26. However, depending upon the sophistication of the technique of sampling, it may be desirable to condense the effluent from reactor 24 and then use the conventional sampling means in order to properly charge chromatographic column 26. The sample size may vary considerably; for instance, 3 microliter sample may be used or more. The predetermined value for the presence of toluene after conversion in the miniature reactor was chosen at 8% toluene. In other words, it was the desire to charge a material in line 20 to the catalytic reformer which comprised precursors which would yield 92% xylene and only 8% toluene from the commercial unit. Satisfactory control of distillation column 17 was achieved in that the lapsed time between the determination of percent toluene in line 20 to a change of operating conditions was only approximately 20 minutes.

Therefore, the present invention provided a facile and economical manner of controlling the prefractionation section which prepared a selected feedstock for a catalytic reforming process unit. It should be noted that the material in line 20 contained a considerable variety of C₇ to C₉ hydrocarbons and therefore on the basis of hydrocarbon type it would have been extremely difficult to determine from the breakdown shown in the table exactly how much xylene would have been produced from this kind of a feedstock. Utilizing the miniaturized reactor technique coupled with chromatographic detection means enabled the refiner to achieve excellent control over the subsequent catalytic reforming process unit in terms of maximizing benzene and xylene production while minimizing or excluding entirely any significant production of toluene.

Preferred embodiment

It can be seen from the description of the invention so

far that the present invention in its preferred embodiment provides a method for preparing selected feedstock for a catalytic reforming process to produce aromatic hydrocarbons which comprises the steps of: (a) introducing a hydrocarbon mixture containing precursors for benzene, toluene, and xylene into a first distillation zone and withdrawing therefrom an overhead stream comprising benzene precursors and a bottoms stream comprising precursors for toluene and precursors for the xylenes; (b) passing said bottoms stream into a second distillation zone and withdrawing therefrom a distillate stream comprising precursors for toluene and a heavier boiling fraction comprising precursors for the xylenes, said second zone being maintained under distillation conditions including temperature sufficient to maintain the concentration of toluene precursors in said heavier boiling fraction at a preselected value; (c) passing a minor portion of said heavier boiling fraction through a conversion zone maintained under aromatization conditions sufficient to convert precursors therein into aromatic hydrocarbons comprising toluene and the xylenes; (d) introducing the aromatic-containing effluent from the conversion zone together with hydrogen carrier gas into chromatographic means under conditions sufficient to resolve said effluent into bands of said aromatic hydrocarbons; (e) detecting said bands and obtaining from such detection a signal quantitatively correlatable to at least one of said detected bands; (f) employing said signal to vary the distillation temperature of Step (b) in response to the quantitative determination of Step (e); and (g) recovering from said second distillation zone the heavier boiling fraction as the selected feedstock to a catalytic reforming process.

Another preferred embodiment of the invention includes the preferred method hereinabove wherein said preselected value for the concentration of toluene in said selected feedstock is less than 10% by volume.

The invention claimed:

1. Method for preparing selected feedstock for a catalytic reforming process unit which comprises:

- (a) introducing a hydrocarbon mixture comprising precursors for single ring aromatic hydrocarbons into a separation zone under conditions sufficient to separate said mixture into a relatively light precursor concentrate stream, a relatively intermediate precursor concentrate stream, and a relatively heavy precursor concentrate stream;
- (b) passing a portion of a selected precursor concentrate stream through a miniaturized conversion zone maintained under conditions sufficient to convert precursors in said selected concentrate stream into single ring aromatic hydrocarbons;
- (c) resolving the hydrocarbon effluent from said conversion zone into bands of identifiable aromatic hydrocarbons using chromatographic means;
- (d) obtaining from said chromatographic means a signal quantitatively correlatable to a predetermined single ring aromatic hydrocarbon;
- (e) employing said signal to vary said separation zone conditions in response to said quantitative measurement, thereby maintaining the amount of at least one precursor in said selected concentrate stream at a predetermined value; and
- (f) removing from said separation zone the remaining portion of the concentrate stream of Step (b) as the selected feedstock for a catalytic reforming process unit.

2. Method according to claim 1 wherein said concentrate stream of Step (b) is selected from the group consisting of said intermediate stream and said heavy stream.

3. Method according to claim 2 wherein said single ring aromatic hydrocarbons comprise benzene, toluene, and xylene and wherein said light precursor is for benzene, said intermediate precursor is for toluene, and said heavy precursor is for the xylenes.

4. Method according to claim 1 wherein said signal

in Step (e) varies a temperature of the separation zone.

5. Method for preparing selected feedstock for a catalytic reforming process to produce aromatic hydrocarbons which comprises the steps of:

- (a) introducing a hydrocarbon mixture containing precursors for benzene, toluene, and the xylenes into a first distillation zone and withdrawing therefrom an overhead stream comprising benzene precursors and a bottoms stream comprising precursors for toluene and precursors for the xylenes;
- (b) passing said bottoms stream into a second distillation zone and withdrawing therefrom a distillate stream comprising precursors for toluene and a heavier boiling fraction comprising precursors for the xylenes, said second zone being maintained under distillation conditions including temperature sufficient to maintain the concentration of toluene precursors in said heavier boiling fraction at a preselected value;
- (c) passing a minor portion of said heavier boiling fraction through a conversion zone maintained under aromatization conditions sufficient to convert precursors therein into aromatic hydrocarbons comprising toluene and the xylenes;
- (d) introducing the aromatic-containing effluent from the conversion zone together with hydrogen carrier gas into chromatographic means under conditions sufficient to resolve said effluent into bands of said aromatic hydrocarbons;
- (e) detecting said bands and obtaining from such detection a signal quantitatively correlatable to at least one of said detected bands;
- (f) employing said signal to vary the distillation temperature of Step (b) in response to the quantitative determination of Step (e); and
- (g) recovering from said second distillation zone the heavier boiling fraction as the selected feedstock to a catalytic reforming process.

6. Method according to claim 5 wherein said preselected value for the concentration of toluene in said selected feedstock is less than 10% by volume.

7. Method according to claim 6 wherein said signal of Step (e) is quantitatively correlatable to the toluene band.

8. In a distillation process for separating precursors of aromatic hydrocarbons into a first fraction comprising precursors of relatively light aromatic hydrocarbons and a second fraction comprising precursors of relatively heavy aromatic hydrocarbons wherein said distillation is influenced by temperature, the improvement which comprises passing sample of one of said fractions into a miniaturized conversion zone under conditions sufficient to convert precursors therein to aromatic hydrocarbons, resolving the hydrocarbon effluent from said conversion zone into bands of identifiable aromatic hydrocarbons using chromatographic means, obtaining from said chromatographic means a signal quantitatively correlatable to a preselected converted aromatic hydrocarbon, and employing said signal to vary said distillation temperature in response to the quantitative measurement thereby maintaining the amount of at least one aromatic hydrocarbon precursor in said sampled fraction at a predetermined value.

9. Improvement according to claim 8 wherein said sampled fraction comprises said second fraction and said preselected converted aromatic hydrocarbons comprises said light hydrocarbons.

10. Improvement according to claim 9 wherein said first fraction comprises precursors for toluene and said second fraction comprises precursors for the xylenes.

11. System for controlling a distillation column which comprises in combination, a distillation column, means for introducing a feed mixture into said column, means for withdrawing an overhead product fraction from the top of the column, means for withdrawing a heavier

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product fraction from the column, means for controlling the temperature in an upper portion of said column, sampling means for at least one of said product fractions, means for converting a component in said sampled fraction to a preselected identifiable compound, means for analyzing the product from said converting means for said identifiable compound, means for generating a signal from said analyzing means quantitatively correlatable to said identifiable compound, and, means for employing said signal to vary said temperature control means responsive to said quantitative measurement.

12. System according to claim 11 wherein said sampling means comprises means for sampling said heavier product fraction.

13. System according to claim 12 wherein said pre-

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selected identifiable compound is the major constituent in said overhead product fraction.

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10 HERBERT LEVINE, *Primary Examiner*.

U.S. Cl. X.R.

23—230, 253, 288; 196—132; 202—160; 203—3; 208—134; 260—668