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PRODUCTION OF AROMATIC HYDROCARBONS

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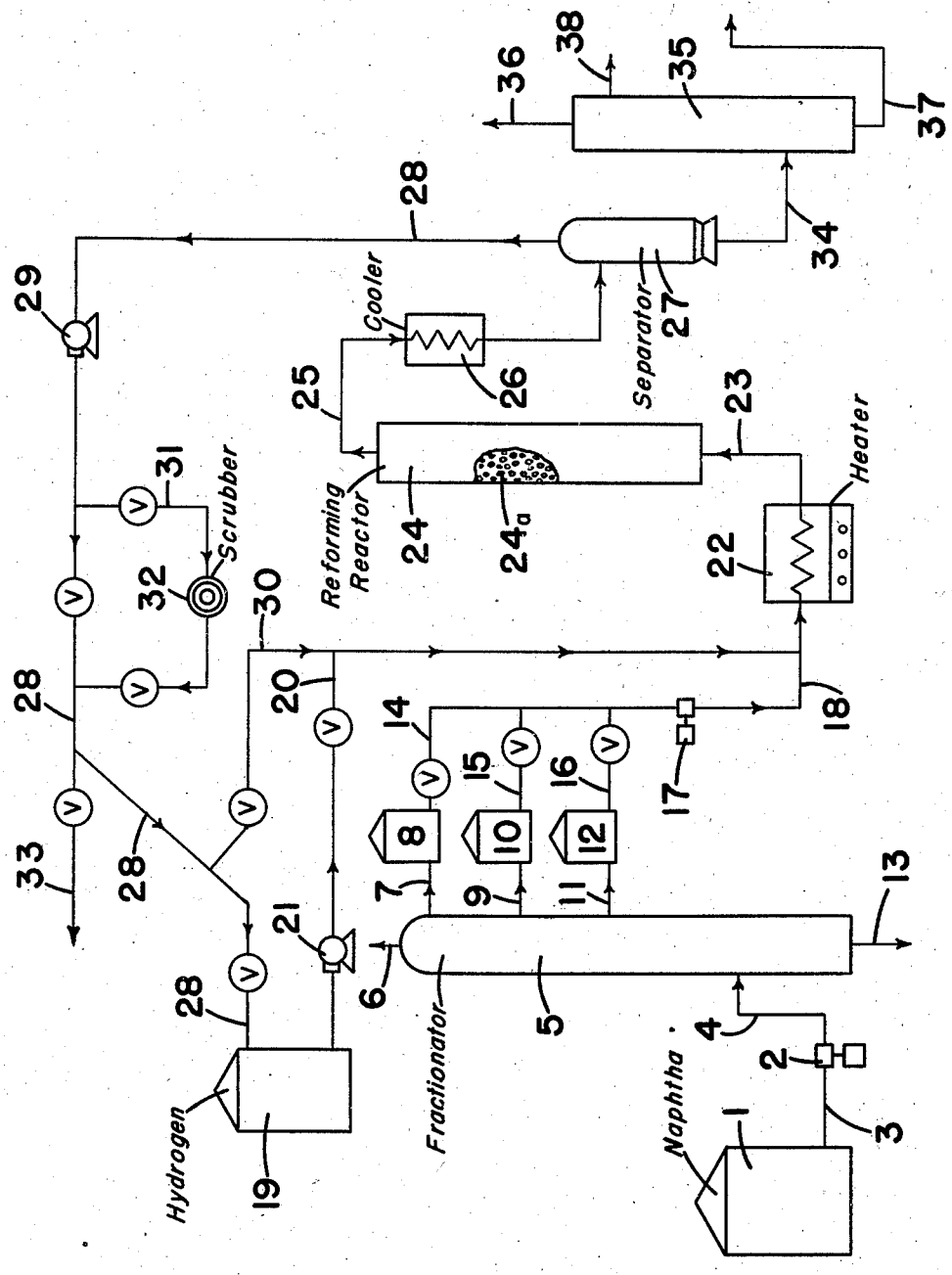

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PRODUCTION OF AROMATIC HYDROCARBONS

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3 Claims. (Cl. 260—668)

This invention relates to the preparation of aromatic hydrocarbons. It is particularly concerned with a process wherein naphthene (cycloparaffin) hydrocarbons boiling in the range between about 280° and 350° F. are converted into aromatic hydrocarbons by catalytic dehydrogenation, and the newly formed aromatic hydrocarbons are segregated from the unreacted charge stock by fractional distillation.

It is known that naphtha distillates derived from some crudes, for example naphthenic or asphaltic base crudes, contain appreciable quantities of aromatic hydrocarbons such as benzene, toluene, xylene, etc. The aromatic hydrocarbons are often segregated from these distillates by extracting them with a selective solvent such as SO_2, furfural or other similar solvents. The extracted aromatics, after some purification such as is effected by neutralization and/or distillation, are then used as commercial solvents, as high-octane-number gasoline blending stocks, and as the source of charge stock in the preparation of other products. For these uses it is usually not necessary or desirable to isolate a particular aromatic hydrocarbon. Instead, it is quite satisfactory to employ a mixture of various aromatic hydrocarbons since all of them have the desirable solvent properties and high-octane-number characteristics.

It is known also that some naphtha distillates contain appreciable amounts of naphthene hydrocarbons and that these naphthene hydrocarbons can be converted into aromatic hydrocarbons, usually with the corresponding number of carbon atoms, by subjecting the naphtha distillates to catalytic dehydrogenation treatment such as catalytic reforming or catalytic reforming in the presence of hydrogen. The term "catalytic reforming" shall be understood to mean a process in which hydrocarbon oils comprising naphthene hydrocarbons and boiling within the gasoline range are subjected to heat treatment at a temperature in excess of about 500° F. and in the presence of a suitable catalyst to produce a dehydrogenated or otherwise chemically reconstructed product of substantially higher aromaticity than the starting material, with or without an accompanying change in molecular weight. The term "catalytic reforming" shall be understood to include chiefly dehydrogenation of the naphthenes but some aromatization and isomerization may also occur. The term "catalytic reforming in the presence of hydrogen" shall be understood to mean a process of catalytic reforming carried out in the presence of substantial quantities of added or recycled hydrogen or in gases rich in free hydrogen under conditions such that there is either no overall net consumption of free hydrogen or there is an overall net production of free hydrogen.

Aromatic types of commercial solvents and high-octane-number gasoline blending agents have been prepared from broad-cut naphtha distillates containing appreciable amounts of naphthenes by first subjecting the distillate to dehydrogenation treatment for conversion of the naphthenes to aromatics, and then extracting the dehydrogenated naphtha mixture with a selective solvent, such as SO_2, furfural, etc., to recover the aromatics as an extract. The aromatic extract is then neutralized and/or distilled to obtain the desired solvent or gasoline blending stock. In operations wherein the catalytic reforming charge stock is a broad-cut of naphtha, it is practically impossible to separate any appreciable portion of the aromatic conversion products from the unconverted charge stock by fractional distillation since the conversion products boil within the boiling range of the charge stock. The solvent extraction feature of a process of this type is not entirely satisfactory since it is complicated and requires expensive equipment. Furthermore, its use results in a loss of an appreciable amount of valuable aromatics in the form of degradation products.

I have now discovered an improved method of converting naphthene hydrocarbons present in naphtha distillates boiling in a range between about 280° F. and 350° F. to aromatic hydrocarbons and then recovering the aromatic reaction products from the hydrocarbon reaction mixture. In accordance with my method a naphtha distillate boiling in the range between about 280° F. and 350° F. and containing appreciable amounts of naphthene hydrocarbons is prefractionated under efficient distillation conditions to separate naphtha fractions having boiling ranges not greater than about 40 Fahrenheit degrees, and preferably between 10 to about 25 Fahrenheit degrees. The narrow boiling range naphtha fractions are then separately subjected to catalytic reforming treatment for conversion of the naphthene hydrocarbons to aromatic hydrocarbons. The process of this invention is primarily concerned with the conversion of substituted cyclohexanes to the corresponding substituted benzene hydrocarbons. However, it is recognized that the catalytic reforming treatment also isomerizes and dehydrogenates substituted cyclopentanes and cycloheptanes to aromatic hydro-

carbons, at least to some extent. The aromatic hydrocarbons derived from the substituted cyclopentanes and cycloheptanes have good solvent properties and high-octane-number characteristics; therefore, they are desirable products. Hence, in its broad scope, the process of this invention may be employed as a means of recovering from the hydrocarbon reaction mixture by fractional distillation aromatic hydrocarbon conversion products boiling at least 10° F. above or below the boiling points of the particular naphthene hydrocarbons from which they are derived through catalytic reforming treatment.

In order to make the process of this invention operative it is necessary to exercise care in selecting the temperature range through which the hydrocarbon charge undergoing catalytic reforming treatment boils. That is, the charge stock boiling range should be selected so that the desired aromatic conversion products boil a few degrees above or below the upper or lower limits, respectively, of the charge stock boiling range. This point can be better clarified by reference to the table which gives a comparison of the boiling points of some of the substituted cyclohexanes boiling in the range between about 280° F. and 355° F. with the corresponding substituted benzenes.

Table

Substituted side chain(s)	Boiling point, °F.		Difference in boiling points, °F., substituted benzene relative to substituted cyclohexane	
	Substituted cyclohexane	Substituted benzene	Above	Below
1,3,5-trimethyl	283.6	328.3	44.7	
1-methyl, 3-ethyl	300.5	322.7	22.2	
1-methyl, 4-ethyl	301.9	322.2	20.3	
1-methyl, 2-ethyl	308.5	328.8	20.3	
Isopropyl	310.1	306		4.1
Propyl	311.0	317.5	6.5	
1-methyl, 4-isopropyl	335.1	351.1	16.0	
Tertiary-butyl	339.1	332.6		6.5
Isobutyl	340.2	338.0		2.2
1-methyl, 3-propyl	341.6	358.7	17.1	
1,3-diethyl	345.2	356.9	11.7	
1,4-diethyl	347.9	361.4	13.5	
1-methyl, 4-propyl	348.3	360.5	12.2	
1-methyl, 2-propyl	349.0	363.2	14.2	
Secondary-butyl	354.2	339.6		14.6

It will be noted from the table that if the catalytic reforming charge stock boils through a temperature range from about 280° F. to 315° F. and is comprised of 1,3,5-trimethylcyclohexane, 1-methyl, 3-ethylcyclohexane, 1-methyl, 4-ethylcyclohexane, 1-methyl, 2-ethylcyclohexane, isopropylcyclohexane and propylcyclohexane which are converted to the corresponding substituted aromatic hydrocarbons, it is possible to separate, as a mixture of substantially pure aromatic hydrocarbons, all of the trimethyl- and methylethylbenzenes from the hydrocarbon reaction mixture by efficient fractional distillation, since these all boil several degrees Fahrenheit above the upper limit or the boiling range of the reforming charge stock. Where a substantially pure aromatic conversion product is not required, such as for use as a commercial solvent or a high-octane-number blending agent, it is possible to recover all or the greater part of the propylbenzene along with the trimethylbenzene and the methylethylbenzenes without seriously contaminating the desired product with unconverted charge stock. It is not desirable ordinarily to recover isopropylbenzene from a catalytic reformed charge stock boiling through the range from 280° F. to 315° F., unless it is present in an appreciable quantity, since the boiling point of the isopropylbenzene falls well within the boiling range of the charge stock. If the catalytic reforming charge stock boils within the limit of from 300° F. to 340° F. and is comprised of methylethylcyclohexanes which the catalytic reforming treatment converts to the corresponding methylethylbenzenes, it is impossible to separate the methylethylbenzenes from the reformed hydrocarbon mixture by fractional distillation without some contamination with unconverted charge stock since the methylethylbenzenes boil within the boiling range of the charge stock. However, if the methylethylcyclohexanes are present in appreciable quantities in the catalytic reforming charge stock, it is possible to separate from the reformed hydrocarbon mixture a fraction boiling between about 320 and 330° F. which is sufficiently high in aromatic content to be employed as a commercial solvent or as a gasoline blending agent. In general, the narrower the boiling range of the reforming charge stock, the easier it is to recover the conversion products by fractional distillation and the higher will be their purity or their aromatic content.

The process of this invention may be more fully understood by reference to the attached drawing which is a diagrammatical flow plan of a preferred embodiment.

Referring to the drawing, numeral **1** designates a supply of hydrocarbon oil boiling in the naphtha boiling range and which contains an appreciable quantity of naphthene hydrocarbons, such as the substituted cyclopentanes, cyclohexanes and cycloheptanes. Pump **2** withdraws oil from tank **1** through line **3** and forces it through line **4** into distillation means **5**. Distillation means **5** comprises any suitable number of highly efficient fractionating units which are collectively capable of separating from the charge oil a fraction boiling below about 280° F. and a fraction boiling above 350° F., both of which are discarded from the system, and which is also capable of separating the constituents boiling in the range between about 280 and 350° F. into any suitable number of distillate fractions having desirable boiling ranges not greater than about 40° F. For purpose of description, it will be assumed that the charge oil is fractionated into a cut boiling below 280° F. which is removed from the system through line **6**, a cut boiling between 280° and 315° F. which is withdrawn through line **7** and passed to intermediate storge tank **8**, a cut boiling between 315° and 340° F. which is passed to intermediate storage tank **10** by means of line **9**, a cut boiling between 340° and 350° F. which is removed to intermediate storage tank **12** through line **11**, and a cut boiling above 350° F. which is discarded from the system by means of line **13**.

In successive order, the narrow-boiling-range oils in tanks **8**, **10** and **12** may be separately withdrawn through lines **14**, **15** and **16**, respectively, by means of pump **17** and forced through line **18**.

Numeral **19** designates a supply of hydrogen or a gas rich in free hydrogen. Hydrogen or hydrogen-containing gas is withdrawn from storage **19** and passed to line **18** by means of line **20** and compressor **21**. In line **18**, the hydrogen becomes admixed with the oil flowing therethrough, and the mixture flows through a heating means **22**, wherein it is heated to a temperature suitable for maintaining the desired temperature in the reac-

tion zone 24 in which it is presently to be introduced by means of line 23. If desired, the oil and the hydrogen may be heated separately instead of being heated in admixture with each other. The oil-hydrogen mixture is heated in means 22 to a temperature which is from 100 to 150° F. above the average temperature maintained in reaction zone 24.

Reaction zone 24 is provided with a catalyst material 24a which is capable of catalytically reforming the oil in the presence of hydrogen. Suitable materials for this purpose comprise aluminum oxide in any of its various forms such as bauxite, acid treated bauxite, aluminum hydrate, alumina gel, activated alumina, partially or completely peptized alumina or alumina gels, silica-alumina gels, and hydrofluoric acid treated alumina, together with from 1 to 50% by weight of an oxide or sulfide of a metal of the IV, V, VI, or VIII groups of the periodic system. Especially suitable catalysts are activated alumina mixed or impregnated with from 1 to 20% of oxides or sulfides of molydenum, chromium, tungsten, vanadium, cobalt or nickel.

Reaction zone 24 is maintained at a temperature between 850° and 1,000° F. and under a pressure between slightly above atmospheric pressure and about 600 lbs. per sq. in., preferably between 30 and 400 lbs. per sq. inch. The oil is passed through the reaction zone at a relatively low rate, usually between 0.1 and 3.0, preferably between 0.5 and 1.5 vol. of liquid oil per vol. of catalyst per hour. The quantity of gas passed through the reaction zone along with the oil should be between 1000 and 6000 cu. ft. per barrel of oil, and this gas should contain between 30 and 90 mol per cent of free hydrogen.

The products of reaction leave reaction zone 24 through line 25, and flow through a cooling means 26 before being discharged into separator means 27 wherein gaseous and liquid products may be separated. The gaseous products, which consists principally of hydrogen and relatively small amounts of low molecular weight hydrocarbons such as methane, ethane, and propane, are removed from separating means 27 through line 28 and may be returned by means of compressor 29 directly to hydrogen supply tank 19. As an alternative procedure, the gaseous products may be recycled directly to the system by means of lines 28 and 30. Where desirable, a substantial portion of the hydrocarbon constituents may be removed from the gaseous products before returning the latter to the system. In this latter case, the gaseous products may be passed through line 31 which is provided with a scrubber 32 for removal of the undesired hydrocarbon constituents. Scrubber 32 may be any means suitable for the purpose of separating hydrogen from mixtures of the same with hydrocarbons. Perhaps the most convenient method is to scrub the gaseous products with a light hydrocarbon oil under conditions such that hydrocarbon constituents but substantially no hydrogen will be absorbed from the gaseous products. Gas may be removed from the system through vent line 33.

The liquid products separating in separating means 27 are removed through line 34 and introduced into fractionating means 35 wherein conversion products are separated from the charge stock. In most instances the converted products boil above the boiling range of the charge stock and accordingly are removed by line 37 while the unchanged charge stock is removed as overhead by line 36. However, if the converted materials have a boiling range below that of the charge stock it will be understood that they will be removed as overhead and the charge stock will be removed through line 37. Under some conditions converted material will be present having boiling points above and below that of the charge stock in which instance the charge stock will be removed by a side stream 38 and converted material will be removed as overhead by line 36 and as bottoms by line 37.

The following example illustrates the application of the process of this invention to the preparation of aromatic hydrocarbons for use as solvents or high-octane-number blending agents.

Example

A naphtha fraction boiling from 280° F. to 350° F. and containing appreciable quantities of naphthene hydrocarbons is distilled under efficient fractionating conditions to obtain a cut boiling from about 280° F. to 315° F., a cut boiling from about 315° F. to 340° F., and a cut boiling from about 340° F. to 350° F. These narrow boiling naphtha cuts are separately subjected to catalytic reforming treatment in the presence of hydrogen under the following conditions:

Average catalyst temperature, °F.	913
Pressure, pounds per square inch	200
Oil feed rate, volumes of liquid oil per volume of catalyst per hour	0.5
Recycle gas rate, cubic feet per barrel of oil	2,600
Per cent H_2 in recycle gas	85
Catalyst	Mixture of aluminum and molydenum oxides
Length of reaction cycle, hours	6

The liquid products secured from the catalytic treatment of these various narrow boiling fractions are separately distilled under efficient fractionating conditions to obtain aromatic fractions boiling above the boiling range of their respective reforming charge stocks. The aromatic content of the conversion products separated in this manner is in the order of 85 per cent and higher.

Having fully described and illustrated the practice of the present invention, what I desire to claim is:

I claim:

1. A process of treating a hydrocarbon distillate boiling in the range of 280° to 350° F. and containing appreciable quantities of naphthenes comprising the steps of distilling said fraction to obtain a first cut boiling from 280° to 315° F., a second cut boiling from 315° to 340° F. and a third cut boiling from 340° to 350° F., separately heating and reacting each cut in a reaction zone in the presence of hydrogen and a dehydrogenation catalyst and under temperature and pressure conditions suitable for converting naphthenes to aromatics and passing the products of said reaction zone to a distillation zone to obtain fractions containing a major portion of aromatics and fractions containing a major portion of unconverted hydrocarbons.

2. A method of processing hydrocarbons comprising the steps of subjecting a naphtha fraction containing appreciable quantities of napthene hydrocarbons and boiling from 280° to 350° F. to distillation to separate the naphtha into a first cut boiling from 280° to 315° F., a second cut boiling from 315° to 340° F. and a third cut boiling from 340° to 350° F., separately mixing each of said cuts with hydrogen to obtain mixtures, separately passing each of said mixtures through

a heater to raise the temperature thereof above 850° F. and to a reaction zone where they are maintained in the presence of a dehydrogenation catalyst and under conditions suitable for converting substantial amounts of naphthene hydrocarbons to aromatic hydrocarbons, removing the products of reaction from the reaction zone, cooling them, separating gaseous products from liquid products and fractionating the liquid products by distillation to obtain fractions comprising major amounts of aromatic hydrocarbons and major amounts of unconverted hydrocarbons.

3. A process in accordance with claim 2 in which the separated gases are admixed with the liquid being passed to the heating zone.

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