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TREATMENT OF CRACKED NAPHTHA

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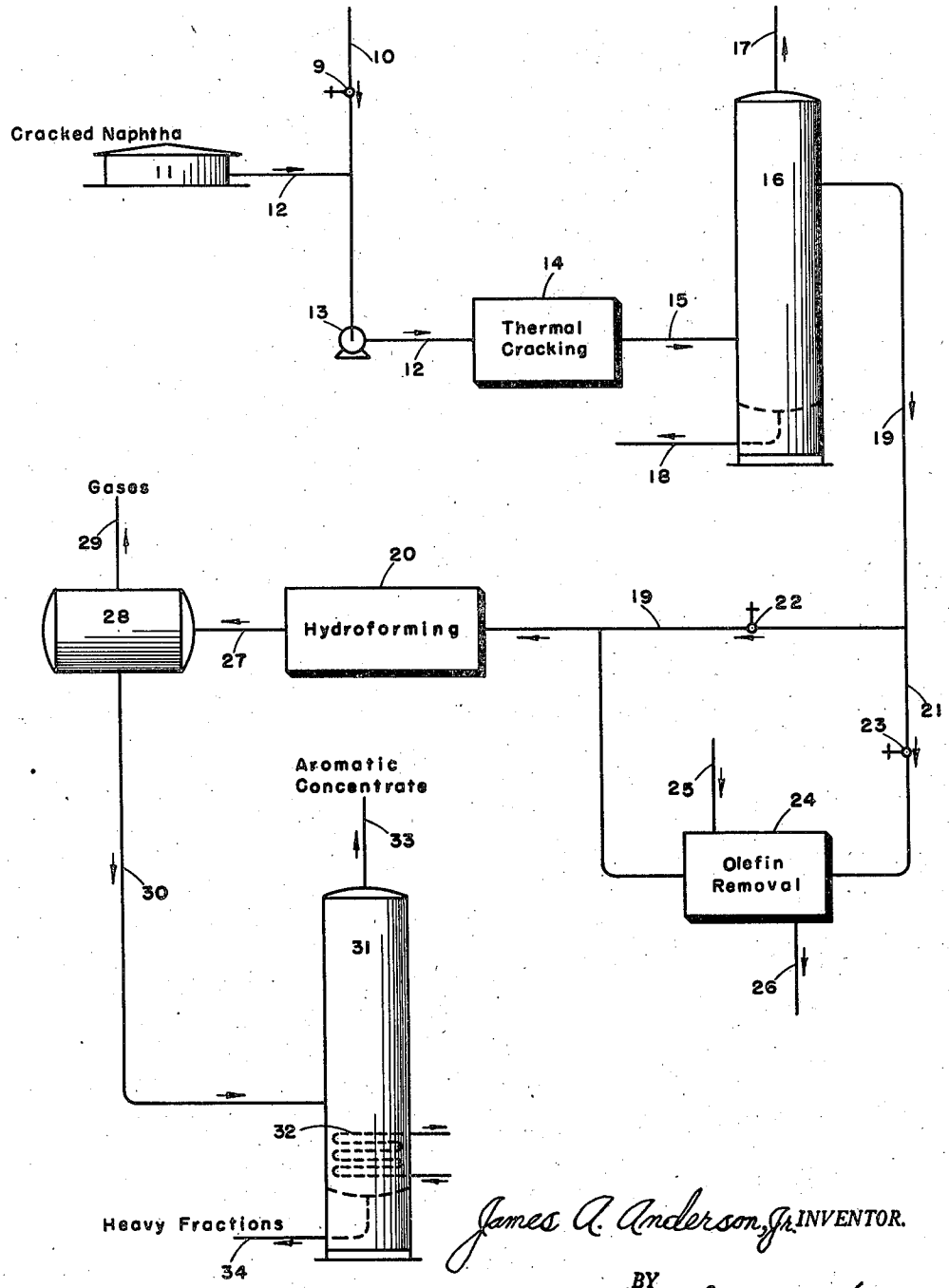

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TREATMENT OF CRACKED NAPHTHA

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4 Claims. (Cl. 260—668)

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The present invention is concerned with a method of conditioning cracked naphthas whereby they are made suitable for production of aromatic fractions. More particularly, the invention is concerned with the thermal cracking of a cracked naphtha to reduce the amount of acyclic compounds present therein and hydroforming the so treated cracked naphtha fractions.

Methods available for producing aromatic hydrocarbons usually include a hydroforming step whereby the naphthenes are converted to aromatic hydrocarbons. Hydroforming operations have been described in the literature, for example, in the Oil and Gas Journal, March 27, 1941, page 86, and in the Journal of the Institute of Petroleum, January 1944, pages 3 and 4, and may be characterized as those chemical reactions which take place when hydrocarbons react in the presence of hydrogen and a reforming catalyst involving a net effect of taking hydrogen away from the hydrocarbon molecules; the chemical reactions involved in such processes are complex but are generally considered to consist mainly of dehydrogenation and cyclization, although other reactions, such as cracking, hydrogenation and desulfurization may also occur. In general, the processes which involve a hydroforming stage include subsequent solvent extraction and distillation stages for recovery of the aromatic hydrocarbons produced during the hydroforming operation. For example, the aromatics may be concentrated by solvent extraction and the extract distilled for recovery of the desired aromatic.

There are produced in the petroleum industry enormous quantities of cracked material which contain appreciable amounts of aromatic compounds. These aromatic compounds are usually associated with naphthenic hydrocarbons which can be converted by hydroforming to aromatics for recovery with the natural aromatics present in the feed to the hydroforming stage. However, these cracked naphthas contain, besides the aromatics and naphthenes, appreciable amounts of acyclic compounds which contaminate them and make the recovery of the aromatics and converted naphthenes difficult. In the present invention the large quantities of aromatics and compounds convertible to aromatics are made available by pretreating the feed to a hydroformer operation by thermal cracking.

In the present invention advantage is taken of the higher cracking rate for acyclic compounds as compared to aromatic compounds when a mixture of these materials is subjected to thermal cracking conditions. A cracked naphtha, such as one produced by thermal or catalytic cracking or reforming and including both acyclic and aromatic compounds, is subjected to vapor phase cracking conditions for the removal of non-aromatic constituents. The recracked naphtha resulting from the thermal treatment is then subjected to hydroforming whereby the naphthenic and cyclo-olefinic hydrocarbons contained in the recracked naphtha fraction are largely converted to aromatic hydrocarbons. The product from this hydroforming step is then distilled to separate a fraction containing large quantities of aromatic hydrocarbons which may be further concentrated by solvent extraction or other well known means.

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The thermally recracked naphtha fraction may be given a treatment intermediate between the thermal cracking and hydroforming stages to remove mono- and diolefinic hydrocarbons. This removal of olefins may be accomplished by treatment of the fraction with strong sulfuric acid. Alternately, the fraction may be treated with organic acids and boron trifluoride in accordance with the method described in pending application U. S. Serial No. 512,494 filed December 1, 1943, for Joseph T. Horeczy.

Usually, however, it will be undesirable to include this treating operation since the treatments described above may result in the removal of some of the naphthenic or cyclo-olefinic hydrocarbons which are hydroformed or converted in substantial amount to the aromatics. Removal of olefins will be desirable only when it is necessary to restrict the quantity of feed to the hydroforming stage.

One of the chief advantages of the present invention is that a relatively purified product is obtained from the hydroforming stage. Stating this in another way, the hydroformed product requires less purification than is required by conventionally produced aromatic fractions. A further advantage obtained by operating in accordance with the present invention is that more aromatics per barrel of hydrocarbon fraction charged to the hydroforming stage are obtained than when the cracked naphtha is charged thereto without a thermal cracking treatment or when a thermal cracking treatment follows the hydroforming operation.

The thermal cracking of naphtha to remove acyclics without substantial destruction of aromatic nuclei present in the naphtha is known to the art. A detailed account of such a thermal cracking step will accordingly not be given here. It may be stated by way of example that it is preferred to subject the cracked naphtha feed stock to vapor phase cracking conditions in which the pressure is no greater than 1,000 pounds per square inch, the temperature is within the range of 500° to 1100° F., and with the time of exposure to cracking conditions within the range of 10 seconds to 60 seconds, and preferably within the range between 15 seconds and 40 seconds.

The hydroforming stage of the present inven-

tion is also conducted in a conventional manner. It is usual practice to employ in the hydroforming stage a catalyst selected from the oxides and sulfides of the metals selected from the VI group of the periodic table under temperature conditions between 875° and 1000° F. and at pressures between about 150 and 250 pounds per square inch.

The invention will be better understood by reference to the drawing in which the single figure is a flow diagram of a preferred embodiment for conducting the invention. In the following description read in conjunction with the figure it is to be understood that each one of the stages described includes all auxiliary equipment usually associated with those stages.

Referring now to the drawing, numeral 11 designates a storage tank containing a naphtha produced by thermal or catalytic cracking, or reforming operations. The naphtha contained in storage tank 11 in admixture with natural naphtha introduced through valve 9 and line 10 is conducted, by way of line 12 and pump 13, to thermal cracking stage 14, wherein, under suitable conditions of temperature and pressure, the acyclic compounds contained in the naphtha are subjected to decomposition reactions such that the acyclic compounds are converted to higher or lower boiling hydrocarbon fractions, while substantially leaving the aromatic fractions unaltered. The recracked naphtha fraction is removed from thermal cracking stage 14 by line 15 and is discharged into a suitable means such as fractionating tower 16 capable of removing undesired constituents from a fraction in the gasoline boiling range. Tower 16 may be operated to remove fixed gases and hydrocarbons boiling below the gasoline boiling range as overhead by means of outlet 17, hydrocarbons boiling above the gasoline boiling range from outlet 18, and a side stream including the desired constituents in the gasoline boiling range by means of outlet 19.

It is preferred to discharge the fraction in the gasoline boiling range separated from the recracked naphtha directly into hydroforming stage 20. However, as an alternative operation, the fraction in line 19 may be sent through a bypass 21 by closing valve 22 in line 19 and opening valve 23 in by-pass line 21. By-pass line 21 discharges into olefin separation stage 24.

In the olefin separation stage 24 the thermally recracked fraction in the gasoline boiling range is subjected to treatment with strong sulfuric acid or other chemicals whereby the mono- and diolefins are substantially removed without destroying the aromatic hydrocarbons. The sulfuric acid may be charged into the olefin removal stage by means of inlet 25, and the acid having the mono- and diolefins dissolved therein removed by means of outlet 26. The amount of acid used will depend to a large extent on the amount of monoolefins contained in the thermally cracked naphtha, as well as the degree of olefin removal desired. Generally, it will be undesirable to employ more than 30 pounds of sulfuric acid per barrel of thermally cracked naphtha. When it is desired to employ olefin separation stage 24 and sulfuric acid is employed as the treating reagent therein, it will be preferred to conduct the treating operation at reduced temperatures to avoid sulfonation of the aromatic compounds contained in the fraction undergoing treatment.

As stated previously, it is usually preferable to by-pass the olefin separation stage 24 because

the chemical reagents removing the mono- and diolefins may also destroy or remove cyclo-olefins which are convertible to aromatic materials under conditions of hydroforming. If the olefin separation stage is to be by-passed, valve 23 is closed and valve 22 is opened and the fraction in the gasoline boiling range removed from tower 16 is passed by means of line 19 directly to hydroforming stage 20.

In the hydroforming stage 20 the naphthenes and cyclo-olefins, as well as a portion of the mono-olefins, are converted into aromatics. The product from this stage is passed by means of line 27 into separator 28, from which undesirable gases may be removed through outlet 29. The remainder of the product is withdrawn from separator 28 by means of line 30 and introduced into a fractionating stage 31, which will usually comprise distillation equipment. In the drawing, the separation means is shown as a single fractionating tower. It is to be understood, of course, that separation stage 31 may include 2 or more fractionating towers, as desired. In separation stage 31 conditions of temperature and pressure are adjusted by heating means 32 so that a concentrate of aromatics is removed as overhead by way of line 33 and heavy fractions are discarded by way of line 34. The fractions recovered as overhead from separation stage 31 by means of line 33 may then be subjected to further purification treatment, such as solvent extraction, if desired.

The present invention may be practiced with a variety of charge stocks. For example, the fraction contained in storage tank 11 or introduced through line 10 may be a relatively narrow boiling fraction boiling between 200° and 250° F., or the boiling range may vary between 200° and 350° F., depending on the type of aromatics desired. In some instances it may be desirable to operate with fractions boiling initially as low as 150° F. when the first compound of the homologous series beginning with benzene is desired.

The present invention will be further illustrated by the following run on a catalytically cracked naphtha boiling between 200° and 300° F. This catalytically cracked naphtha had the following analysis:

Table 1

	Percent by volume
Naphthenes	33.2
Aromatics	37.3
Acyclics	29.5

One hundred volumes of the naphtha having the above composition was subjected to conditions of thermal cracking which included a temperature of 998° F. and a pressure of 801 pounds per square inch with a contact time of 38.6 seconds. The fraction having the same boiling range (200° to 300° F.) recovered from the thermal cracking treatment described was analyzed and found to have the following composition:

Table 2

	Percent by volume
Naphthenes	27.4
Aromatics	60.2
Acyclics	12.4

It is noteworthy from a comparison of the data in Tables 1 and 2 that the amount of acyclics has been decreased over 50% with a corresponding increase in aromatic compounds, with the naphthenic hydrocarbons being largely unconverted.

The products from the thermal cracking operation having the analysis shown in Table 2 were

then subjected to hydroforming conditions which included a temperature of 930° F. and a pressure of 215 pounds per square inch in the presence of a molybdenum sulfide catalyst. A fraction of comparable boiling range to the boiling range of the original catalytically cracked naphtha was found to contain 87% aromatics.

When operating in a conventional manner without the conditioning treatment by thermal cracking of the catalytically cracked naphtha, the product from the hydroforming operation contained only 74% aromatics. By comparison with the product obtained when operating in accordance with the present invention it will be immediately apparent that the present invention allows obtaining of an aromatic fraction which will require less purification than the product obtained when operating in a conventional manner.

To emphasize the improved results of the present invention, results obtained when conducting a run in accordance with the present invention are compared with the results obtained when practicing a process including the steps of hydroforming and the subsequent destruction of aliphatic hydrocarbons in the hydroformed product by thermal cracking.

In the example given above, 88.2 barrels of a fraction containing 87% aromatics was recovered for each 100 barrels of cracked naphtha charged to the hydroforming stage. A portion of the same naphtha was hydroformed and then thermally cracked, the conditions during the hydroforming and thermal cracking stages being maintained the same as in the preceding run for purposes of comparison. The product recovered when first hydroforming and subsequently thermally cracking yielded only 68.5 barrels of an aromatic fraction of the same purity as in the preceding example for each 100 barrels of hydroformer feed.

The nature and objects of the present invention having been described and illustrated, what I wish to claim as new and useful and to secure by Letters Patent is:

1. A process for producing aromatics from a cracked naphtha fraction boiling no lower than 150° F. and not above 350° F. comprising a mixture of naphthenes, aromatics and acyclic compounds which comprises subjecting said fraction to a thermal cracking operation to cause the cracking of substantial amounts of acyclic compounds without substantially decreasing the amount of cyclic compounds therein, separating uncondensable gases from the products of said thermal cracking operation, recovering from said thermally cracked product a fraction having substantially the same boiling range as the charge thereto, hydroforming said thermally cracked product and subsequently distilling to obtain a fraction high in aromatic content.

2. A process in accordance with claim 1 in which the thermally cracked fraction having a boiling point substantially that of the material undergoing thermal cracking is treated for removal of olefins.

3. A process for treating hydrocarbons comprising the steps of subjecting a petroleum fraction to cracking conditions and subsequently recovering therefrom a fraction having a boiling range of approximately 200° to 300° F. and including cyclic and acyclic compounds, subjecting said fraction to thermal cracking conditions to cause cracking of acyclic compounds without substantially altering cyclic compounds, removing product from said thermal cracking step, recovering therefrom a portion having a boiling range of approximately 200° to 300° F., subjecting said portion to hydroforming conditions and subsequently distilling to obtain a product high in aromatic content.

4. A process for treating hydrocarbons comprising the steps of subjecting a cracked petroleum fraction having a boiling range of approximately 200° to 300° F. and including a mixture of naphthenes, aromatic and acyclic compounds to thermal cracking conditions in the vapor phase to cause the cracking of substantial amounts of acyclic materials therein without substantially decreasing the amount of cyclic materials therein, removing the product from the thermal cracking step and distilling it to separate a fraction having a boiling range of approximately 200° to 300° F., treating said fraction with sulfuric acid to remove olefins therefrom and subsequently hydroforming to increase the amount of aromatic compounds therein, removing product from the hydroforming step and distilling to separate a fraction high in aromatic content.

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