Patented Feb. 15, 1944 2,342,090

UNITED STATES PATENT OFFICE

2,342,090

PRODUCTION OF AROMATIC COMPOUNDS

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No Drawing. Application February 21, 1940, Serial No. 320,096

5 Claims. (Cl. 260—668)

This invention relates to the production of aromatic hydrocarbons from petroleum products and particularly to the production of fractions containing substantially one class of aromatic compounds such as bicyclic or tricyclic aromatics.

Heretofore alkylated naphthalenes, for instance, have been obtained mainly from coal tar directly or by alkylation of naphthalene. Since the yield of alkyl naphthalenes from coal tar is rather limited and since processes of alkylation of naphthalene are relatively expensive, alkyl naphthalenes are practically non-available as a commercial product. For these reasons and the fact that aromatics in general are so important commercially, various processes have been proposed for producing valuable aromatics from petroleum rather than from coal tar. Usually these proposals involve the use of relatively high temperatures and for one reason or another have not met with any considerable commercial success.

It is an object of our invention to supply valuable aromatic compounds from petroleum products.

A more specific object is to provide a process for supplying a highly aromatic product composed principally of bicyclic aromatic compounds from petroleum.

A further specific object is to provide a process for supplying a highly aromatic product composed principally of tricyclic aromatic compounds from petroleum.

Another specific object of the invention is to afford means for obtaining alkylated naphthalenes and tetralins from petroleum products.

Still another object is to provide a process for utilizing certain heavy petroleum products for the production of valuable aromatic compounds.

In accordance with our invention we have found that when certain high specific gravity petroleum products are subjected to a cracking operation, fractions may be obtained from the cracked product which are almost exclusively aromatic in nature. It has been found, for instance, that, if contrary to prior practices, such high specific gravity stocks are subjected to what might be termed a light cracking therefor, i. e., a cracking under substantially the conditions used for cracking a gas oil to gasoline, an aromatic product may be recovered comprising a fraction composed almost entirely of bicyclic aromatic compounds and another fraction composed almost entirely of tricyclic aromatic compounds. It has been found further that the fraction composed of bycyclic aromatic compounds comprises a predominant amount of alkyl naphthalenes and alkyl tetralins.

Our invention is to be clearly distinguished from the conventional cracking processes of the petroleum industry and the cracked products obtained therefrom. In general, the materials cracked heretofore have been comparatively low gravity stocks which possess relatively low aromatic content. As is well known, these materials, as, for instance, straight run gas oil, are usually cracked to produce gasoline and yield a cracked tar as the residual product. In these conventional cracking processes, bubble tower recycle stocks are also used. The content of aromatics in both gas oils and these usual recycle stocks is relatively quite low and as is well known, the cracked distillate products therefrom are quite limited as to their content of alkylated bicyclic and tricyclic aromatic hydrocarbons. Since alkylated bicyclic and tricyclic aromatic hydrocarbons cannot produce any substantial amount of gasoline because of their refractoriness except by complete molecular disruption accompanied by excessive coke and gas formation, it is obvious the materials cracked conventionally contain very little, if any, such compounds.

Highly aromatic petroleum products of the nature of those employed in our process have been cracked in the past. However, heretofore, these heavier and more aromatic petroleum products have been cracked mostly in the presence of large excesses of low specific gravity stocks whereby obviously the highly aromatic fractions of our invention would not be obtained. In certain cases the above heavy petroleum products have been processed alone; however, in such cases they have been cracked very heavily to produce a maximum possible amount of gasoline. In such process the high boiling alkyl bicyclic and tricyclic aromatic hydrocarbons, which were present in the virgin stocks, have been condensed into heavy tars, and these tars have been completely decomposed with a predominant formation of gas and coke.

Thus while the cracking conditions of our process have been used before it has only been on low gravity stocks of low aromatic content, and while pertroleum materials such as this invention is concerned with have been cracked alone before, such has only been done under very severe conditions and to produce predominantly gasoline, gas and coke. Accordingly, it appears that in the prior methods of cracking known to the industry, not only has it not been appreciated

that the valuable aromatic compounds discovered by us can be produced to any appreciable extent, but also it appears that fractions comprising the high content of aromatic compounds, as, for instance, alkyl naphthalenes and tetralins as obtained by our process have never been produced as a final product.

The petroleum products to be cracked by our process comprise highly aromatic products of relatively high boiling point, as, for example, highly aromatic fractions having an initial boiling point of at least 550–650° F. and preferably higher. These charging stocks for the production of alkyl naphthalenes and other aromatics should contain a large amount of hydrocarbons soluble in concentrated (95%) sulfuric acid (2 volumes of H_2SO_4 per 1 volume of stock). The amount of such hydrocarbons should be not less than about 35–40% by volume. The hydrocarbons soluble in sulfuric acid are either aromatic hydrocarbons (derivatives of benzene, naphthalene, anthracene, etc.) or aromatic-hydroaromatic hydrocarbons (e. g. partially hydrogenated alkyl naphthalenes, anthracenes, etc.) Accordingly, herein where the aromaticity of the stocks is referred to, it is to be understood reference is made to cyclic hydrocarbons soluble in concentrated sulfuric acid. Since the specific gravity is to a certain degree a measure of aromaticity, the petroleum products suitable for our process may also be roughly defined as petroleum products of the boiling range of gas oil and higher having a specific gravity higher than a straight run or recycle fraction of similar boiling range and in all cases higher than about 0.92–0.94. Some specific examples of materials that may be used in our process which have an aromatic content within the range above specified comprise, for example, solvent tars, cracked residua (particularly from vapor phase cracking or from naphthenic crudes), and distillates from solvent tars and cracked residua.

Thus, we have found when our particular petroleum products are subjected to a cracking operation, fractions boiling between about 220° C. and about 320° C. may be obtained from the cracked product and these fractions are composed almost entirely of aromatic compounds which consist of alkyl naphthalenes and tetralins and other bicyclic aromatic hydrocarbons. We have found further that a higher fraction boiling between 320° C. and 420° C. may be obtained from our cracked residium which may have an aromaticity as high as 97–100% and which consists predominantly of alkyl tricyclic aromatic compounds, i. e., alkyl derivatives of anthracene, phenanthrene and similar hydrocarbons.

A complete investigation of the aromatics boiling between 220°–320° C. shows that the fraction boiling up to 275° C. consists predominantly of alkyl naphthalenes and tetralins with short side chains, while the fraction boiling above 275° C. contains in addition to alkyl naphthalenes with longer side chains, a considerable amount of alkyl diphenyls and similar hydrocarbons with two phenyl rings. The alkylated bicyclic aromatics boiling in the range of 220°–320° C. produced by our cracking process usually have a specific gravity of about 0.97 to 0.99. These alkylated bicyclic aromatics are soluble in concentrated sulfuric acid (one volume of product per two volumes of 95% H_2SO_4) up to 85 to 95% and contain about 10 to 15% olefines and have a Kauri-Butanol number of around 85 to 100. The alkylated bicyclic aromatics produced from petroleum products by our process may be successfully used as solvents, for production of sulfonic acids and detergents and for various other purposes to which such compounds are put.

The actual cracking temperatures and pressures of our process are not substantially different from those employed in the usual cracking processes for the production of gasoline from gas oil and the like. For instance, in a continuous operation of cracking highly aromatic petroleum products by our process, the cracking may be performed at temperatures of about 900° F. in conventional cracking equipment in a once-through operation. The synthetic crude obtained is separated and fractionated for the separation of the fraction boiling in the range of about 220 to 320° C. which comprises alkylated bicyclic aromatics, and the fraction boiling in the range of about 320°–420° C. which comprises alkylated tricyclic aromatics. The fractionation of the synthetic crude may be carried out continuously and simultaneously with the cracking operation.

The cracking operation for our process may be performed also in batch operation, if desired. For instance, the cracking operation may be carried out at temperatures around 850 to 900° F. with a reaction time of about 30 minutes to 60 minutes depending upon the refractoriness of the stock.

It is to be understood that the above specific cracking temperatures given by way of illustration are in no way to be construed as limiting, since, as stated hereinabove, the actual cracking conditions of temperature and pressure of our process are essentially those of conventional cracking operations for cracking gas oil to gasoline, and accordingly the corresponding well known temperature ranges may be used with the same relationship between temperature and time existing, e. g., decreased time with increased temperature. Therefore, contrary to prior processes for producing aromatics from petroleum and for treating materials such as those with which we are concerned, which prior processes treated at temperatures of 1100° F. and higher, our process treats at a temperature below 1000° F., and usually around 900° F.

The following specific examples are given in order to further illustrate the invention. However, it is to be understood that these examples are not to be construed as limiting, since they may be wide variations without departing from the spirit of the invention.

Example I

A flash residuum from reforming heavy naphtha, sp. gr. 1.02, was cracked in batch operation at 875° F., 900 lbs. per sq. in. pressure, and 40 minutes reaction time. The results of the cracking were as follows:

	Per cent
Coke and gas	23.2
Gasoline, sp. gr. 0.810	10.5
Alkyl bicyclic aromatics, sp. gr. 0.986	28.4
Residuum, sp. gr.>1.0	37.9

The 37.9% of residuum was then fractionated to give the following yield:

	Per cent
Alkyl tricyclic aromatics, sp. gr. 1.07	17.1
Residuum, >400° C	20.8

Example II

A distillate of a residuum from vapor-phase cracking was cracked in batch operation at 900° F., 1200 lbs. per sq. in. pressure, and 60 minutes

reaction time. The results of the cracking were as follows:

	Per cent
Coke and gas	31.1
Gasoline, sp. gr. 0.820	16.7
Alkyl bicyclic aromatics, sp. gr. 0.977	27.3
Residuum, sp. gr. >1.0	24.9

The 24.9% residuum was then fractionated to give the following yield:

	Per cent
Alkyl tricyclic aromatics	17.5
Residuum, >400° C	7.4

Example III

A furfural extract from Mirando Neutrals (sp. gr. 0.985) was cracked in batch operation at 875° F., 1300 lbs. per sq. in. pressure, and 40 minutes reaction time. The results of the cracking were as follows:

	Per cent
Coke and gas	20.0
Gasoline, sp. gr. 0.800	16.6
Alkyl bicyclic aromatics, sp. gr. 0.974	16.7
Alkyl triccylic aromatics+residuum, sp. gr. >1.0	46.7

We claim:

1. A process for obtaining high yields of alkyl bicyclic aromatic hydrocarbons boiling between about 220° C. and about 320° C. and alkyl tricyclic aromatic hydrocarbons boiling between about 320° C. and about 420° C., in substantially pure state, from an aromatic petroleum stock having an initial boiling point of at least 550° F., having a specific gravity of at least 0.92 and containing upwards of 40% aromatic hydrocarbons including aromatic hydrocarbons having complex aromatic structures, other than said alkyl bicyclic aromatic hydrocarbons and said alkyl tricyclic aromatic hydrocarbons, and the balance normally liquid non-aromatic hydrocarbons, which comprises subjecting said aromatic petroleum stock in a reaction zone, to thermal cracking conditions including temperatures varying between about 850° F. and about 1000° F., for a eriod of time sufficient to crack substantially all the non-aromatic hydrocarbons boiling within the boiling ranges of said alkyl bicyclic and alkyl tricyclic aromatic hydrocarbons, to produce gas, liquid non-aromatic hydrocarbons boiling within the gasoline boiling range and coke, and to simplify the complex aromatic structures initially present in said aromatic petroleum stock, to yield a liquid consisting essentially of a mixture of said liquid non-aromatic hydrocarbons and aromatic hydrocarbons boiling within the gasoline boiling range, and polycyclic aromatic hydrocarbons, withdrawing said liquid from said reaction zone, and subjecting said liquid to distillation to obtain fractions of a mixture of hydrocarbons boiling within the gasoline boiling range, and said alkyl bicyclic aromatic hydrocarbons and said alkyl tricyclic aromatic hydrocarbons, in substantially pure state.

2. A process for obtaining high yields of alkyl bicyclic aromatic hydrocarbons boiling between about 220° C. and about 320° C. and alkyl tricyclic aromatic hydrocarbons boiling between about 320° C. and about 420° C., in substantially pure state, from an aromatic petroleum stock having an initial boiling point of at least 550° F., and a specific gravity of at least 0.92 and containing upwards of 40% aromatic hydrocarbons including aromatic hydrocarbons having complex aromatic structures, other than said alkyl bicyclic aromatic hydrocarbons and said alkyl tricyclic aromatic hydrocarbons, and the balance normally liquid non-aromatic hydrocarbons, which comprises subjecting said aromatic petroleum stock in a reaction zone, to thermal cracking conditions including temperatures varying between about 900° F. and about 1000° F., for a period of time sufficient to crack substantially all the non-aromatic hydrocarbons boiling within the boiling ranges of said alkyl bicyclic and alkyl tricyclic aromatic hydrocarbons, to produce gas, liquid non-aromatic hydrocarbons boiling within the gasoline boiling range and coke, and to simplify the complex aromatic structures initially present in said aromatic petroleum stock, to yield a liquid consisting essentially of a mixture of said liquid non-aromatic hydrocarbons and aromatic hydrocarbons boiling within the gasoline boiling range, and polycyclic aromatic hydrocarbons, withdrawing said liquid from said reaction zone, and subjecting said liquid to distillation to obtain fractions of a mixture of hydrocarbons boiling within the gasoline boiling range, and said alkyl bicyclic aromatic hydrocarbons and said alkyl tricyclic aromatic hydrocarbons, in substantially pure state.

3. A process for obtaining high yields of alkyl bicyclic aromatic hydrocarbons boiling between about 220° C. and about 320° C. and alkyl tricyclic aromatic hydrocarbons boiling between about 320° C. and about 420 C., in substantially pure state, from an aromatic petroleum stock having an initial boiling point of at least 550° F., having a specific gravity of at least 0.92 and containing upwards of 40% aromatic hydrocarbons including aromatic hydrocarbons having complex aromatic structures, other than said alkyl bicyclic aromatic hydrocarbons and said alkyl tricyclic aromatic hydrocarbons, and the balance normally liquid non-aromatic hydrocarbons, which comprises subjecting said aromatic petroleum stock in a reaction zone, to thermal cracking conditions including a temperature of about 900° F., for a period of time sufficient to crack substantially all the non-aromatic hydrocarbons boiling within the boiling ranges of said alkyl bicyclic and alkyl tricyclic aromatic hydrocarbons, to produce gas, liquid non-aromatic hydrocarbons boiling within the gasoline boiling range and coke, and to simplify the complex aromatic structures initially present in said aromatic petroleum stock, to yield a liquid consisting essentially of a mixture of said liquid non-aromatic hydrocarbons and aromatic hydrocarbons boiling within the gasoline boiling range, and polycyclic aromatic hydrocarbons, withdrawing said liquid from said reaction zone, and subjecting said liquid to distillation to obtain fractions of a mixture of hydrocarbons boiling within the gasoline boiling range, and said alkyl bicyclic aromatic hydrocarbons and said alkyl tricyclic aromatic hydrocarbons, in substantially pure state.

4. A process for obtaining high yields of alkyl bicyclic aromatic hydrocarbons boiling between about 220° C. and about 320° C. in substantially pure state, from an aromatic petroleum stock having an initial boiling point of at least 550° F., having a specific gravity of at least 0.92 and containing upwards of 40% aromatic hydrocarbons including aromatic hydrocarbons having complex aromatic structures, other than said alkyl bicyclic aromatic hydrocarbons, and the balance normally liquid non-aromatic hydrocarbons, which comprises subjecting said aromatic petroleum stock in a reaction zone, to thermal

cracking conditions including temperatures varying between about 850° F. and about 1000° F., for a period of time sufficient to crack substantially all of the non-aromatic hydrocarbons boiling within the boiling range of said alkyl bicyclic aromatic hydrocarbons, to produce gas, liquid non-aromatic hydrocarbons boiling within the gasoline boiling range and coke, and to simplify the complex aromatic structures initially present in said aromatic petroleum stock, to yield a liquid consisting essentially of a mixture of said liquid non-aromatic hydrocarbons and aromatic hydrocarbons boiling within the gasoline boiling range, and polycyclic aromatic hydrocarbons, withdrawing said liquid from said reaction zone, and subjecting said liquid to distillation to obtain fractions of a mixture of hydrocarbons boiling within the gasoline boiling range, and said alkyl bicyclic aromatic hydrocarbons in substantially pure state.

5. A process for obtaining high yields of alkyl tricyclic aromatic hydrocarbons boiling between about 320° C. and about 420° C. in substantially pure state, from an aromatic petroleum stock having an initial boiling point of at least 550° F., having a specific gravity of at least 0.92 and containing upwards of 40% aromatic hydrocarbons including aromatic hydrocarbons having complex aromatic structures, other than said alkyl tricyclic aromatic hydrocarbons, and the balance normally liquid non-aromatic hydrocarbons, which comprises subjecting said aromatic petroleum stock in a reaction zone, to thermal cracking conditions including temperatures varying between about 850° F. and about 1000° F., for a period of time sufficient to crack substantially all the non-aromatic hydrocarbons boiling within the boiling range of said alkyl tricyclic aromatic hydrocarbons, to produce gas, liquid non-aromatic hydrocarbons boiling within the gasoline boiling range and coke, and to simplify the complex aromatic structures initially present in said aromatic petroleum stock, to yield a liquid consisting essentially of a mixture of said liquid non-aromatic hydrocarbons and aromatic hydrocarbons boiling within the gasoline boiling range, and polycyclic aromatic hydrocarbons, withdrawing said liquid from said reaction zone, and subjecting said liquid to distillation to obtain fractions of a mixture of hydrocarbons boiling within the gasoline boiling range, and said alkyl tricyclic aromatic hydrocarbons in substantially pure state.

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