

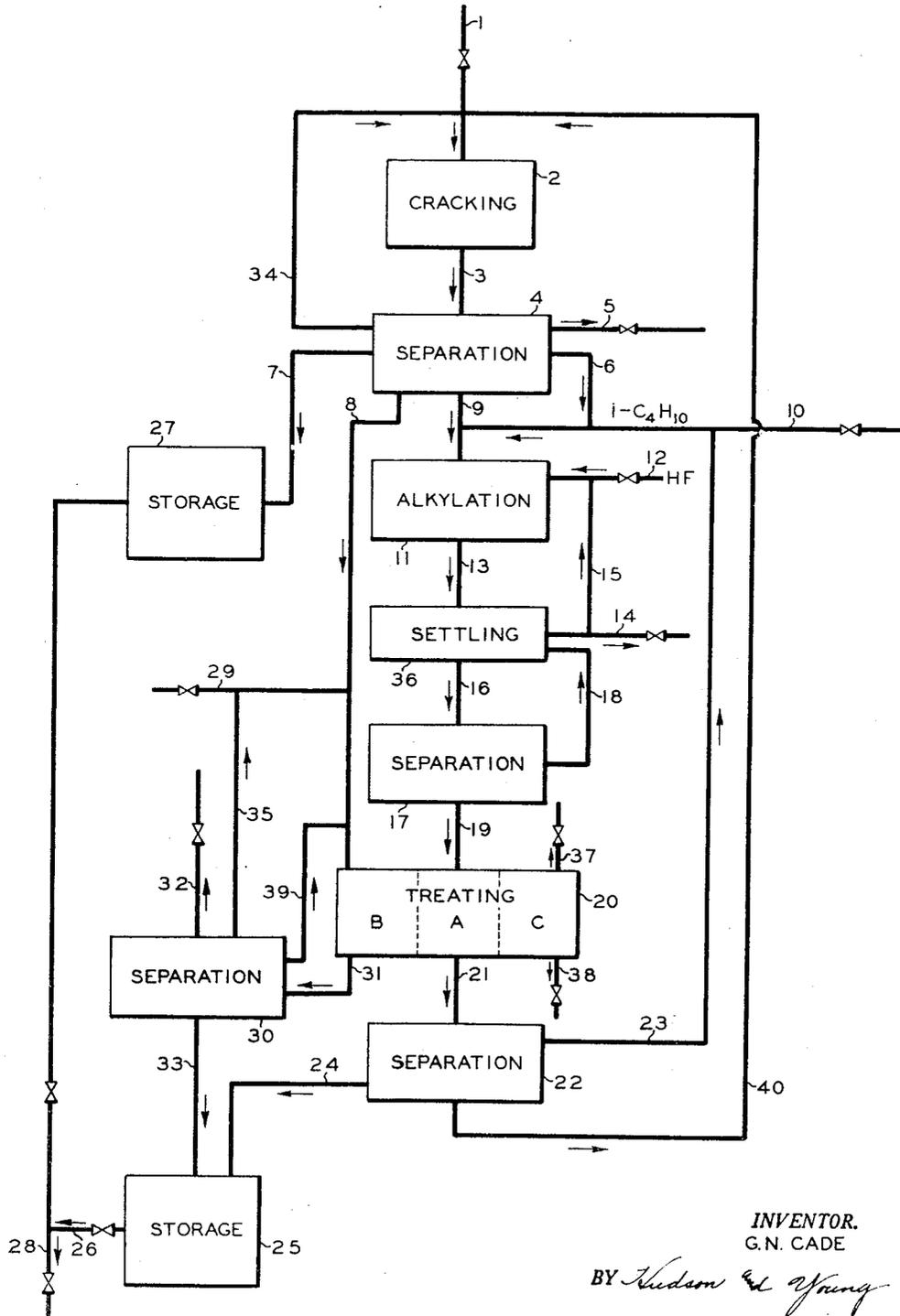
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CONVERSION OF POLYALKYL AROMATICS TO MONOALKYL AROMATICS

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CONVERSION OF POLYALKYL AROMATICS TO MONOALKYL AROMATICS

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This invention relates to the manufacture of gasoline. In another aspect this invention relates to a process for the manufacture of premium gasoline stocks from cracking. In a more specific aspect this invention relates to a process for obtaining improved yields and quality of gasoline product from cracking hydrocarbon oils.

This invention has for an object to provide a process for the manufacture of gasoline stocks.

Another object is to provide a process for the manufacture of premium gasoline stocks in improved yield and quality from hydrocarbon cracking products.

Another object is to provide a process for the utilization of a spent catalyst previously used for removing organically combined fluorine from hydrocarbons.

Still another object of this invention is to provide a process for the manufacture of monoalkyl aromatic hydrocarbons from a fraction rich in polyalkyl aromatics.

Other objects and advantages will be apparent to one skilled in the art from the accompanying discussion and disclosure.

This invention provides a novel and unitary combination process for increasing the yield and quality of gasoline obtained by cracking. Briefly, a preferred embodiment of the invention may be summarized as follows:

1. A cracked hydrocarbon oil is fractionated to obtain a light gasoline fraction, a heavy gasoline fraction, and an aromatic naphtha fraction.

2. The heavy gasoline fraction is treated with isobutane and hydrofluoric acid under alkylation conditions to obtain a substantially non-olefinic gasoline fraction containing branched-chain octanes, which is defluorinated with bauxite and rebled with the light gasoline fraction.

3. The aromatic naphtha is mixed with benzene and contacted with bauxite that has been used in the defluorination mentioned above. The product is a fraction containing monoalkylated aromatics boiling in the gasoline range. It is blended with the light gasoline fraction and the heavy alkylated gasoline fraction mentioned above.

A more detailed explanation will be given with reference to the attached drawing.

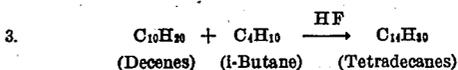
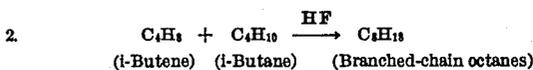
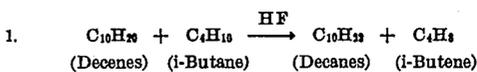
A cracking stock, e. g. a topped crude, enters cracking zone 2 through inlet 1. Cracking zone 2 may be a conventional thermal or a catalytic cracking system; in many cases, it will be a thermal cracking unit and may be considered so here for illustration purposes. It may be operated at about 800 to 950° F. and about 300 to 800 p. s. i., specific conditions depending on the feed used and the degree of conversion desired. When catalytic cracking is used, the feed oil is vaporized, diluted with steam, and heated to about 850-1100° F. The vaporized and diluted oil is then contacted with a catalyst at about

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0-100 p. s. i. and a liquid space velocity of about 1 to 10 volumes of oil per volume of catalyst per hour. Suitable catalysts are mixtures comprising silica and alumina, acid-treated clays, and alumina promoted with minor proportions of oxides of elements of groups V and VI of the periodic table. The exact conditions used will depend on the type of oil to be cracked, the properties of the catalyst, and the technic of contacting the catalyst with the oil.

The cracked effluent passes through conduit 3 to separation zone 4, which is usually a series of fractionation columns. A light gas fraction is withdrawn through outlet 5. A C₄ fraction is passed through conduit 6 to inlet 10. A light gasoline fraction boiling below about 250° F. passes through conduit 7 to storage means 27. A heavy gasoline fraction having a boiling range of about 250 to 400° F. is passed through conduit 9 to alkylation zone 11. An aromatic naphtha fraction having a boiling range of about 400 to 500° F. is passed through conduit 8 to treating zone 20. A heavy fraction is recycled through conduit 34.

The heavy gasoline fraction is mixed with isobutane, which enters through inlet 10, and the C₄ fraction from conduit 6 and is passed to alkylation zone 11. In this zone, the mixture is intimately contacted with concentrated hydrofluoric acid, supplied through inlet 12. Conditions in alkylation zone 11 are the paraffin-olefin alkylation conditions known to the art; for example, the temperature may be about 75-150° F., the contact time 5-30 minutes, the volume ratio of acid phase to hydrocarbon phase about 1:1, and the isobutane-to-olefin mol ratio about 5:1 to 15:1. Sufficient pressure to maintain substantially liquid-phase operation is usually used. Under these conditions, so-called "hydrogen-transfer alkylation" takes place, hydrogen apparently being transferred from the isobutane to the heavy olefins of the gasoline fraction. The net effects of this reaction are: the heavy olefins become saturated; branched-chain octanes are formed; and some ordinary alkylation takes place. Some of the reactions occurring in alkylation zone 11 may be exemplified as follows:



Reaction 3 accounts for a relatively small proportion of the product. It will thus be seen that

the heavy olefins, undesirable in motor gasoline, are converted to the corresponding paraffins, and branched-chain octanes, which are desirable, are produced.

The effluent from alkylation zone 11 is passed through conduit 13 to settling zone 36, in which a hydrocarbon phase is separated from an acid phase. The acid phase may be withdrawn through conduit 14 and passed to regeneration means, not shown; preferably, part is recycled through conduit 15. The hydrocarbon phase is passed through conduit 16 to separation zone 17, from which the dissolved hydrogen fluoride is distilled as an azeotropic mixture with light hydrocarbons and recycled through conduit 18 to settling zone 36. Acid-free hydrocarbon material containing organically combined fluorine as a by-product of the alkylation is passed to treating zone 20.

Treating zone 20 is a system comprising at least three bauxite treaters connected in parallel. The three treaters are diagrammatically indicated by A, B, and C. Treater A contains calcined bauxite, which removes organically combined fluorine from the hydrocarbon material entering through conduit 19. Treater B contains bauxite that has been used for defluorinating the material passing through conduit 19. The material in treater B is used as a catalyst to effect the so-called "benzene exchange" reaction. The aromatic naphtha from separation zone 4 passes through conduit 8 and is mixed with benzene, supplied through inlet 29. The mixture is reacted in treater B of treating zone 20. Treater C of treating zone 20 contains material that has been used for both the defluorination and the benzene exchange reaction. Superheated steam is supplied to treater C through inlet 37 to remove fluorine from the bauxite and is withdrawn through outlet 38.

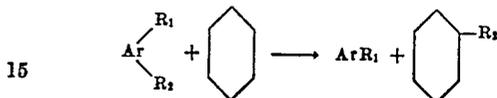
Material passing through conduit 19 is contacted with calcined bauxite in section A at about 100 to 300° F., sufficient pressure to maintain the hydrocarbon in the liquid phase, and a liquid space velocity of about 1 to 10.

The removal of small proportions of organic fluorine compounds from hydrocarbons by contacting with granular metal oxides has been disclosed and claimed by F. E. Frey in U. S. Patent 2,347,945 (1944). A suitable oxide for this purpose is granular calcined bauxite. The mechanism by which the fluorine removal proceeds is imperfectly understood, but, after contacting with the bauxite under suitable conditions (150-500° F. and liquid space velocities ranging from about 1 to 10 volumes of hydrocarbon per volume of bauxite per hour), the hydrocarbon material is rendered substantially fluorine free (usually less than 0.001 weight per cent F.), the fluorine remaining, in undetermined chemical form, in admixture and/or chemical combination with the bauxite. In commercial practice in which HF-alkylate is defluorinated with bauxite, it has been customary to discard the bauxite when the fluorine content has risen to about 15 to 40 per cent, because, when the fluorine content reaches this range, small amounts of hydrogen fluoride begin to appear in the bauxite-treated hydrocarbon. The present invention utilizes the spent or fluorine-containing bauxite, formerly considered a waste material, to effect another valuable conversion of hydrocarbons, to be described subsequently.

The aromatic naphtha in conduit 8 contains appreciable amounts of polyalkyl aromatics. A two to five-fold molar excess of benzene is added

to this material through inlet 29, and the mixture is contacted with the fluorine-containing bauxite in treater B at about 800 to 1000° F., pressures up to 600 p. s. i., and space velocities up to 10 liquid volumes per volume of catalyst per hour. This treatment converts polyalkyl aromatics to monoalkyl aromatics suitable for use in gasoline.

The reaction of high-boiling, polyalkylated aromatics with benzene in the presence of the fluorine-containing bauxite may be exemplified by the following equation:



in which Ar represents an aromatic nucleus and R_1 and R_2 alkyl radicals, which may be identical or different. This type of reaction is sometimes called the "benzene exchange reaction." It will thus be seen that higher-boiling, polyalkyl aromatics are converted to lower-boiling, monoalkyl aromatics, including monoalkyl benzenes, which are desirable constituents of motor fuels. In processes such as polyforming and cracking, substantial amounts of higher-boiling aromatics are present in recycle fractions higher-boiling than gasoline. The present invention converts such materials to gasoline constituents and utilizes, as a catalyst for this conversion, the fluorine-containing bauxite produced in the defluorination step previously described. A stoichiometric excess of benzene promotes the formation of monoalkyl benzenes. As previously mentioned, a two- to five-fold excess of benzene is ordinarily used. In some cases, however, a smaller proportion of benzene may be used, particularly when polymethyl benzenes are desired.

After the benzene exchange reaction has continued for some time the activity of the catalyst decreases as a result of the deposition of coke and/or other carbonaceous matter on the catalyst. These deposited materials are removed by the steam treatment subsequently described.

When the material in treater A has been used for a sufficient length of time so that it contains up to about 20 weight percent or more of fluorine, the material in conduit 19 is switched to treater C, in which the bauxite has previously been treated with superheated steam to remove the fluorine. The material in conduit 8 is then switched to treater A, and steam, introduced through conduit 37, is switched to treater B. This switching operation is accomplished by suitable manifolding means not shown in the drawing.

The steam treatment or regeneration in treater C is conducted at about 1000° F., as taught by J. D. Gibson in U. S. Patent 2,419,558 (1947). The regeneration is conducted by passing superheated steam at 600-1000° F. and space velocities equivalent to 0.1 to 5 liquid volumes of water per volume of the spent bauxite per hour. This treatment removes the fluorine, as hydrofluoric acid, from the bauxite and renders the bauxite suitable for further use in the defluorination described. The steam treatment or regeneration also removes the carbonaceous materials deposited on the bauxite during the benzene exchange reaction. It is further advantageous to add air or other oxygen-containing gas to the steam to aid in removing such deposits. The effluent steam, containing hydrofluoric acid, is withdrawn through outlet 38. The acid may be recovered from the steam, for example by absorption with an alkali-metal fluoride and sub-

sequent desorption, as taught in the Gibson patent cited above.

Thus, in accordance with this invention, the bauxite in a given treater is used in a cyclic series of operations, namely, defluorination, benzene exchange reaction, regeneration with steam, defluorination, benzene exchange, etc.

Defluorinated hydrocarbon material treated in treater A is passed through conduit 21 to separation zone 22. From separation 22, a fraction comprising isobutane is recycled through conduit 23. A fraction boiling in the gasoline range is passed through conduit 24 to storage means 25. A fraction comprising material higher-boiling than gasoline is recycled to cracking zone 2 through conduit 40.

The effluent material from treater B is passed through conduit 31 to separation zone 30. From separation zone 30, a light gas fraction is withdrawn through outlet 32. A fraction comprising unreacted benzene is recycled through conduit 35. A monoalkyl aromatic fraction is passed through conduit 33 to storage means 25. A fraction boiling above the gasoline range and comprising unreacted polyalkyl aromatics is recycled through conduit 39.

The material in storage means 27 is a low-boiling gasoline fraction comprising olefins. The material in storage means 25 is a relatively heavy gasoline fraction comprising isoparaffins and aromatics. The materials from these two storage means are blended in desired proportions to form a premium grade gasoline having a high anti-knock road rating. This gasoline is withdrawn through outlet 28 as a product of the process. Other hydrocarbons may be added to this product, as desired, to meet volatility specifications.

The invention is not necessarily limited to the specific fractions and boiling ranges mentioned above. For example, the aromatic fraction treated in treater B of zone 20 may be any aromatic fraction boiling between about 300 and 700° F. Refractory recycle stocks obtained in catalytic cracking and in polyforming, as well as in thermal cracking, are suitable. The chief object of the treatment by the benzene exchange reaction is to convert relatively high-boiling, polyalkylated aromatics to compounds suitable for use in motor fuel. Non-gasoline materials are thus used to increase yield and quality of gasoline from a given feed.

In another embodiment of the invention, polyalkyl aromatics may be separated from the cracking or polyforming effluent streams by solvent extraction and fractionation before being subjected to the benzene exchange reaction. The benzene for this reaction may be similarly concentrated.

Advantages of this invention are illustrated by the following example. The reactants and their proportions and other specific data are presented as being typical and should not be construed to limit the invention unduly.

A gas oil is cracked over a catalyst comprising alumina and silica at 980° F. and at a space velocity of 1.1 liquid volumes of oil per volume of catalyst per hour. The oil is diluted with steam at a ratio of 60 pounds of steam per barrel of oil. The effluent is treated by conventional methods to remove steam and tar. The resulting hydrocarbon product is fractionated to recover a light gasoline fraction having an end point of about 235° F., a heavy gasoline fraction boiling at 235-400° F., and a heavier recycle stock, which

contains an appreciable proportion of aromatics. Part of the recycle stock is fractionated to obtain a fraction boiling at about 400-550° F. This fraction is extracted with furfural to obtain an extract, which, after removal of the furfural, comprises an aromatic concentrate boiling at about 410-530° F.; the raffinate is recycled to the cracking step.

The heavy gasoline fraction is mixed with about 5 volumes of isobutane, and the mixture is contacted with about an equal volume of commercial anhydrous hydrofluoric acid at 115° F. and a contact time of 15 minutes. The effluent is freed of acid and normally gaseous hydrocarbons to obtain a liquid alkylate containing about 0.01 weight per cent organically combined fluorine.

The liquid alkylate is contacted with granular bauxite previously calcined at about 700° F. This contacting takes place at 180° F. and a liquid space velocity of about 1. The effluent alkylate is substantially fluorine-free. It is then fractionated to obtain an alkylate fraction boiling in the motor fuel range and a heavier alkylate fraction. The heavier alkylate is recycled to the cracking step previously described.

After the fluorine content of the bauxite used for the defluorination of the alkylate has risen to about 20 weight per cent, the alkylate stream is switched to a mass of previously used bauxite that has been regenerated by contact with steam and air at 1000° F.

The 410-530° F. aromatic concentrate obtained as described previously is mixed with about 2 volumes of benzene and contacted with the fluorine-containing bauxite at 1000° F., 75 p. s. i., and a liquid space velocity of about 0.9. The product of this step contains about 2 volume per cent of light gas and about 20 volume per cent of an alkyl aromatic fraction boiling in the motor fuel range, the remainder comprising unreacted benzene and apparently unreacted material higher-boiling than motor fuel. About 1.5 weight per cent of the charge to this step is converted to carbon, which is deposited on the fluorine-containing bauxite catalyst. After the activity of this catalyst has declined to an undesirably low level as a result of carbon deposition, the catalyst is regenerated with steam and air, as previously mentioned, and is then again suitable for defluorinating the liquid alkylate.

The light gasoline fraction from the cracking step, the motor-fuel alkylate, and the alkyl aromatic motor fuel fraction produced by the reaction of the 410-530° F. aromatic concentrate with benzene are blended to obtain a premium gasoline stock. This stock comprises olefins boiling below 250° F., isoparaffins (including branched-chain octanes), and alkyl aromatics. It may be blended with conventional base stocks and stabilized in known manner to obtain finished gasoline.

This invention affords utilization of a spent bauxite defluorination catalyst of any hydrocarbon conversion process employing a catalyst comprising hydrofluoric acid by which catalyst is meant liquid hydrogen fluoride either alone or in mixture with minor amounts of compounds exerting a promoting or modifying effect upon the activity thereof. Such compounds are, for example, boron fluoride or certain metalloidal halides, etc.

In one modification, the aromatic product of the benzene exchange reaction may be processed by fractionation and/or solvent extraction to

recover individual alkyl aromatics in purified form.

As will be evident to those skilled in the art, various modifications can be made or followed, in the light of the foregoing disclosure and discussion, without departing from the spirit or scope of the disclosure or from the scope of the claims.

I claim:

1. A process for producing monoalkyl aromatic hydrocarbons which comprises reacting benzene with a polyalkyl aromatic-rich stock in the presence of spent bauxite/defluorination catalyst to form monoalkyl aromatic hydrocarbons, and recovering said monoalkyl aromatic hydrocarbons from the total reaction product; said spent defluorination catalyst having previously been used for removing organically combined fluorine from hydrocarbons until having become spent as a result of accumulation of fluorine-containing compounds thereon.

2. A process for producing monoalkyl aromatic hydrocarbons which comprises admixing benzene in molar excess with a polyalkyl aromatic-rich stock in a ratio in the range of 2:1 to 5:1, contacting the admixture with spent bauxite defluorination catalyst at a temperature in the range of 800 to 1000° F., at a pressure within the limits of 0 and 600 p. s. i. g. and at a liquid space velocity in the range of 1 to 10; said spent defluorination catalyst comprising bauxite, previously utilized in a hydrocarbon conversion process employing a catalyst comprising hydrofluoric acid to remove from the liquid hydrocarbon conversion effluent organically combined fluorine present therein and formed as a by-product of said conversion, said bauxite having been so utilized until spent as a result of accumulation of fluorine containing compounds thereon.

3. A process for the utilization of spent bauxite defluorination catalyst comprising bauxite utilized in a defluorination step of a hydrocarbon conversion process employing a catalyst comprising hydrofluoric acid to remove from liquid hydrocarbon alkylation effluent organically combined fluorine present therein and formed as a

by-product of said alkylation, said bauxite having an accumulation of fluorine compounds thereon, which process comprises effecting such a defluorination step in a hydrofluoric acid hydrocarbon conversion process in the presence of a first bauxite catalyst until said first catalyst becomes spent, reacting benzene with a polyalkyl aromatic-rich stock in the presence of a second bauxite catalyst comprising catalyst spent in such a defluorination step to form monoalkyl aromatic hydrocarbons while concomitantly depositing carbonaceous material on said second catalyst thereby reducing the catalytic activity thereof, in a regeneration step contacting a third bauxite catalyst used previously in such a benzene polyalkyl aromatic reaction with steam and an oxygen-containing gas so as to remove carbonaceous materials and fluorine compounds deposited thereon; when said first catalyst becomes spent diverting the flow of fluorine-containing hydrocarbon material from said first catalyst to said third catalyst regenerated as aforesaid, diverting the flow of benzene-polyalkyl aromatic feed from said second catalyst to said first catalyst, and in a regeneration step contacting said second catalyst with steam and an oxygen-containing gas to remove carbonaceous material and fluorine compounds deposited thereon.

GEORGE N. CADE.

REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
2,276,171	Ewell	Mar. 10, 1942
2,322,863	Marschner et al.	June 29, 1943
2,347,945	Frey	May 2, 1944
2,360,358	Mattox	Oct. 17, 1944
2,389,713	Atwell	Nov. 27, 1945
2,394,905	Frey	Feb. 12, 1946
2,419,558	Gibson	Apr. 29, 1947
2,420,073	Frey	May 6, 1947
2,432,482	Matuszak	Dec. 9, 1947
2,476,750	Matuszak	July 19, 1949