

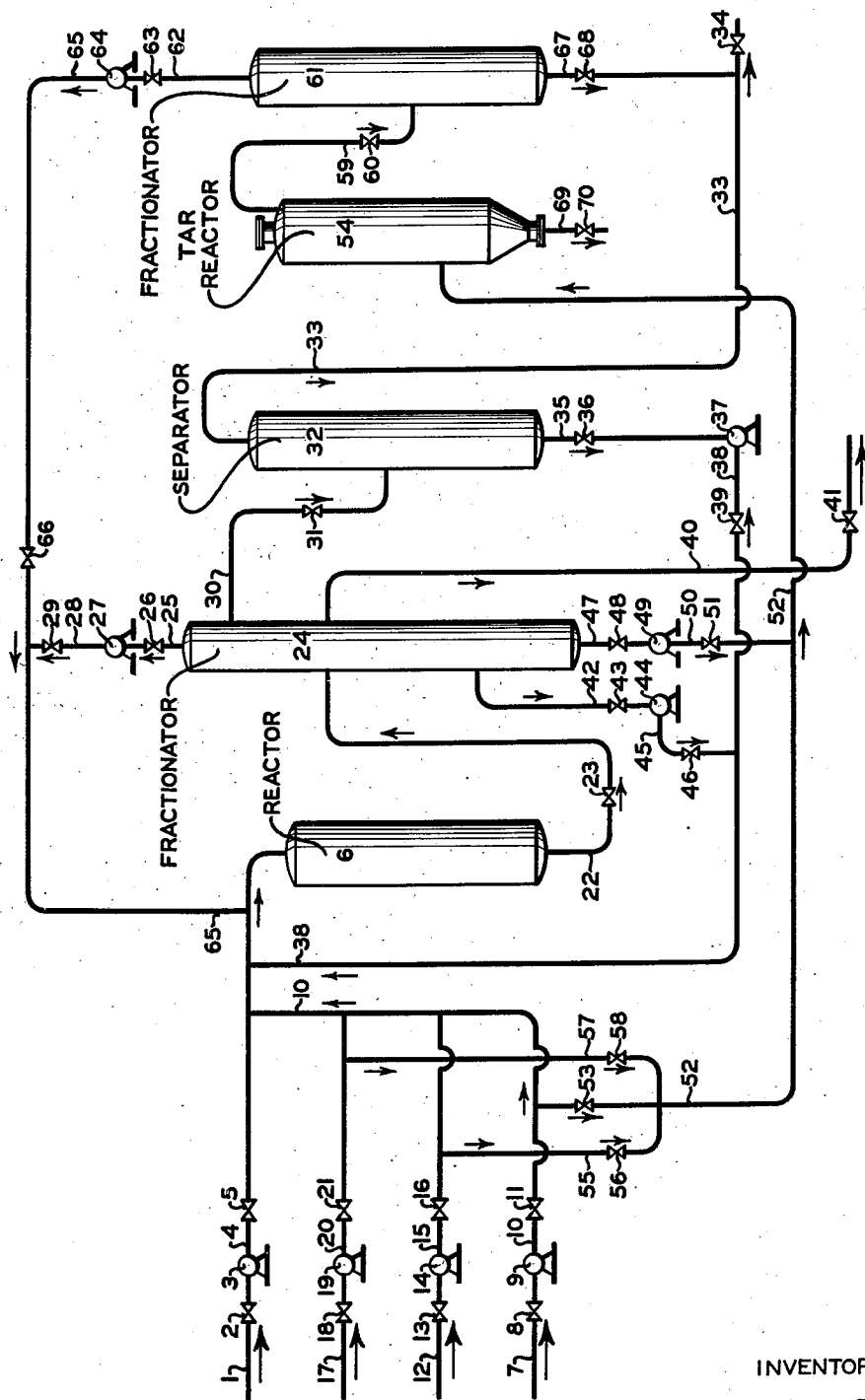
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H. S. BLOCH

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TREATMENT OF HYDROCARBONS

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INVENTOR
HERMAN S. BLOCH
BY *Lee J. Gary*
ATTORNEY

UNITED STATES PATENT OFFICE

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TREATMENT OF HYDROCARBONS

Herman S. Bloch, Chicago, Ill., assignor to Universal Oil Products Company, Chicago, Ill., a corporation of Delaware

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This invention relates to the treatment of hydrocarbon oils comprising essentially paraffins and naphthenes and preferably relatively free from olefins and aromatics, to produce therefrom lower boiling hydrocarbons, chiefly isoparaffins. In a more specific sense the invention is concerned with a process for converting a hydrocarbon oil into a gaseous product rich in isobutane and higher boiling normally liquid hydrocarbons of motor fuel boiling range and high antiknock value.

The formation of isobutane and of other isoparaffins or more highly branched chain paraffin hydrocarbons from less-branched chain liquid paraffins and from naphthenic hydrocarbons is desirable because of the generally higher antiknock value of the isomeric paraffin hydrocarbons so formed. Furthermore, the branched chain paraffins, both gaseous and liquid, are generally more reactive than the corresponding normal hydrocarbons and consequently these may be utilized in the production of other branched chain paraffins by so-called alkylation reactions in the presence of suitable catalysts. Also, lower boiling isoparaffins, such as isobutane and isopentane, may be dehydrogenated to the corresponding branched chain olefins which in turn may be converted into normally liquid polymers hydrogenatable by hydrogen-containing gases derived from the dehydrogenation step to produce substantially saturated motor fuel of high antiknock value.

In one specific embodiment the present invention comprises a process for converting a substantially saturated hydrocarbon oil into substantial yields of a light hydrocarbon fraction rich in isobutane and a substantially saturated gasoline of high octane number which comprises treating said hydrocarbon oil with hydrogen in the presence of a mixture of boron fluoride and hydrogen fluoride to form reaction products; separating said reaction products into a light hydrocarbon fraction rich in isobutane, a substantially saturated gasoline, a recycle oil, and a tar; returning said recycle oil to commingle with the hydrocarbon oil being charged to the process; directing said tar to a subsequent treatment in the presence of hydrogen at a relatively higher temperature to decompose said tar and form light hydrocarbons and a mixture comprising essentially boron fluoride, hydrogen, and hydrogen fluoride; and recycling said mixture to commingle with the hydrocarbons being charged to the process.

The substantially saturated hydrocarbons com-

prising essentially paraffins and naphthenes, with which the treatment of the process of the present invention is concerned, are normally liquids with relatively low octane number. Such substantially saturated hydrocarbons are produced in considerable quantities in the oil-refining industry from paraffinic, naphthenic, and mixed base crudes. Further, paraffins occur in substantial amounts in other gasolines and in the higher boiling constituents of natural gas commonly known as "casing head gasoline," in certain hydrocarbon materials produced synthetically, and in gasolines produced in relatively high yields by the cracking of relatively heavy petroleum fractions. In the case of cracked gasolines produced from paraffinic and naphthenic oils, the relative proportions of isoparaffins, normal paraffins, and naphthenes may vary over a considerable range.

The preferred catalyst suitable for use in effecting the process of the present invention comprises essentially a mixture of boron trifluoride and hydrogen fluoride. Boron trifluoride, BF_3 , is normally a colorless gas, having a boiling point of -101°C . and a melting point of -120°C . so that it is most readily handled for catalytic work in a vaporous condition. Hydrogen fluoride has a boiling point of $+20^\circ \text{C}$. and therefore the proposed catalytic mixture of these compounds is readily employed in vapor phase reactions or for the treatment of hydrocarbons in liquid phase under selected conditions of temperature and pressure. In accordance with the present invention, it has been found that various proportioned mixtures of boron trifluoride and hydrogen fluoride have catalytic effects in destructive hydrogenation of hydrocarbon oils to produce lower boiling isoparaffinic hydrocarbons so that there is obviously a joint promoting action although it is recognized that promoter catalysis is not understood entirely and the term is sometimes abused. As a rule the amount of boron trifluoride is in excess of the hydrogen fluoride in the most efficient mixtures, but this is not to be taken as an invariable rule as widely different effects may be obtained by varying the proportions of the two catalytic components of the preferred mixtures.

An important feature of the present invention consists in the treatment of normally liquid paraffins and naphthenes in the presence of both boron fluoride and hydrogen fluoride under a superatmospheric pressure of hydrogen. Tar formation is the predominant reaction when a substantially saturated hydrocarbon oil is treated with boron fluoride and hydrogen fluoride in the absence of added hydrogen but under a super-

atmospheric pressure of another gas such as nitrogen. Also the desired conversion to gaseous and liquid isoparaffins does not occur to a substantial degree when hydrogen fluoride and boron fluoride are used singly. In order to obtain the desired destructive hydrogenating action, it is necessary that hydrogen fluoride and boron fluoride be employed simultaneously.

The process of the present invention comprises essentially two stages, namely, (1) destructive hydrogenation of a substantially saturated hydrocarbon oil in the presence of boron fluoride and hydrogen fluoride to produce a light fraction containing isobutane and higher boiling isoparaffins and a relatively heavy fraction or tar containing a substantial proportion of the hydrogen fluoride and boron fluoride utilized as catalyst; and (2) a subsequent treatment of said tar with or without addition of more hydrogen under more severe conditions of temperature and pressure. In the first stage of the process the temperature, pressure, and time of contact necessary for effecting an optimum amount of destructive hydrogenation will vary with the composition of the reaction mixture so that only broad ranges for these operating conditions need be given. In general, the temperature employed in treating both the primary charging stock and the tar is within the approximate limits of 50° and 350° C. while the pressure is from substantially atmospheric to approximately 2000 pounds per square inch. When desired, boron fluoride may be employed together with water which causes hydrolysis and thereby generates hydrogen fluoride in situ.

Destructive hydrogenation products formed as hereinabove set forth are separated by fractional distillation into hydrogen, hydrogen fluoride, and boron fluoride catalyst, a light hydrocarbon fraction containing isobutane, a substantially saturated gasoline, a higher boiling recycle oil, and a residue or tar which is subjected to further treatment as hereinafter set forth. The light fraction containing isobutane and a substantially saturated gasoline fraction are conducted to storage while the recovered mixture of hydrogen, hydrogen fluoride, and boron fluoride and also the recycle oil are returned to further destructive hydrogenating treatment. The relatively high boiling residue or tar generally containing a substantial proportion of hydrogen fluoride and boron fluoride is subjected to a further treatment with hydrogen in the presence or absence of additional boron fluoride and/or hydrogen fluoride and under sufficiently severe conditions of temperature and hydrogen pressure to convert into light hydrocarbons a substantial proportion of the tar and to regenerate the boron fluoride and hydrogen fluoride contained therein.

The accompanying drawing is essentially a flow diagram embodying conventional apparatus for illustrating one specific combination of steps contemplated by the invention for producing isobutane and normally liquid isoparaffins of gasoline boiling range from a relatively higher boiling hydrocarbon oil comprising essentially paraffins and naphthenes, and preferably relatively free from olefins and aromatics.

Referring to the drawing, a hydrocarbon oil comprising essentially paraffins and naphthenes is introduced through line 1 and valve 2 to pump 3 which discharges through line 4 and valve 5 into reactor 6. Simultaneously hydrogen is directed through line 7 and valve 8 to compressor 9 which discharges through line 10 and

valve 11 into line 4, already mentioned. Also, boron fluoride is introduced through line 12 and valve 13 to pump 14 which discharges through line 15 and valve 16 into line 10 in which the hydrogen and boron fluoride are commingled with hydrogen fluoride introduced thereto by way of line 17, valve 18, pump 19, and line 20 containing valve 21. The commingled mixture of hydrocarbon oil, boron fluoride, hydrogen fluoride, and hydrogen in reactor 6 is subjected to a temperature within the approximate limits of 50° and 350° C. under a pressure of from substantially atmospheric to approximately 2000 pounds per square inch for a time sufficient to convert a substantial proportion of the hydrocarbon oil into a mixture comprising essentially isobutane, higher boiling isoparaffinic hydrocarbons of motor fuel boiling range, and higher boiling products together with the catalyst and added hydrogen.

From reactor 6 the entire reaction mixture is directed through line 22 and valve 23 to fractionator 24 of conventional design adequate to separate a mixture of hydrogen and boron fluoride, a light hydrocarbon fraction containing isobutane, a substantial gasoline fraction, and recycle oil and a residue or tar from which may be recovered gaseous hydrocarbons, hydrogen fluoride, and boron fluoride. The mixture of recovered hydrogen and boron fluoride is directed from fractionator 24 through line 25 and valve 26 to compressor 27, next through line 28, valve 29, lines 65 and 4, and thence to reactor 6, already mentioned. A mixture of hydrogen fluoride and light gases containing isobutane is directed from fractionator 24 through line 30 and valve 31 to separator 32 of adequate design for separating the lighter hydrocarbon layer from the generally heavier liquefied hydrogen fluoride. Said light hydrocarbons are directed from separator 32 through line 33 and valve 34 to storage, fractional distillation, or other treatment as desired.

Used hydrogen fluoride recovered by separation from the destructive hydrogenation products in separator 32 is withdrawn therefrom through line 35 and valve 36 to pump or compressor 37 which discharges through line 38 and valve 39 into line 4, already mentioned, through which the hydrocarbon fraction charged is introduced to the process. The gasoline fraction is directed from fractionator 24 through line 40 and valve 41 to storage. A higher boiling recycle oil is conducted from fractionator 24 through line 42 and valve 43 to pump 44 which discharges through line 45 and valve 46 to line 38, already mentioned, and is therein recycled to line 4 and thence to destructive hydrogenating reactor 6, already mentioned.

Heavy residual hydrocarbons and tar are directed from the bottom of fractionator 24 through line 47 and valve 48 to pump 49 which discharges through line 50, valve 51, and line 52 into tar reactor 54 which comprises a suitable chamber operating preferably at a slightly higher temperature than reactor 6, although within the same general limits of about 50° and about 350° C., and in the presence of fresh hydrogen supplied from line 10 through line 52 and valve 53 either at the same pressure as that utilized in reactor 6 or at a higher pressure. The hydrogen being directed to reactor 54 through line 52 may be commingled therein with boron fluoride supplied from line 15 by way of branch line 55 and valve 56 and with hydrogen fluoride

conducted from line 20 through branch line 57 and valve 58. Also, when desired, reactor 54 may be supplied, by means not shown, with additional quantities of hydrogen fluoride and/or boron fluoride derived from the products of reactor 6.

In reactor 54 the residue or tar from the destructive hydrogenation treatment in reactor 6 is converted into hydrogen fluoride and/or boron fluoride together with light hydrocarbon gases, a considerable proportion of which is isobutane. The hydrocarbon products from reactor 54 are directed therefrom through line 59 and valve 60 to fractionator 61 which consists of either a single fractionating column or a series of fractionators in which a mixture of hydrogen, hydrogen fluoride, and boron fluoride is separated from a light hydrocarbon fraction containing isobutane. Said mixture of hydrogen, hydrogen fluoride, and boron fluoride is directed from fractionator 61 through line 62 and valve 63 to compressor 64 which discharges through line 65 and valve 66 into line 4, already mentioned, through which the charged hydrocarbon oil and admixed hydrogen, hydrogen fluoride, and boron fluoride are conducted to destructive hydrogenation in reactor 6. The light hydrocarbon fraction separated as bottoms in fractionator 61 is directed through line 67 and valve 68 to line 33, already mentioned, through which a similar light hydrocarbon fraction produced in the destructive hydrogenation step is being conducted to storage. The products formed in reactor 54 contain some difficultly volatile material such as relatively high boiling tars and carbonaceous residues which are withdrawn from the bottom of reactor 54 through line 69 and valve 70 to waste or storage.

The following example is introduced as characteristic of the practical operation of the process although it is not presented with the intention of limiting the scope of the invention in exact correspondence with the numerical data given:

A Pennsylvania gas oil, treated at 150° C. for 4 hours with 10% each of hydrogen fluoride and boron fluoride under an initial hydrogen pressure of 100 atmospheres, yielded 16% by volume of a 400° F. end-point saturated gasoline with 66 octane number, a gas containing isobutane, a tar made up of about 10% by volume of hydrocarbons and a major proportion of the hydrogen fluoride and boron fluoride catalyst, and also about 70% by weight of unconverted hydrocarbon oil suitable for recycling to further destructive hydrogenation treatment.

With recycling of unconverted hydrocarbon oil the ultimate yields, based upon the weight of oil charged, are gasoline, 44%; gas (75 mole per cent isobutane) 18%; and tar about 38%.

The tar produced in the first step and containing the major proportion of the hydrogen fluoride and boron fluoride is treated at 300° C. for 8 hours under an initial hydrogen pressure of 100 atmospheres. Approximately 11% of the tar is converted in one pass into liquid hydrocarbons while hydrogen fluoride and boron fluoride are liberated to the extent of 7.5 and 11%, respectively, of the quantities of these materials charged in the first step of the process. The remainders of the tar, hydrogen fluoride, and boron fluoride remain in the form of an unconverted residue.

The novelty and utility of the process of this invention are evident from the preceding specification and example although neither section is intended to unduly limit its generally broad scope.

I claim as my invention:

1. A process for converting tar or residue containing boron fluoride and hydrogen fluoride into more useful products, which comprises subjecting said tar to the action of hydrogen whereby to form low boiling hydrocarbons and to liberate said boron fluoride and hydrogen fluoride.

2. The process of claim 1 further characterized in that additional boron fluoride and hydrogen fluoride are added to said tar prior to the conversion treatment.

3. In a process for the conversion of substantially saturated hydrocarbon oils wherein the oil is subjected to conversion under cracking and isomerizing conditions of temperature and pressure in the presence of boron trifluoride, hydrogen fluoride and hydrogen and wherein a tar residue is formed comprising hydrocarbons, boron trifluoride and hydrogen fluoride, the method of treating the tar residue which comprises subjecting said tar residue to the action of hydrogen under more severe conditions of temperature and pressure than are maintained in the first mentioned conversion step to liberate at least a portion of said hydrocarbons, boron trifluoride and hydrogen fluoride from said residue.

4. The improved process of claim 3 further characterized in that additional boron trifluoride and hydrogen fluoride are introduced to the tar residue conversion step.

HERMAN S. BLOCH.