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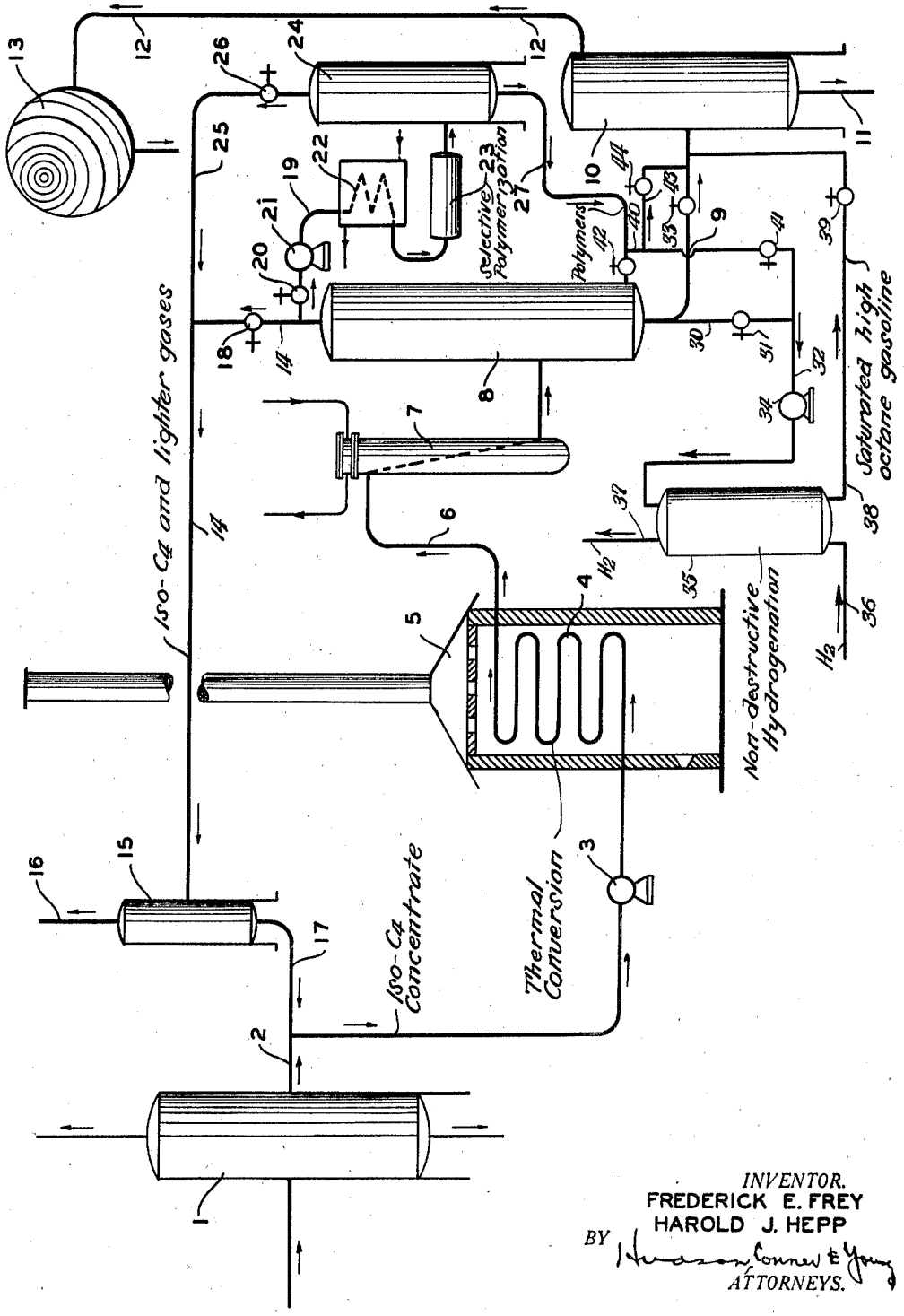

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PROCESS FOR MANUFACTURING HYDROCARBON OILS

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9 Claims. (Cl. 196—10)

This invention relates to the manufacture of volatile hydrocarbon oils and in particular to the manufacture of oils highly branched in structure and peculiarly suitable for motor fuel in an internal combustion engine where paraffinic characteristics and high antiknock value are important. It has been proposed to produce normally liquid volatile hydrocarbons suitable for motor fuel by subjecting normally gaseous hydrocarbons to heat and pressure and thereafter separating from the products of reaction such hydrocarbon products and also the gaseous hydrocarbons suitable for returning to the conversion operation.

We have discovered that if from a mixture of gaseous hydrocarbons there is separated a material consisting of isobutane, or predominating in isobutane, that such a fraction, exposed to suitable conditions of heat and pressure to be set forth, can be converted into volatile normally liquid hydrocarbons almost entirely aliphatic and largely of branched structure. We have discovered that a product of this character is not obtained under conditions of low pressure and with extensive conversion of isobutane in a single thermal treatment which, from the standpoint of economy in conversion alone, is desirable. In our invention we produce volatile normally liquid hydrocarbons largely aliphatic and of branched structure by subjecting isobutane to a temperature within the range 752° to 1292° F., within which range cracking takes place, while maintaining a pressure of at least 500 pounds per square inch.

It is of the essence of this invention that the extent of decomposition of isobutane be limited to 50 per cent or less of the isobutane content of the material subjected to the conversion step in order that products of the aliphatic character described be obtained, and further that an elevated pressure must be maintained of at least 500 pounds per square inch during the conversion and preferably higher pressures, the higher the better, the pressure being limited only by the strength of the apparatus. Isobutane surviving the thermal treatment may be returned to the conversion step to be subjected again to treatment along with fresh isobutane-rich material. Butylenes occurring in the effluents from the thermal treatment, as well as any desired fraction of the propane and propylene, may also be returned for retreatment. In this way recycle operation in which all suitable hydrocarbons are treated will always call for the return of a volume of stock approximately equal to, or greater than, the volume of fresh hydrocarbon to be subjected to the process. The fresh hydrocarbon stock to be subjected to conversion should contain preferably a higher content of isobutane than is found in hydrocarbons extracted from natural gas or from the gas derived from oil cracking stills and should contain accordingly at least 50 per cent of isobutane, but the higher the isobutane content up to 100 per cent the more highly branched will be the structure of the normally liquid hydrocarbons produced and the more efficiently will they perform in internal combustion engines of high compression ratio.

The time during which the hydrocarbon should be exposed to a conversion temperature is determined by the restriction that at least 50 per cent of the isobutane survive the thermal treatment and the time of reaction will consequently be decreased with elevation of the temperature employed and will be of the order of 0.2 to 1 minute at about 1050° F. A lower extent of destruction of the isobutane during the thermal treatment will increase the proportion of branched aliphatic hydrocarbons in the normally liquid products but an extent of decomposition of isobutane much below 10 per cent will result in a small production of normally liquid products and an attendant increased expense.

The figure which forms a part of this specification diagrammatically illustrates one form of apparatus for practicing this present invention.

A hydrocarbon mixture containing isobutane is subjected to fractional distillation in fractionating element (1) and a concentrate high in isobutane passes through conduit (2) to pump (3) wherein the pressure is raised to the desired pressure for the conversion. From the pump the said hydrocarbon fraction passes through a tube coil (4) situated within the furnace (5) wherein the hydrocarbon passing continuously through the tube coil may be subjected to the desired pyrolysis temperature for the desired time. The thermally treated hydrocarbon passes through conduit (6) and heat exchanger (7) wherein a part of the heat may be extracted, to fractionating column (8) wherein said thermally treated hydrocarbon is separated into a fraction composed primarily of normally liquid hydrocarbons and a fraction composed of gaseous hydrocarbons. The first mentioned fraction is passed through conduit (9) to fractionating column (10) wherein hydrocarbons boiling above the desired range are separated from the mixture and removed through conduit (11), while the volatile normally liquid hydrocarbon product is isolated and withdrawn through conduit (12) and collected in the container (13). The gases passing from fractionating column (8) through conduit (14) enter separator (15) wherein light gases are separated from the mixture and discharged from the system through conduit (16), and normally gaseous hydrocarbons of three and four carbon atoms per molecule containing the unconverted isobutane are returned through conduit (17) to the inlet of pump (3).

A further increase in antiknock value of the

motor fuel produced is obtained by subjecting the normally gaseous hydrocarbons resulting from the thermal conversion to a selective catalytic polymerization whereby the isobutylene present, which we have found to be formed in substantial amount, is converted into di-polymer and tri-polymer which may be incorporated in the hydrocarbon product to increase the antiknock value both of the motor fuel as produced thermally and after subjecting it to non-destructive hydrogenation.

With further reference now to the figure, it will be seen that conduit (14) includes a valve (18), which when closed will allow normally gaseous hydrocarbons flowing through conduit (14) from the fractionating column (8) to pass into conduit (19), which is controlled by a valve (20) and in which is provided a pump (21) to force the normally gaseous hydrocarbons through a heating element (22) and a polymerization catalyst chamber (23). The polymers produced in the chamber (23) are then passed along with other material present to the chamber (24) wherein unreacted gases are separated and removed through conduit (25) to the conduit (14) so that they may ultimately pass into the separator (15). Conduit (25) is provided with a valve (26) which will remain open when valve (20) is open, and be closed when the valve (18) is open. From the separator (24) the polymers pass through conduit (27) to the fractionating column (8).

The catalytic polymerization may be effected by a variety of catalysts which comprise sulfuric acid, phosphoric acid, aluminum chloride, and activated fuller's earth, the polymerization is selective for isobutylene at temperatures somewhat below those required to polymerize propylene and butenes. The temperature for such selective polymerization is readily determined by experiments and usually lies between 100° and 300° F., the exact temperature depending upon the activity of the catalyst.

The normally liquid hydrocarbon product obtained by the process set forth is predominantly aliphatic but contains small proportions of olefine hydrocarbons particularly when the lower operating pressures in the range are employed for the thermal treatment. It is an object of our invention to produce a more highly saturated product of more completely paraffinic characteristics by subjecting the said material to non-destructive hydrogenating conditions with the aid of a catalyst. For this purpose chromium oxide catalyst (U. S. P. 1,905,383, April 25, 1933, Frey and Huppke) or other catalysts, such as nickel and molybdenum sulfide, may be used with elementary hydrogen preferably as the source of hydrogen though light paraffinic hydrocarbons, preferably butanes, may be used for the purpose, the hydrogen in such a case being extracted from the butane with the formation of butylene as a product of the process. The hydrogen or hydrogen-supplying agent is passed together with the normally liquid hydrocarbon product over the catalyst at a reaction temperature which will vary widely with the catalyst selected, being usually between 200° and 500° F., and from the effluents of the catalytic treatment the normally liquid product of saturated type may be separated.

Non-destructive hydrogenation, either of the polymers from the selective polymerization effected in polymerization catalyst chamber 23, or of the liquid material from the thermal process as effected in tube coil 4, or of mixtures of these two, may take place in the following manner.

Effluents of the fractionating column (8) passing through conduit (9) are passed through conduit (30) and valve (31) and into conduit (32), while valve (33) in conduit (9) is closed. Pump (34) in conduit (32) compresses the hydrocarbons to a desired hydrogenating pressure, and forces them to the hydrogenating chamber (35) which contains any suitable catalyst of the type herein taught. Hydrogen under suitable pressure is introduced into this chamber through conduit (36), and passes countercurrent to the hydrocarbons being treated therein. Gases containing or consisting of excess hydrogen are withdrawn from chamber (35) through conduit (37). Hydrogenated hydrocarbons are passed from the chamber (35) through conduit (38) and valve (39) and into conduit (9) and then to the fractionating column (10) for further separation as has been herein described.

If the process is operated to include selective polymerization of isobutylene, the polymers from polymerization catalyst chamber (23) passing through conduit (27) may be subjected to hydrogenation by passing them into fractionating column (8) and out conduit (9), however, if desired, they need not be passed into the column (8), but may be passed from conduit (27) directly into conduit (32) through conduit (40) and valve (41), while valve (42) in conduit (27) is closed. If it is desired to mix the polymers from the catalytic polymerization with the hydrogenated hydrocarbons from the thermal treatment, this may be done by closing both valves (41) and (42) and passing the polymers through conduit (43) and valve (44) to conduit (9).

It is also a part of this invention to produce paraffin hydrocarbons of highly branched structure in concentrated form. This is accomplished by subjecting the normally liquid product of the thermal treatment, either hydrogenated or unhydrogenated, to fractional distillation in efficient apparatus whereby highly branched hydrocarbons, notably isohexanes, isoheptanes and isooctanes, may be obtained in a concentrated form.

A paraffinic motor fuel may also be obtained without the hydrogenation step by treating the normally liquid product or fractions thereof with a polymerizing agent such as sulfuric acid or aluminum chloride and removing heavier polymer so formed by distillation.

Example 1.—Isobutane was passed at a temperature of 1022° F. and under a pressure of 2420 pounds through a heated tube at such a rate of flow that the stream was exposed to reaction temperature for 3.0 minutes. The effluents were of the following composition:

	Weight per cent
H_2	0.1
CH_4	6.6
C_2H_4	0.2
C_2H_6	1.2
C_3H_6	3.0
C_3H_8	5.2
C_4H_8	3.8
C_4H_{10}	70.0
Gasoline	8.9
Tar	1.0
	100.00

The normally liquid products contained 10 per cent of hydrocarbons boiling above 350° F. The

gasoline was found to contain less than 10 per cent of cyclic hydrocarbons and to consist of hydrocarbons of 5, 6, 7, and 8 carbon atoms per molecule, present in the following percentages and predominating in branched paraffins:

C_5	23
C_6	15
C_7	37
C_8	15
Heavier	10
	100

The normally liquid hydrocarbons with the high boiling material removed, subjected to an engine knock test, showed a high antiknock rating.

Example 2.—Normally liquid hydrocarbons produced substantially in accordance with Example 1, except that hydrocarbons of 3 and 4 carbon atoms per molecule, separated from the products were returned to the thermal treatment accompanied by fresh isobutane, and boiling below 350° F. were admixed with five times their vapor volume of hydrogen and passed over chromic oxide gel catalyst maintained at a temperature of 642° F. The olefin content was thereby reduced from 25 per cent to 2 per cent. The engine antiknock test rating was virtually the same as for the product in Example 1 but the addition of small amounts of tetraethyl lead was found to effect a considerable improvement in knock rating, the addition of 3 cc. of tetraethyl lead fluid per gallon producing a fuel of 98 octane number, as determined by the A. S. T. M. method D 357–34T.

Example 3.—Normally liquid hydrocarbons obtained substantially as described in Example 1 were subjected to fractional distillation and the fraction consisting largely of branched heptanes of high antiknock value was isolated between 165° and 185° F. distilling temperature (atmospheric pressure) as well as fractions distilling in the range 130° to 146° and 205° to 215° F. likewise of high antiknock value and composed predominantly of isohexanes and iso-octanes respectively.

Having described our invention, what we claim is:

1. A process for producing special motor fuels of high antiknock quality and consisting predominantly of aliphatic hydrocarbons of branched structure, which comprises subjecting a normally gaseous hydrocarbon mixture comprised predominantly of isobutane to thermal treatment at 752° to 1292° F. and at a pressure exceeding 500 pounds per square inch for such a time as will effect the conversion of no more than 50 per cent of the isobutane initially present, and then separating from the effluents normally liquid hydrocarbons in the gasoline boiling range.

2. A process for producing special motor fuels of high antiknock quality possessing paraffinic characteristics and of special boiling range, which comprises subjecting a normally gaseous hydrocarbon mixture comprised predominantly of isobutane to thermal conversion at 752° to 1292° F. and at a pressure exceeding 500 pounds per square inch for such a time as will effect the conversion of no more than 50 per cent of the isobutane initially present to form normally liquid aliphatic hydrocarbons, separating said normally liquid hydrocarbons from the thermally converted hydrocarbons, subjecting the said normally liquid hydrocarbons to non-destructive hydrogenation, and finally subjecting the resulting normally liquid hydrocarbons to fractional distillation to separate highly branched paraffin hydrocarbons in concentrated form for use as special motor fuels.

3. A process for producing normally liquid hydrocarbons predominantly aliphatic and of branched structure, which comprises subjecting hydrocarbons comprised predominantly of isobutane to thermal conversion at 752° to 1292° F. and at a pressure exceeding 500 pounds per square inch for such a time as will effect the conversion of no more than 50 per cent of the isobutane initially present producing normally liquid aliphatic hydrocarbons and normally gaseous hydrocarbons of an appreciable isobutylene content, separating the thermally converted hydrocarbons into normally liquid hydrocarbons and normally gaseous hydrocarbons, passing the normally gaseous hydrocarbons into contact with a polymerization catalyst under such conditions that isobutylene is selectively polymerized into aliphatic hydrocarbon polymers in the motor fuel boiling range, separating said polymers from the remaining normally gaseous hydrocarbons and mingling them with said normally liquid hydrocarbons, and separating from said normally liquid hydrocarbons a selected normally liquid hydrocarbon fraction in the motor fuel boiling range.

4. A process as in claim 3 wherein the mingled normally liquid hydrocarbons are subjected to non-destructive hydrogenation, and a highly paraffinic, high antiknock motor fuel separated therefrom.

5. A process for the production of special motor fuels containing essentially aliphatic hydrocarbons of branched structure, which comprises separating from a normally gaseous hydrocarbon mixture an isobutane fraction comprising isobutane in essentially a pure state, mixing said isobutane fraction with a recycle stock consisting of at least 50 per cent isobutane and minor portions of other three and four carbon atom hydrocarbons, subjecting the mixture to thermal conversion at 752° to 1292° F. and at a pressure exceeding 500 pounds per square inch for such a time as will effect the conversion of no more than 50 per cent of the total isobutane initially present to form normally liquid aliphatic hydrocarbons, separating the effluents into a fraction of normally liquid hydrocarbons and removing same from the process and a fraction containing hydrocarbons of three and fewer carbon atoms per molecule and removing this fraction from the process and an intermediate fraction consisting of at least 50 per cent of isobutane and minor portions of other three and four carbon atom hydrocarbons and returning at least a portion of said intermediate fraction as recycle stock to be admixed with the aforesaid isobutane fraction.

6. A process for the production of special motor fuels essentially composed of selected aliphatic hydrocarbons of branched structure, which comprises subjecting hydrocarbons comprised predominantly of isobutane to thermal conversion at 752° to 1292° F., and at a pressure exceeding 2000 pounds per square inch for such a time as will effect the conversion of no more than 50 per cent of the isobutane initially present, producing normally liquid aliphatic hydrocarbons, and separating from the effluents of said conversion a fraction distilling between 130° and 215° F.

7. A process for producing special motor fuels

of high antiknock quality and consisting predominantly of aliphatic hydrocarbons of branched structure, which comprises subjecting a normally gaseous hydrocarbon mixture comprised predominantly of isobutane to thermal treatment at 752° to 1292° F. and at a pressure exceeding 500 pounds per square inch for such a time as will effect the conversion of between 10 and 50 per cent of the isobutane initially present, and then separating from the effluents normally liquid hydrocarbons in the gasoline boiling range.

8. A process for producing normally liquid hydrocarbons predominantly aliphatic and of branched structure, which comprises subjecting hydrocarbons comprised predominantly of isobutane to thermal conversion at 752° to 1292° F. and at a pressure exceeding 500 pounds per square inch for such a time as will effect the conversion of between 10 and 50 per cent of the isobutane initially present producing normally liquid aliphatic hydrocarbons and normally gaseous hydrocarbons of an appreciable isobutylene content, separating the thermally converted hydrocarbons into normally liquid hydrocarbons and normally gaseous hydrocarbons, passing the normally gaseous hydrocarbons into contact with a polymerization catalyst under such conditions that isobutylene is selectively polymerized into aliphatic hydrocarbon polymers in the motor fuel boiling range, separating said polymers from the remaining normally gaseous hydrocarbons and mingling them with said normally liquid hydrocarbons, and separating from said normally liquid hydrocarbons a selected normally liquid hydrocarbon fraction in the motor fuel boiling range.

9. A process for the production of special motor fuels containing essentially aliphatic hydrocarbons of branched structure, which comprises separating from a normally gaseous hydrocarbon mixture an isobutane fraction comprising isobutane in essentially a pure state, mixing said isobutane fraction with a recycle stock consisting of at least 50 per cent isobutane and minor portions of other three and four carbon atom hydrocarbons, subjecting the mixture to thermal conversion at 752° to 1292° F. and at a pressure exceeding 500 pounds per square inch for such a time as will effect the conversion of between 10 and 50 per cent of the total isobutane initially present to form normally liquid aliphatic hydrocarbons, separating the effluents into a fraction of normally liquid hydrocarbons and removing same from the process and a fraction containing hydrocarbons of three and fewer carbon atoms per molecule and removing this fraction from the process and an intermediate fraction consisting of at least 50 per cent of isobutane and minor portions of other three and four carbon atom hydrocarbons and returning at least a portion of said intermediate fraction as recycle stock to be admixed with the aforesaid isobutane fraction.

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