

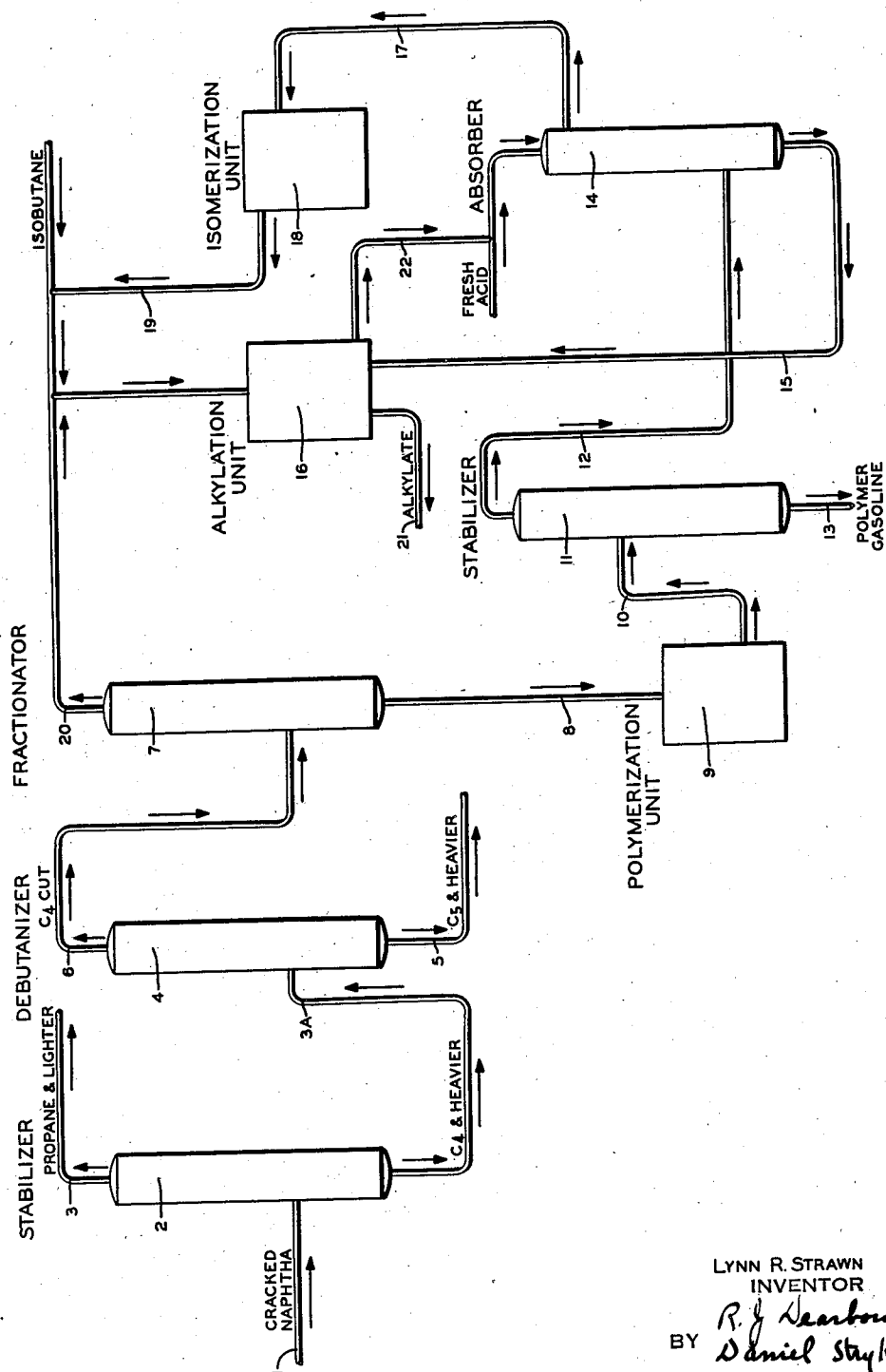
Feb. 16, 1943.

L. R. STRAWN

2,311,096

MANUFACTURE OF MOTOR FUEL

Filed April 6, 1940



LYNN R. STRAWN
INVENTOR

BY *R. J. Searles*
Daniel Strayker
HIS ATTORNEYS

UNITED STATES PATENT OFFICE

2,311,096

MANUFACTURE OF MOTOR FUEL

Lynn R. Strawn, Port Arthur, Tex., assignor, by
mesne assignments, to The Texas Company,
New York, N. Y., a corporation of Delaware

Application April 6, 1940, Serial No. 328,195

11 Claims. (Cl. 196—10)

This invention relates to the manufacture of motor fuel and particularly to its manufacture from a hydrocarbon fraction comprising saturated and unsaturated hydrocarbons having four carbon atoms per molecule.

Broadly the invention comprises a process which involves segregating a C_4 hydrocarbon fraction, such as obtained in the stabilization of cracked naphtha, into a cut containing branched chain hydrocarbons and a cut containing straight chain hydrocarbons. The branched chain cut is subjected directly to alkylation, while the straight chain cut is subjected to polymerization to remove olefin constituents by polymerization. The unconverted hydrocarbons are further treated to remove remaining olefin constituents to produce a straight chain hydrocarbon cut consisting essentially of normal butane. This normal butane is then converted to isobutane and the resulting isobutane utilized for alkylation with the olefin hydrocarbons by contact with a suitable alkylation catalyst.

In accordance with the invention cracked naphtha is subjected to stabilization to remove propane and lighter constituents. The stabilized naphtha is then subjected to fractionation to remove a fraction comprising C_4 hydrocarbons, namely iso and normal butane, isobutylene and normal butylenes, including butylene-1 and butylene-2.

This C_4 hydrocarbon fraction is then subjected to further fractionation to separate it into a cut containing isobutane, isobutylene and butylene-1, and another cut containing normal butane and butylene-2. The branched chain cut contains butylene-1 since the boiling point of the latter is only slightly lower than that for isobutylene. This branched chain hydrocarbon cut is passed directly to an alkylation plant.

The straight chain hydrocarbon cut is subjected to polymerization so as to convert at least a substantial proportion of the butylene-2 to normally liquid hydrocarbons, which are subsequently removed as polymer gasoline. The remaining straight chain hydrocarbons, retaining some olefin hydrocarbons, are then subjected to extraction with concentrated sulphuric acid, advantageously a portion of the catalyst used in the alkylation plant, to absorb the retained olefin. The acid and absorbed hydrocarbons are then passed to the alkylation plant, while the remaining normal butane, substantially free from olefin, is subjected to isomerization. The resulting isobutane is then utilized in the alkylation plant for alkylating the olefin hydrocarbons to produce

normally liquid hydrocarbons of high anti-knock value.

The object of the invention is to effect alkylation of olefin hydrocarbons with isobutane in the substantial absence of straight chain hydrocarbons and particularly normal butane. Normal butane is unreactive in the alkylation reaction. Its presence in that reaction results in a substantial reduction in the yield of alkylated hydrocarbons and also causes substantial deterioration of the catalyst.

A further object of the invention is to segregate the normal butane contained in the hydrocarbon feed in a relatively pure form so that it may be effectively isomerized to isobutane without substantial deterioration of the isomerization catalyst. It has been found that in isomerizing normal butane by contact with aluminum chloride as a catalyst it is desirable to effect the isomerization reaction in the substantial absence of the olefin hydrocarbons. The olefin hydrocarbons tend to react with the catalyst to form complex compounds which, in themselves, are ineffective as catalysts, at least relatively so, and whose presence soon renders the metallic halide catalyst ineffective.

In order to describe the invention more fully reference will now be made to the accompanying drawing showing a diagram of flow suitable for carrying out the process.

As indicated in the drawing, a cracked naphtha, such as obtained in the cracking of gas oil or topped crude, is conducted from a source not shown through a pipe 1 to a stabilizer 2. The stabilization is effected under conditions of temperature and pressure adapted to remove propane and more volatile constituents, so as to produce a stabilized naphtha. The propane and lighter constituents are discharged through a pipe 3. The stabilized naphtha, comprising C_4 hydrocarbons and higher molecular weight hydrocarbons, are drawn off through the pipe 3A to a fractionator 4 wherein conditions are maintained so as to vaporize and remove from the stabilized naphtha a fraction comprising C_4 hydrocarbons, including saturated and unsaturated hydrocarbons both of branched chain and straight chain structure.

The resulting debutanized naphtha is withdrawn through a pipe 5 for such further treatment as may be desired.

The fraction comprising gaseous C_4 hydrocarbons is drawn off through a pipe 6 to a fractionator 7 wherein it is separated into a branched chain hydrocarbon cut containing isobutane, isobutyl-

ene and butylene-1, and a straight chain hydrocarbon cut containing normal butane and butylene-2.

The straight chain hydrocarbon cut is passed through a pipe 8 to a polymerization unit 9 wherein the hydrocarbons are subjected to contact with a polymerization catalyst, such as phosphoric acid, at a temperature of around 400° F. and under a pressure of around 750 pounds. The operation is advantageously effected in the liquid phase, although it is contemplated that the conditions of temperature and pressure may be varied as desired. The polymerization is carried out under conditions such that at least a substantial proportion of the butylene present in the feed mixture is converted to polymer suitable as a component of gasoline or motor fuel.

From the polymer unit the treated hydrocarbons pass through a pipe 10 to a stabilizer 11 wherein low boiling constituents, including normal butane and some olefins, are removed and discharged through a pipe 12. The stabilized polymer gasoline is discharged through a pipe 13 for such further treatment as may be deemed appropriate.

The hydrocarbons passing through the pipe 12 are conducted to an absorber 14. In the absorber 14 the hydrocarbons are subjected to contact with concentrated sulphuric acid. The acid may be fresh acid or used acid withdrawn from the alkylation stage of the process. The purpose of the absorption step is to selectively absorb olefin hydrocarbons associated with the normal butane passing from the stabilizer 11.

The acid containing absorbed olefins is withdrawn through a pipe 15 and passed to an alkylation plant 16.

The normal butane, now substantially free from olefin hydrocarbons, is passed from the upper portion of the absorber 14 through a pipe 17 to an isomerization unit 18. In the unit 18 the normal butane is subjected to contact with a catalyst comprising a metallic halide, such as aluminum chloride, in the presence of a small amount of hydrogen halide, such as hydrogen chloride. The isomerization is advantageously effected in the gas phase at a temperature of around 150 to 250° F. and, preferably, at around 210 to 220° F., with a time of contact of around 1 to 5 minutes. The hydrogen halide promoter is introduced to the reaction in the proportion of around 1 to 5% by weight of the butane charge.

Under these conditions around 50 to 55% by volume of the normal butane is converted to isobutane without substantial cracking and without substantial deterioration of the catalyst. Thus, the cracked products produced will not exceed around 3% by volume of the butane charge.

The resulting isobutane is conducted through a pipe 19 to the alkylation unit 16, previously mentioned.

The branched chain hydrocarbon cut containing isobutane, isobutylene and butylene-1, produced from the fractionator 7, is also passed through a pipe 20 to the alkylation unit 16. In the alkylation unit the olefin hydrocarbons are subjected to alkylation with the isobutane by contact with an alkylation catalyst, namely, sulphuric acid having a concentration in the range 90 to 100% H₂SO₄. The temperature of reaction is maintained in the range about 40 to 125° F. and preferably around 60 to 80° F., with a time

of reaction from about 10 to 90 minutes and preferably about 20 to 60 minutes.

The isobutane and olefin hydrocarbons are charged to the alkylation unit so as to maintain a substantial excess of isobutane, for example, a ratio of isobutane to olefins of between about 3:1 and 5:1 or over. Lower ratios may be employed but in excess of 1:1.

The resulting alkylated hydrocarbons are withdrawn through a pipe 21 for further processing as may be deemed necessary to render them suitable as merchantable gasoline.

As indicated, a stream of used or partially spent catalyst is withdrawn from the unit through a pipe 22 and passed to the previously mentioned absorber 14 for absorption of butylene-2 and the like from the hydrocarbons passing from the polymerization unit 9. The fresh concentrated acid may be introduced to the system through the pipe 22, as indicated, or, if desired, it may be introduced directly to the alkylation unit 16.

While concentrated sulphuric acid has been mentioned as a suitable alkylation catalyst, it is, of course, contemplated that other liquid alkylation catalysts may be employed, as, for example, a catalyst prepared by passing BF₃ into water to complete saturation, producing a complex having the formula BF₃·nH₂O, where n has a value ranging from about 1 to 1.5.

Obviously many modifications and variations of the invention, as hereinbefore set forth, may be made without departing from the spirit and scope thereof, and therefore only such limitations should be imposed as are indicated in the appended claims.

I claim:

1. A process for the manufacture of high anti-knock gasoline hydrocarbons from a hydrocarbon fraction containing mainly C₄ saturated and unsaturated hydrocarbons, which comprises fractionating said fraction into an iso C₄ cut containing isobutane, isobutylene and butylene-1, and a normal C₄ cut containing normal butane and butylene-2, passing said iso C₄ cut to an alkylation zone wherein it is subjected to contact with a liquid alkylation catalyst, subjecting the normal C₄ cut to polymerization such that butylene-2 is converted to polymer liquid, withdrawing the polymer liquid, subjecting the unconverted normal C₄ cut to contact with a stream of said alkylation catalyst in an absorption zone so that remaining butylene-2 is absorbed, removing the unabsorbed butane, passing the absorbed butylene-2 to said alkylation zone, and alkylating isobutane with said absorbed butylene-2 and olefins of said iso C₄ cut in said alkylation zone in the presence of said alkylation catalyst and in the substantial absence of normal butane such that substantial conversion to high anti-knock gasoline hydrocarbons is secured.

2. The method according to claim 1 in which the alkylation catalyst comprises concentrated sulphuric acid.

3. A process for the manufacture of high anti-knock gasoline hydrocarbons from a hydrocarbon fraction containing mainly C₄ saturated and unsaturated hydrocarbons, which comprises fractionating said fraction into an iso C₄ cut containing isobutane, isobutylene and butylene-1, and a normal C₄ cut containing normal butane and butylene-2, passing said iso C₄ cut to an alkylation zone wherein it is subjected to contact with a liquid alkylation catalyst, subjecting the normal C₄ cut to polymerization such that butyl-

ene-2 is converted to polymer liquid, withdrawing the polymer liquid, subjecting the unconverted normal C₄ cut to contact with a stream of said alkylation catalyst in an absorption zone so that remaining butylene-2 is absorbed, removing the unabsorbed normal butane, subjecting the removed butane to isomerization by contact with an isomerization catalyst in the substantial absence of olefins, passing the resulting isobutane and the absorbed butylene-2 to said alkylation zone, and subjecting the absorbed butylene-2 and the olefin hydrocarbons of said iso C₄ cut to reaction with isobutane by contact with said alkylation catalyst in said alkylation zone in the substantial absence of normal butane such that substantial conversion to high anti-knock gasoline hydrocarbons is secured.

4. A process for the manufacture of high anti-knock gasoline hydrocarbons from a hydrocarbon fraction containing mainly C₄ saturated and unsaturated hydrocarbons, which comprises fractionating said fraction into an iso C₄ cut containing isobutane, isobutylene and butylene-1, and a normal C₄ cut containing normal butane and butylene-2, passing said iso C₄ cut to an alkylation zone, subjecting the normal C₄ cut to polymerization such that butylene-2 is converted to polymer liquid, withdrawing the polymer liquid, subjecting the unconverted normal C₄ hydrocarbons to contact with a stream of concentrated sulphuric acid so that remaining butylene-2 is absorbed while normal butane remains unabsorbed, introducing the acid and absorbed butylene-2 to the alkylation zone, subjecting the unabsorbed normal butane to isomerization in the substantial absence of olefins so as to effect conversion to isobutane, passing the resulting isobutane to said alkylation zone, and subjecting the isobutane and the absorbed butylene-2 and the olefin hydrocarbons of said iso C₄ cut in said alkylation zone to reaction by contact with concentrated sulphuric acid in the substantial absence of normal butane such that substantial conversion to high anti-knock gasoline hydrocarbons is secured.

5. A process for the manufacture of high anti-knock gasoline hydrocarbons from a normally gaseous hydrocarbon fraction comprising C₄ olefins and paraffins of branched and straight chain structure, which comprises separating said fraction into a cut comprising branched chain hydrocarbons and a cut comprising straight chain hydrocarbons, subjecting the straight chain cut to polymerization so that olefin constituents are converted to normally liquid hydrocarbons, removing the converted hydrocarbons, extracting remaining olefins from said straight chain cut by absorption with concentrated sulphuric acid, removing the unabsorbed straight chain hydrocarbons consisting of normal butane and subjecting the absorbed hydrocarbons and the branched chain cut to alkylation by contact with concentrated sulphuric acid in the presence of excess isobutane and in the substantial absence of normal butane such that substantial conversion to high anti-knock gasoline hydrocarbons is secured.

6. The method according to claim 5 in which the removed unabsorbed normal butane is sub-

jected to isomerization in the substantial absence of olefins to produce isobutane and the resulting isobutane utilized in the alkylation reaction.

7. A process for the manufacture of high anti-knock gasoline hydrocarbons from a hydrocarbon fraction containing mainly C₄ saturated and unsaturated hydrocarbons which comprises fractionating said C₄ fraction into an iso C₄ cut containing isobutane, isobutylene and butylene-1 and a normal C₄ cut containing normal butane and butylene-2, passing the iso C₄ cut to an alkylation zone, subjecting said normal C₄ cut to separate treatment including contact with a polymerization catalyst to partially polymerize and remove butylene-2 as polymer liquid, and then contact with sulfuric acid to absorb and remove remaining butylene-2 in said cut and leave a purified normal butane, passing the acid and absorbed butylene to said alkylation zone, subjecting said purified normal butane to contact with an isomerization catalyst under isomerizing conditions and in the substantial absence of olefins thereby forming isobutane, passing the resulting isobutane to the alkylation zone and reacting the isobutane with the absorbed butylene-2 and the olefins of said iso C₄ cut in the presence of concentrated sulfuric acid in said alkylation zone and in the substantial absence of normal butane such that substantial conversion to high antiknock gasoline hydrocarbons is secured.

8. A process for the manufacture of high anti-knock gasoline hydrocarbons from a hydrocarbon fraction containing mainly C₄ saturated and unsaturated hydrocarbons, which comprises separating said hydrocarbon fraction into an iso C₄ cut containing isobutane, isobutylene and butylene-1, and a normal C₄ cut containing normal butane and butylene-2, subjecting said normal C₄ cut to catalytic polymerization to partially convert butylene-2 to polymer liquid, separating the polymer liquid from the remaining unconverted normal C₄ cut, subjecting said remaining unconverted normal C₄ cut to contact with an absorption liquid to absorb remaining butylene-2 therefrom, separating said absorbed butylene-2 from resulting unabsorbed normal butane, and alkylating a low-boiling isoparaffin with said absorbed butylene-2 in the presence of an alkylation catalyst and in the substantial absence of normal butane to produce gasoline hydrocarbons of high anti-knock value.

9. The method in accordance with claim 8, wherein the unabsorbed normal butane is subjected to catalytic isomerization in the substantial absence of olefins to thereby convert normal butane to isobutane, and resulting isobutane is employed as the low-boiling isoparaffin in the said alkylation step.

10. The method in accordance with claim 8, wherein the iso C₄ cut is also supplied to the said alkylation step, whereby isobutane of said iso C₄ cut is alkylated with the absorbed butylene-2 and the olefins of said iso C₄ cut.

11. The method in accordance with claim 8, wherein the said alkylation catalyst is a liquid, and the said liquid catalyst is employed as the absorption liquid in said absorption step.

LYNN R. STRAWN.