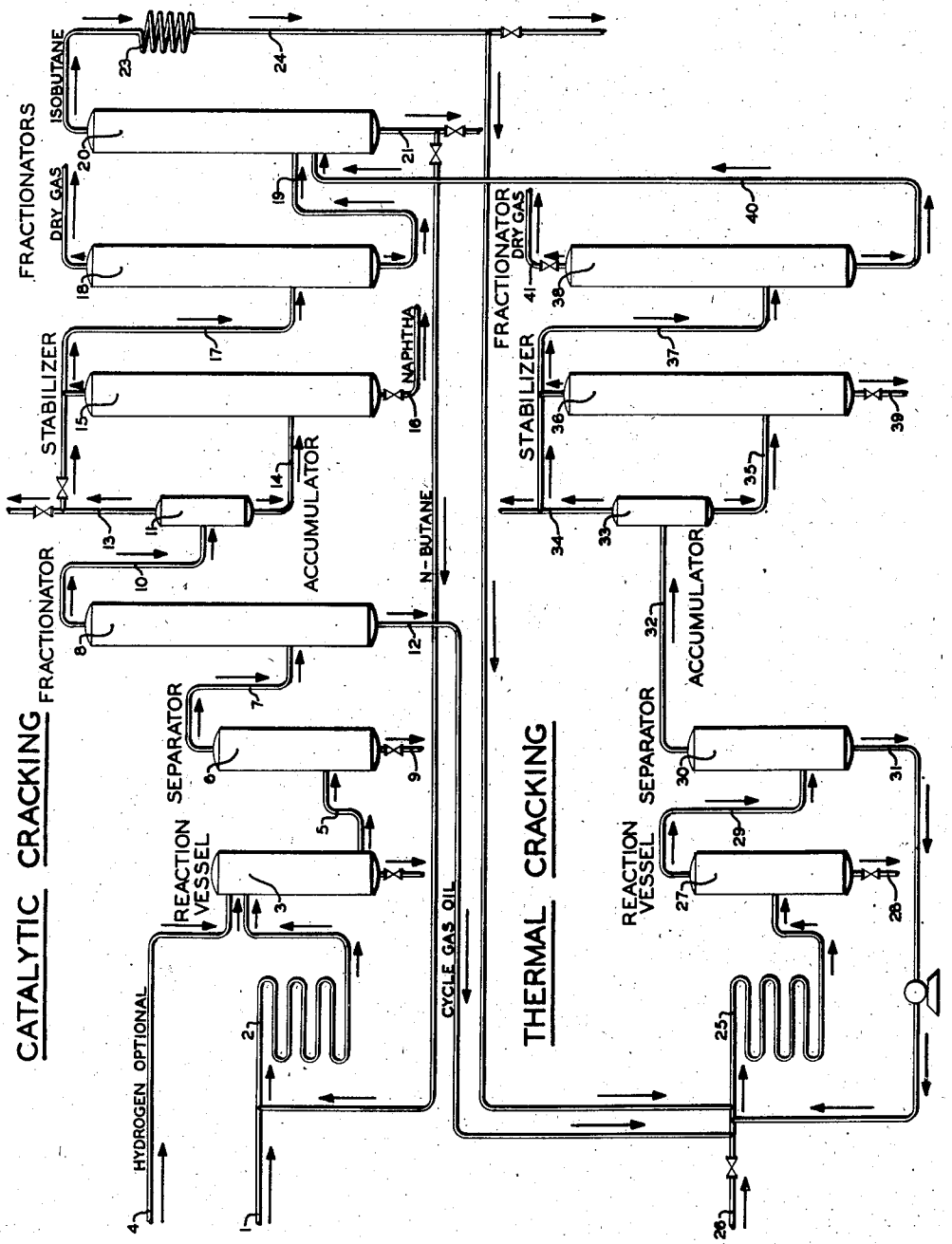
Dec. 10, 1940. LE ROY G. STORY 2,224,840

CONVERSION OF HYDROCARBON OILS

Filed July 24, 1939



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Patented Dec. 10, 1940 2,224,840

UNITED STATES PATENT OFFICE

2,224,840

CONVERSION OF HYDROCARBON OILS

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Application July 24, 1939, Serial No. 286,106

5 Claims. (Cl. 196—9)

This invention relates to the conversion of hydrocarbon oils and has to do particularly with a process of conversion for the production of gasoline hydrocarbons suitable in the manufacture of motor fuel.

Broadly, the invention contemplates a process of conversion wherein hydrocarbon oils are subjected to catalytic cracking such that the products of conversion contain a substantial amount of a low-boiling isoparaffin such as isobutane. The catalytically cracked oil is separated into a gas oil fraction and a naphtha fraction containing gasoline hydrocarbons, including isoparaffins. The gas oil fraction is subjected to thermal conversion in the presence of a low-boiling isoparaffin hydrocarbon such as isobutane separated from the naphtha produced in the catalytic conversion.

The products of thermal conversion are likewise fractionated to separate a naphtha fraction, comprising gasoline and lighter hydrocarbons, and a gas oil fraction, which may be recycled. The naphtha fraction is stabilized to remove low-boiling constituents which may include both normal and isoparaffin hydrocarbons. The low-boiling isoparaffin hydrocarbons are recycled through the thermal conversion operation, while the low-boiling normal paraffin hydrocarbons, as well as any unsaturated low-boiling hydrocarbons, are recycled to the catalytic conversion operation.

More specifically, the invention involves operating a catalytic cracking unit in conjunction with a thermal cracking unit wherein the isobutane produced from the catalytic unit is recycled to the thermal unit and the normal butane from the thermal unit is recycled to the catalytic unit. The gas oil produced from the catalytic unit forms all or a portion of the gas oil charge to the thermal unit.

The catalyst employed in the catalytic unit may be a metallic halide such as aluminum chloride, although other catalysts having a cracking and isomerizing effect may be used, including phosphoric acid, antimony and molybdenum sulfides, etc. The catalyst may be supported on an adsorptive solid such as activated alumina or silica, or acid treated clays. Hydrogen may also be used in the catalytic cracking step.

In the cracking of oil with a catalyst such as aluminum chloride there is a substantial amount of isobutane evolved, whereas in the conventional thermal cracking there is a considerable amount of normal butane and butylenes produced. The normal butane and the butylenes may be used to advantage in the catalytic cracking operation to obtain isomerization of the normal butane and polymerization of the butylenes. On the other hand, the isobutane is useful for injection into the thermal cracking operation.

As described in pending application Serial No. 274,514 filed May 19, 1939 relating to improvements in Conversion of hydrocarbon oils it has been found highly beneficial to inject a comparatively high proportion of isobutane in the oil which is undergoing thermal conversion. Moreover, it is desirable that the isobutane so injected be in a relatively concentrated form; that is, relatively free from normal butane and other gaseous hydrocarbons. When thermal cracking is carried out in the presence of isobutane in this manner substantially no coke or tar formation occurs. The reactions are not understood fully, but may include splitting of hydrogen from the isobutane and hydrogenation of the products which otherwise would tend to be converted into tar or coke. Substantial alkylation by the isobutane, or products thereof, may occur. It is also possible that the isobutane has a direct or indirect inhibiting effect on reactions tending to form tar and coke.

The beneficial effect of the presence of isobutane in thermal cracking is illustrated in the case of cracking an East Texas gas oil having a gravity of 34.6° A. P. I. and a boiling range of 454° F. to 704° F. In one instance a portion of this oil was cracked at a temperature of about 750° F. under a pressure of 4,150 pounds, with a ratio of isobutane to oil of about 6.7:1, the time of reaction being one hour. Under these conditions there was obtained about 31% of 410° F. end point stabilized gasoline, on the basis of the total stabilized liquid product, without any tar or coke formation.

In another instance, a portion of this same oil was cracked under the same conditions of temperature and time under a pressure of 2,350 pounds, but with an isobutane to oil ratio of only 4.5:1. Under these conditions the yield of 400° F. end point gasoline was only 10.6% and was accompanied with considerable tar and coke formation, indicating that the ratio of isobutane to oil was insufficient for this temperature.

Cracking the same oil under a temperature of 825° F. and a pressure of 6000 pounds with a ratio of isobutane to oil of 20:1 produced a 70% yield of 400° F. end point gasoline with no coke or tar formation.

The process is applicable to the cracking of various types of oils, either distillate or residual, as well as to the reforming of naphtha or certain constituents of naphtha.

The invention will be understood more fully

from the following description read in connection with the accompanying drawing, which shows a diagrammatic sketch of one arrangement of flow for carrying out the process of the invention.

Referring to the drawing, the oil to be cracked as, for example, a reduced crude, is charged through a line 1 to a heating coil 2 wherein it may be heated to a temperature ranging from around 400–750° F. while under a pressure ranging from atmospheric to about 100 pounds per square inch gauge.

The heated oil is passed to a reaction vessel 3 wherein it is brought into contact with a cracking catalyst such as aluminum chloride. If desired, hydrogen may be introduced to the reaction vessel through a pipe 4.

The products of conversion are removed from the reaction vessel 3 through a pipe 5 leading to a separator 6.

In the separator 6 gas oil and lower-boiling hydrocarbons are removed in vapor form through pipe 7 leading to a fractionator 8. High-boiling hydrocarbons of a tarry nature are drawn off from the bottom of the separator 6 through a pipe 9 and may be disposed of as desired.

In the fractionator 8 the gasoline hydrocarbons and gaseous constituents are separated as a vapor fraction which is drawn off through pipe 10 leading to an accumulator 11. The higher-boiling constituents comprising gas oil hydrocarbons are drawn off from the bottom of the fractionator through a pipe 12 leading to the thermal cracking unit, to which reference will be made later.

In the accumulator 11 gaseous constituents, including fixed gases and normally gaseous hydrocarbons, separate and are withdrawn through a pipe 13. The gasoline hydrocarbons are drawn off through a pipe 14 to a stabilizer 15 operated under suitable conditions of temperature and pressure to remove gaseous hydrocarbons, including C_4 hydrocarbons and lighter. The operation may be regulated so as to retain in the gasoline any desired proportion of the C_4 hydrocarbons in order to produce a fuel of the desired volatility and boiling point characteristics. The stabilized gasoline is drawn off through a pipe 16.

The gaseous hydrocarbons separated in the stabilizer 15 are removed overhead through a pipe 17 and these gases together with all or a portion of the gases removed from the accumulator 11 are introduced to a fractionator 18 for the purpose of recovering C_4 hydrocarbons, particularly normal butane and isobutane. This butane fraction is drawn off from the bottom of the fractionator 18 through a pipe 19 leading to another fractionator 20 wherein it is resolved into an isobutane fraction and a normal butane fraction. The normal butane fraction is drawn off in liquid form from the bottom of the fractionator 20 through a pipe 21 and returned, all or in part, to the pipe 1 leading to the heater 2 wherein the recycled butane and any butylenes associated therewith are mixed with feed hydrocarbons.

The isobutane fraction is removed overhead from the fractionator 20 through a condenser 23 and the condensate passed through a pipe 24 to the inlet of thermal cracking heater 25.

The gas oil fraction drawn off through pipe 12 from the fractionator 10, as previously described, is introduced to the inlet of the heater 25 along with the isobutane from the fractionator 20. If desired, additional fresh feed, including gas oil or isobutane or both, may be introduced through a pipe 26.

The mixture of hydrocarbons passing through the heater 25 is heated to a temperature which may range from about 650–1000° F. and under pressure which may range from 300–7000 pounds. Advantageously, the ratio of isobutane to oil passing through the heater 25 is maintained between about 2:1 and 50:1. The higher pressures and higher ratios of isobutane to oil are ordinarily associated with the higher temperatures, while the lower pressures and lower ratios of isobutane to oil are more suitable for the lower temperatures.

It is contemplated that the more common conditions will be pressures of about 2000–4000 pounds and temperatures of about 700–850° F. with ratios of isobutane to oil of between about 10:1 and 30:1.

The reaction time will vary with the temperature and may range between about two minutes and two hours and, preferably, between about twenty and forty-five minutes.

The heated hydrocarbons are discharged from the heater 25 into a reaction vessel 27 wherein they are subjected to cracking conditions for the desired length of time. The high-boiling tarry constituents formed in the reaction vessel are withdrawn from the reaction vessel through pipe 28. The lower-boiling cracked hydrocarbons are removed from the vessel 27 through a pipe 29 leading to a separator 30 wherein the gasoline and lighter constituents are separated from the higher-boiling gas oil constituents. The gas oil constituents are drawn off from the separator through a pipe 31 communicating with the inlet to the heater 25.

The vaporized gasoline and gaseous hydrocarbons are drawn off from the separator 30 through a pipe 32 leading to an accumulator 33. Gaseous constituents separating in the accumulator 33 are drawn off through a pipe 34, while the gasoline hydrocarbons are drawn off through a pipe 35 leading to a stabilizer 36.

Gaseous constituents, including all or a portion of the C_4 hydrocarbons, are removed from the gasoline in the stabilizer 36 and conducted through a pipe 37 leading to a fractionator 38. Gaseous constituents removed from the accumulator through pipe 34 also may be passed through pipe 37 leading to the fractionator 38.

The stabilized gasoline is drawn off from the bottom of the stabilizer through a pipe 39.

In the fractionator 38 gaseous constituents, commonly referred to as dry gas, are separated and discharged through the pipe 39 while a fraction comprising C_4 hydrocarbons is formed and drawn off through a pipe 40 leading to the previously described fractionator 20. In this way the C_4 fraction is resolved into normal butane and isobutane, which are separately recycled, as previously described.

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. In the conversion of hydrocarbon oil for production of motor fuel, the steps comprising subjecting the oil to catalytic cracking such that the products of conversion contain a substantial amount of C_4 hydrocarbons, including isobutane, separating the catalytically cracked oil into a catalytic gas oil fraction and a catalytic naphtha fraction, removing from said naphtha fraction

fractions respectively rich in normal and isobutane, recycling the normal butane fraction to the catalytic conversion step, and subjecting the catalytic gas oil fraction to thermal cracking in the presence of said isobutane fraction.

2. In the conversion of hydrocarbon oil for production of motor fuel, the steps comprising subjecting the oil to catalytic cracking such that the products of conversion contain a substantial amount of C_4 hydrocarbons, including isobutane, removing from the catalytically cracked oil a catalytic gas oil fraction and a catalytic naphtha fraction, removing from said naphtha fraction a fraction comprising C_4 hydrocarbons, subjecting said C_4 fraction to fractionation to produce an isobutane fraction and a fraction comprising normal butane, subjecting the catalytic gas oil fraction to thermal cracking in the presence of said isobutane fraction, removing from the thermally cracked oil a thermal gas oil fraction and a thermal naphtha fraction, separating C_4 hydrocarbons from said thermal naphtha fraction, subjecting said C_4 fraction to fractionation with the C_4 fraction produced in the catalytic cracking step and recycling the normal butane produced in said fractionation through the catalytic cracking step.

3. The method according to claim 2 in which the thermal gas oil fraction is recycled through the thermal cracking step.

4. The method according to claim 1 in which the thermal cracking is effected under superatmospheric pressure at a temperature in the range 650 to 1000° F., the ratio of isobutane to oil undergoing cracking being maintained between about 2:1 and 50:1.

5. The method according to claim 1 in which the catalytic cracking is effected in the presence of a catalyst comprising aluminum chloride.

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