July 11, 1944. J. NOORDUYN 2,353,490

CRACKING AND REFORMING OF HYDROCARBONS

Filed July 21, 1941 2 Sheets-Sheet 1

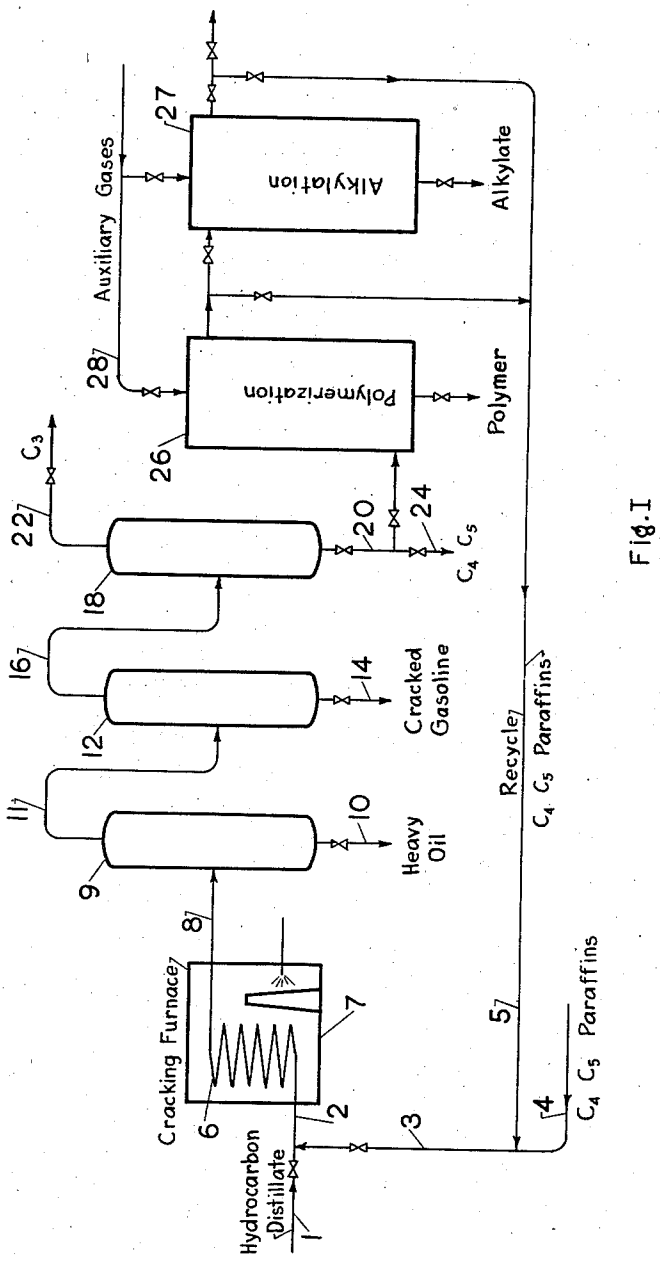


Fig. I

Inventor: Jan Noorduyn

By his Attorney: [signature]

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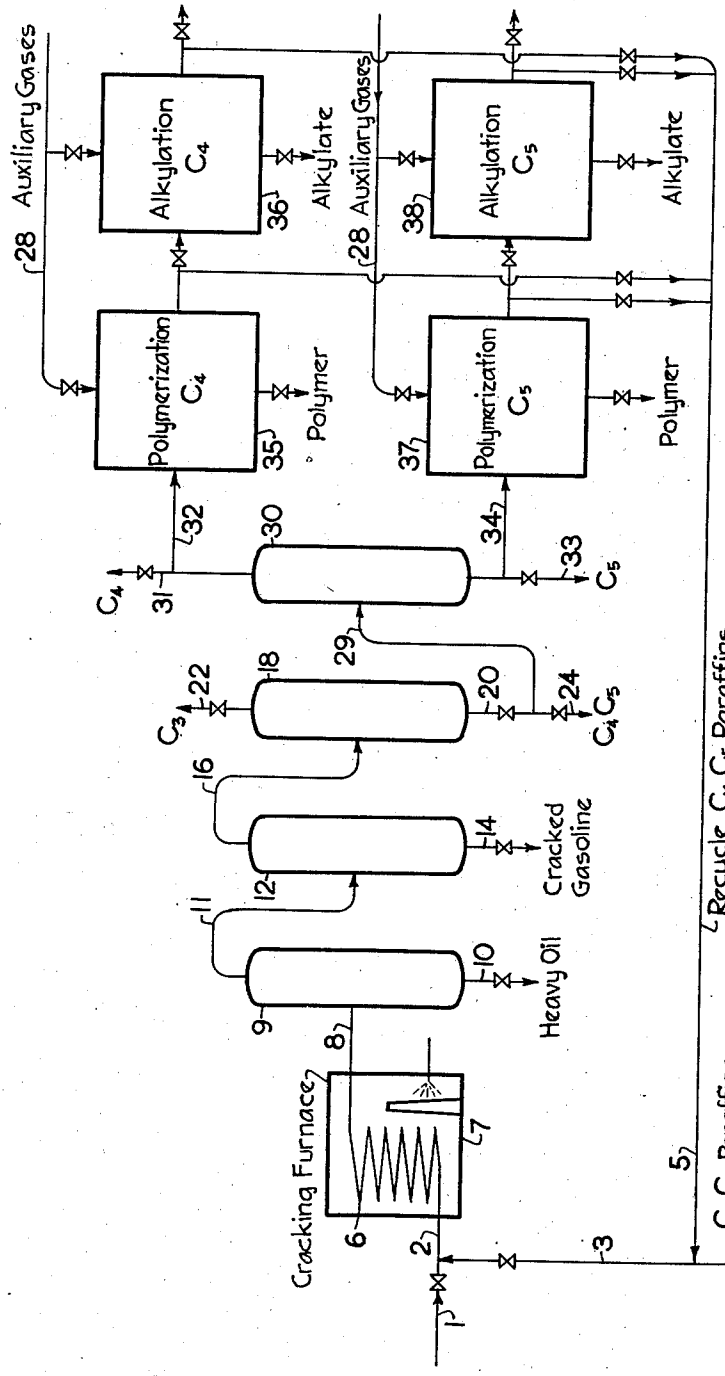


Fig. II

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2,353,490

CRACKING AND REFORMING OF HYDROCARBONS

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Application July 21, 1941, Serial No. 403,331

5 Claims. (Cl. 196—66)

This invention relates to the manufacture of motor fuels by cracking of hydrocarbon distillates and especially to the art of cracking low octane naphtha to produce an improved motor fuel of high anti-knock value.

It is well known that by subjecting naphthas of low octane rating to high temperatures and pressures the naphthas are cracked so that gasolines having higher octane numbers are produced. At the same time varying amounts of products having boiling points too high and too low to be incorporated in the gasolines are formed resulting in reduced yields of the improved gasolines.

It is also known that as the thermal treatment becomes more severe, i. e., the temperature, pressure, residence time or combinations thereof are increased, the octane number of the treated gasoline is, within limits; further improved and its yield further decreased. When a certain severity of the thermal treatment is reached, deposition of coke in the different parts of the cracking apparatus becomes so rapid that further useful operation is impossible.

It is known also that more severe cracking conditions can be maintained without objectionable coking by introducing into the cracking zone, together with the naphtha, gaseous hydrocarbons such as those having one to five carbon atoms in the molecule. In general, however, very large quantities, i. e., 100% or more, of these gases had to be used to obtain substantially improved operation, an expedient which very appreciably raised the cost of heating, compressing and pumping.

The object of this invention is to produce improved motor fuels by reforming or cracking hydrocarbon distillates or naphtha in the presence of certain added normally gaseous hydrocarbons. Other objects are to make use of the cracking in the presence of added hydrocarbon gases at reduced cost and to utilize certain less valuable hydrocarbon gases for this purpose. Further objects include the transformation of less valuable gases into more useful ones. Still further objects will be found in the improvements hereinafter disclosed.

This invention is based on the discovery that the addition of relatively small amounts of normal paraffinic hydrocarbons having four and five carbon atoms to a distillate oil or naphtha makes possible the practical application of an appreciable increase in the severity of cracking conditions and that at the same time these light hydrocarbons are transformed into others which are more useful.

According to this invention, a relatively heavy feed, i. e., a hydrocarbon distillate oil, is commingled with about 10% to 30% or more of a lighter feed comprising predominantly paraffin hydrocarbons having four and five carbon atoms in the molecule and preferably consisting essentially of normal butane and normal pentane.

The commingled hydrocarbons are then subjected to heat and pressure to result in cracking, and the treated hydrocarbons are separated into heavier-than-gasoline products, gasoline and lighter products. The heavy part is withdrawn and may be utilized to suit convenience. The gasoline has improved anti-knock properties and may be treated, blended and utilized in any conventional manner. The lighter-than-gasoline products may also be withdrawn and utilized conventionally, but it is more advantageous to separate the butanes and pentanes, and preferably the normal butane and pentane, therefrom and to use them alone or in admixture with other C_4 and C_5 paraffin hydrocarbons for the above-mentioned light feed, while remaining olefines and other gases may be put to any desirable useful purpose.

The preferred way of producing these butanes and pentanes is to separate from the cracked product a fraction comprising predominantly hydrocarbons of four and five carbon atoms in the molecule and subject it to polymerizing and alkylating conditions so as to produce unsaturated gasoline by polymerization of the olefines and saturated gasoline by alkylating isoparaffins with olefines. Simultaneously, the normal paraffins are prepared for the light feed to be used in the above cracking operation.

The term "cracking" as herein used is meant to cover thermal non-catalytic reactions resulting in carbon-carbon scission or dehydrogenation, or both, and thus includes "reforming." In this process the conditions of temperature, time and pressure depend on the exact result desired. In general, it is possible to, and I do, maintain conditions more severe than those maintainable without rapid coking if the heavier distillate were charged alone, as a result of which a greater increase in octane number can be secured than is normally possible.

The hydrocarbon distillate which is the heavy feed of this process may be any gasoline, naphtha, gas oil, etc., or a fraction thereof, boiling within the range of about 100° F. to 800° F. This feed is preferably free from gum-forming constituents which would tend to form deleterious tars.

Straight run distillates, especially from paraffinic crudes, are very suitable.

When it is desired to further improve the octane numbers of cracked distillates, it is preferable to remove highly unstable components formed incidentally during the cracking operations, such as those generally known as gum-forming compounds, e. g., diolefines, certain branched and other highly reactive olefines, styrene, etc., because they are most prone to form tars. Nitrogen, sulfur and oxygen derivatives of hydrocarbons such as nitrogen bases, amines, phenols, naphthenic acids, mercaptans, sulfonic acids, etc., which are often found in cracked distillates may also favor deleterious coke formation, if present in excessive amounts. These objectionable hydrocarbons and derivatives may be removed satisfactorily in most cases by conventional methods such as by extraction with a liquid having greater solvent power for unsaturated than for saturated hydrocarbons, for example, liquid SO_2, nitrobenzene, methyl acetate, phenyl acetate, methyl or ethyl cellosolve, furfural, acetone, aniline, cresylic acids, dichlorethyl ether, SO_2-benzene mixtures, etc., or by a combination of solvent and anti-solvent such as phenol or cresol with propane, etc.; by treatment with adsorption agents such as clay, bauxite, fuller's earth, diatomaceous earth, silica gel, etc., preferably at elevated temperatures below incipient cracking; by sulfuric acid or phosphoric acid treatment at suitable concentrations to produce a sludge containing the undesirable constituents which can be separated; etc.

If desired, suitable selected distillates formed within the process may be recycled to the cracking zone to form part of the heavier feed. This may be especially useful if a substantial proportion of the heavy feed introduced into the system boils above the gasoline boiling range, and after cracking gives a middle oil distillate heavier than gasoline. The recycle oil, like the cracked naphtha, may be treated to remove coke-forming substances as described. Recycle oils of high aromatic contents but low olefine contents frequently aid in reducing coke deposition by virtue of their solvent power for tars before they are converted to coke.

The light feed normally constitutes between 10% and 30%, as already stated, and preferably 15% to 25% of the total feed. This light feed comprises predominantly butanes and pentanes, preferably normal butane and normal pentane, and may contain substantial amounts of hexanes, preferably normal hexane. It is desirable that it be substantially free from olefines. A preferred composition is one containing less than 5% olefines, over 50% of normal pentane and over 35% of normal butane, the remainder being predominantly hexane.

The following considerations serve to explain some of the factors which are believed to contribute to the success of this process.

Objectionable deposition of coke in cracking coils and other parts of the apparatus is probably due to formation of heavy aromatic and tarry materials during cracking, which materials readily separate from the heated hydrocarbons, especially in the skin layer which exists along heating surfaces. As a result these tarry materials deposit on the heating walls where they stick and progressively are transformed into coke.

It is generally believed that the harmful coke-forming tars are produced from the initial feed by recurring cracking or dehydrogenation, and polymerization. Lower olefines, particularly the branched ones, undergo these reactions much more rapidly than corresponding paraffins, and by eliminating them from the feeds and especially from the light feed, the tendency to form tars and coke within the time required to raise the octane number of the cracked gasoline to a certain predetermined level is greatly diminished.

It is already known that the tendency for tars (once they are formed) to deposit from a hydrocarbon mixture under cracking conditions can be lowered by adding thereto normally gaseous hydrocarbons at elevated pressures. I have found that C_4 and C_5 hydrocarbons are particularly valuable from this point of view, as apparently under the conditions maintained they are effective in much lower concentrations than the still lower hydrocarbons. It is for this reason that a material increase in the severity of cracking conditions above the normal limits can successfully be maintained in the presence of relatively small amounts only of the preferred light feed. While, if desired, amounts in excess of about 30% of the total feed may be introduced, the excess of the light feed above about 30% has little, if any, additional beneficial effect on the octane number improvement, while the cost of the treatment increases more nearly proportionally with increases in the amounts of the added light feed.

The normal saturated hydrocarbons which comprise the light feed are of relatively little value in the manufacture of polymer and alkylation gasoline as they are too unreactive. However, when they are subjected, together with gasoline, to the intense cracking conditions of my process, part of them at least undergo transformations such as isomerization, dehydrogenation, cracking, and possibly polymerization, etc., so that more valuable hydrocarbon gases are produced. C_3 and lighter paraffin hydrocarbons, being more stable thermally, do not undergo transformations as useful under the same conditions.

As indicated above, the cracked gases resulting from this process, being rich is reactive components, are subjected to polymerization or alkylation, or both. If desired, the polymerization of olefines and alkylation of olefines with isoparaffins can be achieved as part of the thermal reaction taking place during cracking by including them in the light feed. In general, however, this is not very desirable as it involves less controllable and less efficient reactions than the separate polymerization and alkylation of selected fractions, particularly when employing moderate temperatures below cracking in conjunction with catalysts. Moreover, as pointed out, the introduction of olefines into the cracking zone as part of the light feed is liable to defeat in part at least the very purpose of this invention because they are prone to speed up coke formation. Furthermore, separate alkylation and polymerization processes result in an efficient separation of olefines and isoparaffins from the normal paraffins and thus furnish the preferred light feed of this process.

The process of this invention is illustrated in the accompanying drawings which represent specified flow diagrams of two alternative forms of this process. Figure I discloses the combined polymerization and alklation of the C_4 and C_5 cut. Figure II shows the separate polymerization and alkylation of the C_4 and C_5 cut.

In Figure 1, a suitable relatively heavy feed, i. e., a hydrocarbon distillate from a source not

shown, and a lighter feed having a composition as hereinbefore defined are introduced through conduits 1 and 3, respectively, into pipe 2.

The light feed may comprise predominantly gases produced within the process, as will be described later, admitted through conduit 5, or, if desired, gases from an outside source not shown (such as a stabilizer for straight run gasoline) introduced through line 4, or both. If the light feed contains substantial amount of C_3 and lighter components, it may be advantageous to scrub it with the heavier feed under conditions to absorb in the latter mainly the pentanes and the butanes, thereby producing the desired mixed feed, or else the light and heavy feeds may simply be mixed and compressed by conventional means not shown.

The mixed feed in conduit 2 proceeds to cracking coils 6 in furnace 7 in which the desired conditions of temperature, time and pressure are maintained to effect the cracking. Depending upon the compositions and the proportions of the heavy and light feeds, suitable temperatures and pressures may vary between about 950° F. and 1100° F. at 500 to 2000 pounds, and preferably between 1000° F. to 1050° F. at 800 to 1200 pounds. These temperatures refer to exit temperatures, while the pressures refer to pressures at the entrance of coils 6. The time of cracking may be controlled with the aid of a reaction chamber, not shown.

The heat-treated hydrocarbons now pass by way of conduit 8 to fractionator 9 wherein they are separated into the different fractions in the usual way, i. e., tar and heavy distillates boiling above the motor fuel range which are withdrawn through line 10 and a lighter fraction including motor fuel which is taken overhead through line 11.

The overhead products from fractionator 9 are further separated in fractionator 12 to which line 11 leads. The bottom product which is a cracked naphtha or gasoline distillate containing hydrocarbons of six or more carbon atoms is withdrawn through line 14, while the gas fraction withdrawn through line 16 contains the C_5 hydrocarbons and lighter components.

The C_5 and lighter fraction is further separated in fractionator 18 to produce a light gaseous fraction composed essentially of C_3 and lighter components, e. g., hydrogen, methane, ethane, ethylene, propane and propylene, which is taken overhead through line 22, and a bottom fraction comprising predominantly hydrocarbons having four or five carbon atoms, which is withdrawn through line 20.

The C_3 and lighter fraction is withdrawn from the process and may be utilized in any desired manner not shown.

The C_4—C_5 fraction may, if desired, be eliminated from the process through line 24 provided a suitable light feed is introduced into the system in sufficient amounts from an outside source, not shown, through line 4. However, it is preferred to proceed as follows:

The C_4—C_5 fraction from fractionator 18 enters a polymerization plant 26 through line 20 where it is subjected to polymerizing conditions in the presence of a polymerization catalyst, for example, to a temperature of about 440° F. to 500° F. and a pressure of about 500 to 1000 pounds p. s. i. over a solid phosphoric acid catalyst. Preferably, the polymerization is regulated so as to predominantly polymerize iso-olefines, leaving normal olefines substantially unchanged. The resulting hydrocarbons are fractionated to separate the polymer gasoline which is withdrawn.

Remaining gases are than further treated in an alkylation plant 27 to react the normal olefines with isoparaffins, for example, in the presence of concentrated sulfuric acid under alkylating conditions, thereby producing a high octane number saturated gasoline which is separated from the gases unaffected by the reaction and withdrawn. Normally, the isoparaffin content of this gas is insufficient to alkylate all of the olefines present and therefore isobutane may have to be admitted to the alkylation plant through line 28 from a source not shown. Moreover, as is well known, the best alkylating conditions require in the reaction zone the presence of a large excess of the isoparaffins over the olefines, and after completed reaction this excess is separated from the residue gases and is returned to the alkylation process.

In a variation of this process which may sometimes be preferred, the polymerization is conducted more thoroughly so as to polymerize substantially all of the olefines. In this case the alkylation plant is by-passed.

Instead of polymerizing, or polymerizing and alkylating, the C_4—C_5 fraction as described, I may first fractionate it to produce a fraction consisting predominantly of C_4 and another of C_5 hydrocarcarbons, respectively, which fractions may be processed separately by the above methods, as shown in Figure II.

Cracking furnace 7 and fractionating columns 9, 12 and 18 are exactly the same in Figure II as in Figure I. The difference lies in the addition of column 30 for the separation of the C_4—C_5 fraction withdrawn from the bottom of column 18 through line 20. This fraction is conducted through line 29 into the column 30 and the C_4 fraction is withdrawn from the top of this column through line 31 or 32, and the C_5 fraction is withdrawn from the bottom of this column through line 33 or 34. The C_4 fraction from the fractionator 30 enters the polymerization plant 35 through line 32, where it is subjected to polymerizing conditions in the presence of a polymerization catalyst, as previously described, and similarly the C_5 fraction from fractionator 30 enters the separate polymerization plant 37 through line 34, where it is subjected to polymerizing conditions in the presence of a polymerization catalyst. The advantage of separating the C_4 from the C_5 fraction for separate polymerization is that different polymerizing treatments may be employed so as to obtain the highest yield of desired products from each.

Remaining gases may then be further treated in alkylation plants 36 and 38 respectively, to react the normal olefins with isoparaffins, for example in the presence of concentrated sulfuric acid, under alkylating conditions, thereby producing a high octane number saturated gasoline, which is separated from the gases unaffected by the reaction and withdrawn.

Furthermore, isopentane being itself a valuable component of motor fuels, I may recover it from the pentane fraction and blend it with gasoline. In this case, isobutane from an outside source may be used for alkylating the normal pentenes.

Residual gases from the above separations usually consist mainly of normal pentane and normal butane. They are returnd to the cracking operation through line 5.

Various auxiliary gases which may be needed in the polymerization and/or alkylation reactions, e. g., steam, isoparaffins, etc., may be introduced into the system through line 28.

Methods other than those described may be used for eliminating olefines or isoparaffins, or both, from the C_4—C_5 fraction while leaving the normal paraffins unchanged. Such methods, which are well known, include polymerization with different catalysts such as listed, for example, in National Petroleum News of November 20, 1935, page 45 and following, U. S. Patent 2,171,207, and other references; alkylation of aromatic or isoparaffinic hydrocarbons by olefines in the presence of similar catalysts; hydration of olefines to alcohols in the presence of acids, or their oxidation in the presence of metal catalysts as silver, or their halogenation, hydrohalogenation, etc.

The following data from plant scale operation further illustrate my invention:

Straight run Venezuelan naphtha was cracked under conditions close to coking alone and then in the presence of a light feed. The following table gives comparative results and shows that while the yields of cracked gasoline have been diminished, its octane number is raised and the amount of high grade polymer and alkylate gasoline available is increased.

	Conventional cracking	Improved cracking of invention
Percent light feed on intake	0	19.9
Percent C_5 in light feed on intake	0	10.73
Percent C_4 in light feed on intake	0	6.52
Cracking coil outlet temperature, °F.	1,013	1,049
Cracking coil inlet pressure, pounds	900	900
Percent yield on naphtha intake:		
Cracked gasoline	67.7	59.2
n-C_4 and n-C_5 paraffins	3.3	14.2
Polymer gasoline available from iso-C_4 olefines	2.8	4.8
Alkylate gasoline available from remaining C_3-C_4-C_5 olefines	14.7	32.4
Octane number of cracked gasoline	76.4	79.0
Average octane number of polymer and alkylate gasolines	90	90
Total yield of gasoline	85.2	96.4
Octane yield [1]	6,750	8,020

[1] Octane yield = sum of products of octane numbers $\times$ % yields of the several gasolines.

I claim as my invention:

1. In the process of cracking hydrocarbon distillates, the improvement comprising commingling said distillates with a light feed to produce a mixture, said light feed constituting between about 10 and 30% of said mixture, consisting essentially of normal butanes and normal pentanes, and produced at least in part of said process, subjecting said mixture to non-catalytic cracking in a cracking zone at a temperature between about 950 and 1100° F. and a pressure between about 500 and 2,000 pounds p. s. i., fractionating the resulting cracked products to obtain at least two fractions, a gasoline distillate and a lighter fraction consisting essentially of hydrocarbons of four and five carbon atoms and containing olefines and isoparaffins, treating said lighter fraction to convert said olefines and isoparaffins to higher boiling products, separating said products from residual gases, and returning at least a part of the latter to said cracking zone.

2. In the process of cracking hydrocarbon distillates, the improvement comprising commingling said distillates with a light feed to produce a mixture, said light feed constituting between about 10 and 30% of said mixture, consisting essentially of normal butanes and normal pentanes, and produced at least in part in said process, subjecting said mixture to non-catalytic cracking in a cracking zone at a temperature between about 950 and 1100° F. and a pressure between about 500 and 2,000 pounds p. s. i., fractionating the resulting cracked products to obtain at least two fractions, a gasoline distillate and a lighter fraction consisting essentially of hydrocarbons of four and five carbon atoms and containing olefines and isoparaffins, subjecting said lighter fraction to polymerizing and alkylating conditions to convert said olefines and isoparaffins to higher boiling products, separating said products from the residual gases, and returning at least a part of the latter to said cracking zone.

3. In the process of cracking hydrocarbon distillates, the improvement comprising commingling said distillates with a light feed to produce a mixture, said light feed constituting between about 10 and 30% of said mixture, consisting essentially of normal butanes and normal pentanes, and produced at least in part in said process, subjecting said mixture to non-catalytic cracking in a cracking zone at a temperature between about 950 and 1100° F. and a pressure between about 500 and 2,000 pounds p. s. i., fractionating the resulting cracked products to obtain at least two fractions, a gasoline distillate and a lighter fraction consisting essentially of hydrocarbons of four and five carbon atoms and containing olefines and isoparaffins, subjecting said lighter fraction to polymerizing conditions in the presence of solid phosphoric acid catalysts and to alkylating conditions in the presence of sulfuric acid to convert the major part of said olefines and isoparaffins to motor fuels, separating said motor fuels from residual gases, and returning at least a part of the latter to said cracking zone.

4. In the process of cracking hydrocarbon distillates, the improvement comprising commingling said distillates with a light feed to produce a mixture, said light feed constituting between about 10 and 30% of said mixture, consisting essentially of normal butanes and normal pentanes, and produced at least in part in said process, subjecting said mixture to non-catalytic cracking in a cracking zone at a temperature between about 950 and 1100° F. and a pressure between about 500 and 2,000 pounds p. s. i., fractionating the resulting cracked product to obtain at least three fractions, a gasoline distillate and two lighter fractions, one consisting essentially of hydrocarbons of four carbon atoms and the other of hydrocarbons of five carbon atoms, both containing olefines and isoparaffins, treating said latter fractions to convert said olefines and isoparaffins to higher boiling products, separating said products from residual gases, and returning at least a portion of the latter to the said cracking zone.

5. In the process of cracking hydrocarbon distillates, the improvement comprising commingling said distillates with a light feed to produce a mixture, said light feed constituting between about 10 and 30% of said mixture, consisting essentially of normal butanes and normal pentanes, and produced at least in part in said process, subjecting said mixture to non-catalytic cracking in a cracking zone at a temperature between about 950 and 1100° F. and a pressure between about 500 and 2,000 pounds p. s. i., fractionating the resulting cracked product to obtain at least three fractions, a gasoline distillate and two lighter fractions, one consisting essentially of

hydrocarbons of four carbon atoms and the other of hydrocarbons of five carbon atoms, both containing olefines and isoparaffins; treating the C_4 lighter fractions to convert the olefines and isoparaffins contained therein to higher boiling products and separating said products from residual gases; treating the C_5 lighter fractions to convert the olefines contained therein to higher boiling products, separating said products and subjecting the remainder of said C_5 fraction to fractional distillation to separate isopentane from residual gases; and returning part at least of the residual gases so obtained from said lighter fractions to said cracking zone.

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