

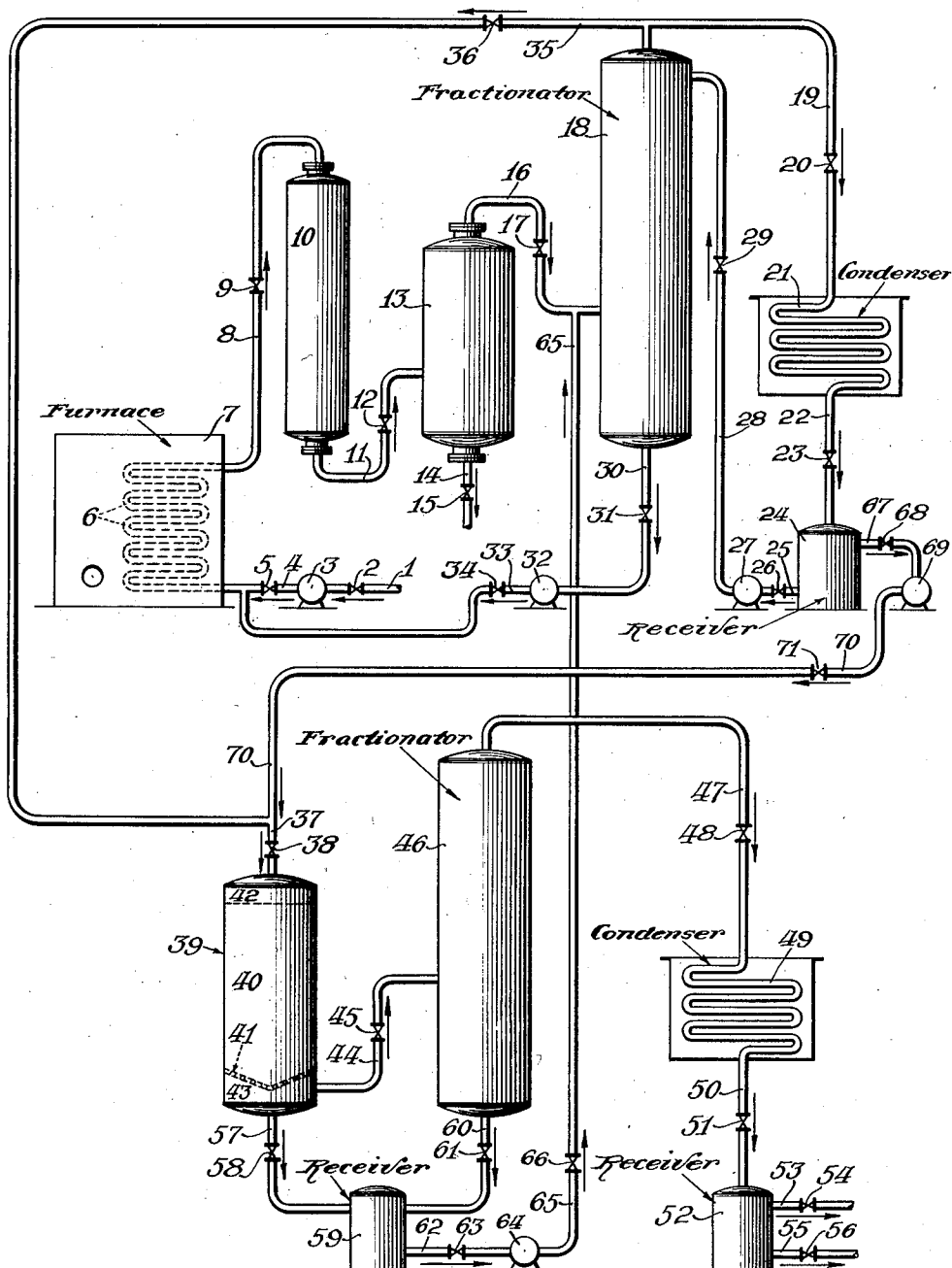
Dec. 15, 1936.

V. IPATIEFF

2,063,933

CONVERSION OF HYDROCARBON OIL

Filed Dec. 28, 1933



Inventor:
Vladimir Ipatieff,
By: *Lee J. Gary*
Attorney

UNITED STATES PATENT OFFICE

2,063,933

CONVERSION OF HYDROCARBON OIL

Vladimir Ipatieff, Chicago, Ill., assignor to Universal Oil Products Company, Chicago, Ill., a corporation of Delaware

Application December 28, 1933, Serial No. 704,220

1 Claim. (Cl. 196—36)

This invention relates more particularly to the conversion of heavy hydrocarbons such as the heavier and less valuable distillate and residual portions of petroleum into low boiling distillates suitable for use as motor fuel.

In a more specific sense the invention has reference to a process which employs pyrolytic decomposition processes in operative conjunction with catalytic polymerization in such a way that the overall yield and quality of gasoline is better than that currently obtained in contemporaneous cracking processes.

As a result of numerous experiments and researches, the mechanism of the cracking reaction involving the conversion of heavy molecules into lighter is fairly well understood at the present time. The primary reactions of decomposition involve loss of hydrogen, splitting of chain compounds into equimolecular portions of olefins and paraffins and the release of side chains from cyclic hydrocarbons. In the secondary reactions which follow if sufficient time factor is permitted at the cracking temperature, polymerization and recombination reactions take place resulting in the formation of cyclic compounds from olefins and other reactions not entirely understood.

The object of the majority of commercial cracking processes is to produce maximum quantities of motor fuel of gasoline boiling range having sufficient antidetonating quality to meet present day requirements. In such cases a compromise must be effected between yield and quality of gasoline from an anti-knock standpoint since the anti-knock value corresponding to maximum yield is not the highest obtainable but usually corresponds to a high gas loss and the formation of heavy liquid residue or coke. It is with improvements in this balancing process between yield and quality that the present invention is concerned.

In one specific embodiment the present invention comprises cracking hydrocarbon oils at elevated temperatures and pressures, fractionating the resultant products to produce a mixture of fixed gases and overhead vapors of approximate gasoline boiling range, subjecting said gas-vapor mixture to the action of composite solid catalysts comprising phosphoric acid and finally recovering gasoline as an overhead product.

The process as thus briefly outlined exerts a control upon the cracking step in that the lighter olefinic portions of the cracked products are controllably repolymerized to liquids boiling within the range of gasoline, thus increasing the overall yield from the process, while the products of gasoline boiling range resulting from the cracking

step are simultaneously treated to improve their quality.

Obviously, the aforementioned combination of steps may be conducted in interconnected cracking and catalytic apparatuses which are of different types and which bear different relationships to each other in regard to special design and capacity. To thoroughly and accurately describe the nature of the process, use will be made of the attached drawing which shows the essential details of a combination cracking and polymerizing plant though the invention is not limited to the particular modifications shown. The elements of the plant are shown in side elevation by the use of conventional figures and the drawing is not to scale.

Heavy oils to be cracked may be supplied to the plant through a line 1, containing control valve 2, and pumped by a pump 3 through a line 4, containing a control valve 5, into and through a tubular heating element 6 disposed to receive heat from a furnace setting 7. The severity of conditions embodied in a heating step in regard to temperature and pressure will depend upon the physical and chemical character of the charging oil and the benefit derived from utilizing the secondary catalytic polymerizing step so that only broad ranges can be laid down for general use. Present day cracking plants are commonly designed to operate at temperatures of approximately 850 to 1,000° F. and pressures of 100 to 500 pounds per square inch or higher. Any combination of temperature and pressure within these approximate limits may therefore be employed at the exit of heating element 6.

The heated and partially cracked products are then passed through a line 8, containing a control valve 9, and may pass through an unheated vaporizing or reaction chamber 10 having sufficient capacity to permit the substantial completion of conversion reactions at any desired point. The pressure in the reaction chamber may be substantially the same as that obtaining at the exit of the heating element or may be reduced if desired.

The cracked products then pass through a line 11, containing control valve 12, and enter a vaporizer 13 which operates preferably at a reduced pressure, usually in the neighborhood of 50 to 100 pounds per square inch, the function of this element being to effect a rough separation of the residual heavy tars which have little or no value as stock for further cracking, these

tars being quickly removed through line 14, containing control valve 15, to prevent their coking.

The vapors from vaporizer 13 pass through a line 16, containing control valve 17, and enter a fractionator 18 which is preferably operated to produce vapors of approximate gasoline boiling range and bottom refluxes of a character suitable for further conversion in the heating element. To control the boiling range of the emergent vapors a portion thereof may be recovered for recirculating purposes in auxiliary equipment to avoid bringing back treated material.

Thus, a portion of the fractionated gasoline boiling range vapors may pass through a line 19, containing control valve 20, and be condensed during passage through a condenser 21, flowing therefrom through line 22, containing control valve 23 to a receiver 24. The liquid accumulating in this receiver is then recirculated by way of line 25, valve 26, recirculating pump 27, line 28 and valve 29 to the top plate of the fractionator. The disposal of gases accumulating in the receiver at this point will be described later.

The main body of gases and vapors to be subjected to the secondary catalytic polymerizing and treating step pass through line 35, containing control valve 36, and line 37, containing control valve 38, to enter the catalytic treater 39 which contains a stationary catalytic body 40 supported upon a perforated false bottom 41 and dividing the treater into upper and lower vapor spaces 42 and 43, respectively.

The catalytic materials which may be employed as filler in treater 39 are of a peculiar nature and merit special description. The reactive constituent of such solid materials is phosphoric acid which may comprise ortho, pyro or meta phosphoric acids singly or in combination.

The spacing or carrying materials which may be employed in connection with these acids may be divided roughly into three general classes:

1. Siliceous or aluminous materials of an active character which exert a variable promoting action as a component of the catalytic mass. This class includes such materials as activated alumina, the mineral bauxite, fuller's earth, bentonite and other selected clays, kieselguhr or infusorial earth, tonsil and some artificially prepared forms of silica (such as Sil-o-Cel) or aluminum silicates. The influence of different materials of this character on the activity of the total catalyst mixture will depend upon their individual characteristics and their physical condition, particularly in regard to porosity, and each substance will exert its own individual effect when employed alternatively, which is not exactly equivalent to the other materials which may be employed.

2. Materials of an essentially siliceous character which have substantially no catalytic or promoting action but which function principally as carriers and in strengthening the catalyst structure. This class includes such materials as fire clays, silica fragments of varying fineness, pumice, et cetera, which may be used alternatively depending upon which is at hand in greatest quantity. These materials have substantially no reactivity with phosphoric acid and consequently do not yield phosphates.

3. Organic materials which yield some type of carbonaceous residue on heating. This class includes such materials as cellulose, starches, sugars, glue, gelatin, flour, molasses, agar-agar, et cetera. They evidently function as binders in

increasing the strength and resistance to disintegration of the contact masses in service.

In catalyst mixtures of the simplest character as comprised within the scope of the present invention, a phosphoric acid, usually ordinary orthophosphoric acid (H_3PO_4) is mixed in suitable proportions with an inert carrier such as kieselguhr and the mass is heated to some optimum temperature, usually within the range of 180 to 220° C. to drive out water and produce a solid mass which can be ground and sized to produce graded particles to act as filler in the catalyst tube or tower.

When carbonaceous materials are used in the initial mixtures somewhat higher temperatures may be employed to decompose them. Good results have been obtained at 300° C. and in some instances it would appear that too high temperatures above this point have deleterious effect. The exact maximum temperature employed in the ignition step will be to some extent a matter of trial.

The oxides which may be employed comprise those of the alkaline earth metals, calcium, barium, strontium, and magnesium and also zinc oxide. In the ignition step a considerable percentage of these oxides may be converted to phosphates by the action of the phosphoric acid, thus partially neutralizing the acid and rendering the contact masses less corrosive without apparently reducing their treating efficiency.

The chlorides of the base elements disclosed in the preceding paragraph may also be employed to advantage in the original mixtures from which the catalyst masses are produced by controlled heating. The chlorides are decomposed to some extent by the stronger acid and apparently the evolution of hydrochloric acid functions to increase the porosity of the masses. The extent of this action is variable and it merely acts in conjunction with the other materials to produce a solid catalyst of the desired physical structure.

Catalysts of the present character are hygroscopic to a variable extent and are best ground, sized and preserved for use out of contact with moist air.

Owing to the possibilities of varying the ingredients which go to form the catalyst masses, a number of alternatives exist, each of which will have its own peculiar catalyzing and polymerizing effect which will not be exactly equivalent to that of masses of different composition.

As the mixture of gases and vapors passes through solid catalysts of the above general character, olefins are polymerized, pronounced effects being noticeable among the gaseous olefins of 3, 4, and 5 carbon atoms including propylene, alpha and beta butene, isobutylene and the various isomeric amylenees. These compounds under suitably chosen conditions in regard to efficiency of catalyst, temperature, pressure and rate of treatment, may be made to polymerize principally to dimers and trimers rather than to heavier polymers so that they are converted into hydrocarbons boiling within the range of gasoline and which have exceptionally high anti-knock value approximately equal to that of the iso octane employed motor fuel in test blends as a standard of reference. The increase in gasoline yield due to this polymerizing action is often considerable as will be shown in later examples.

The gases separating in auxiliary reflux accumulator 24 may be added to the mixture undergoing treatment in catalytic treater 39, by way of line 67, control valve 68, gas pump 69, line 70 and control valve 71. If the quantity of gas obtained

at this point is sufficient to have any appreciable influence upon the temperature of the gas-vapor mixture passing through the solid catalyst, they may be heated although means for accomplishing this end are not shown in the drawing.

The effect upon primary olefins of gasoline boiling range present in the vapors entering the catalytic treater is usually somewhat less pronounced than the effect upon the low boiling olefins and if any effect is present it generally results in the elimination of gum-forming compounds so that the gasoline condensed from the overhead vapors is more stable. Thus, heavy polymers produced in the treatment may be withdrawn from the lower part of treater 39 by way of line 57, containing control valve 58, to an accumulator 59 which also receives heavy refluxes from fractionator 46 by way of line 60, containing control valve 61.

The mixture of gases and gasoline containing vapors pass from the catalytic treater through line 44, containing control valve 45, and are subjected to a final fractionation in fractionator 46 to separate compounds boiling higher than the desired end point of the final product and vapors and fixed gases which pass together through a line 47, containing control valve 48, the condensible components being liquefied during passage through condenser 49 and following line 50, containing control valve 51, to final receiver 52, this receiver having a gas release line 53, containing a control valve 54, and a liquid draw line 55, containing a control valve 56.

The gases recovered at this point will be substantially devoid of the more readily polymerizable 3, 4, and 5 carbon atom olefins, though they will contain at times considerable quantities of ethylene in admixture with gaseous paraffin hydrocarbons, since ethylene is not affected to any considerable extent by the preferred types of catalyst.

In order to conserve recycle stock, the heavy polymers accumulating in receiver 59 are passed to a recycling pump 64 through line 62, containing control valve 63, and returned to vapor line 16 by way of line 65, containing valve 66. In this way they ultimately reach the heating zone in admixture with the refluxes from fractionator 18.

The following data summarizes the main results obtained in operating according to the present process and furnishes an illustrative example of its commercial value.

A mixture of equal volumes of Mid-Continent residuum and heavy distillate having an A. P. I. gravity of 26 was subjected to cracking at a temperature of approximately 930° F. and a pressure of 250 pounds per square inch maintained throughout the reaction chamber following the heating element. In the ordinary operation without employing the polymerizing step of the present process, the ultimate yield of untreated 400° F. end point gasoline was 55%, and

there was concurrently produced per barrel of charging stock 600 cubic feet of a gas mixture comprising 35% of olefins containing 3 and 4 carbon atoms to the molecule.

When operating according to the present process with a solid catalyst manufactured by suitably calcining and sizing a mixture composed of 20 parts by weight of kieselguhr and 80 parts by weight of 89% orthophosphoric acid, the yield and quality of the 400 end point gasoline was materially improved, as shown by the succeeding tabulation. The temperature employed in the polymerizer was 375° F. and the pressure 75 pounds per square inch.

Results of cracking with and without polymerization

	Without polymerization	With polymerization	
Yield of gasoline, % by volume---	55.0	60.0	20
A. P. I. gravity---	56	56.5	
End point °F.---	400	400	
Mg. of gum by copper dish----	200	25	25
Octane number--	70	75	

The benefits gained by the use of the polymerizing step in conjunction with the cracking process are indicated by the preceding data and these benefits are further emphasized by a consideration of the fact that the catalyst mass maintained its activity until approximately 4,000 pounds of gasoline vapors were passed through it. After this time regeneration was effected by simple air oxidation, the vapor stream being meanwhile diverted into a similar polymerizer in parallel connection.

The novelty and the commercial utility of the preceding process in contrast to the ordinarily used pyrolytic processes for the manufacture of gasoline from heavy oils is evident from the preceding specification and example although the invention is not limited to the specific descriptive material nor the data presented.

I claim as my invention:

In the cracking of hydrocarbon oils wherein there is produced a fractionated vaporous mixture of gasoline and olefinic gases, the method of increasing the gasoline yield of the cracking process and the quality of the cracked gasoline which comprises subjecting said mixture to the action of a solid calcined mixture of siliceous material and phosphoric acid under temperature and pressure conditions such as to polymerize olefinic gases contained therein into high anti-knock hydrocarbons boiling within the gasoline range and to remove gum-forming compounds from the gasoline, and recovering the thus polymerized gasoline hydrocarbons of high anti-knock value in admixture with the cracked refined gasoline.

VLADIMIR IPATIEFF.