

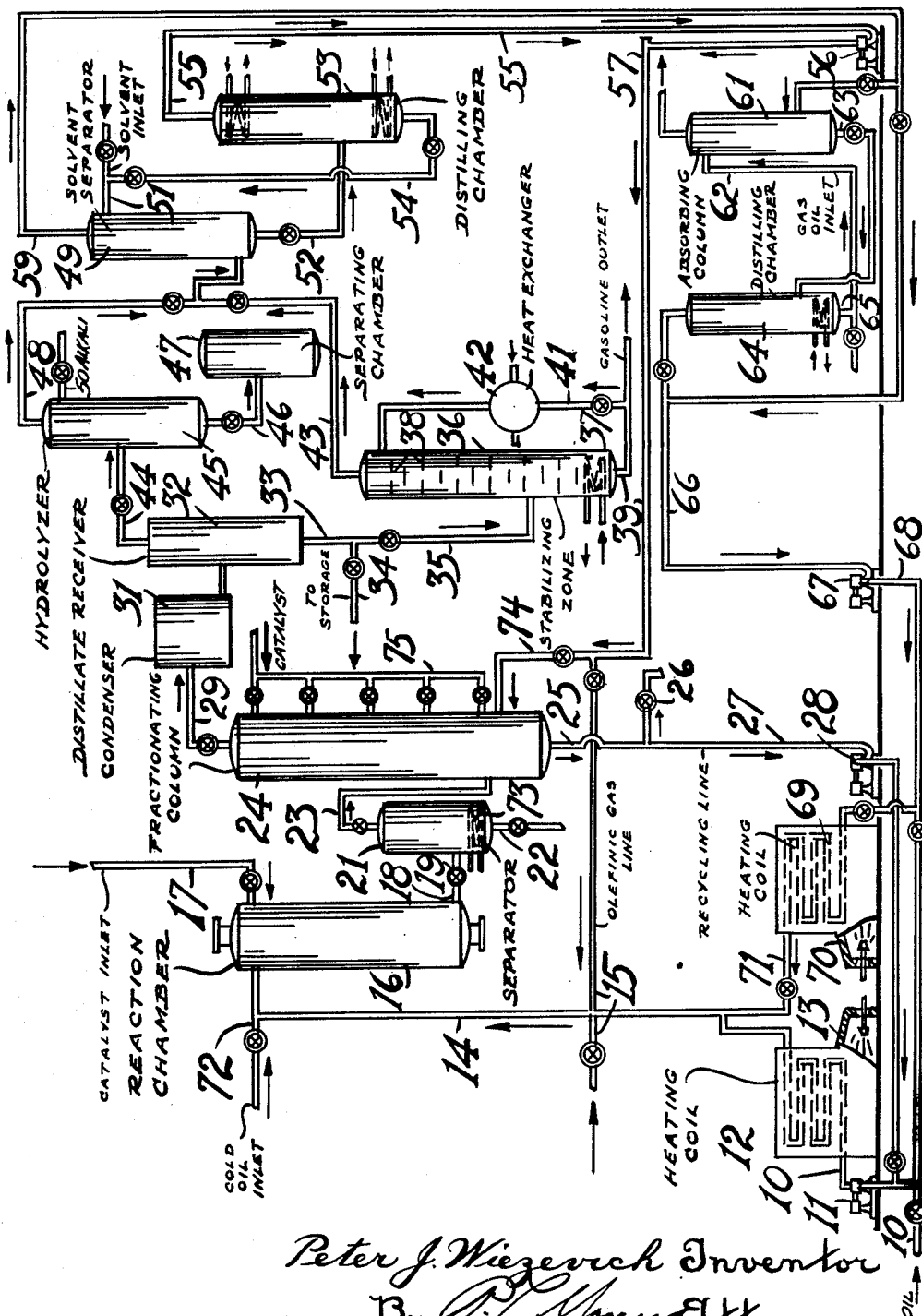
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P. J. WIEZEVICH, NOW BY JUDICIAL CHANGE OF NAME P. J. GAYLOR

PROCESSING HYDROCARBON OILS

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Peter J. Wiezevich Inventor  
By *P. J. Young* Attorney

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## PROCESSING HYDROCARBON OILS

Peter J. Wiczevich, Elizabeth, N. J., now by  
judicial change of name Peter J. Gaylor, as-  
signor to Standard Oil Development Company,  
a corporation of Delaware

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## 4 Claims. (Cl. 196—9)

This invention relates to the processing of hydrocarbon oils to produce motor fuel and pertains more particularly to a combined process for cracking high-boiling hydrocarbons into lower-boiling hydrocarbons within the motor fuel boiling range, and the reversion of the light normally gaseous hydrocarbons, or hydrocarbons too light for use in motor fuel, into higher-boiling hydrocarbons within the motor fuel boiling range.

The principal object of my invention is to provide a process for converting hydrocarbon oil into gasoline which will materially improve the yield and quality of motor fuel produced. A further and more specific object of my invention is to reduce the gas loss incident to the cracking process.

In the conversion of hydrocarbon oil into gasoline by conventional pyrolytic and catalytic processes there is formed concurrently with a gasoline, intermediate condensate boiling above the gasoline boiling range amenable to further cracking treatment, heavy residual tarry material unsuitable for cracking and light gaseous hydrocarbons boiling below the normal gasoline boiling range. Since the intermediate condensate is usually returned to the cracking zone and subjected to further cracking, the ultimate gasoline yield is limited by the formation of gases and tar. In many commercial cracking processes the formation of troublesome coke deposits in the cracking zone is the limiting factor determining the extent of cracking. In other processes, particularly the vapor phase processes operating at high temperature and at relatively low pressure and processing light clean condensate, the permissible gas loss is the controlling factor determining the gasoline yield. Expressed in other words, in many high temperature vapor phase cracking operations, the limiting factor is the amount of gas formed rather than the formation of troublesome coke deposits.

Various processes have been developed for reverting or polymerizing these cracked residual gases into higher-boiling hydrocarbons within the gasoline boiling range. Most of these processes involve the separate polymerization of the residual gases, either catalytically or pyrolytically in apparatus separate and distinct from the cracking equipment, although I understand that in some instances it has been proposed to return a part of the residual gases to the cracking coil to thermally polymerize such gases concurrently with the cracking of the heavier oil.

In accordance with my invention, the fresh charging oil which may be a gas oil, crude or

reduced crude, is first subjected to cracking and the total cracked effluent, or a vapor fraction thereof enriched with gaseous olefins is subjected to further treatment which will effect reversion of gases formed during the cracking treatment into higher-boiling hydrocarbons suitable for motor fuel.

The terms "reversion of gases" and "gas reversion" as herein employed may be defined as the formation of higher-boiling hydrocarbons from gases whether it result from the condensation or polymerization of like molecules or by the union of unlike molecules, known as alkylation. Since in my invention the reversion of the gases is in admixture with high-boiling constituents, it is impossible to determine whether the mechanism by which the gases are caused to unite to form higher-boiling hydrocarbons is one of straight polymerization of like molecules or the alkylation of higher molecular weight hydrocarbons.

Further, in accordance with my invention, the vapor products from the reversion zone or the combined reversion and cracking zone, in case the latter is employed as hereinafter described, is separated into a condensate fraction boiling above the range of gasoline, a desired distillate fraction, a saturated gas fraction and an unsaturated gas fraction. The condensate and the saturated gas fraction is then subjected to further cracking either independently or in admixture with the fresh charging oil as circumstances may dictate and the resulting cracked products passed to the reversion zone hereinbefore described. The unsaturated olefinic gas fraction is returned directly to the reversion zone where it reacts to form higher-boiling hydrocarbons.

In accordance with the preferred form of my invention, the reversion of the cracked gases is effected in the presence of a polymerizing catalyst. As a catalyst I prefer to employ a volatile metallic halide such as boron and aluminum chloride, although other catalysts such as phosphorus pentoxide, zinc chloride, clay, and phosphoric acid may be used and still retain a number of the advantages of my invention. Boron fluoride is preferred however, since it is more easily recovered and does not form a sludge with the oil.

Other objects and advantages of my invention will be apparent from the more detailed description hereinafter in which reference will be made to the accompanying drawing which is a diagrammatic illustration of an apparatus suitable for carrying my invention into effect.

Referring to the drawing, the reference character 10 designates a charging line provided with a pump 11, which forces the charging oil, which is preferably a gas oil, but which may be a crude or reduced crude, into the heating coil 12 located in the furnace 13. The oil during its passage through the heating coil 12 is raised to cracking temperature and subjected to cracking therein. The oil may be heated, for example, to a temperature of from 850 to 1100° F., during its passage through the heating coil 12.

The cracked products from the heating coil 12, pass through transfer line 14 wherein they admix with olefinic gases introduced through line 15 and the combined products pass to the reaction chamber 16.

In accordance with one mode of operating my process, the cracked products, enriched with additional olefinic gases are contacted within the reaction chamber 16 with a catalyst capable of causing gaseous olefins to combine to form higher-boiling hydrocarbons. Boron fluoride is particularly suitable for effecting such combination, and for convenience and simplicity the specific embodiment will be described employing boron fluoride as a catalyst, it being understood that other polymerizing catalysts may be employed.

The catalyst is introduced into the reaction chamber through line 17. The products from the reaction chamber 16, after undergoing the desired reaction therein, pass through line 18, provided with a reducing valve 19 to a separator 21 wherein the vapors separate from residue. The unvaporized residue is withdrawn from the separator 21 through line 22 and is rejected from the process. This residue may be subjected to any further treatment desired. The vapors separated in the separator 21 pass overhead through line 23 to a fractionating column 24, wherein insufficiently converted constituents are condensed, while the gasoline and lower-boiling constituents are retained in vapor form. The insufficiently converted constituents condensed in fractionating tower 24 are withdrawn therefrom through line 25 and may be withdrawn from the system through line 26, or part or all of said constituents may be recycled through line 27 provided with pump 28 to the inlet side of the heating coil 12 and subjected to further cracking therein.

Vapors remaining uncondensed in the fractionator 24 pass overhead through line 29 to a condenser 31 wherein the gasoline constituents are condensed. The total effluent from the condenser 31 passes to a distillate receiver 32 wherein the gasoline distillate separates from the gases. The gasoline distillate is withdrawn from the receiver 32 through line 33 and may be passed to suitable storage through line 34, but is preferably subjected to further stabilizing treatment. In the latter case, the distillate passes through lines 33 and 35 to a stabilizing zone 36 wherein it is subjected to distillation and fractionation to liberate low-boiling constituents therefrom and produce a stable gasoline. To this end, the stabilizer is suitably heated, such as by means of a steam coil 37, and is also provided with fractionating elements 38. The stabilized gasoline is withdrawn from the stabilizer through line 39 and passed to a suitable storage tank (not shown). A portion of the stabilized gasoline may be passed through line 41 and after being cooled by passing through heat exchanger 42 introduced into the top of the stabilizer as a reflux therefor. The light gases liberated during the stabilizing action pass overhead

from the stabilizer 38 through line 43 and is subjected to further treatment for separation of the same into saturates and unsaturates as herein-after described.

Returning now to the distillate receiver 32, the gases separated therein pass overhead through line 44 to a hydrolyzer 45, wherein they are treated to separate the boron fluoride therefrom. The gases after being introduced into the hydrolyzer 45 pass in countercurrent contact with a dilute alkali solution, such as sodium hydroxide supplied through a pipe 50, which reacts with the boron fluoride to form a sodium fluoroborate. This salt solution is withdrawn from the hydrolyzer 45 through line 46 and is passed to a separating chamber 47 wherefrom the boron fluoride is regenerated in a manner well known in the art.

The vapors, after removal of the boron fluoride therefrom in hydrolyzer 45, are passed through line 48 to a solvent extraction zone 49, wherein they are treated with a selective solvent capable of separating the gases into a rich unsaturated fraction and a lean unsaturated fraction. This separation may be accomplished, for example, by methyl alcohol or other solvents known to selectively dissolve olefines and diolefines from mixed gases. The solvent is introduced into the solvent separator 49 through line 51 and passes countercurrent to the flow of gases or liquified gases therethrough.

The solvent containing the olefine or unsaturated constituents is withdrawn from the separator 49 through line 52 and passes to a distilling chamber 53, wherein it is subjected to distillation to fractionally distill the olefinic gases from the solvent. The lean solvent separated in the distilling chamber 53, is removed therefrom through line 54 and is recycled to the top of the solvent separator.

The unsaturated gases liberated in the distilling chamber 53 pass overhead through line 55 provided with pump 56 and may be passed via line 57 to the transfer line 14 where they combine with products from the cracking coil 12.

Returning now to the solvent separator 49, the gases remaining undissolved in the separator pass overhead through line 59 to a hydrogen and methane separating unit, wherein the hydrogen and methane is separated therefrom. This hydrogen and methane separating unit may comprise an absorbing column 61 into which an absorbing medium, such as gas oil, may be introduced into the top through line 62. The gases from the line 59 pass into the bottom of the absorbing tower and pass upwardly therein countercurrent to the downward flow of the absorbing medium. The absorber oil selectively absorbs the higher-boiling constituents of the gases and separates the same from hydrogen and methane. The fat absorber oil is withdrawn from the bottom of the absorbing column 61 through line 63 and is passed to a distilling chamber 64, wherein the absorbed gases are distilled therefrom. The lean absorber oil from the distilling chamber 64 is withdrawn from the bottom thereof through line 65 which merges with line 62, and is returned to the top of the absorbing column 61. Gases liberated in distilling chamber 64 pass overhead through line 66, provided with pump 67, and may be recycled to the inlet side of the heating coil 12, wherein it is subjected to cracking conditions to form olefines along with the fresh oil to be cracked, or a portion or all of the gases may be passed through line 68 to a separate heating coil 69 (which may contain a dehydrogenation or

cracking catalyst), located in furnace 70, and subjected to separate cracking conditions, pyrolyzing or dehydrogenating the saturated constituents into a maximum yield of olefines. In the latter case, the products from the heating coil 69 pass by way of line 71 to the transfer line 14 and are there merged with the cracked products from coil 12.

From the foregoing, it should be evident that, in accordance with my invention, residual gases resulting from the combined cracking and polymerization unit are separated into saturated and unsaturated constituents. The saturated constituents, after removal of hydrogen and methane, are then subjected to cracking for conversion thereof into olefines, while the unsaturated constituents of the gases are returned to the transfer line 14 and merged with cracked products therein. The combined products then pass to the reaction chamber 16 wherein they undergo further reaction resulting in the formation of motor fuel and higher-boiling constituents.

The reaction chamber 16 may be maintained at a temperature ranging from reforming temperature to active cracking temperature (800-1000° F.), and if desired, even above active cracking temperature, such as from 1000 to 1200° F. in which case the reversion of gases and cracking of heavier products takes place concurrently. It is preferred, however, to maintain the reaction chamber at or somewhat below active cracking temperature and preferably between 600-1000° F. The reaction chamber is maintained under super-atmospheric pressure ranging from 200-1000 lbs./sq. inch. The time of contact with the catalyst may vary over relatively wide limits from a fraction of a second to fifteen minutes or more depending on the temperature and pressure.

When operating the reaction chamber below active cracking temperature, the cracked products may be cooled either by indirect contact with a cooling medium in a heat exchanger or the cracked products may be combined with a relatively cold oil preferably a relatively heavy oil. In the drawing, a line 72 is shown merging with transfer line 14 through which the relatively colder oil may be introduced.

When operating the reaction chamber 16 at low temperature, the products therefrom are subjected to further heating to effect the desired distillation. The separating chamber 21 is shown provided with a heating coil 73 to effect the required heating, it being understood that other types of heating may be employed.

According to another mode of operating my process, the olefinic gases are charged into the fractionating tower 24 rather than to the reaction chamber 16, so that the gases are first combined with vapors from cracking operation rather than with the total cracked products. To this end, a branch line 74 is shown connecting the olefinic gas line 57 with the bottom of the fractionating tower 24. In such case, the tower 24 serves as a combined fractionating and gas reversion zone and the vapor catalyst is contacted with the lighter constituents of the vapors for a materially longer period than with the heavier constituents condensed in the bottom of the fractionating tower. When operating in this manner, a part or all of the catalyst may be introduced into the fractionating zone at any one or more of a plurality of spaced points through inlets leading from a common manifold 75 so that the catalyst may be caused to contact with any desired portion of the vapors undergoing fractionation. For ex-

ample, by introducing the catalyst adjacent to the top of the fractionating tower only the very lightest fraction of the vapors are caused to contact with the catalyst. In such a case the temperature of the oil vapors to be so treated would be in the neighborhood of 400-800° F., or thereabouts.

When operating the process in this manner, the reaction chamber 16 functions principally as a cracking chamber rather than as a gas reversion zone or as a combined cracking and gas reversion chamber although if desired a relatively small amount of catalyst may also be introduced into this chamber.

According to either mode of operating my process, the amount of cracking effected during a single passage of the oil through the cracking zone is not limited by the amount of gas loss permissible since with the exception of the hydrogen and methane all of the gas is ultimately converted into higher-boiling constituents. My invention makes it possible to attain an ultimate gasoline, of high anti-knock gasoline of from 85 to 95% with a crack per pass based on the total oil charge of from 30 to 60%.

The amount of catalyst employed may range from a fraction of a percent, say 0.001 to 0.5% to 10% or more of the olefine gases introduced to the reversion zone.

For purposes of simplicity, I have in the drawing diagrammatically illustrated only the conventional equipment, it being understood that other pertinent equipment such as heat exchangers, flow meters, thermostats, etc. will be provided. The process may be operated under a substantially uniform pressure throughout, except for the necessary differential to effect the desired flow hereinbefore described, or a differential pressure between the various portions of the equipment may be maintained. For example, the combined cracking and polymerization portion of the equipment may be maintained under a relatively high pressure, whereas the hydrolyzer 45 and the solvent separator 49 may be maintained under a materially lower pressure.

Having described the preferred embodiment, it is understood that my invention embraces such other variations and modifications as come within the spirit and scope thereof and that it is not my intention to unnecessarily limit my invention or to dedicate any novel features thereof.

I claim:

1. A method of processing hydrocarbon oil which comprises passing a stream of oil through a cracking zone and subjecting the same to cracking therein, thereafter separating the cracked products into vapors containing unsaturated gases and residue, fractionating said vapors in a fractionating zone to condense insufficiently cracked constituents as reflux condensate, contacting said vapors in said fractionating zone with a catalyst capable of causing said unsaturated gases to react to form higher boiling hydrocarbons, removing vapors remaining uncondensed in said fractionating zone, further cooling said vapors to separate the same into a desired distillate fraction and a normally gaseous fraction containing saturated and unsaturated constituents, separating said gaseous fraction into a saturated component and an unsaturated component and passing said unsaturated component to said fractionating zone.

2. A method of processing hydrocarbon oil which comprises passing a stream of oil through a cracking zone and subjecting the same to

cracking therein, thereafter separating the cracked products into vapors containing unsaturated gases and residue, fractionating said vapors in a fractionating zone to condense insufficiently cracked constituents as reflux condensate, contacting said vapors in said fractionating zone with a catalyst capable of causing said unsaturated gases to react to form higher boiling hydrocarbons, removing vapors remaining uncondensed in said fractionating zone, further cooling said vapors to separate the same into a desired distillate fraction and a normally gaseous fraction containing saturated and unsaturated constituents, separating said gaseous fraction into a saturated component and an unsaturated component, subjecting said saturated component to dehydrogenation to remove hydrogen therefrom and thereby convert said saturated constituents into unsaturated constituents and passing the dehydrogenated component and said unsaturated component to said fractionating zone.

3. A method of processing hydrocarbon oil which comprises passing a stream of oil through a cracking zone and subjecting the same to cracking therein, thereafter separating the cracked products into vapors containing unsaturated gases and residue, fractionating said vapors in a fractionating zone to condense insufficiently cracked constituents as reflux condensate, contacting said vapors in said fractionating zone with boron fluoride to thereby cause said unsaturated gases to react to form higher boiling hydrocarbons, removing vapors remaining uncondensed in said fractionating zone, further cooling said vapors to separate the same into a desired distillate fraction and a normally gase-

ous fraction containing saturated and unsaturated hydrocarbon constituents and boron fluoride vapors, separating the boron fluoride vapors from said gaseous fraction and returning it to the fractionating zone, separating the remaining gaseous fraction into a saturated component and an olefinic component and returning the olefinic component to the fractionating zone for further treatment therein.

4. A method of processing hydrocarbon oil which comprises passing a stream of oil through a cracking zone and subjecting the same to cracking therein, thereafter separating the cracked products into vapors containing unsaturated gases and residue, fractionating said vapors in a fractionating zone to condense insufficiently cracked constituents as reflux condensate, contacting said vapors in said fractionating zone with boron fluoride to thereby cause said unsaturated gases to react to form higher boiling hydrocarbons, removing vapors remaining uncondensed in said fractionating zone, further cooling said vapors to separate the same into a desired distillate fraction and a normally gaseous fraction containing saturated and unsaturated hydrocarbon constituents and boron fluoride vapors, separating the boron fluoride vapors from said gaseous fraction and returning it to the fractionating zone, separating the remaining gaseous fraction into a saturated component and an olefinic component, dehydrogenating the saturated component of said gaseous fraction to convert the same into unsaturated constituents and passing the dehydrogenated component to the fractionating column for further treatment.

PETER J. WIEZEVICH.