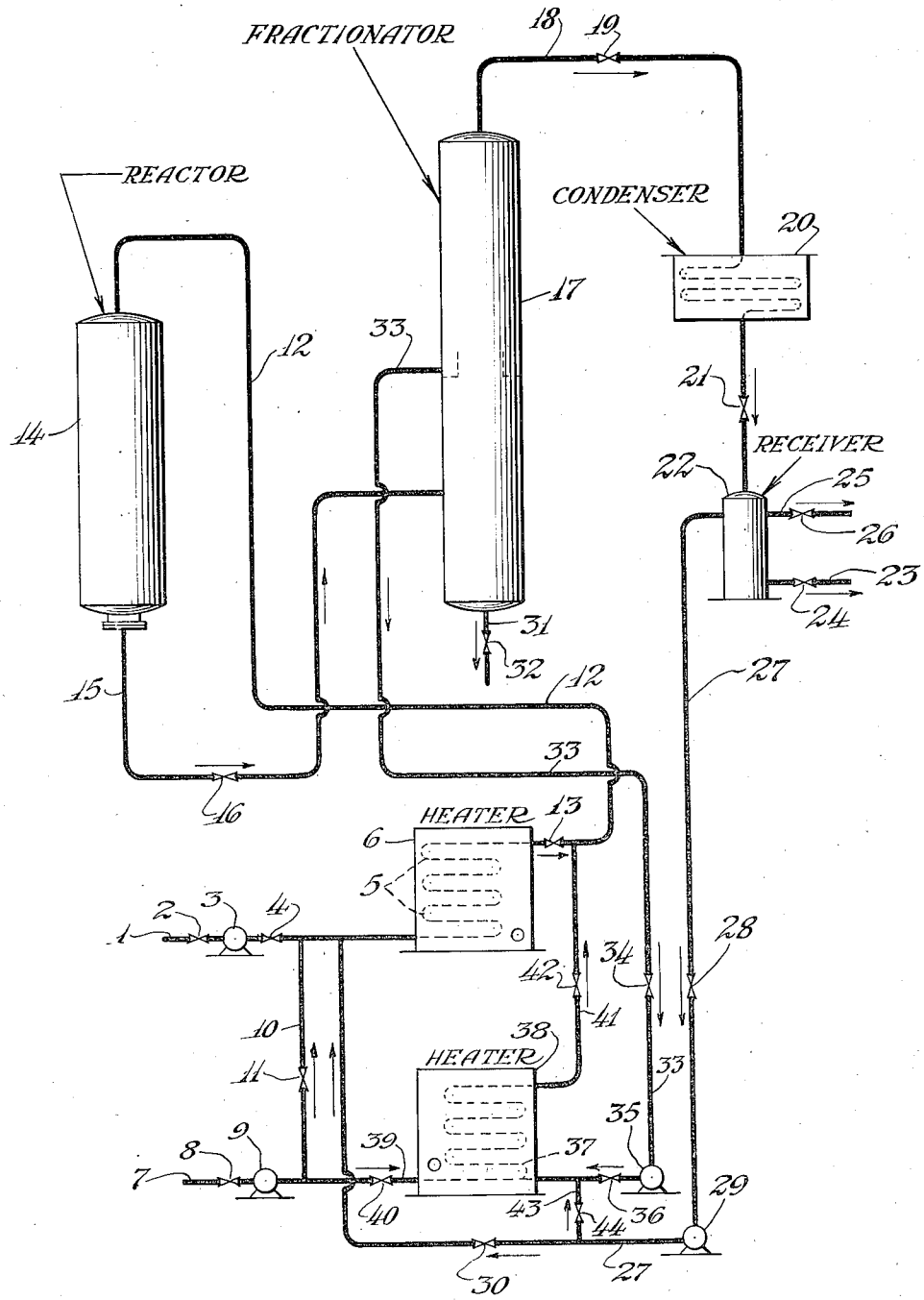
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TREATMENT OF HYDROCARBONS

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TREATMENT OF HYDROCARBONS

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5 Claims. (Cl. 196—26)

This invention relates to a process for refining hydrocarbon oils, and more particularly, distillate fractions of such oils containing major percentages of motor fuels.

The object of the invention is to improve the motor fuel properties of the gasoline by reducing the sulfur content thereof, and otherwise improving the antiknock characteristics of the oil undergoing treatment. The hydrocarbon oils treated may be obtained by the straight run distillation of crude oils, or by cracking or reforming gasoline, naphtha or higher boiling oils to produce distillates having relatively large proportions of motor fuel contained therein. Mixtures of straight run and cracked products may also be treated according to this process.

In one specific embodiment the present invention comprises a process for improving the antiknock properties of hydrocarbons boiling within the motor fuel range by heating a mixture of said hydrocarbons with zince chloride, separately heating material boiling above the gasoline range produced as hereinafter described in the presence of zinc chloride combining the reactants in a common reaction zone and fractionating them to recover gas, gasoline, an intermediate fraction boiling above gasoline and another fraction unsuitable for further conversion, treating the intermediate fraction boiling above gasoline as previously indicated, withdrawing the fraction unsuitable for further conversion together with spent catalyst, and supplying a portion of the gases produced to the treating steps.

The invention is further understood by reference to the accompanying diagrammatic drawing, but should not be interpreted as limited to the exact apparatus shown therein.

The hydrocarbons undergoing conversion are composed largely of gasoline, but may contain some higher boiling oil for example, kerosene. This oil, in the course of the process, may undergo some further conversion to motor fuel. The charging stock may be the so-called pressure distillate, produced by the pressure cracking, either catalytic or non-catalytic, of higher boiling hydrocarbon oils, or may be composed of straight run distillate such as naphtha, or may comprise a blend of straight run and cracked products. The oil is introduced through line 1, valve 2, pump 3 and valve 4 to coil 5 which is disposed in heater 6. The treating agent, which comprises zinc chloride, and may be a solution of zinc chloride but is preferably composed of zinc chloride disposed on a relatively inert carrier such as charcoal, activated carbon, pumice, silica-alumina composites, alumina, silica gel, clays, acid-treated clays, porcelain, heavy metal oxides, magnesite, firebrick, etc., is introduced through line 7, valve 8, pump 9, line 10 and valve 11 joining with the charging stock in line 1. The zinc chloride may be in the form of a slurry or emulsion in oil, or may be introduced in any other suitable manner. It is preferably introduced in a form in which it is readily carried through the subsequent reaction coils by means of the hydrocarbons undergoing treatment. The reaction mixture is heated, for example, to a temperature within the range of approximately 200–800° F. at pressures of substantially atmospheric to 1000 pounds per square inch or more. The mixture passes through line 12 containing valve 13, to reactor 14. The temperature in the reactor may be approximately the same or higher than that in coil 5. The reaction products pass through line 15 containing valve 16 to fractionator 17. Gasoline, together with relatively small amounts of gas formed during the process, is passed through line 18 containing valve 19, through condenser 20 and valve 21 to receiver 22. The treated gasoline is removed through line 23 and valve 24 to suitable stabilizers and thence passed to storage. The gasoline is of low sulfur content and highly resistant to oxidation reactions or to deterioration on storage. The cracked gasolines treated in this way are of low gum content and have a long induction period which may be further increased by the addition of minor amounts of gum inhibitors. The antiknock properties with and without added tetraethyl lead are improved over that of the untreated gasoline because of the low sulfur content and other catalytic effects of the zinc chloride under the treating conditions. The lead susceptibility is improved particularly. The gasoline is usually completely sweetened or may be made so by a wash with an alkaline reagent such as caustic soda. The improvements may be due in part to reduction in sulfur content of the gasoline, in part to catalytic reforming which may occur, and in part to isomerization of some of the straight chain or slightly branched chain hydrocarbon constituents to more highly branched chain hydrocarbons of higher antiknock value and lead susceptibility than those of the original gasoline. It is not intended to limit the invention to any explanation set forth herein.

A relatively small amount of gas which is formed in the process may be withdrawn from receiver 22 through line 25 and valve 26 to suitable gas recovery system not shown. A further portion may be recycled through line 27 contain-

ing valve 28, pump 29 and valve 30 joining with line 1. Returning to fractionator 17, the catalytic material suspended in high boiling oil may be withdrawn through line 31 and valve 32. The catalyst may be recovered and reactivated for further use in the process. An intermediate boiling fraction containing substantially no gasoline is removed through line 33 containing valve 34, pump 35 and valve 36, being passed to coil 37 which is disposed in heater 38. Zinc chloride is introduced from line 7 through line 39 containing valve 40. The reaction mixture is heated to a temperature at which decomposition of the higher boiling hydrocarbons into lower boiling hydrocarbons occurs. This is preferably somewhat higher than the temperature used in coil 5, and may be of the order of approximately 400–1100° F. and is preferably of the order of 700–900° F. Pressures of atmospheric to 1000 pounds per square inch or higher may be used. The mixture is passed through line 41 and valve 42 to line 12 wherein it joins with the reaction products from coil 5 and is thence passed to reactor 14. In coil 37 occurs catalytic reforming and catalytic cracking reactions whereby the higher boiling constituents contained in the charging stock and some higher boiling constituents formed by polymerization reactions in the lower temperature operation in coil 5 are converted to gasoline. The receiver gases may be introduced from line 27 through line 43 containing valve 44.

The following example is given to illustrate the usefulness and practicability of the process but should not be construed as limiting it to the exact conditions given therein.

A mixture of straight run and cracked West Texas naphtha boiling in the range of approximately 200–500° F. may be treated according to the present invention, using a temperature of 750° F. in the primary step (coil 5) and a temperature of 900° F. in the secondary step (coil 37). The sulfur content may be reduced from approximately 0.25% to 0.005%. The octane number of the gasoline fraction may be increased from approximately 60 to 70, which is further increased to 85 by the addition of 3 cc. of tetra-ethyl lead per gallon. The product is sweet to the doctor test and is 30°+ Saybolt color, which is stable in both light and dark storage. The copper dish gum content is less than 10 mg. per 100 cc. and the gasoline has an induction period of more than 500 minutes in the oxygen bomb method.

I claim as my invention:

1. A process for refining hydrocarbon distillate containing gasoline to improve the antiknock properties thereof which comprises adding to said distillate a suspension of a treating agent comprising essentially zinc chloride as the active constituent, heating the mixture to a desulfurizing temperature, separating spent treating agent, recovering the refined gasoline, separating a fraction boiling above gasoline, adding a portion of the treating agent thereto, heating the mixture to a cracking temperature in excess of the first mentioned temperature and combining the reaction products with those from the first-mentioned step.

2. A process for refining hydrocarbon distillate containing a major portion of gasoline which comprises heating said distillate to a desulfurizing temperature with a suspension of a treating catalyst comprising zinc chloride as its active constituent, separately heating a fraction produced as hereinafter set forth, boiling above gasoline with another portion of said treating catalyst but at a substantially higher temperature in the cracking range, combining the reaction products, fractionating them to recover gas and gasoline and a higher boiling fraction, supplying said higher boiling fraction to the second-mentioned treating step and removing spent treating reagent from the system.

3. A process for refining hydrocarbon distillate containing motor fuel which comprises treating said distillate with a catalyst comprising zinc chloride as its major constituent at a temperature of approximately 750° F. whereby refining occurs with a relatively minor amount of decomposition fractionating the reaction products, recovering gasoline, removing spent catalyst, separating a fraction boiling above the gasoline range, adding a portion of said catalyst thereto and treating the mixture at a temperature of approximately 900° F. whereby decomposition of said hydrocarbons to material boiling in the gasoline range occurs, and combining the reactants with those from the first-mentioned treating step.

4. A process for refining hydrocarbon distillate containing gasoline which comprises treating said distillate in the presence of a catalyst comprising essentially zinc chloride as its active constituent under desulfurizing conditions of temperature and pressure, fractionating the reaction products into gas, gasoline and a portion boiling above the gasoline range, subjecting the latter-named portion to cracking conditions of temperature and pressure in the presence of said catalyst, combining the reaction products therefrom with the first-mentioned treating step and supplying at least a portion of the gas produced in the process to each of said treating steps.

5. A process for improving hydrocarbon distillates containing gasoline fractions which comprises heating the distillate to a desulfurizing temperature in the presence of zinc chloride, fractionating the resultant products to separate gasoline and a condensate heavier than gasoline, heating said condensate in the presence of additional zinc chloride to a cracking temperature in excess of the first-mentioned temperature, and supplying the cracked products to said fractionating step.

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