March 7, 1944. C. E. HEMMINGER 2,343,770

CHEMICAL PROCESS

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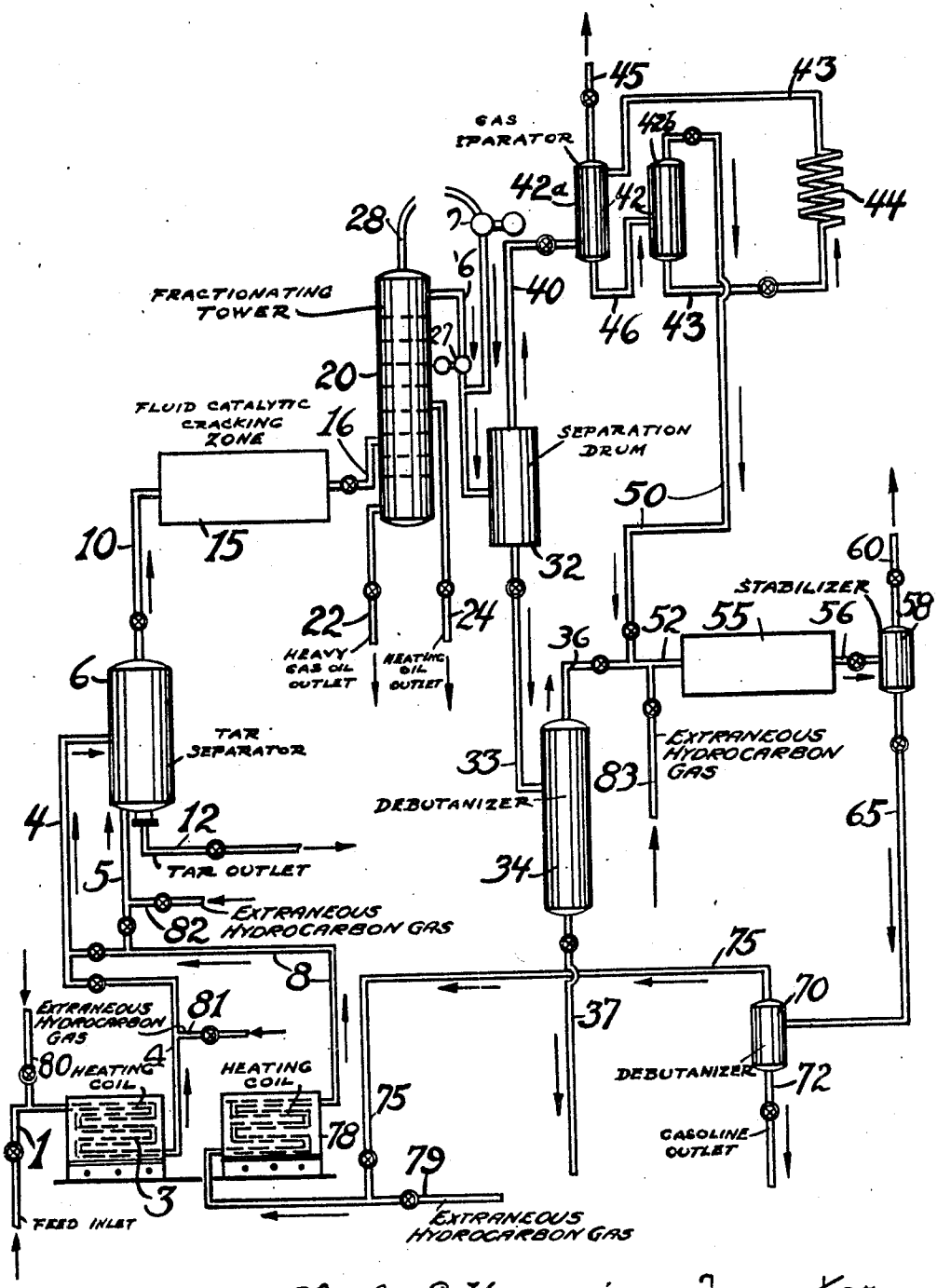

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CHEMICAL PROCESS

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4 Claims. (Cl. 196—52)

The present invention relates to the art of treating hydrocarbons, and it involves improved methods of cracking a relatively heavy hydrocarbon oil to obtain gasoline.

The main object of my invention is to treat hydrocarbon oil and normally gaseous hydrocarbons, such as butane, butylenes and/or propane, propylene by cracking the oil catalytically in the presence of the separately preheated gases and thereafter forming gasoline from the cracked gases by alkylation and/or polymerization.

Other and further objects of the present invention will appear more fully hereinafter.

The present invention will be best understood by reference to the accompanying drawing which shows diagrammatically a flow plan which may be employed to carry my invention into effect.

Referring in detail to the drawing, a reduced crude, such as a topped East Texas crude petroleum oil having an A. P. I. gravity of about 18°, is introduced into the system through line 1 and thence discharged into a heater 3 where it is heated to a temperature of about 800° F. The preheated oil is withdrawn from the heater through line 4 and discharged into a tar separator 6. As shown in the drawing, a conduit 8 also discharges into line 4, and this conduit contains C_3 and C_4 hydrocarbons preheated to a temperature within the range of from about 900° F. to 1400° F. The confluence of the heated crude oil and the superheated light hydrocarbons results in a heat transfer with the final result that the mixture of crude oil and heated gases discharged into separator 6 is at a temperature of about 800° F. to 950° F. and pressure from 2 to 150 pounds/square inch. This may be accomplished by mixing the crude oil and the gaseous hydrocarbons in the ratio varying from 0.5 to 5 parts by weight of gaseous hydrocarbons to 1 part of crude oil. In vessel 6 the volatile constituents of the charging oil are vaporized, aided by the preheated gaseous hydrocarbons, and these volatilizable constituents, together with the added hydrocarbon gases, are withdrawn from separator 6 through line 10.

The heavier oil and tar are withdrawn from the separator 6 through line 12 and these may be processed in any known manner to obtain asphalt, bunker fuel, and the like.

About 25% of the heated gaseous hydrocarbons may be introduced as shown through line 5 to the bottom of separator 6 where they serve to strip the tar of vaporizable oil fractions.

The volatile hydrocarbons in line 10 are admixed with a powdered catalyst, such as an acid treated clay in powder form, according to known methods, in apparatus illustrated diagrammatically by reference character 15 and cracked to form cracked gasoline, olefins and other products. The technique of employing a powdered catalyst to crack hydrocarbons in the vapor phase per se forms no part of my invention and previously known methods may therefore be employed in this step, including separation of the catalyst from the vapors and regeneration of the catalyst.

The cracked products are withdrawn from 15 through line 16 and discharged into a fractionating column 20. From column 20 a heavy gas oil is withdrawn through line 22, and this fraction may be recycled to coil 3 for further cracking.

A heating oil may be withdrawn from fractionating column 20 through line 24.

Gasoline is withdrawn from column 20 through line 26 and pumped by pump 27 into drum 32.

From column 20, normally gaseous hydrocarbons are withdrawn through line 28, then pumped by pump 30 into drum 32.

Preferably the gases in line 28 are cooled somewhat, and also the gasoline in line 27, but in any event conditions prevailing in drum 32 are such that a superatmospheric pressure, say up to 100 pounds/square inch gauge, exists therein and a temperature of about 100° F.

From drum 32 gasoline is withdrawn through line 33 and since this gasoline contains excess butane, it is delivered to a debutanizing drum 34 from which stable gasoline may be withdrawn through line 37 and delivered to a final treatment to produce finished gasoline, or sent to storage.

Referring again to drum 32, gaseous hydrocarbons are withdrawn therefrom through line 40, and delivered to a gas absorption system 42. The gases withdrawn from drum 32 contain C_1, C_2, C_3 and C_4 hydrocarbons, and the purpose of the treatment in gas absorber 42 is to remove C_1 and C_2 hydrocarbons. The absorption system operates under substantially the same pressure as that prevailing in 32 and is manipulated as follows:

A lean oil is present in this system in line 43, passing continuously through a cooler 44 and thence discharging into the top of drum 42—*a* where it flows countercurrent to gas entering at the bottom of said drum and serves to wash out of the gaseous mixture at least the greater portion of the C_3 and C_4 hydrocarbons. The undissolved gas is withdrawn through line 45 and may be disposed of in any desirable manner, such as burning in a furnace. The solution containing the dissolved gases is withdrawn from

42—*a* through line 46 and delivered to drum 42—*b*. In drum 42—*b* a separation is effected between the gases and the solvent oil, and the solvent oil returns again to line 43 for reuse. The gases consisting essentially of C_3 and C_4 hydrocarbons are withdrawn from 42—*b* through line 50 and discharged into line 52. The debutanizer gases from drum 34 containing essentially C_4 hydrocarbons, but also some C_3 hydrocarbons, are withdrawn from drum 34 through line 36 and discharged into line 52. Gases from the absorber system and the debutanizer are discharged into a polymerizing or alkylation unit 55, where the C_3 and C_4 hydrocarbons are converted, at least in part, to products boiling within the gasoline range. The alkylation and/or polymerization of the gases in unit 55 per se forms no part of my present invention, and these processes may be carried out according to any known method. The product from unit 55 is withdrawn through line 56 and delivered to a primary separation drum 58 from which tail gas may be withdrawn through line 60, the liquid product being withdrawn through line 65 and delivered to debutanizer 70 where excess butane and the remaining C_3 hydrocarbons are separated from the gasoline in debutanizer 70, and these are withdrawn through line 75 and recycled to coil 78.

Stable gasoline is withdrawn through line 72 from debutanizer 70, and this may be mixed with gasoline in line 37. Due to the manner in which the gasoline is produced, that is by cracking and alkylation or polymerization, the total gasoline is of improved octane number since it contains substantial amounts of branch chain paraffinic hydrocarbons.

In order to supply normally gaseous hydrocarbons from some extraneous source, I have provided means for introducing such extroneous gas through lines 79, 80, 81, 82, and 83, respectively, to points in the system where it may be desirable to add such extraneous gas. For example, it will usually be advisable to add extraneous gas, such as field butane, through line 79 discharging into line 75, rather than to depend on the gas which is formed in my present process. Less rarely it may be necessary to add gas through line 81 to the oil in line 4, or through line 82 to the gas in line 5. With respect to the gas added in line 83, it may be, and often is, desirable to add iso-paraffins through said last-named lines, such iso-paraffins as isobutane being preferred for the reason that the gases in line 50 will contain substantial amounts of olefins which may be readily alkylated by the extraneous iso-paraffins in unit 55.

To review briefly, my invention contemplates carrying out a combination process in which hydrocarbon oils are catalytically cracked in the presence of added C_3 and C_4 hydrocarbons, the latter being preheated, and thus supplying at least a part of the heat which is necessary to maintain the hydrocarbon oil undergoing cracking, and is further broadly characterized by the feature that gases resulting from the cracking operation, particularly the C_3 and C_4 hydrocarbons, are either alkylated or polymerized to form hydrocarbons boiling within the gasoline range. The process is unitary in that at least a part of the gas which is supplied to the cracking zone is obtained from the alkylation or polymerization step, and, furthermore, the presence of these gases in the cracking zone tends to repress excessive amounts of gas formation, so that from a given quantity of say gas oil, the amount of undesired gases produced in the cracking zone is reduced.

Many modifications of my invention will readily occur to those who are skilled in this particular art.

What I claim is:

1. In the process of treating hydrocarbons to form gasoline, the improvement which comprises heating a topped crude petroleum oil to a temperature within the range of from about 700° F. to 900° F., separately preheating gas comprising C_3 and C_4 hydrocarbons to a temperature within the range of from about 900° F. to 1400° F., discharging the heated oil and the heated gas into a flash zone to assist in the vaporization of the volatile constituents of the oil, withdrawing oil vapors and gas from the flash zone, dispersing a powdered cracking catalyst in the vapors and gas, permitting the oil vapors and gas to remain in contact with the catalyst under cracking conditions for a sufficient period of time to effect cracking of the oil vapors and the gas, separating by fractional distillation the C_3 and C_4 hydrocarbons from the cracked products, causing conversion of the C_3 and C_4 hydrocarbons to products boiling within the gasoline range, separating C_3 and C_4 hydrocarbons from converted C_3 and C_4 hydrocarbons and recycling the separated C_3 and C_4 hydrocarbons to said flash zone and recovering gasoline from both the cracked oil and the C_3 and C_4 hydrocarbons.

2. The process set forth in claim 1 in which the C_3 and C_4 hydrocarbons recovered from the cracking zone are catalytically polymerized to form gasoline.

3. The process set forth in claim 1 in which during the preheating of the C_3 and C_4 hydrocarbons they undergo cracking and in which condition they are mixed with a heavy oil in said flash zone.

4. A process according to claim 1 wherein the C_3 and C_4 hydrocarbons recovered from the cracking step are subjected to alkylation to form gasoline.

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