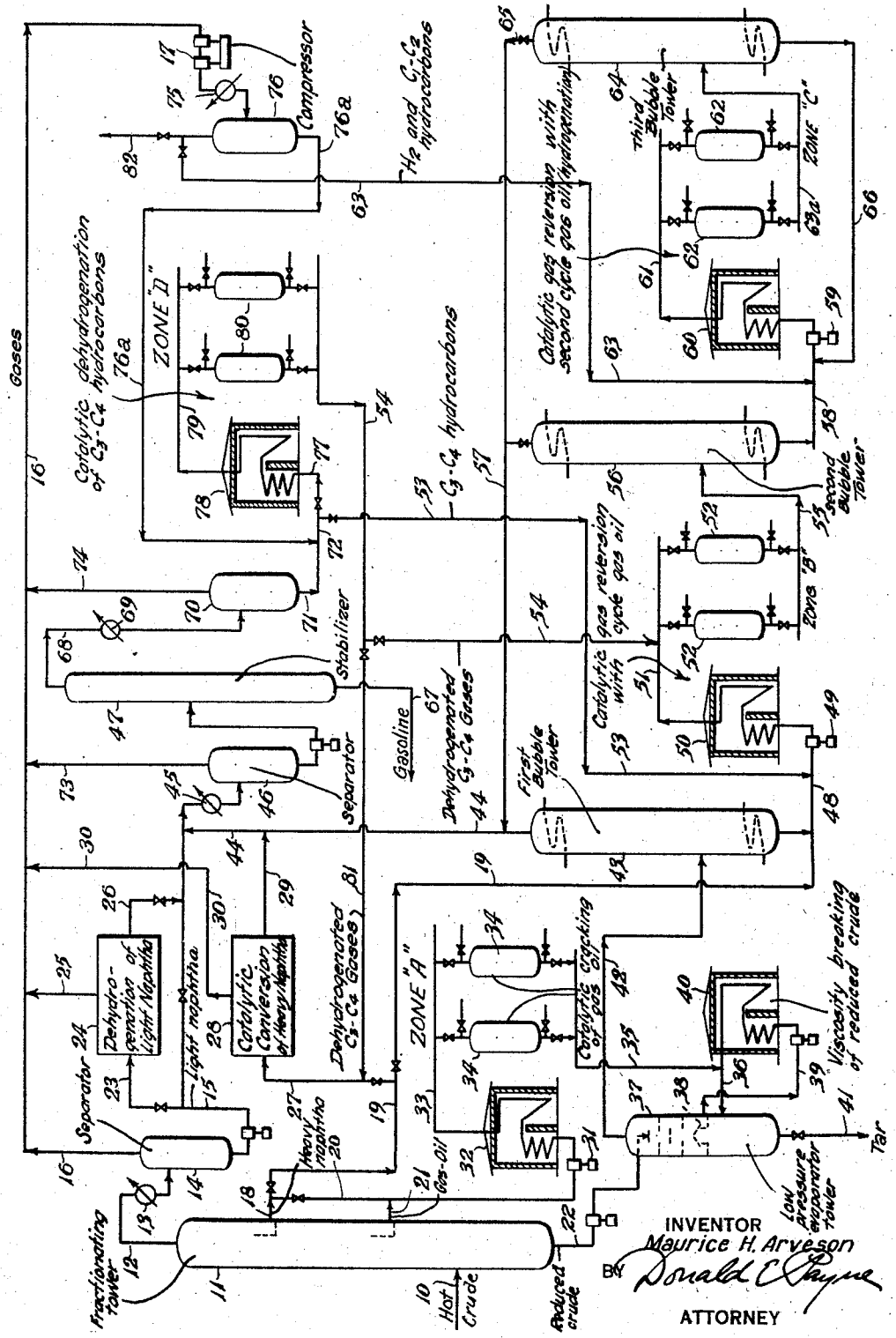
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PRODUCTION OF MOTOR FUEL

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PRODUCTION OF MOTOR FUEL

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This invention relates to the production of motor fuel from petroleum oil, and it pertains more particularly to processes for converting a wide variety of petroleum fractions into high octane number gasoline. The invention is applicable to the production of gasoline from crude oil, but while this is a preferred embodiment, it should be understood that the invention is equally applicable to the wide variety of petroleum fractions from various refining processes.

The object of my invention is to increase the yield and quality of gasoline obtainable from crude oil. A further object is to increase the yield and quality of gasoline obtainable from various oils and gases resulting from petroleum refinery operations.

A further object of my invention is to provide an integrated system of thermal and catalytic processes wherein each specific process is correlated with the other processes so that maximum thermal and operating efficiency is secured throughout the whole system, and wherein the products from one process may be most effectively utilized in each of the correlated processes.

A further object is to provide an improved combination of conversion processes operating with different feed stocks and under the same or different conditions of temperature and pressure, either with or without the presence of specific catalysts, so that optimum conditions are obtained in each conversion process, optimum charging stocks are available for each conversion process, and optimum refining methods are provided for the products of each process.

A further object is to simplify the apparatus and operation of a system for converting crude oil to high quality motor fuel, to decrease the cost and increase the efficiency of such systems. Other objects will be apparent as the detailed description of my invention proceeds.

My process comprises three major conversion steps:

(1) Catalytic conversion of gas oil, either with or without heavy naphtha to produce high-anti-knock motor fuel, a certain quantity of hydrocarbon gases and first cycle gas oil;

(2) Catalytic conversion of this first cycle gas oil fraction, with or without the heavy naphtha, along with propane-butane fractions to produce high anti-knock motor fuel, a certain quantity of gases and a second cycle gas oil;

(3) The catalytic conversion of the second cycle gas oil along with light hydrocarbon gases and hydrogen to produce high anti-knock motor fuel, a certain quantity of gases and a third cycle stock, the third cycle stock being recycled with the second cycle stock in this step.

Other steps in the process include the dehydrogenation of light naphtha, the viscosity breaking of reduced crude and optionally the catalytic dehydrogenation of the propane-butane fraction. The gases from each of the above steps are combined and then separated into light and heavy fractions, the heavy fractions either with or without dehydrogenation going to the second step, and the light gases, together with hydrogen, going to the third step.

The temperatures and pressures in each of these steps necessarily vary with the particular stocks treated and the particular catalysts employed, all of which will be hereinafter set forth in more detail. A common stabilizer is used for the three conversion processes. Hot products from one process are introduced directly into the hot feed stocks entering another process so that maximum thermal efficiency is obtained. By the particular combination of processes hereinabove described I can not only markedly increase the yield of gasoline obtainable from any given crude, but I can obtain a higher quality motor fuel, one which is particularly characterized by a very high knock rating.

The invention will be more clearly understood from the following detailed description, and from the accompanying drawing which forms a part of this specification and which diagrammatically represents the arrangement of a preferred embodiment of my apparatus or system.

Crude oil is heated in conventional exchangers and coils and is introduced at a temperature of about 500° F. to 800° F. through line 10 into crude oil fractionating tower 11, wherein it may be separated into as many fractions as desired. Preferably, the vapors from the top of the tower pass through line 12 and cooler 13 to separator 14, a light naphtha being withdrawn from the bottom of the separator through line 15, and uncondensed gases being transferred through line 16 to compressors 17.

Heavy naphtha is taken off as a side stream through line 18 and it may optionally be passed through line 19 to be processed with first recycle gas oil, or through line 20 to be processed with gas oil. The gas oil is withdrawn as a side stream through line 21 and reduced crude is withdrawn from the bottom of the tower through line 22.

The light naphtha may be suitable for blending without further treatment, but if desired, its octane number may be increased by subjecting it to a catalytic dehydrogenation of the type which will be hereinafter described. Such a dehydrogenation process will not only increase the knock rating of the light naphtha, but it will furnish useful hydrogen for step 3, hereinabove described. If the naphtha is dehydrogenated it will be by-passed through line 23 through dehydrogenation system represented by the rectangle 24, the hydrogen being passed through line 25 to

gas line 16, and the dehydrogenated light naphtha being returned through line 26 to line 15 and thence to the stabilizer, as will be hereinafter described.

The heavy naphtha may be processed in one of the ways hereinafter described or it may be treated catalytically, passed through line 27 to a catalytic conversion system represented by rectangle 28 for increasing its octane number, the treated heavy naphtha being introduced through line 29 to the stabilizer, and any gases produced in the catalytic treatment being passed through line 30 to the gas line 16. If conversion system 28 is employed it is preferably carried out at a temperature of about 700 to 850° F. in the presence of activated clay of the same general type which is hereinafter described with regard to the treatment of gas oil.

Gas oil from line 21, which may contain heavy naphtha from line 20, is forced by pump 31 through pipe still 32 and lines 33 to one or more of a battery of catalyst chambers 34. The particular temperature and pressure will depend somewhat upon the nature of the crude oil and the boiling range of the gas oil, but preferred temperatures are of the order of 750 to 1000° F., preferably 850 to 925° F. The pressure in the catalyst zone is preferably low, i. e., atmospheric or below fifty pounds per square inch.

I may use any one of a variety of catalysts known to be effective for the conversion of gas oils and naphthas to low boiling hydrocarbons of high anti-knock rating. Such catalysts include activated hydrosilicates of alumina, both natural and synthetic, particularly such compositions wherein the mol percent of alumina is of the order of 10% to 40%. The acid treated natural clays such as Attapulgus or Death Valley clay may be used. The catalysts also include boron silicate, alumina mounted on silica, and other mixed catalysts involving one element from the third group and one element from the fourth group in the periodic system. Nickel borite has been found to be an excellent catalyst, either alone or admixed with some other material to decrease its carbon-forming tendencies, i. e., with cobalt, borite, clay, bauxite, etc. Any and all of the above catalysts may be impregnated with other metallic oxides, including nickel, copper, cadmium, cobalt, thoria, manganese and the like. If desired, certain promoters may be introduced along with the hydrocarbon stream entering the reaction zone, such promoters including the hydrogen halides, organic halides and easily decomposable oxides. When using oxide promoters, some improvement is effected in the cracking reaction itself, but what is more important, the life of the catalyst is extended by virtue of the consumption of carbonaceous matter on the catalyst while the process is in operation. These oxides include the organic peroxides and the oxides of nitrogen.

In this process, which will be referred to as zone A, there is no recycling, the unconverted gas oil being further processed in zone B and tar and heavy gas oil being converted in the viscosity breaker, which will be hereinafter described.

In accordance with conventional practice, one or more of the catalyst chambers are revivified or regenerated by oxygen-containing gases, while other catalyst chambers are on stream. Such regeneration is well-known in the art and needs no further description.

The reaction products leaving catalyst chambers 34 are passed through line 35, through line 36 to the low pressure evaporator tower 37.

Reduced crude from line 22 is introduced into this low pressure evaporator 37 above trap-out pan 38, where it picks up heat and where the light ends are stripped therefrom. The hot stock from the trap-out pan is charged through line 39 to viscosity breaker furnace 40, wherein it is heated to a temperature of about 850 to 950° F., at about the same pressure as the catalytic cracking system hereinabove described. The hot products from pipe still 40 mixed with catalytic cracking products from line 35 are introduced through line 36 underneath trap-out pan 38. Tar is withdrawn from the base of the evaporator through line 41, and vapor, comprising the first recycle oil, gasoline fractions, and gases are taken overhead through line 42 to the first bubble tower 43. The heavier gas oil fractions are condensed with the reduced crude in the evaporator tower and continuously recycled to the vis breaker pipe still until converted into lighter products and tar, respectively.

In bubble tower 43 the gasoline and gases are separated from the first cycle gas oil, the former being withdrawn from the top of the tower through line 44 to cooler 45, separator 46 and stabilizer 47. Suitable reflux means will, of course, be supplied in the top of the bubble tower, and a reboiler or heating means may be supplied at the bottom thereof.

The first cycle gas oil from the base of bubble tower 43 is withdrawn through line 48 and forced by pump 49 through pipe still 50, thence through line 51 to one or more of a battery of catalyst chambers 52. As above stated, heavy naphtha from line 19 may be admixed with this first cycle gas oil in line 48, and a C_3–C_4 gas fraction from line 53 may be introduced into the line between pump 49 and the pipe still. The C_3–C_4 fraction is obtained, as hereinafter described, and consists chiefly of propane, propylene, normal and iso-butanes, normal butenes and iso-butylene, although small amounts of other hydrocarbons may be used. If the C_3–C_4 fraction is catalytically dehydrogenated, as hereinafter described, it may be introduced directly into line 51 through line 54.

The temperatures employed in catalyst chambers 52 (zone B of my system), are about the same as those employed in zone A, namely, from 800 to 1000° F., and preferably from 850 to 925° F. The pressures in this zone may also be similar to those used in zone A, but they are preferably higher, and may be up to 200 or 300 pounds per square inch or even higher. The catalysts in zone B may be the same as those used in zone A, but they may in addition be impregnated with, or physically admixed with, one of the known dehydrogenation catalysts. For example, pellets or particles of chrome oxide gel or metallic chromites, such as magnesium chromite, may be admixed with the extruded sticks or hollow cylinders of clay material used in zone A. It is particularly desirable to employ such dehydrogenation catalysts in zone B if the gases charged thereto have not been previously dehydrogated. By carrying out the process of zone B in the presence of normally liquid and normally gaseous hydrocarbons, it is found that while the yield is approximately the same as that which would be obtained by processing the two stocks separately, the octane number obtained is considerably higher.

Reaction products from zone B are introduced through line 55 to bubble tower 56. The gasoline

and gases are withdrawn overhead through a suitable reducing valve to line 57, to line 44, cooler 45, gas separator 46 and stabilizer 47.

The second cycle gas oil is withdrawn from the base of bubble tower 56 through line 58, and is forced by pump 59 through the coils of pipe still 60, thence through line 61 to the catalyst chambers 62 of zone C. This second cycle gas oil is admixed with hydrogen, methane, ethane, ethylene, etc., from line 63, which may be introduced in line 58 ahead of the pump or compressor 59, or which may be separately compressed and introduced into the line between pump 59 and the coils of the pipe still 60. The temperatures in catalyst chambers 62 of zone C are somewhat higher than those used in zone B and may range from 900 to 1050° F. Pressures in zone C are preferably considerably higher than those used in zone B, and may range from 200 to 2000 pounds per square inch. The catalysts in zone C are preferably those commonly described as sulfur containing hydrogenation catalysts of which molybdenum sulfide is an example. The purpose of zone C is to obtain an effective reaction between gases rich in hydrogen and a cycle stock of low hydrogen content, so that a maximum yield of gasoline of comparatively high octane number can be produced with a minimum amount of coke formation, and preferably without the formation of tar.

The products from zone C are introduced through line 63a to bubble tower 64, the gasoline and gases being withdrawn from the top of this tower through line 65 containing a suitable pressure reduction valve to line 57, and the heavier products being withdrawn from the base of this bubble tower through line 66 and recycled along with second cycle stock from line 58 through the coils of pipe still 60 and through the zone C catalyst chambers.

The gasoline and gases from all of the bubble towers is cooled in condenser 45 and introduced into separator 46, the condensate being introduced into stabilizer 47, as hereinabove described. This stabilizer is preferably operated at a pressure of about 100–300 pounds per square inch, and it may therefore be desirable to provide separate separators for the gasoline from low pressure and high pressure bubble towers. Finished gasoline is withdrawn from the base of the stabilizer tower through line 67. The overhead from the stabilizer is withdrawn through line 68 to cooler or condenser 69 and thence to separator 70. Liquid from this separator may be used as reflux in the stabilizer or passed by line 71 to line 72.

Uncondensed gases from separator 46 are introduced through line 73 to line 16, and uncondensed vapors from separator 70 are introduced through line 74 to line 16. Line 16 will thus conduct all of the hydrogen, methane, ethane, ethylene and perhaps some propane, propylene, butanes and butylenes to compressor 17 which will boost the pressure of these gases to about 300 pounds per square inch, or higher. The compressed gases are partially condensed in cooler 75 and introduced into separator 76. A fraction containing predominately hydrogen, C_1 and C_2 fractions is withdrawn through line 63 for introduction into feed stock going to zone C, as hereinabove described. The condensate from separator 76, which contains chiefly C_3 and C_4 fractions, is withdrawn through line 76a to line 72, from which it may be passed through line 53 to the feed stock entering zone B. A light pressure absorber and stripper may be substituted for separator 76 with certain resultant economies in which case line 74 may lead directly to the absorber.

These fractions from line 72 may alternatively be passed through line 77, pipe still coils 78 and line 79 to dehydrogenation catalyst chambers 80 of zone D. The temperature of this zone is of the same order as that used in zone B, namely, about 800 to 1000° F., and the pressures may likewise be about the same as used in zone B. The catalyst used in the dehydrogenation of zone D is preferably a chrome oxide gel or a magnesium chromite, although it should be understood that any well-known dehydrogenation catalyst may be employed. Dehydrogenated C_3–C_4 fractions are withdrawn from zone D through line 54 for admixture with hot vapors entering zone B, in which case the pressure in zone B will preferably be maintained at below 200 pounds per square inch, or, they may be introduced through line 81 for use in the catalytic conversion of heavy naphtha, as hereinabove described. This conversion of heavy naphtha with dehydrogenated C_3-C_4 fractions may be effected either catalytically or thermally. The catalytic reaction conditions will be approximately the same as those hereinabove described in connection with zone B. If a thermal process is used, temperatures of the order of 1050 to 1100° F. are preferred, with pressures upwards of 500 pounds per square inch.

While I have described a common stabilizer tower for light naphtha, converted heavy naphtha, and gasoline from bubble towers 43, 56, and 64 it should be understood that each or any of these gasoline fractions may be separately stabilized if desired, without departing from the spirit of my invention. The finished gasoline is preferably a blend of the products produced in each of the above-enumerated steps, but it should be understood that particular products may be segregated for special use.

It will be noted that all of the gases from all of the zones of my system are fractionated in a common separator, segregated and utilized in those processes for which they are most suitable. Reaction in zone B, for instance, effects a certain amount of reaction of gaseous olefins with normally liquid paraffins or gaseous paraffins with normally liquid olefins. These reactions produce highly branched paraffin and olefin hydrocarbons of high knock rating. Similarly, in zone C there will be a certain amount of polymerization, hydrogenation, alkylation and gas reversion, so that the resulting motor fuel will consist of branched chain hydrocarbons which are richer in hydrogen than the second cycle gas oil charging stock, and which are characterized by a very high antiknock rating.

Widely varying fractions of crude oil are thus converted almost entirely into gasoline of high antiknock value, only a small amount of tar being withdrawn through line 41. It may be necessary from time to time to vent a portion of the light gas component from the system through line 82 to the burner gas lines.

While I have described in detail a preferred embodiment of my invention, it should be understood that I do not limit myself to any of the details hereinabove described, and it should also be understood that the above description has been simplified by purposely omitting details of heat exchange expedients, and of a large num-

ber of steam lines, water lines, pumps, compressors, valves, etc., which will be necessary for operation, but which are not shown for reasons of clarity. Regeneration equipment and catalyst chamber construction has not been described in detail for the same reason. Such details of construction and operation are well-known to those skilled in the art, and their inclusion in this description would tend to confuse rather than to clarify the description of the invention.

I claim:

1. The method of converting petroleum oil to high antiknock motor fuel which comprises fractionating said oil into naphtha, virgin gas oil and reduced crude, thermally converting the reduced crude into tar and light products including gas oil, gasoline and gases, catalytically cracking the virgin gas oil, fractionating the products from the catalytic cracking together with the products from the thermal conversion to separate gasoline and gases from a first cycle gas oil, separating hydrogen and methane from said gases to obtain a C_3–C_4 hydrocarbon fraction admixing said C_3–C_4 fraction with said first recycle gas oil, and catalytically converting said mixture to form a second cycle gas oil, and a high antiknock gasoline characterized by branched chain structure.

2. The process of claim 1 which includes the further step of admixing a gas rich in hydrogen with the second cycle gas oil, and catalytically converting said mixture into high antiknock gasoline under a pressure of about 200 to 2000 pounds per square inch in the presence of a hydrogenation catalyst.

3. The method of converting crude petroleum oil into high quality motor fuel, which comprises fractionating said oil into naphtha, gas oil and reduced crude, catalytically converting said naphtha to form high antiknock motor fuel and gases, catalytically cracking said gas oil to form high antiknock motor fuel, together with gases, a cycle gas oil, and heavier products, thermally converting said reduced crude, together with said heavy products from the catalytic cracking step to form tar, first cycle gas oil, gasoline and gases, separating the gasoline and gases produced in the catalytic cracking and thermal conversion steps from the combined gas oils produced therein, catalytically converting said combined gas oil, together with an admixed C_3–C_4 fraction to produce high quality gasoline, gas, and a second cycle oil, separating said second cycle oil from said gasoline and gas, catalytically converting said second gas oil in the presence of a gas rich in hydrogen to form high quality gasoline and gas and separating the gas from the gasoline produced in each of the above steps, fractionating said gas into a C_3–C_4 fraction, and a fraction rich in hydrogen, returning the C_3–C_4 fraction for conversion with first cycle gas oil, and returning said fraction rich in hydrogen for conversion with said second cycle gas oil.

4. In the process of claim 3, wherein the C_3–C_4 fraction is dehydrogenated before it is returned for admixture with said first cycle gas oil.

5. The method of claim 3 wherein the catalytic cracking is effected at a pressure of about atmospheric to 50 pounds per square inch and a temperature of about 800 to 1000° F., wherein the conversion of the first cycle stock with the C_3–C_4 fraction is effected at a temperature of about 800 to 1000° F. and at a pressure of about atmospheric to 200 pounds per square inch, and wherein the catalytic conversion of the second cycle stock with the fraction rich in hydrogen is effected at a temperature of about 900 to 1050 F. under a pressure of about 200 to 2000 pounds per square inch.

6. The process of claim 3 wherein the catalyst employed in the conversion of the first cycle gas oil with the C_3–C_4 fraction is a mixture of a dehydrogenation catalyst with a cracking catalyst.

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