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REFINING OF SYNTHETIC HYDROCARBON MIXTURES

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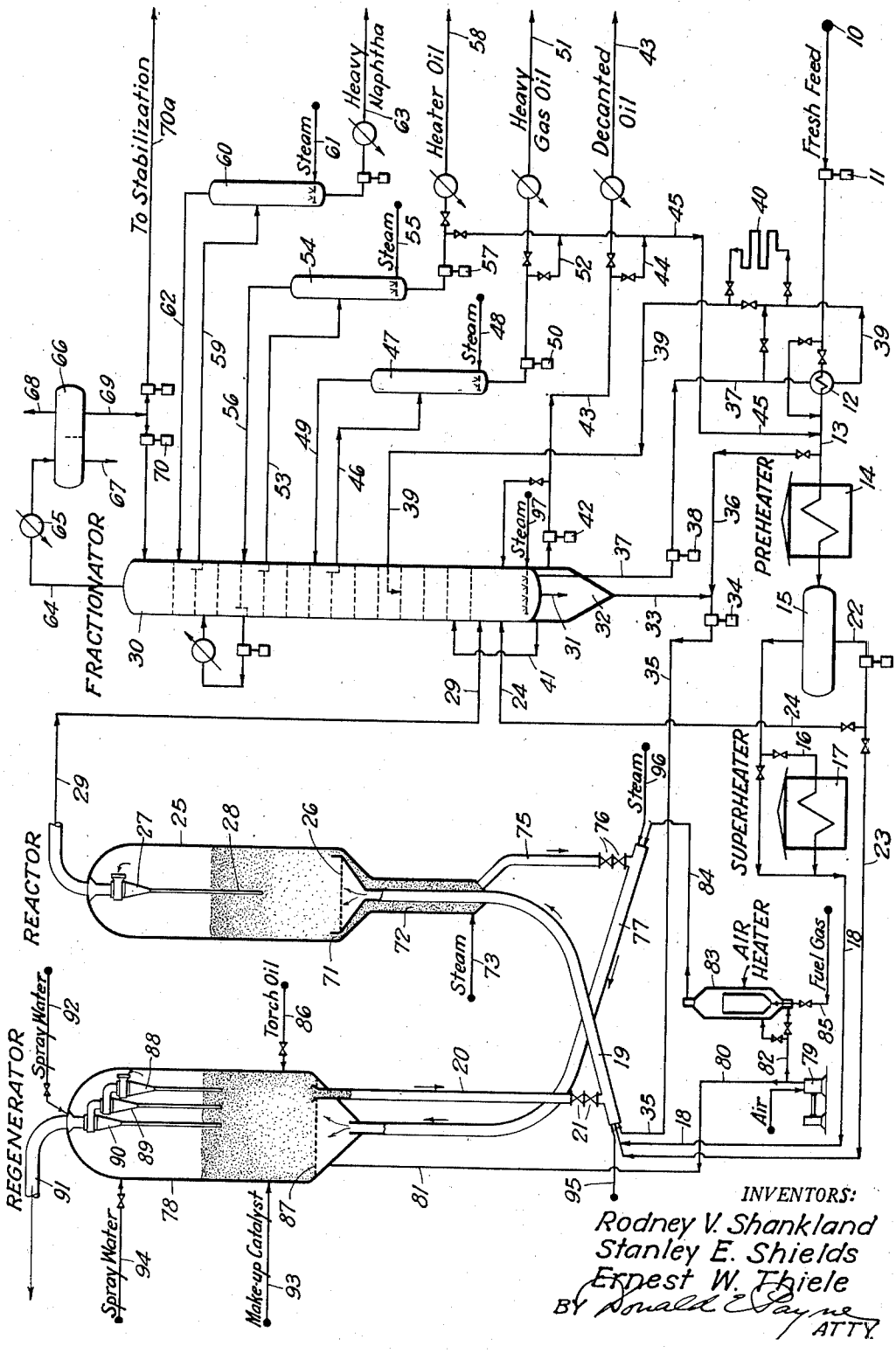

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REFINING OF SYNTHETIC HYDROCARBON MIXTURES

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5 Claims. (Cl. 260—450)

1

This invention relates to the refining of synthetic hydrocarbon mixtures, such for example as are obtained by synthesis from hydrogen and carbon monoxide. The invention pertains more particularly to an improved method and means for obtaining high quality distillate fuel oils as well as high quality gasoline.

When hydrocarbons are synthesized by reaction of carbon monoxide and hydrogen over an iron catalyst, the gasoline fraction of the product liquid has a relatively low octane number and a bad odor and it is extremely unstable toward oxygen, i. e. toward gum formation and discoloration. The fraction boiling above gasoline is likewise characterized by bad odor and instability toward oxygen so that it is unsuitable for use as distillate fuels such as kerosene, burner oils and furnace oils. The obtaining of maximum yields of distillate fuel oils is a matter of outstanding importance; such products were heretofore amply supplied as by-products from ordinary refining operations but the increase in demand therefor coupled with the decrease in crude petroleums of suitable quality for supplying such demand has presented the petroleum industry with a serious problem which the present invention will help to alleviate. An object of this invention is to provide a method and means for treating the synthesis product liquid for producing maximum quantities of high quality distillate fuels and gasoline by a reaction which is primarily reforming and deoxygenation as distinguished from cracking.

A further object is to provide an improved method for treating synthesis hydrocarbon product mixtures which will minimize degradation thereof to carbon and light hydrocarbon gases. A further object is to obtain from synthesis hydrocarbon mixtures maximum yields of gasoline and distillate fuels at minimum refining costs and to provide a refining system which can be built and operated at minimum expense.

A further object of the invention is to provide an improved treating method for deodorizing synthetic hydrocarbon products of the gasoline and distillate fuel boiling range and for making said products stable against discoloration and gum formation. Another object of the invention is to provide optimum operating conditions for effecting such treatment with particular catalysts. A further object is to provide an improved correlation of temperature, catalyst and severity of treatment whereby maximum yields of high quality distillate fuel oil and gasoline are obtainable from synthesis hydrocarbon mixtures with minimum degradation to coke and light hydrocarbon gases. A further object is to provide improved methods and means for removing combined oxygen from synthesis hydrocarbon products. Other objects will be apparent as the detailed description of the invention proceeds.

2

In a preferred method of practicing the invention the synthesis product liquid is heated to effect vaporization of substantially all components except those which might form carbonaceous deposits in heating tubes, the vaporized portion is separated from unvaporized liquid, and the vaporized portion is then superheated. Unvaporized liquid may be commingled with the superheated vapors when said vapors are contacted with conversion catalyst. The catalyst is preferably a synthetic silica alumina gel which contains about 10% to 25% of alumina and which has been dried and heated to high temperature to produce hard, porous particles characterized by a gel structure. The catalyst is of small particle size chiefly in the range of 2 to 100 microns and it is employed in fluidized dense phase condition in a reaction and regeneration system similar to that conventionally employed in so-called fluid catalytic cracking systems.

The severity of treatment in our process is materially lower than that employed for catalytic cracking. The reaction temperature of about 700° F. is much lower than ordinary cracking temperature. The intensity of treatment depends not only upon temperature but upon the activity of the catalyst, the catalyst-to-oil weight ratio (C/O) and the weight space velocity or amount by weight of oil charged per hour per amount by weight of catalyst in the reactor ($W_o/hr./W_c$). After catalyst has been on stream for some time its activity is considerably less than that of freshly prepared catalyst and its relative weight activity (A) may be defined as the number of parts by weight of fresh catalyst which would correspond in effectiveness to 100 parts by weight of the catalyst being evaluated. Equilibrium catalyst in a fluidized system may have a relative weight activity in the range of about 10 to 40, e. g. about 15 to 20. At such catalyst activity the severity factor may be expressed as:

$$\frac{C/O}{(W_o/hr./W_c)1.5}$$

and the severity factor as determined by this formula should be in the approximate range of

.02 to 2.0, the highest severity in this range being employed with the least active catalyst and/or relatively low operating temperatures. At 700° F. and with catalyst of average equilibrium activity, the use of a severity factor less than .02 results in products of inferior odor and stability against gum and color formation while severity factors greater than 2.0 result in impaired quality and an undesirable amount of cracking, loss to coke and gas formation.

The reactor is operated at a dilute phase pressure of about 12 pounds per square inch gauge, the pressure in the lower part of the reactor being somewhat higher since the catalyst therein is maintained in turbulent condition at a density of about 25 to 35 pounds per cubic foot by passing a gasiform charge stream upwardly therein at about 1.2 to 1.5 feet per second (measured in the dilute phase).

Catalyst regeneration is effected at about 1000 to 1050° F. at a dilute phase pressure of approximately 10 pounds per square inch gauge. The catalyst in the lower part of the regenerator is maintained in turbulent condition at a density of about 25 to 35 pounds per cubic foot by passing regeneration gas upwardly therein at about 1.3 to 1.6 feet per second (measured in the dilute phase). The catalyst is stripped with steam before it enters the regenerator from the reactor.

The products from the reactor enter the lower scrubbing section of a fractionator wherein residual catalyst particles are scrubbed out and settled for return to the stream entering the reactor. Naphtha, heater oil and gas oil streams are separately recovered. In the absence of preliminary adsorption of oxygen compounds from the synthetic hydrocarbon mixture with silica gel or the like, the heater oil and/or gas oil streams should either be recycled to the reactor with incoming synthesis hydrocarbon product or may be recycled in a blocked out operating in the absence of synthesis hydrocarbon product. These particular fractions require more drastic treatment than the gasoline fraction for deodorizing stabilizing against color and gum formation and quality improvement generally.

The invention will be more clearly understood from the following detailed description of a specific example read in conjunction with the accompanying drawing which is a flow sheet of a commercial system for treating about 4500 barrels per day of a synthesis hydrocarbon product.

The plant illustrated in the drawing was designed for the treating of a synthesis hydrocarbon mixture produced by reacting carbon monoxide and hydrogen in the presence of a fluidized iron catalyst at a temperature in the range of about 600 to 700° F. and a pressure in the range of about 200 to 450 pounds per square inch, the total effluent synthesis stream being fractionated to remove normally gaseous components and oxygen compounds that are readily removable by feasible fractionation, extraction or other separation means. The remaining synthesis hydrocarbon mixture consists essentially of hydrocarbons having about 5 to 20 carbon atoms or more per molecule with combined oxygen in amounts of .5 to 5% or more.

The treatment of fractions containing less than 5 carbon atoms per molecule or even the C_5 fraction is usually unnecessary because oxygen compounds can readily be removed from such fractions by simple and well known extraction or fractionation procedures. Any waxy products having appreciably more than 20 carbon atoms per molecule may be removed by distillation or other known means. The inspection of a representative synthesis hydrocarbon mixture is as follows:

API gravity	55.2
Combined oxygen	2.12 weight %
Initial boiling point	128° F.
10% over at	168° F.
30% over at	218° F.
50% over at	270° F.
70% over at	339° F.
90% over at	474° F.
End point	650° F.

The combined oxygen is usually rather uniformly distributed throughout the entire boiling range. This synthesis hydrocarbon mixture usually contains about 78 to 82 volume percent of hydrocarbons in the gasoline boiling range, a representative inspection of the gasoline fraction being approximately as follows:

API gravity	61.1
Odor	bad
Color	3.5 NPA
ASTM gum	111.4 mg.
Induction period (with and without inhibitor)	<40 min.
Aniline point, °F	74
Oxygen content	2.16 wt. %
Clear ASTM motor octane number	58.8
Motor octane number with 1 cc. of lead tetraethyl	66.4
Motor octane number with 3 cc. of lead tetraethyl	74.1
CFR research octane number clear	63.8
CFR research octane number+1 cc. of lead tetraethyl	70.4
CFR research octane number+3 cc. of lead tetraethyl	83.7
Initial boiling point	122° F.
10% over at	166° F.
30% over at	196° F.
50% over at	228° F.
70% over at	266° F.
90% over at	328° F.
End point	395° F.

The fraction of the charge in the heater oil range is characterized by a bad odor and a marked tendency toward discoloration and gum formation on storage.

About 4500 barrels per day of total synthesis hydrocarbon mixture of this general type is charged from source 10 by pump 11 through heat exchanger 12 and line 13 to preheater 14 wherein it is heated to a sufficient temperature for vaporizing all but the highest boiling fractions of the charge, e. g. to a temperature in the range of 500 to 600° F. or about 550° F. The heated charge is then introduced into separator 15 from which the vapors may be passed by line 16 through coils in superheater furnace 17 and thence passed by line 18 to transfer line 19 for picking up hot catalyst discharged from the base of standpipe 20 in amounts controlled by valves 21. A by-pass may be provided around heat exchanger 12 and around superheater 17 for at least a part of the stream normally passing through lines 13 and 18 in order to obtain desired temperature control. The unvaporized liquid from the base of separator 15 is withdrawn through line 22 and it may be in whole or in part introduced by line 23 to transfer line 19 or introduced by line 24 to the base of the

product fractionating tower. The vapors passed through superheater 17 may be heated to a temperature of the order of 650 to 700° F. the precise amount of preheat depending upon the amount of unvaporized charge introduced through line 23 to transfer line 19 and the amount of heat available as sensible heat in the hot regenerated catalyst. By eliminating the highest boiling components from materials passing through the superheater coke deposition in the superheater coils is substantially avoided and coke formation in the reactor is substantially reduced.

The catalyst-to-oil weight ratio of materials passing through transfer line 19 to the reactor is preferably in the range of about 2:1 to 5:1 and it may be varied within or even outside of this range to maintain the desired heat balance, i. e. to maintain the temperature in the reactor at about 700° F. The hot charge and catalyst mixture passes through transfer line 19 at a velocity of about 25 to 30 feet per second to the base of reactor 25 into which it is distributed by grid plate 26 designed to give a pressure drop of about 1 pound per square inch and to effect uniform distribution of the incoming mixture throughout the cross-sectional area of the reactor. The reactor itself may be about 40 feet or 50 feet high and about 11 feet in diameter so that in recycle operation the vertical gas velocity in the upper portion thereof will be in the range of 1.2 to 1.5 or about 1.35 feet per second. Under such operating conditions the catalyst density will be in the range of about 25 to 35 pounds per cubic foot in the lower part of the reactor. The pressure in the dilute phase above the dense phase level is of the order of about 10 to 12 pounds per square inch gauge and a dilute phase or disengaging space of at least about 15 feet should be maintained above the dense phase level. For average equilibrium catalyst activity the weight space velocity in the reactor should usually be in the range of about 2 to 10 pounds of oil charged per hour per pound of catalyst in the reactor at any instant.

The reaction products pass from the upper part of the dilute phase to cyclone separator 27 from which separated catalyst particles are returned by dip leg 28 to a point below the dense phase level in the reactor. The product stream then passes by line 29 to the lower part of fractionator tower 30 wherein high boiling product components are condensed and solids are scrubbed out of the product stream. Condensate and solids are withdrawn through line 31 to settling chamber 32. Settled solids may be returned from the base of the settler by line 33, pump 34 and line 35 to transfer line 19 along with a small portion of the charge stream introduced through line 36. Another portion of the liquid from the base of tower 30 is withdrawn through line 37 and forced by pump 38 through exchanger 12 and then returned by line 39 as scrubbing liquid for the lower part of tower 30. For further temperature control a part of this recycled stream may be passed through auxiliary temperature control means 40. Solids settling chamber 32 is connected by vent line 41 to a point in tower 30 above the inlet of line 29. The heavy oil separated from solids in settler 32 may be withdrawn by pump 42 and either discharged from the system by line 43 or returned through lines 44 and 45 to inlet charge line 13.

A heavy gas oil side stream is withdrawn from tower 30 through line 46 to stripper 47 into which

steam is introduced through line 48, the stripping steam and overhead fraction being returned to the tower through line 49 and the heavy gas oil fraction being withdrawn by pump 50 and line 51 or returned by lines 52 and 45 to inlet charge stream in line 13.

A heater oil fraction boiling in the range of about 350 to 600° F. is withdrawn from tower 30 to line 53 to side stream stripper 54 wherein it is stripped with steam introduced through line 55 the steam and overhead products being returned to the tower through line 56 and the heater oil being withdrawn by pump 57. All or a part of the heater oil is withdrawn from the system through line 58 although a substantial part of the heater oil may be returned by line 45 to the charge stream in line 13.

A heavy naphtha fraction is withdrawn from tower 30 through line 59 to stripper 60 into which steam is introduced through line 61 and from which overhead is returned to the tower through line 62. The heavy naphtha is withdrawn from the system through line 63.

Light naphtha together with uncondensed gases leave the top of tower 30 through line 64 to cooler-condenser 65 and is thence introduced into separator 66 from which condensed water is withdrawn through line 67. Uncondensed gases leave separator 66 through line 68 and are subsequently processed to recover the desired components thereof. Condensate from the base of separator 66 is withdrawn through line 69 a part of it being returned by pump 70 for use as reflux and the remainder being withdrawn through line 70a for stabilization.

Referring to the catalyst system generally, a substantially constant catalyst inventory is maintained therein and relatively spent catalyst may be withdrawn from the system and fresh catalyst added thereto at such a rate as to maintain a predetermined weight activity which may, for example, be about 20. Catalyst is removed from the reactor at substantially the same rate as it is introduced thereto from the regenerator, the catalyst from the reactor being withdrawn directly from the dense phase at a point below the upper level thereof. When the stripper is at the base of the reactor and in the same chamber, the catalyst may be withdrawn through annular space 71 to stripping section 72 into which steam is introduced through line 73 at the rate of about 6 pounds per thousand pounds of catalyst passing through the stripper. If desired, an external stripper may be employed in which case dense phase catalyst may be transferred laterally thereto through a valve conduit and the stripped products may be returned by an upper conduit to the reactor. The stripping steam replaces the hydrocarbon suspension gas and even when the stripper is in the base of the reactor very little if any steam passes upwardly into the dense catalyst phase in the reactor. We have found that it is detrimental to introduce any substantial amount of steam into the dense phase portion of the reaction zone as will be hereinafter pointed out in more detail.

The stripped catalyst is downwardly withdrawn through standpipe 75 and introduced in amounts regulated by valve 76 into transfer line 77 which leads to regenerator 78. From blower 79 a portion of the air may pass directly through lines 80 and 81 to the base of the regenerator but sufficient air is introduced through line 82, vessel 83 and line 84 for carrying catalyst back to the regenerator at a velocity of about 25 to 30

feet per second in transfer line 77. During the starting up procedure a portion of the air may support combustion in chamber 83 of fuel gas introduced through line 85 the hot combustion products serving to bring the catalyst up to desired temperature. If the amount of carbon deposited on the catalyst in the combustion step is not sufficient, when burned in the regenerator, to maintain desired regenerated catalyst temperature, torch oil may be directly introduced into the regenerator through line 86.

The regenerator may be of substantially the same general design as the reactor but somewhat larger and in this case may be a vessel of about 40 to 50 feet in height and about 13½ feet in diameter (making allowance for maximum coke to be handled). The regenerator is preferably operated at a temperature of about 1000 to 1050° F. and at a dilute phase pressure of about 10 to 12 pounds per square inch gauge. The incoming spent catalyst stream is uniformly distributed across the entire cross-sectional area by a grid 87 which may be designed for a pressure drop of about 1 pound per square inch. The regenerator should be designed for a dilute phase upward gas velocity in the range of about 1.3 to 1.6, e. g. about 1.45 feet per second. Here again the dense phase catalyst in the lower part of the regenerator should have a density of about 25 to 35 pounds per cubic foot, the bed depth may be about 15 feet and at least about 15 feet should be provided above the dense phase level for disengagement of carry-over catalyst particles. Primary, secondary and tertiary cyclone separators 88, 89 and 90 remove the bulk of the remaining entrained catalyst particles from the flue gas and these particles are returned to the dense phase by dip legs which extend below the dense phase level. Flue gas is discharged from line 91 through a valve which controls the pressure in the top of the regenerator and, in order to protect such valve means, spray water is introduced through line 92 to cool the exit gases to a temperature of approximately 700° F.

Regenerated catalyst may be withdrawn directly from the dense phase in the regenerator into the top of standpipe 20. It should be understood of course that standpipes 20 and 75 are both provided with conventional aeration means at a point immediately above valves 21 and 76 and at other points along the standpipe lengths. Make-up catalysts may be introduced into the system through line 93, emergency spray water may be introduced into the upper part of the regenerator through 94 and emergency steam may also be introduced through line 95 and transfer line 19 and/or through line 96 to transfer line 77. Likewise, steam may be introduced through line 97 at the base of fractionator 30.

As illustrative of results obtainable by our process, a charge, as hereinabove described, was treated with a fluidized silica alumina catalyst having a particle size chiefly within the range of about 1 to 100 microns and synthetically prepared to have a gel structure and to have an alumina content in the range of about 10 to 25%. The charge was treated at about 700° F. with a weight space velocity of about 3.9 pounds of charge per hour per pound of catalyst in the reactor and with a catalyst-to-oil weight ratio of about 2.5:1 at a pressure of about 10.7 pounds per square inch, the regeneration of the catalyst being effected at about 1000° F. The catalyst had a relative weight activity of about 20 to 30 and the severity factor was about 0.33. On a once-through product output basis there was obtained:

5.0 volume percent total C_4 hydrocarbons
78.7 volume percent of gasoline (C_5–400° F.)
9.3 volume percent heater oil
3.6 volume percent heavy gas oil
2.0 weight percent water
1.3 weight percent dry gas
1.84 weight percent coke

The C_4–400° F. gasoline fraction had the following properties:

API gravity	61.5
Odor	O. K.
Color	11 Saybolt
Aniline point, °F	97
ASTM gum	2.2 mg.
Induction period without inhibitor	480 min.
Induction with .003% du Pont No. 22	705 min.
ASTM motor octane No. clear	76.4
ASTM motor octane No. + 1 cc. lead tetraethyl	81.6
ASTM motor octane No. + 3 cc. lead tetraethyl	84.3
CFR–R octane No. clear	85.3
CFR–R octane No. + 1 cc. lead tetraethyl	91.4
CFR–R octane No. + 3 cc. lead tetraethyl	95.3
Reid vapor pressure	4 lbs.
Initial distillation temperature	120° F.
10% over at	166° F.
30% over at	204° F.
50% over at	239° F.
70% over at	283° F.
90% over at	350° F.
End point approximately	390° F.

The heater oil, which constituted 9.3% of the total product, had the following inspection:

API gravity	35.4
Odor	Fair
Color	1.5 NPA
Initial boiling point	436° F.
10% over at	448° F.
30% over at	458° F.
50% over at	467° F.
70% over at	480° F.
90% over at	506° F.
End point	528° F.

While the above inspection shows that a remarkable improvement was effected in the heater oil over the corresponding fraction in the initial charge, best results are obtainable if a substantial portion of the heater oil fraction, as well as the heavy gas oil fraction, is recycled to the conversion zone or separately retreated with the catalyst at substantially the same temperature. Thus when about two parts of product boiling above 400° F. is recycled for each three parts of fresh charge introduced, the dry gas yield may be increased by about .3%, the total C_4 hydrocarbons may be increased by about the same amount, the gasoline fraction may be increased by about 1 or 2% and the heater oil fraction decreased by about 1 or 2%, slightly more water being produced in the recycle operation and the coke being increased by about .8% based on total charge. Such a recycle operation markedly improves the heater oil fraction with regard to odor, color and stability against gum formation. In the recycle operation we may recycle all of the heavy gas oil and all but the net production of the heater oil. For best results the recycle ratio of total feed

to fresh feed should be in the range of 1.2:1 to 3:1; based on components in the fresh feed boiling above 400° F. the ratio should be in the range of 2:1 to 11:1.

Instead of employing recycle operation the heater oil and/or heavy gas oil may be separately charged to the reactor at about 700° F. under substantially the same conditions as hereinabove set forth. In fact the gasoline fraction and the higher boiling fraction of the original synthesis mixture may be separately treated in which case the gasoline fraction may be subjected to somewhat higher temperatures and correspondingly higher space velocities and the heater oil and gas oil fractions may be contacted at temperatures of approximately 700° F. at somewhat lower space velocities, e. g. of the order of 0.1 to 3 pounds of oil per hour per pound of catayst in the reactor at any instant. Thus a fraction of the original synthesis hydrocarbon mixture having an API gravity of 35.4 and a distillation range of about 400 to 675° F. was treated with silica alumina catalyst at a temperature of 700° F. with a weight space velocity of .22 pound of oil per hour per pound of catalyst in the reactor at a pressure of 15 pounds per square inch to give a 92% volume yield of a product of which the kerosene and heater oil fractions, on standing 100 hours in the daylight at room temperature, had a saybolt color shade of plus 20 and plus 11 respectively. The odor of the kerosene and heater oil was good after 500 hours. The color stability of the heater oil was even greater than that of kerosene produced from crude petroleum.

While a fluidized treating system has been hereinabove described in considerable detail, it should be understood that the treating may be effected in either fixed bed or moving bed operations although such operations (particularly fixed bed) are not as advantageous, economical or desirable as the fluid catalyst system. When fixed bed or moving bed operations are employed, the on-stream period (or catalyst holding period in moving bed) should be less than 2 hours and preferably from about 1 minute to about 1 hour, the space velocity in this case being within a range of about .1 to 2.5 pounds of oil charged per hour per pound of catalyst in the reactor at any instant. The use of short on-stream reaction periods between catalyst regenerations has a remarkable effect in increasing the rate of conversion and product quality and in decreasing the losses to dry gas and coke. Since it is desired that cracking of hydrocarbons, particularly in the distillate fuel boiling range, should be minimized and that the conversion should be chiefly reforming and deoxygenation, the very short catalyst holding time (or on-stream period in fixed bed operations) is a matter of considerable importance.

The reaction temperature of 700 degrees is predicated on the use of average equilibrium catalyst originally prepared as a synthetic, gel-type silica-alumina catalyst containing about 10 to 25% of alumina (altho the alumina content may be more or less than that stated as the preferred range). An example of the preparation of such a catalyst is as follows: dissolve about 50 to 75 kg. of sodium aluminate in about 500 liters of water. If the sodium aluminate is of sufficient purity the solution should be substantially complete. If a technical grade of sodium aluminate is employed the solution should be filtered to remove insoluble materials. Dissolve 700 liters of sodium silicate (water glass) in 2100 liters of water. Pour the sodium aluminate into the water glass solution at ordinary room temperature with stirring to avoid any precipitation and to obtain a sol of uniform consistency. Permit the sol to set for several hours or longer to form a gel. Wash the gel thoroughly with distilled water and then with a weak acid or a concentrated salt solution, e. g., an 8% ammonium chloride solution, for removing sodium ions as completely as possible. Then thoroughly wash the gel with water and slowly dry the gel to such degree that it can be broken into small lumps. Continue the drying of the lumps of broken gel at higher temperatures and finally heat the lumps of gel to a temperature of about 850 to 1150° F., preferably about 1000° F. The resulting product will consist of hard glassy-appearing (i. e. not dull or chalky) particles which are remarkably resistant to abrasion and which are characterized by a high degree of porosity. The resulting catalyst is a dense form of silica and alumina which is in intimate physical admixture, which is highly porous and which has remarkable activity. Synthetic silica alumina catalysts of similar activity can be prepared by other methods well known to those skilled in the art and the invention is applicable to the use of any such catalysts.

Considerable improvement in gasoline and heater oil properties may be obtained by the use of activated montmorillonite clay (Super Filtrol) or by the use of activated alumina catalysts prepared from alumina gels or bauxite. Such activated alumina catalysts however are not equivalent to the synthetic silica alumina catalysts hereinabove described and they require somewhat different operating conditions. When activated alumina catalysts are employed the treating temperature should be about 100 degrees higher and the contact time should be somewhat longer, i. e. the weight space velocity should be somewhat lower and the severity factor correspondingly increased. Activated alumina catalysts tend to form more carbon or coke and to result in somewhat lower product quality. The use of fuller's earth (Gray process) at 500° F., 200 p. s. i. g. and a weight space velocity of 1 pound of oil charged per hour per pound of fuller's earth in the treating zone gave some improvement in stability but no appreciable improvement in odor and insufficient improvement in octane number; the failure of this treating method to produce a satisfactory gasoline is striking evidence of the fact that the odor and instability of the synthetic hydrocarbon mixture are caused by very different types of compounds from those which are responsible for instability and/or poor color in ordinary petroleum refining processes.

When we refer to a temperature of about 700° we mean 700° F. plus or minus 75° F. Similarly, in the case of bauxite, a temperature of about 800° means a temperature of 800° F. plus or minus 75° F. Preferably, the temperature should be in the range of plus or minus 50° F. and for best results should be in the range of plus or minus 25° F. Higher temperatures produce too much cracking, coke deposition and gas formation and result in products of lower quality. Lower temperatures do not accomplish the desired product improvement at reasonable severity factors.

Addition of steam to the reactor at higher temperatures tends to somewhat reduce the coke deposition but in this process steam has a deleterious effect on the stability of the gasoline

obtained and its use also impairs the odor of the gasoline produced; the use of steam seems to destroy the effectiveness of the process toward the removal of oxygen in the synthetic hydrocarbon mixture. Although small amounts of steam may be tolerated in the reactor, e. g. the amounts that might come from the stripping zone, we prefer to avoid the introduction of steam into the dense phase catalyst portion of the reactor.

As hereinabove pointed out, the severity of treating is of great importance. The severity should be such as to avoid cracking as a predominant reaction and to effect instead chiefly isomerization and oxygen removal. The term "isoforming" has been applied to this treating step because of the high liquid yields, octane number improvement and relatively small amount of cracking; it should be pointed out, however, that this process is markedly different from the process described, for example in U. S. Letters Patents 2,326,705 and 2,410,908, in that the problem in this case is that of removing or altering very different types of compounds, the temperature employed is of a different order of magnitude, the optimum severity factor is likewise considerably different and the use of steam, which was beneficial in the prior process, appears to be detrimental in this process. In the prior isoforming process the charge to the treating step was fractionated to improve components boiling above 400 to 450 F. while in this process advantageous results are obtained by treating the entire synthetic hydrocarbon mixture except perhaps for a very small amount of heavy waxy materials the amount of which is usually less than about 5%. In our process the coke yield appears to be approximately the same under a given set of operating conditions regardless of whether the feed stock is the gasolne fraction, the gas oil fraction or the total synthetic hydrocarbon mixture (provided that the small amount of waxy bottoms is not included). Considerable economy is therefore effected by simultaneously treating the total gasoline plus gas oil fraction and then recycling or retreating the heater oil fraction to obtain the desired odor, color, stability against oxidation and gum formation and burning quality index. Our treating of the heater oil fraction does not improve its cetane number and for preparation of diesel fuel it is preferred to subject such fractions to hydrogenation.

As above pointed out, the severity of the treating must be maintained within narrow limits, i. e. the severity factor, as above defined, should be in the range of about .02 to 2.0 at about 700° F. with average equilibrium catalyst. Such severity factor sharply distinguishes this process from the prior proposals to subject synthetic hydrocarbon mixtures to catalytic cracking. Thus U. S. 2,264,427 teaches the contacting of synthesis hydrocarbon product mixtures and particularly the gas oil fractions thereof with conventional cracking catalysts under cracking conditions with the object of converting the higher boiling components to gasoline. In our process we seek to obtain deoxygenation without substantial cracking so that we may avoid the large losses to coke and fixed gases, effect substantial savings in operating costs, and produce a high quality heater oil as a separate fraction instead of converting such heater oil fraction to gasoline by destructive cracking.

If the synthesis hydrocarbon mixture is contacted with an adsorbent such as silica gel prior to our treating step the severity of treating required for obtaining good odor and stability is somewhat decreased but the indicated severity of treatment may be required to obtain a product of desired octane number improvement. If such a silica gel adsorption step is employed for minimizing the amount of oxygen compounds in the mixture undergoing treatment, a once-through operation may be all that is required to provide a distillate fuel of required odor and stability. While the use of such an adsorption step may be employed in our invention with advantageous results, the invention is not limited thereto.

While our process is specifically designed for the treating of synthesis hydrocarbon mixtures obtained from synthesis with hydrogen and carbon monoxide over iron catalyst, it is believed that the process may also be applicable to the treatment of synthetic hydrocarbon mixtures obtained by oxidation of hydrocarbons and/or by the distillation of shale provided that the products in those gases contain the same types of objectionable components that are contained in the charging stocks hereinabove described. The term "synthetic hydrocarbon mixture" as used herein is intended to mean a hydrocarbon mixture containing oxygen compounds which cannot be separated therefrom by conventional fractionation or extraction procedures, the amount of combined oxygen in said mixture usually being in the range of about .5% to 5% or more, e. g. about 2%.

While our invention has been described in considerable detail with respect to specific examples thereof, it should be understood that many modifications of apparatus and operating procedures and alternative operating conditions will be apparent to those skilled in the art from the above description.

We claim:

1. The method of treating a synthetic mixture of hydrocarbons and oxygenated compounds, which mixture boils within the range of about 100° F. to about 700° F. and contains chiefly components in the gasoline boiling range, which mixture contains combined oxygen distributed throughout the entire boiling range and present in an amount in the range of .5 to 5 weight per cent and which mixture is characterized by a bad odor and extreme instability toward oxygen with a marked tendency toward discoloration and gum formation, which method comprises contacting said mixture with a silica alumina catalyst of gel structure containing an amount of alumina in the range of about 10% to 25% by weight, which is sufficiently spent so that its catalytic activity is only one-tenth to four-tenths the catalytic activity of fresh catalyst, at a temperature in the range of 625° F. to 775° F. and with a severity factor in the range of .02 to 2.0 sufficiently low to substantially avoid cracking and to produce a product of good odor and stability toward oxygen, said severity factor being the catalyst-to-oil weight ratio divided by the weight space velocity taken to the 1.5 power.

2. The method of claim 1 wherein the mixture is one containing components having about 5 to 20 carbon atoms per molecule and produced by carbon monoxide-hydrogen synthesis in the presence of fluidized iron catalyst at a temperature in the range of about 600 to about 700° F. and under a pressure in the range of about 200 to 450

pounds per square inch, the total effluent synthesis stream being fractionated to remove normally gaseous components, higher boiling components and extractable oxygen compounds.

3. The method of claim 1 which includes the step of recontacting a portion of the product from a previous contacting step, which portion is higher boiling than gasoline, said recontacting being under conditions for the production chiefly of a heater oil of good color and stability toward oxygen.

4. The method of claim 1 which includes the steps of employing a weight space velocity in the contacting step in the range of about 2 to 10 pounds of oil introduced per hour per pound of catalyst in the contacting zone and effecting said contacting in the absence of any substantial amount of added steam.

5. The method of claim 1 which includes the steps of superheating vapors of said mixture prior to the contacting step and effecting said contacting by commingling superheated vapors with hot catalyst of small particle size and passing said vapors upwardly through a fluidized dense phase mass of said catalyst while employing a catalyst-to-oil weight ratio of materials introduced in the contacting zone in the range of about 2:1 to 5:1, a weight space velocity in the contacting zone in the range of about 2 to 10 pounds of oil introduced per hour per pound of catalyst maintained in the contacting zone, and fractionating products from the contacting zone to obtain a gasoline boiling range fraction of improved octane number, good odor and stability toward oxygen and a burning oil boiling range fraction also characterized by improved odor and stability toward oxygen.

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