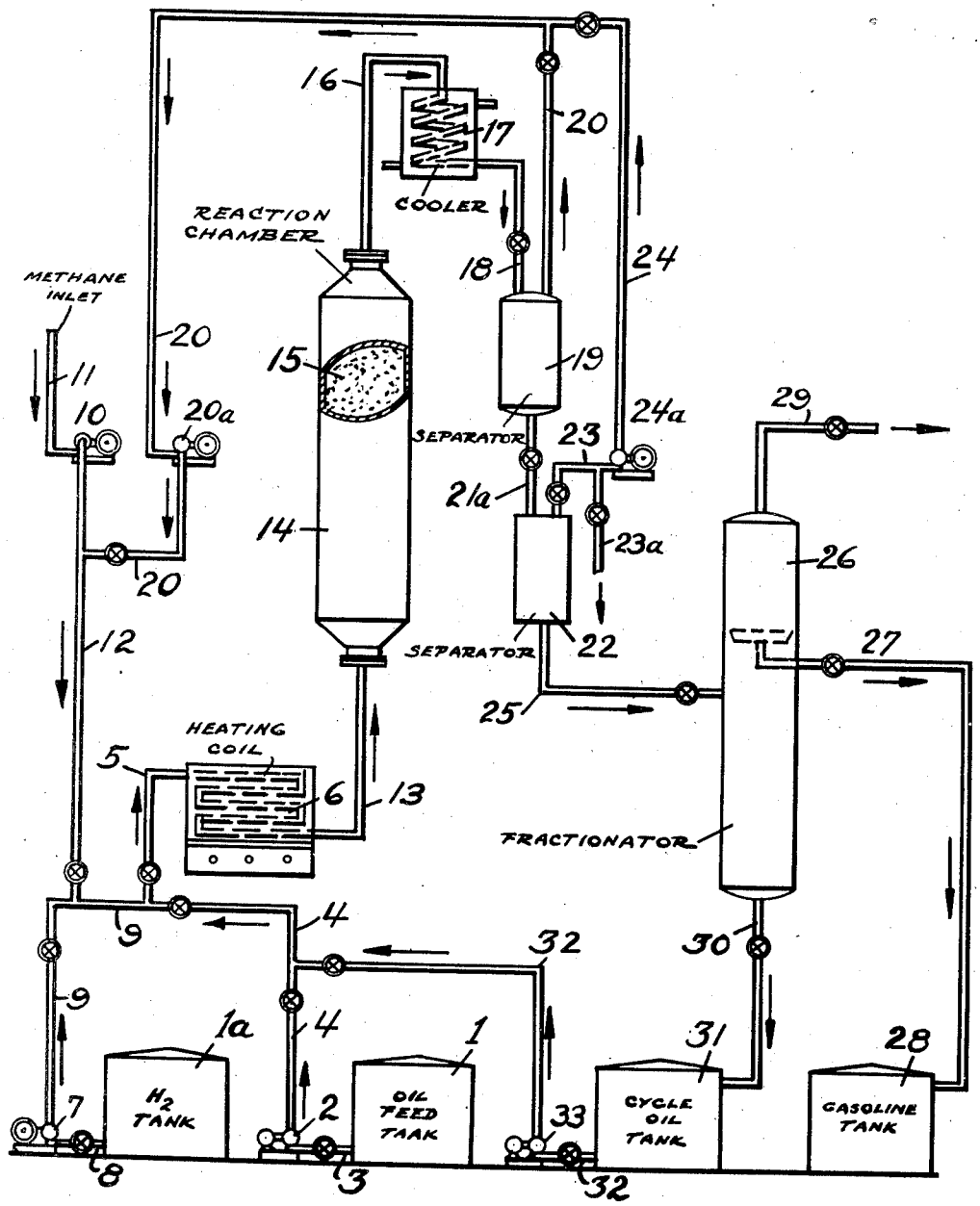
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DESTRUCTIVE HYDROGENATION

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DESTRUCTIVE HYDROGENATION

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1 Claim. (Cl. 196—53)

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This invention relates to the destructive hydrogenation of hydrocarbon oils and is more particularly concerned with the destructive hydrogenation of hydrocarbon oils of the type of middle oils, gas oils and the like conducted in the presence of substantial quantities of methane.

The destructive hydrogenation of gas oils for the production of motor fuels of high octane number and other desirable characteristics is ordinarily carried out at pressures of the order of 200 atmospheres and in the presence of recycle gases containing 80% or more of free hydrogen. Heretofore it has been found necessary to operate in the presence of gases of such high hydrogen content in order to avoid rapid deterioration of the activity of the catalysts used. The necessity for continuously supplying substantially pure hydrogen is an important item of expense in such processes and it can readily be seen that anything which makes it possible to reduce the quantity of free hydrogen required is particularly desirable from an economic standpoint.

I have now found that it is possible to conduct such destructive hydrogenation processes in the presence of substantial quantities of methane. The dilution of the hydrogen with methane has four important advantages over the use of substantially pure hydrogen, namely (1) the amount of free hydrogen which must be produced and supplied to the process is greatly reduced; (2) an appreciable quantity of the methane is caused to react with the hydrocarbon oil and is thereby converted to a useful liquid product; (3) the octane number of the motor fuel produced is markedly higher than that of the product produced when operating in the absence of substantial quantities of methane and (4) the use of methane and its conversion to a useful liquid product provides an outlet for an otherwise refractory material which is commercially available in large quantities.

The manner in which the improved process is carried out will be fully understood from the following description when read with reference to the accompanying drawing which is a semi-diagrammatic view in sectional elevation of one type of apparatus suitable for the purpose.

Referring to the drawing, numeral 1 designates a supply tank of a hydrocarbon oil to be converted to motor fuel. This hydrocarbon oil consists essentially of hydrocarbons boiling in the range of kerosenes and gas oils and may have been derived from any source, for example from the products of the distillation, destructive distillation, cracking, catalytic cracking, hydrogenation, destructive hydrogenation or other treatment of coals, tars, peats, mineral oils, petroleum, shales, lignite, brown coal, pitches, bitumens and other solid, semi-solid or liquid carbonaceous materials. Numeral 1a designates a supply tank of free hydrogen or a gas consisting essentially of free hydrogen. Pump 2 draws hydrocarbon oil from tank 1 through line 3 and forces it through lines 4 and 5 into a heating means 6. Compressor 7 draws hydrogen from tank 1a through line 8 and forces it through lines 9 and 5 also into heating means 6. Compressor 10 draws methane or a gas rich in methane, such as natural gas, for example, through line 11 from any convenient source and forces it through line 12 which meets line 9 carrying hydrogen. A mixture of hydrogen and methane is thereby formed at this point, and this mixture passes with the oil through the heating means 6. The heated mixture of oil, hydrogen and methane flows from heating means 6 through line 13 into a reaction chamber 14 containing a catalyst 15, the nature of which will be described below. Reaction chamber 14 is adapted to withstand high pressures and high temperatures and is resistant to attack by the reacting materials under the operating conditions.

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Reaction chamber 14 is maintained under a pressure between 60 and 1000 atmospheres, preferably between 200 and 600 atmospheres and at a temperature between 500 and 1000° F., preferably between 550 and 850° F. The quantity of gas, consisting of a mixture of hydrogen and methane, which accompanies the oil through the reaction chamber may be between 5000 and 20,000 cubic feet per barrel of oil and the proportion of methane in said gas may be between 40 and 85 mol percent. Small amounts of carbon monoxide, carbon dioxide and water may also be present in the gas mixture. The rate at which the oil passes through the reaction chamber may be between 0.5 and 2.0 volumes of liquid oil per volume of catalyst per hour.

The catalyst 15 in reaction chamber 14 is one characterized by substantial hydrogenating activity. Examples of suitable types of catalyst for this purpose are sulfides of metals of the VI group of the periodic system preferably deposited upon a clay carrier. Sulfides of molybdenum, tungsten or chromium deposited upon clay carriers of the type of natural or activated bentonites and montmorillonites, "Super Filtrol" and the like are especially effective. The carrier may be treated with fluorine compounds such as hydrofluoric acid and fluosilicic acid before the metal sulfide is deposited upon it. The quantity of metal sulfide deposited upon or associated with the carrier may be between 5 and 50% by weight.

Products of reaction leave reaction chamber 14 through line 16, pass through a cooling means 17 and then flow through line 18 into a high pressure separating means 19 wherein gaseous and liquid products may be separated. The gaseous products are removed from separating means 19 through line 20 and are recycled to line 12 by means of a booster compressor 20*a*. The liquid products are removed from separating means 19 through line 21, flow through a pressure reduction valve 21*a* and then discharge into a low pressure separating means 22 wherein the products caused to be vaporized by the reduction in pressure may be separated from the products which remain in liquid phase. The vaporized products, which will contain appreciable quantities of methane and other low molecular weight hydrocarbons, are removed from separating means 22 through line 23 and may be eliminated from the process through line 23*a* or a portion or all of them may be recycled by means of booster compressor 24*a* through line 24 to line 20 where they combine with the gaseous products leaving the high pressure separating means 19. It will be understood that the proper ratio of hydrogen to methane in the recycled gaseous products may be obtained by adjusting the quantities of fresh hydrogen and fresh methane supplied to the recycle gases through lines 8 and 11 respectively.

Liquid products are removed from low pressure separating means 22 through line 25 and introduced into a fractionating means 26. A fraction boiling in the range of gasoline or a motor fuel is withdrawn from the fractionating means through line 27 and collected in a tank 28. Hydrocarbons too volatile for inclusion in the motor fuel are removed from the top of the fractionating means through line 29 and may be discarded, passed to the refinery fuel line or otherwise disposed of. These volatile hydrocarbons will frequently contain large proportions of isobutane which is a valuable feed for alkylation processes. Fractions boiling above the range of the desired motor fuel are removed from the bottom of the fractionating means through line 30 and collected in a tank 31 from which they may be recycled to the fresh feed line 4 by means of line 32 and pump 33.

The following example illustrates the application of the process and indicates the results obtained thereby:

Example

A gas oil having the following characteristics:

Gravity, °A. P. I.	36.5
Initial boiling point, °F	376
Final boiling point, °F	643

is subjected to destructive hydrogenation in the presence of methane at a total pressure of 3000 pounds per square inch and in the presence of a catalyst comprising tungsten sulfide deposited on hydrofluoric acid treated clay. Three experiments are carried out. In the first, the hydrogen partial pressure is 2500 pounds per square inch and the methane partial pressure is 100 pounds per square inch; in the second, the hydrogen and methane partial pressures are 1280 and 1275 pounds per square inch respectively, and in the third, the hydrogen and methane partial pressures are 790 and 1800 pounds per square inch respectively. The following table shows the important operating conditions and the results obtained in each experiment:

	Experiment No.		
	1	2	3
Feed rate, v./v./hour	2.0	2.0	2.0
Total pressure, lbs./sq. in.	3,000	3,000	3,000
Recycle gas rate, cubic feet/bbl. total feed	12,000	12,000	12,000
Average oven temperature, °F.	734	720	763
Hydrogen partial pressure, lbs./sq. in.	2,500	1,280	790
Methane partial pressure, lbs./sq. in.	100	1,275	1,800
Hydrogen consumed, cubic feet/barrel fresh feed	950	700	345
Methane consumed, cubic feet/barrel fresh feed		270	270
Volume percent yield of motor gasoline, on fresh feed	60	54.5	21.2
Volume percent yield of cycle oil, on fresh feed	47	52.4	78.1
Inspection of gasoline:			
Percent off @ 158° F.	14.5	16.0	12.0
Percent off @ 212° F.	32.0	34.0	27.5
Final boiling point, °F.	400	393	378
Acid heat, °F.	1	3	4
Reid vapor pressure	9.0	9.0	9.0
Octane number, ASTM	63.5	68.0	69.0
Inspection of cycle oil:			
Gravity, ° A. P. I.	42.9	41.5	38.6
Aniline point, °F.	176	172	162
Initial boiling point, °F.	431	432	426
Final boiling point, °F.	601	608	621

It will be noted that in Experiments 2 and 3 where the recycle gas contained substantial quantities of methane, there was a consumption of methane of 270 cubic feet per barrel of fresh feed and a substantially smaller consumption of hydrogen than in Experiment 1 where the recycle gas consisted essentially of hydrogen. It will also be noted that the gasoline produced in Experiments 2 and 3 had ASTM octane numbers about 5 points higher than that of the gasoline produced in Experiment 1.

This invention is not limited by any theories of the mechanism of the reactions nor by any details which have been given merely for purposes of illustration but is limited only in and by the following claim in which it is intended to claim all novelty inherent in the invention.

I claim:

An improved process for obtaining lower boiling hydrocarbons suitable for use as motor fuel from a higher boiling hydrocarbon oil of the type of gas oil which comprises subjecting the higher boiling hydrocarbon oil to treatment with between 5000 and 20,000 cubic feet per barrel of oil of a mixture of hydrogen and methane in which the latter is present in a proportion between 40 and 85 mol percent at a temperature between 500° and 1000° F. under a pressure between 60 and 1000 atmospheres and in the presence of a catalyst comprising a minor proportion of a sulphide of a metal of the sixth group of the periodic system and a major proportion of a hydrofluoric acid treated clay so that a substantial proportion of the methane reacts with the oil cooling the products of this treatment without substantial reduction of pressure, separating the liquid and gaseous products, substantially reducing pressure on the liquid products whereby a portion thereof is caused to vaporize, subjecting the products still remaining in liquid phase to fractionation to obtain a fraction boiling in the motor fuel range and a fraction boiling above the motor fuel range, combining the vapors evolved by reduction of pressure with the gaseous products separated before the reduction of pressure, and recycling the mixture to the reaction to provide at least a portion of the mixture of hydrogen and methane required therein.

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