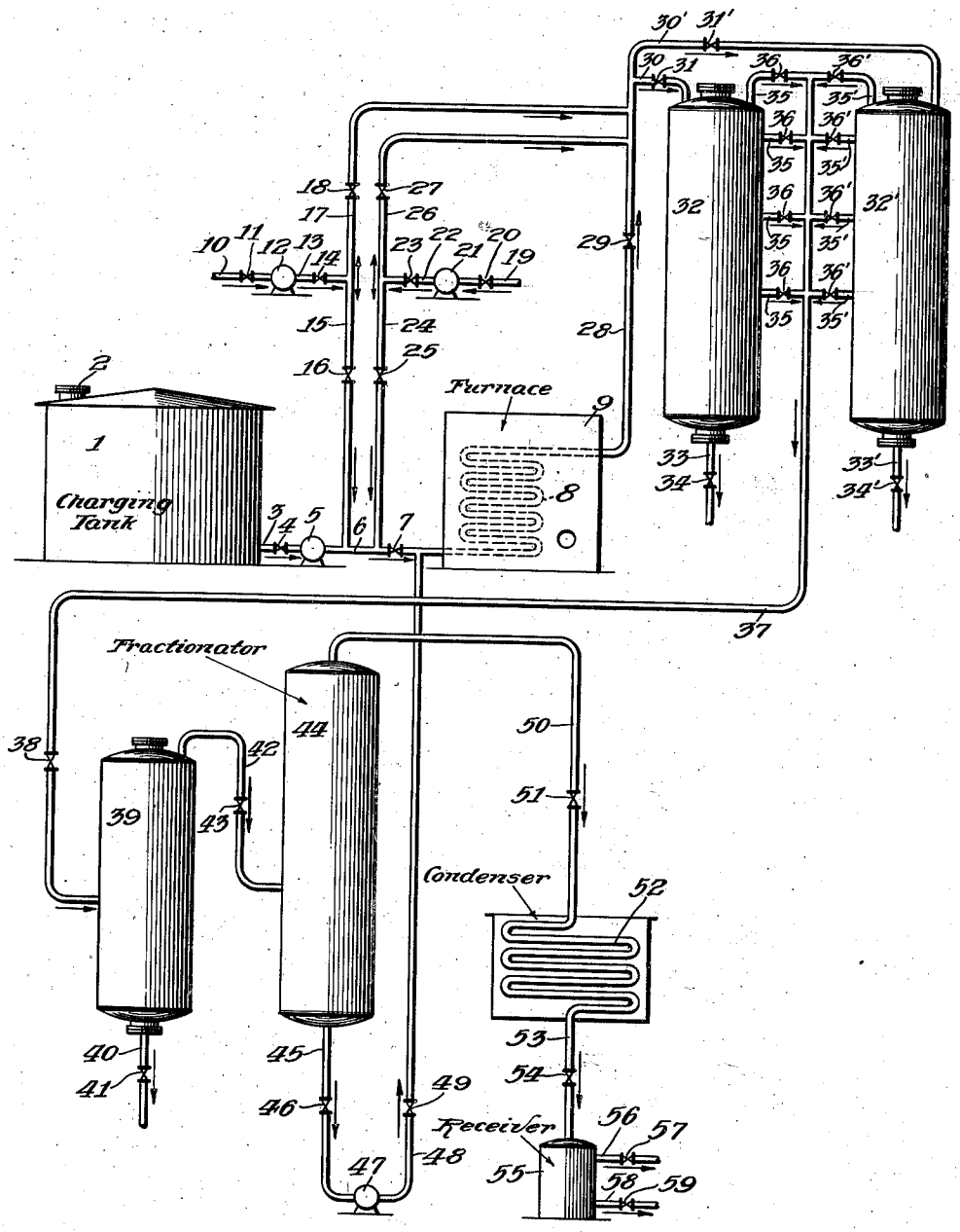
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DESTRUCTIVE HYDROGENATION OF ORGANIC MATERIALS

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DESTRUCTIVE HYDROGENATION OF ORGANIC MATERIALS

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This invention relates more particularly to the treatment of hydrocarbon materials for the production therefrom of high yields of good antiknock value motor fuel and other refined hydrocarbon products.

In a more specific aspect the invention is concerned with a process in which nascent active hydrogen plays an important role in reactions of decomposition and recomposition among various classes of hydrocarbons during their heat treatment, resulting in the production of higher yields of good quality products than those resulting from ordinary pyrolytic processes.

The process may be employed to treat a considerable variety of naturally occurring and synthetic hydrocarbon mixtures such as, for example, petroleum and its fractions resulting from ordinary or destructive distillation, and also coal and closely related minerals such as lignite and their primary or secondary distillation products, including coal tar, lignite tar, and aromatic distillates. Briefly stated, the process of the invention can be applied generally to the treatment or improvement of hydrocarbon or hydrocarbonaceous materials from any source.

Decomposition by heat which has been designated as cracking or pyrolysis, is practiced extensively on heavy hydrocarbon materials with the object of producing maximum yields of low boiling hydrocarbon mixes which have sufficient volatility and proper chemical characteristics for use as internal combustion engine fuels. More extensive cracking is practiced with the object of producing fuel gas and coke.

In cracking any heavy hydrocarbon mixture, the ultimate yield of desired products is definitely limited by the amount of originally combined hydrogen in the stock treated since the desired lower boiling materials have a higher hydrogen-carbon ratio than the original charge and owing to this hydrogen transfer the residues have a much lower ratio, particularly if operations are conducted until heavy liquid residues or solid coke is formed.

Pyrolytic processes are also insufficient in respect to the production of low boiling hydrocarbon liquids in that a certain amount of hydrogen released from its original combination in the primary decomposition reactions does not react further and appears in the molecular and unreactive state in the gaseous products.

Various processes employing extraneous hydrogen have been developed to overcome the more obvious disadvantages inherent in ordinary cracking processes such as the limits of yield of lighter fractions and the heavy character of the residues. Prior to the commercial development of hydrogenation processes, it had been known for a long time that addition of hydrogen to unsaturated compounds could be readily accomplished by employing molecular hydrogen in the presence of certain metallic catalysts, notably freshly reduced nickel which has a high efficiency in effecting the addition of hydrogen to unsaturated compounds such as oleic acid to make stearic acid and also to hydrocarbons characterized by either chain or ring unsaturation. These more active catalysts typified by nickel are at the same time extremely sensitive to poisoning influences due to the presence of sulphur, arsenic, etc., in reaction materials, and are also gradually depreciated by the deposition of small amounts of carbon which decrease their total effective catalytic surface.

Previously known types of active catalysts were found to have substantially no practical value when attempts were made to employ them in hydrogenating coal and other solid mineral hydrocarbons and in cracking and hydrogenating petroluem fractions on account of the invariable presence of prohibitive amounts of sulphur. For this reason hydrogenation processes have been tried which operate without catalysts under very high hydrogen pressure of the order of from 2000 to 5000 pounds per square inch and other processes have sought to treat mixtures of solid and liquid hydrocarbons using catalytic materials of lesser activity but with greater resistance to poisoning influences such as, for example, the oxides and sulphides of the metals of the 6th group of the periodic table including chromium, molybdenum and tungsten with and without promoting substances. The commercial technique of these processes has been developed to a considerable extent. The present process is in a sense a development along the latter line, although it is in another sense a distinct departure therefrom.

In one specific embodiment the present invention comprises destructively hydrogenating hydrocarbonaceous materials using hydrogen generated in situ by the interaction of carbon monoxide and water in the presence of catalytic materials comprising the oxides of the alkaline earth metals, e. g. magnesium and calcium or mixtures of the same.

The term "destructive hydrogenation" is used in the present connection to include the sum total of reactions between added hydrogen and the primary decomposition products of hydrocarbonaceous materials produced at elevated temperatures

and pressures. This definition is used to differentiate the complicated reactions which occur in such cases from the simpler direct hydrogenation reactions which correspond merely to the addition of hydrogen to unsaturated linkages to produce the corresponding saturated compounds. In destructive hydrogenation reactions unsaturated compounds both of a chain and a cyclic character may appear in the final products depending upon the conditions of time, temperature, pressure and hydrogen concentration employed. Thus it is possible to produce high yields of good anti-knock gasoline by destructively hydrogenating heavy hydrocarbon material while suitably correlating the physical and chemical factors involved.

Under the preferred conditions of reaction in the present process nascent hydrogen is liberated in accordance with the following equation:

$$CO+H_2O \rightleftarrows CO_2+HH$$

This reaction and the subsequent reactions in which the hydrogen enters into combination are both catalyzed and further promoted by the fact that the preferred mixture of oxides reacts with the carbon dioxide formed, removing one of the products of the hydrogen-producing reaction and causing it to continue in the desired direction as long as the reacting constituents are present. The carbon dioxide reacts most readily with calcium oxide although some interaction gradually occurs to remove the magnesium oxide also from the sphere of the reaction.

The broad principles of the present process may be successfully applied to the destructive hydrogenation of hydrocarbonaceous materials in numerous ways involving different types of plant equipment of both a batch and a continuous character, although the latter type of operation is practically always used in commercial work. In a batch operation, for example, an intimate mixture of oil or oil and coal with the finely divided oxides obtained, for example, by calcining dolomite is emulsified with water and added to a pressure vessel, the vessel is heated to an optimum temperature within a range which will be later specified and carbon monoxide is introduced to bring about the desired reactions. As an alternative mode of operation carbon monoxide and steam may be added gradually in suitable proportions to the dry mix of hydrocarbons and oxides in the bomb, during mechanical agitation. Some preheating of the gases introduced may be necessary although the reactions are in general exothermic and tend to maintain the desired temperature. It is not necessary to use pure carbon monoxide in the process since the catalysts are not sensitive to ordinary poisoning influences. Water gas and other carbon monoxide-containing gases may be used, although the greater efficiency will result when gases containing relatively higher percentages of this gas are employed.

To illustrate some of the details of a practical continuous operation of the process the attached drawing has been provided which shows in side elevation by the use of conventional figures an arrangement of interconnected elements in which it may be conducted. The plant shown has a certain degree of flexibility but it is not to be inferred that the scope of the invention is limited by the arrangement or proportioning of the drawing since the parts are not drawn to scale and many modifications are possible within the province of the invention.

Referring to the drawing a mixture of fluid hydrocarbon material and finely divided calcined oxides of magnesium and calcium may be made in a supply tank 1 and maintained in suspension by mechanical stirring devices or outside circulating pumps although neither of these two commonly used expedients is shown in the drawing. In operating with coal the fines are suspended in oil along with the oxide catalysts. 2 indicates a hatch through which the solid ingredients of the primary mix may be introduced into the tank depending upon the nature of the materials undergoing treatment and in other alternative modes of operation, a part or all of the water required for the reaction of hydrogen production may also be emulsified with and maintained in suspension in the fluid menstruum along with the suspended solids.

The mixture or slurry of charging material is then taken through line 3 containing control valve 4 by charging pump 5 and brought to the required temperature and pressure for the subsequent reactions, passing through line 6 containing control valve 7 through a tubular heating element 8 disposed to receive heat from a furnace 9. Either carbon monoxide or water or steam required for the hydrogenation reactions may be introduced at this point in whole or in part. 12 indicates a pump or compressor taking suction on a supply of carbon monoxide (or a gas mixture containing a substantial percentage thereof) from a source not shown through a line 10 containing control valve 11 and discharging through a line 13 containing control valve 14 either into line 15 containing control valve 16 and into line 6 or through line 17 containing control valve 18 into line 28 containing control valve 29 and leading from the heating element to subsequent reaction and settling chambers.

21 indicates a water pump taking suction through line 19 containing control valve 20 and discharging through line 22 containing control valve 23 and branching into line 24 containing control valve 25 leading to line 6 or line 26 containing control valve 27 leading to line 28. In lieu of water injection at these points high pressure steam, either saturated or superheated may be added in place of water. It is comprised within the scope of the invention and may be of some advantage at times to add a portion of the mixed catalytic oxides along with the water. Thus the slaked mixture of oxides of magnesium and lime may be pumped in by pump 21.

It is evident from the portion of the description thus far given that water or steam may be added either at the entrance or the exit of the heating element as well as in the primary mix. As a rule it is preferable also to add the carbon monoxide at the same points and in most instances the majority is added in transfer line 28 just prior to the entrance of the heated materials to the reaction and settling chambers.

Two reaction chambers have been shown in parallel arrangement although any number may be employed in this manner so that the precipitated and spent solid catalytic material may be removed from some chambers while they are accumulating in others in the course of the reactions. Thus the drawing shows line 28 branching into line 30 containing control valve 31 and leading to reaction chamber 32 and branch line 30' containing control valve 31' and leading to reaction chamber 32'. Each reaction chamber is provided with upper and lower removable manhole covers for the injection of fresh or removal of spent catalytic material since if desired the amount of oxides added to the hydrocarbon charge

may be augmented by further amounts of granular material added to the reaction chambers in some methods of operation. Chamber 32 is provided with liquid draw line 33 containing control valve 34 and chamber 32' with a corresponding draw line 33' containing control valve 34'. The quantity and quality of liquid products which may accumulate in the reaction chambers will be determined by the character of the charging material and the conditions and objects of the operation. For example, if a mixture of coal and oil is treated to produce increased yields of lubricating or intermediate fractions, a large amount of relatively heavy liquid may accumulate in the reaction chambers and be withdrawn therefrom for subsequent fractionation or reduction. At other times the products from the reaction chamber comprising both vapors and liquids may be continuously withdrawn in a manner to be presently described

The greater portion of the reactions of destructive hydrogenation occur in the reaction and settling chambers according to the equation of hydrogen production already given and the various complicated hydrocarbon decomposition and recomposition reactions. The solid catalytic material, partly or wholly carbonated and possible somewhat carbonized will gradually accumulate in a reaction chamber which is cut out of the system when the reaction space becomes insufficient, at which time other empty chambers are cut in.

To regenerate the partly spent solids accumulating in the reaction chambers they may be separated from adhering oil and tar by treatment with solvents such as gasoline followed by settling and possibly filter pressing, after which the mixture of carbonates and oxides is calcined to produce a mixture containing a higher percentage of oxides and a certain amount of carbon dioxide. This latter gas may be then passed over coke to reduce it to carbon monoxide for further use in the process. The details of such operations are fairly well known in commercial work and an extensive description of operating details is not necessary.

The process may employ temperatures within the approximate range of from 400 to 650° C., and any desired pressure up to, for example, several thousand pounds per square inch, e. g. 3000 pounds per square inch, if such are found to be necessary to the efficiency of the process. Only general ranges can be stated since a great deal will depend upon the degree of contact of the reacting materials which in turn depends upon such factors as the fineness of the solids and the thoroughness of mixing.

Hydrocarbon reaction products pass from chamber 32 through lines 35 containing control valves 36 or from reaction chamber 32' by way of lines 35' containing control valves 36' to enter header line 37 containing control valve 38 and leading to fractionating equipment. The relative proportions of vaporous and liquid products will depend upon the temperature and pressure of the reaction chambers, and if the proportion of liquid is high, the lines shown leading from the side of the chambers at different levels may be employed to continuously remove liquid accumulations along with the vapors removed from the lines leaving the top of the chambers, the liquid-vapor separation then being made in the succeeding flash chamber and fractionating tower.

Products from the reaction chambers may enter a flash chamber 39 under somewhat reduced pressure and separate out heavy residual liquids in cases where gasoline is desired as the main product of the process, the heavy liquid being withdrawn from the flash chamber through a line 40 containing control valve 41. In case the production of heavier liquids is the main object of the process the flash chamber may be employed merely to volatilize light ends.

The vapors from the flash chamber pass through line 42 containing control valve 43 to a final fractionator 44, the design of which will be varied according to the products desired from the operation and which will usually be adapted to produce an overhead gasoline boiling range fraction when the process is operated in connection with petroleum refining. The vapors and fixed gases from the fractionator pass through a line 50 containing control valve 51, after which they pass through a condenser 52 for liquefying the normally liquid components which then pass together with uncondensed gases through line 53 containing control valve 54 to receiver 55 provided with a gas release line 56 containing control valve 57 and a liquid draw line 58 containing control valve 59.

Bottom refluxes from fractionator 44 will usually be of the type adapted to further conversion and are taken through a line 45 containing control valve 46 to a recycling pump 47 and discharged by way of line 48 containing control valve 49 back to combined feed line 6 and thence through the process as already described.

Owing to the wide applicability of the present process upon miscellaneous hydrocarbonaceous materials as previously enumerated, it will be apparent that a large number of examples could be recited in support of its commercial advantages. However, the following will be sufficiently illustrative to assist in describing the character of the invention.

A cracked residuum resulting from the pyrolysis of a Mid-Continent fuel oil was used as starting material. The details of the primary cracking run, which was conducted in a modern type of commercial cracking plant, are given below. The A. P. I. gravity of the fuel oil was 24.3 and it had an initial boiling point of 595° F.

Details of cracking operation

Pressure of reaction zone	250 pounds per sq. in.
Maximum cracking temperature	925° F.
Yield of gasoline	56% by volume.
Yield of residuum	38.5% by volume.
Cu. ft. of gas/bbl. of charge	415
A. P. I. gravity of gasoline	59
Initial boiling point	90° F.
50% over at	265° F.
90% over at	375° F.
End boiling point	395° F.
A. P. I. gravity of cracked residuum	9
B. S	0.3%
Saybolt furol viscosity at 122° F	110 secs.
Cold test	25° F.
I. B. P	420° F.
Percent over at 572° F	8

The above residuum was destructively hydrogenated to produce a high yield of gasoline. For the sake of increased efficiency and ease of manipulation the gasoline production per pass through the process was held down within defi-

nite limits to make the handling of the required oxides easier since these were used in an amount corresponding to total absorption of the carbon dioxide resulting from the hydrogen-producing reaction between carbon monoxide and steam. For the production of 80% by volume of 400 end point gasoline from this residuum a weight consumption of 4% of hydrogen was found to be necessary and with an equimolecular mixture of magnesium and calcium oxides the combined weight of the two amounts to about 850 pounds per barrel of residuum, with complete absorption of the CO_2 by the calcium oxide.

Instead of attempting to cause the complete conversion in one stage, about 20% gasoline was made in four successive operations by utilizing each time about one-fourth of the total required quantities of carbon monoxide and water and the chemically equivalent amount of combined oxides. A summary of the quantities of materials used in each operation per 42 gallon barrel of the cracked residuum treated is given below:

Quantities of treating materials

Water	gallons	5
Carbon monoxide	cu. ft.	850
Calcium oxide	pounds	125
Magnesium oxide	do	90

The combined oxides were mixed with the cracked residuum, pumped through the heating element up to a pressure of about 2000 pounds per square inch and raised to a temperature of about 850° F., the carbon monoxide and water being pumped into the transfer line prior to the admission of the suspension of oxides in oil to the reaction chamber.

The vaporous and hydrocarbon liquid products from the reaction were segregated to produce gasoline and a recycle stock, the latter being resubjected to substantially the same conditions of treatment, and this process was repeated until the required 80% production of gasoline was obtained.

The properties of the finally produced gasoline are given below:

Gravity ° A. P. I.	63
Initial boiling point	100° F.
10% over at	180° F.
50% over at	280° F.
90% over at	390° F.
End boiling point	425° F.
Octane number, motor method	70

The utility and practical advantages of the present process will be evident from the preceding specification which discloses its details and the single instance of results obtainable by its use proves its commercial possibilities. However, neither of the preceding sections are intended to unduly limit its scope.

I claim as my invention:

1. A process for the destructive hydrogenation of hydrocarbonaceous materials to increase the yield of low boiling products therefrom and to improve its characteristics by reducing the boiling range thereof and the carbon-to-hydrogen ratio which comprises subjecting the said hydrocarbonaceous materials while at elevated temperatures of from 400 to 650° C., and superatmospheric pressure up to approximately 3000 pounds per square inch to the simultaneous action of carbon monoxide and water in the presence of a mixture of calcium and magnesium oxides, the magnesium oxide being in sufficient amount to catalyze the hydrogenation reaction and the formation of hydrogen from the carbon monoxide and water and the calcium oxide being in sufficient amount to absorb the carbon dioxide formed by the reaction of the carbon monoxide and water.

2. In the destructive hydrogenation of hydrocarbonaceous material, the improvement which comprises adding magnesium oxide and calcium oxide to the material and generating hydrogen for the hydrogenation in situ by the reaction of carbon monoxide and water within the mixture, the magnesium oxide being in sufficient amount to catalyze the hydrogenation reaction and the formation of hydrogen from the carbon monoxide and water and the calcium oxide being in sufficient amount to absorb the carbon dioxide formed by the reaction of the carbon monoxide and water.

3. In the destructive hydrogenation of hydrocarbonaceous material, the improvement which comprises generating hydrogen for the hydrogenation in situ by the reaction of carbon monoxide and water within the material, the hydrogen-forming reaction and the hydrogenating reaction being effected in the presence of a sufficient quantity of an equimolecular mixture of magnesium and calcium oxides to catalyze said reactions and to absorb the carbon dioxide formed by the first-named reaction.

4. In the destructive hydrogenation of hydrocarbonaceous material, the improvement which comprises generating hydrogen for the hydrogenation in situ by the reaction of carbon monoxide and water within the material, the hydrogen-forming reaction and the hydrogenating reaction being effected in the presence of a sufficient quantity of calcined dolomite to catalyze said reactions and to absorb the carbon dioxide formed by the first-named reaction.

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