



## UNITED STATES PATENT OFFICE

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## COMBINATION HYDROCARBON DEHYDROGENATION AND HYDROGENATION PROCESS

Alexander S. Ramage, Detroit, Mich., assignor to  
Albert A. F. Maxwell, Detroit, Mich., as trustee

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9 Claims. (Cl. 260—673)

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The present invention relates to a novel process for the treatment of hydrocarbons, such, for example, as hydrocarbons contained in crude oils, low temperature tar oils, shale oils, and the like, for the purpose of producing a gas rich in ethylene and containing only small amounts of propylene and butylene, and a high yield of a liquid mixture consisting chiefly of liquid aromatics and the condensation products of the aromatics and gaseous olefins of high octane number.

The present application is a continuation-in-part of my copending application Serial No. 475,468, entitled Treatment of hydrocarbon oils, filed February 11, 1943.

In my prior Patent No. 1,752,692, issued April 1, 1930, and entitled Process for the production of gas and aromatic hydrocarbons from heavy hydrocarbon oils, I have disclosed a process and apparatus in which the hydrocarbons were dehydrogenated in the lower tubes of the converter by contact with ferric oxide as the reactive agent. The dehydrogenated gases and vapors with a large volume of steam were subsequently passed through the upper tubes in the converter which were filled with metallic iron. While the results of this process were quite satisfactory as a gas process, the liquid condensate tested 70 to 75 octane only.

This invention contemplates a process which will give considerably higher yields of ethylene as well as liquid condensate having a much higher octane number.

The hydrocarbons which are to be transformed comprise mainly paraffins ( $C_nH_{2n+2}$ ) and olefins ( $C_nH_{2n}$ ). These hydrocarbons are first dehydrogenated in the presence of heat to form aromatic hydrocarbons and unsaturated aliphatic hydrocarbons. During dehydrogenation the olefins also broke down into hydrocarbons having a lesser number of carbon atoms. After being subjected to the dehydrogenating step, the hydrocarbons are next subjected to a hydrogenating step in the presence of heat in which the unsaturated aliphatic liquid hydrocarbons are hydrogenated to form olefins and paraffins having a lower number of carbon atoms than the paraffins and olefins which constituted the starting hydrocarbons which were to be treated.

The single figure is a drawing diagrammatically illustrating the apparatus used for treating hydrocarbons according to my method.

My process can be carried on in the apparatus shown either in my Patent 1,752,692 or in the

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apparatus disclosed in my copending application Serial No. 475,468 or in many known cracking converters.

In the first step of my process I dehydrogenate the hydrocarbons by bringing the hydrocarbon to be transformed in a state of vapor substantially unmixed with reactive oxygen into contact with a mixture of reducible metal oxides comprising preferably substantially equal parts of molybdenum oxide ( $MoO_3$ ), chromic oxide ( $Cr_2O_3$ ) and ferric oxide ( $Fe_2O_3$ ) which has been activated by approximately ten percent (10%) of vanadium pentoxide ( $V_2O_5$ ). The vanadium pentoxide can be used in amounts falling within a range of from about 2% to about 10% by weight of the total weight of the three oxides; namely, chromic oxide, molybdenum trioxide and ferric oxide. Although the chromium, molybdenum and ferric oxides each preferably comprise approximately 33 1/3% by weight of the mixture, their respective proportions by weight can be varied over a wide range provided the amount of oxygen necessary for dehydrogenation is liberated by the mixture. A variation of as much as 10% more or 10% less than the above proportion of any of the three oxides with a commensurate decrease or increase in the proportions of the other oxide or oxides of the mixture would work but for best results the use of the three oxides in approximately equal amounts by weight is indicated. A mixture of any two of the chromic, ferric and molybdenum oxides can be used if activated with vanadium pentoxide but at a loss in the efficiency of my process.

The hydrocarbons to be transformed, if not already in the gaseous or vapor phase, are preferably vaporized by heating in a pipe still 1 or other suitable heating equipment, or if in the liquid phase may be injected directly through an injector nozzle into the lower tubes 2 of converter 3 in which the dehydrogenation takes place.

The temperature of the reactive oxide mixture will depend on the hydrocarbon to be transformed. Preferably the reactive oxide mixture will be maintained at a temperature falling within a range of from about 800° F. to about 1100° F. The oxide mixture provides a reactive material which gives up oxygen to the hydrocarbon gases and vapors passing through the tubes or contacted therewith and in doing so at the temperature mentioned effects dehydrogenation thereof.

The length of time during which the reactive agent is active in the liberation of oxygen depends upon the analysis of the hydrocarbon being

treated. By calculating the amount of oxygen present in the reactive agent and analyzing the hydrocarbon vapors being treated, a calculation can be made as to the period of time that the process may be operated before revivifying the said reactive agent. The time is gauged on the analysis of the material to be treated, as shown for example in the following chart:

| Formula              | Atomic weight | Pounds per gal. at atmospheric pressure | Cubic ft. per gal. | B. t. u's per gal. | Boiling point, degrees F. | Pounds oxygen required per pound | Pounds oxygen required per gal. to convert to aromatic |
|----------------------|---------------|-----------------------------------------|--------------------|--------------------|---------------------------|----------------------------------|--------------------------------------------------------|
| $C_6H_{12}$ -----    | 72            | 5.26                                    | 27.7               | 109.713            | 97                        | 0.222                            | 1.170                                                  |
| $C_7H_{16}$ -----    | 100           | 5.70                                    | 21.6               | 117.466            | 209                       | .160                             | .912                                                   |
| $C_8H_{20}$ -----    | 128           | 5.98                                    | 17.88              | 122.407            | 303                       | .125                             | .750                                                   |
| $C_{10}H_{22}$ ----- | 142           | 6.08                                    | 16.38              | 124.130            | 345                       | .111                             | .685                                                   |
|                      |               | 23.02                                   | 83.56              | 473.716            | 954                       | .618                             | 3.517                                                  |
| Average-----         |               | 5.75                                    | 2.09               | 118.429            | 238                       | .154                             | .880                                                   |
| $C_{12}H_{26}$ ----- | 170           | 6.259                                   | 13.92              | 131.043            | 418                       | .09418                           | .589                                                   |
| $C_{14}H_{30}$ ----- | 184           | 6.308                                   | 13.00              | 128.522            | 453                       | .08695                           | .548                                                   |
| $C_{16}H_{34}$ ----- | 198           | 6.375                                   | 12.20              | 129.336            | 486                       | .08080                           | .513                                                   |
| $C_{18}H_{38}$ ----- | 212           | 6.407                                   | 11.56              | 129.844            | 518                       | .07347                           | .484                                                   |
| $C_{20}H_{42}$ ----- | 226           | 6.626                                   | 11.11              | 134.125            | 550                       | .07080                           | .469                                                   |
| $C_{22}H_{46}$ ----- | 240           | 6.463                                   | 10.20              | 130.418            | 577                       | .06660                           | .433                                                   |
| $C_{24}H_{50}$ ----- | 254           | 6.473                                   | 9.65               | 130.605            | 605                       | .06300                           | .408                                                   |
|                      |               | 44.911                                  | 81.61              | 913.903            | 3,605                     | .53779                           | 3.446                                                  |
| Average-----         |               | 6.416                                   | 11.66              | 130.557            | 515                       | .07682                           | .492                                                   |

In all of the starting materials commonly employed in carrying out a process of this type, it will be found that there is a mixture of the hydrocarbons present and when such is the case, the average figures included in the above chart may be taken for the purpose of making such calculations. For example, if 1500 pounds of the reactive material is employed in the dehydrogenation tubes, it will be found that approximately one hundred and fifty pounds of oxygen will be liberated. After this amount of oxygen has been liberated, the reactive agent is revivified by blowing with superheated steam for approximately five minutes and then blowing with air at fifteen pounds pressure for approximately twenty-five minutes. By reference to the above chart showing the number of pounds of oxygen required per pound and per gallon of the hydrocarbon materials, it is possible to calculate the time period that the plant may be run without revivifying the reactive agent.

The aliphatic hydrocarbons in the presence of chromic, ferric and molybdenum oxides activated with vanadium pentoxide at the temperature specified are dehydrogenated to form aromatic hydrocarbons and unsaturated aliphatic hydrocarbons. About 80% of the hydrocarbon vapor after dehydrogenation will be aromatic hydrocarbons ( $C_nH_{2n-6}$ ) and the remaining hydrocarbon vapors will be unsaturated aliphatic compounds. These unsaturated vapors will be, in the main, olefins. During the dehydrogenation step the olefins break down into hydrocarbons having a lesser number of carbon atoms. For example,  $C_{12}H_{24}$  splits up at the temperatures specified into  $2C_6H_{12}$  which splits up into  $4C_3H_6$ , or starting with a paraffin,  $C_{16}H_{34}$  is oxidized or dehydrogenated to form  $C_{16}H_{32}$  which at the dehydrogenating temperatures splits up into  $2C_8H_{16}$  and then into  $4C_4H_8$  and finally ethylene,  $8C_2H_4$ .

In the hydrogenation step of the approximately 20% of the vapors the entire mass of hydrocarbons to be treated, subsequent to the dehydrogenation step, are passed in the form of vapors together with superheated steam through the upper tubes 4 of convertor 3 in contact with a

heated mixture of reactive materials comprising essentially finely divided metallic iron activated with finely divided metallic copper. Preferably the mixture comprises approximately 90% of finely divided iron and 10% of finely divided copper, but the mixture by weight can be varied from 90 to 98% of finely divided iron and 2 to 10% of finely divided copper. This mixture of finely

divided iron and copper is positioned in a second group of tubes in which hydrogenation takes place. The temperature of these tubes and the finely divided iron and copper mixture should be maintained within a range of from about 1000° F. to about 1400° F. according to the nature of the hydrocarbons. During the hydrogenation the temperature within the above range will vary inversely to the number of carbon atoms present in the molecule of the material being hydrogenated. For example, a material consisting largely of  $C_5H_{10}$  will use a temperature of about 1400° F. whereas a material consisting largely of  $C_{18}H_{36}$  will require a lower temperature of about 1200° F. Water in the form of superheated steam is blown into the tubes during hydrogenation and reacts with the iron and copper to liberate atomic hydrogen.

During the hydrogenating step the unsaturated aliphatic liquids present in the form of vapors are hydrogenated to form olefins and paraffins but having a lesser number of carbon atoms in a molecule than the paraffins and olefins which formed the starting materials. The vapors from the hydrogenating tubes may be condensed in the usual manner and treated according to normal refinery practice. The gases remaining after condensation may be treated in conventional types of liquefaction apparatus to effect separation of the ethylene from the other gases. The liquid condensate is a mixture of aromatic hydrocarbons and light saturated hydrocarbons and when tested according to the A. S. T. M.-C. F. R. Motor Method it has been found to have an octane number of from 100 to 106 with an end point of 310° F. and a specific gravity of 30 to 35° Baumé. The yield of liquid product may be varied by varying the temperature, the rate of flow, and the type of starting material. A liquid material having a specific gravity of approximately 30° Baumé and an octane number in excess of 100 may be produced in the amount of approximately ten gallons to the barrel of oil, kerosene or low grade gasoline used as a starting material and also about 2800 cubic feet of gas containing 40 to 45%  $C_2H_4$  equal to 78 to 88 pounds  $C_2H_4$  per barrel

will be produced. A liquid product having a specific gravity of approximately 34° Baumé and having an octane number of from approximately 90 to 92 may be produced in an amount of approximately fifteen gallons to the barrel of starting material and also 2200 cubic feet of gas equal to 65 to 75 pounds  $C_2H_4$  per barrel will be produced. Producing 8 gallons per barrel of spirit of 100 plus octane, there would be produced also 2820 cubic feet of gas containing 85 to 95 pounds  $C_2H_4$  per barrel.

From the converter 3 the vapors are quenched, passed through a Gray tower, then through a fractionating tower (the heavy liquid being returned for recycling) and finally passed through a condenser where the aromatic hydrocarbons have a specific gravity of 30-35° Baumé and consisting chiefly of benzoyl, toluene and xylol are condensed out and the uncondensed gas is then passed on for further treatment.

It has been found that as the volume of liquid distillate produced is increased, the octane value and the amount of gas is decreased. The process is, therefore quite flexible as to the relative amounts of liquid condensate and gases to be produced. The composition of the gases varies according to the temperature employed but in the usual instance using temperatures within the ranges above described, it has been found that the gas consists of approximately 40 to 45 percent of ethylene with very low percentages of propylene and butylene, in the usual case not over approximately 4 to 5 percent. The balance of the produced gas is methane.

For each barrel of starting material put through the process, approximately 2600 cubic feet of gas containing approximately 86 pounds of ethylene may be produced when approximately ten gallons to the barrel of the liquid distillate is recovered having the characteristics above described. If the liquid distillate is recovered to the extent of fifteen gallons to the barrel and has the characteristics above described, the gas yield will be reduced to approximately 2200 cubic feet of gas containing approximately seventy-four pounds of ethylene.

I claim:

1. The process of transforming hydrocarbons into other hydrocarbons relatively poorer in hydrogen, which consists in bringing the hydrocarbon to be transformed in a state of vapor substantially unmixed with reactive oxygen, into contact with a mixture of molybdenum oxide, chromium oxide, and ferric oxide and vanadium pentoxide, and so regulating the temperature of the oxide mixture and vapor between about 800° F. and about 1100° F. so as to oxidize a part only of the hydrogen component of the hydrocarbon producing thereby as reaction products hydrocarbons comprising principally aromatics and lesser quantities of other unsaturated hydrocarbons relatively poorer in hydrogen, and steam.

2. The process as set forth in claim 1 wherein the time of contact of the vapor and oxide mixture is regulated so that the hydrocarbons relatively poor in hydrogen split up into lower boiling hydrocarbons of the same chemical group and thereafter contacting the vapor with a mixture of finely divided metallic iron and finely divided metallic copper in the presence of steam to hydrogenate the unsaturated hydrocarbons produced during the dehydrogenating step.

3. The process of transforming hydrocarbons into other hydrocarbons relatively poorer in hydrogen, which consists in bringing the hydrocar-

bon in a state of vapor into contact with a mixture of molybdenum oxide, chromic oxide, ferric oxide activated with vanadium pentoxide, and regulating the temperature of the oxides and vapor between about 800° F. and about 1100° F. and the time of contact of the vapor with the oxides so as to partially dehydrogenate the hydrocarbon producing thereby as reaction products principally aromatic hydrocarbons and a small amount of olefins having a relatively smaller number of carbon atoms per molecule than the olefins produced directly from the hydrocarbon, then hydrogenating some of the olefins to produce lower boiling hydrocarbons than those originally dehydrogenated.

4. The process as set forth in claim 3 wherein the said oxide mixture comprises substantially by weight one-third molybdenum oxide, one-third chromic oxide, and one-third ferric oxide, and the activating oxide, vanadium, pentoxide, comprises about ten percent by weight of the mixture of the other three oxides.

5. The process of transforming hydrocarbons into other hydrocarbons relatively poorer in hydrogen, principally aromatics which consists in bringing the hydrocarbon in a state of vapor into contact with a mixture of molybdenum oxide, chromic oxide, ferric oxide activated with vanadium pentoxide, and regulating the temperature of the oxides and vapor between about 800° F. and about 1100° F. and the time of contact of the vapor with the oxides so as to partially dehydrogenate the hydrocarbon producing thereby as reaction products principally aromatic hydrocarbons and a small amount of olefins having a relatively smaller number of carbon atoms per molecule than the olefins produced directly from the hydrocarbon, and then hydrogenating the olefinic part of the vapors by contacting the same with finely divided metallic iron activated by finely divided metallic copper in the presence of water in the form of superheated steam.

6. The combination as set forth in claim 5 wherein the steam and finely divided copper and iron are maintained at a temperature falling within a range of about 1000° F. to about 1400° F. during the hydrogenating step.

7. A process of transforming hydrocarbons selected from the group consisting of paraffins, olefins, and mixtures of paraffins and olefins, into hydrocarbons comprising principally aromatics and lesser quantities of other hydrocarbons having a lesser number of carbon atoms in the molecule than the hydrocarbons to be transformed, comprising bringing the hydrocarbon to be transformed in a state of vapor into contact with a mixture of at least two metal oxides selected from the group consisting of chromic oxide, molybdenum oxide and ferric oxide, activating said mixture of oxides with vanadium pentoxide and maintaining the temperature of the oxide mixture and vapor within a range of from about 800° F. to about 1100° F. so as to oxidize a part only of the hydrogen component of the hydrocarbon to be transformed producing thereby as reaction products principally aromatics and lesser quantities of unsaturated aliphatics having a lesser number of carbon atoms in the molecule than the hydrocarbon to be transformed, and then bringing the unsaturated aliphatics in a state of vapor into contact with a mixture of finely divided metallic iron and finely divided metallic copper in the presence of superheated steam while maintaining said copper and iron

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mixture and vapors at a temperature within a range of about 1000° F. to about 1400° F. to thereby hydrogenate the unsaturated aliphatics.

8. A process of transforming hydrocarbons selected from the group consisting of paraffins, olefins, and mixtures of paraffins and olefins, into hydrocarbons comprising principally aromatics and lesser quantities of other hydrocarbons having a lesser number of carbon atoms in the molecule than the hydrocarbons to be transformed, comprising bringing the hydrocarbon to be transformed in a state of vapor into contact with a mixture of at least two metal oxides selected from the group consisting of chromic oxide, molybdenum oxide and ferric oxide, activating said mixture of oxides with vanadium pentoxide and so regulating the temperature of the oxide mixture and vapor between about 800° F. and about 1100° F. so as to oxidize a part only of the hydrogen component of the hydrocarbon to be transformed producing thereby as reaction products principally aromatics and lesser quantities of unsaturated aliphatics, and steam, regulating the

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temperature and time of contact of the hydrocarbon vapor and activated oxide mixture so that the olefins present during the dehydrogenating step split up into olefins with a lesser number of carbon atoms and hydrogenating the olefins to form paraffins having a lower boiling point than the paraffins to be transformed.

9. In the hydrogenating of unsaturated aliphatics, the step of bringing the unsaturated aliphatic in a state of vapor into contact with a mixture of finely divided metallic iron and finely divided metallic copper in the presence of superheated steam, the content of iron of said mixture falling within a range of from about 90 to 95% by weight and the content of copper in said mixture falling within a range of from about 2 to about 10% by weight, and maintaining the temperature of the iron-copper mixture and vapor within a range of from about 1000° F. to about 1400° F. whereby said unsaturated aliphatics are hydrogenated.

ALEXANDER S. RAMAGE.