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PROCESS OF PRODUCING HYDROCARBONS

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This invention relates to a process for producing hydrocarbons.

We have discovered that hydrocarbons can be produced by reacting an iron carbide with steam at a superatmospheric pressure and an elevated temperature. Thus gaseous hydrocarbons and normally liquid hydrocarbons, that is, hydrocarbons liquid at atmospheric pressure and temperature conditions, can be produced by carbiding an iron oxide at an elevated temperature in the range of from about 375° to 675° F. to convert the iron oxide to an iron carbide and then reacting the iron carbide with steam at an elevated temperature of about 525° to 650° F. and at a superatmospheric pressure of above about 100 pounds per square inch. This and subsequent pressures are in pounds per square inch gauge. The reaction of the steam with the iron carbide not only produces the desired hydrocarbons when operating in accordance with the process of our invention, but also converts the iron carbide to an iron oxide. The step of carbiding the iron oxide to form an iron carbide and the step of reacting the iron carbide with steam can be alternately repeated and thus a continuous process employing inexpensive raw materials can be employed to produce gaseous and normally liquid hydrocarbons.

The iron oxide which is formed by the reaction of steam with an iron carbide under the conditions described in detail hereafter is usually ferroferric oxide (Fe_3O_4). It is convenient in starting up the process that the iron-containing material be ferroferric oxide in order that all the cycles can be operated under the same conditions. The iron-containing material can, however, initially be other iron oxides such as ferric oxide (Fe_2O_3), or ferrous oxide (FeO), or partially or completely reduced iron, or a mixture of the various oxides and reduced iron. The initial carbiding conditions can be substantially the same as those used in subsequent cycles to carbide the ferroferric oxide. The initial iron-containing material can be in granular, pelleted, or finely divided form. Preferred results are obtained with ferroferric oxide containing from 0.5 to 2.0 weight per cent of a promoter such as potassium carbonate and from 0.5 to 1.5 weight percent of a metal such as copper.

Low temperature carbonization of iron with carbon monoxide produces carbides which have been shown to exist in at least two forms called the Hagg carbide and the hexagonal carbide of iron. These carbides have a composition represented approximately by the formula Fe_2C . In the specification and claims, these carbides will be so identified as Fe_2C . Higher temperature carbonization of iron with carbon monoxide produces Fe_3C which is known as cementite.

Although the iron carbide which is employed for the reaction with steam can be either Fe_2C or cementite, we have found that a better yield of heavier hydrocarbons can be obtained when cementite is employed. Ferroferric oxide can be converted to Fe_2C by passing carbon monoxide over the ferroferric oxide at a temperature of about 375° to about 500° F. Under these conditions the iron

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is about 70 percent converted to Fe_2C which is about the maximum conversion obtained under these conditions. Ferroferric oxide can be converted to cementite by passing carbon monoxide over it at a temperature of about 575° to 675° F. We have found that preferred results are obtained when the carbiding is stopped at the point where there has been about a 100 percent conversion to cementite and before excess carbon has been deposited upon the carbide. A cementite which is free of excess carbon can be produced by subjecting Fe_2C to a temperature in the range of about 750° to about 950° F. for about 1 to 24 hours. The carbiding of an iron oxide to either Fe_2C or cementite with carbon monoxide can be accomplished at a superatmospheric pressure or under vacuum. However, this is not necessary and because it is usually more convenient, atmospheric pressure is usually employed for such carbiding.

We have further found that when an iron carbide is reacted with steam under a pressure in excess of 100 pounds per square inch, although some hydrocarbons are produced at lower temperatures, preferred results are obtained with temperatures of about 525° F. to about 650° F., and particularly from about 550° to about 600° F.; and especially preferred results are obtained with a temperature of about 575° F.

The employment of a pressure in excess of 100 pounds per square inch during the reaction of an iron carbide with steam is an important feature of the process. We have found that when steam is reacted with an iron carbide at atmospheric pressure a very small yield of gaseous and normally liquid hydrocarbons is produced even though all of the other conditions of this process are optimum. To produce reasonable yields of hydrocarbons, the pressure should be maintained above 100 pounds per square inch, and preferably between about 150 and 300 pounds per square inch.

Continuous production of hydrocarbons can be obtained by use of a plurality of reactors and proper arrangement of the time cycle for carbiding and steaming in each reactor in relation to the time cycles in the other reactors.

The time necessary for carbiding the iron oxide and the time necessary for reacting an iron carbide can be varied depending upon process conditions. It will be understood that in operating more than one process zone at the same time and continuously producing hydrocarbons, the time for carbiding the iron oxide and the time for reacting the iron carbide with steam will be determined by economically balancing production costs, yields, and product distributions. In general, an iron oxide can be carbided and an iron carbide can be reacted with steam to give a desirable yield of hydrocarbons with time periods for each step which may vary from about fifteen minutes to about ten hours, five hours usually giving preferred results.

In order that the invention may be understood more fully, reference should be had to the following specific examples.

EXAMPLE 1

Sixty-eight parts of substantially completely reduced iron pellets are carbided by passing carbon monoxide over them for about 19 hours at atmospheric pressure, a temperature of from about 390° to about 485° F., and an average carbon monoxide space velocity of about 375. (Space velocity is the volumes of gaseous reactants at standard temperature and pressure conditions per volume of materials contacted per hour.) The reduced iron is about 71.2 percent converted to Fe_2C which is the maximum conversion obtained under these conditions. 73.2 parts of iron carbide containing 5.25 parts of carbon are produced in this manner.

Steam is then reacted with the carbided material for

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five hours at a pressure of about 150 pounds per square inch, a temperature of about 570° F., and an average steam space velocity of about 750. Under these conditions the carbided material is converted principally to ferroferric oxide and 2.457 parts of carbon are converted. This represents a conversion of 46.9 percent of the available carbon. The reaction products include 0.998 part, or 19.1 percent, of the available carbon as carbon monoxide and carbon dioxide and 1.459 parts, or 27.8 percent, of the available carbon as hydrocarbons. The product distribution is given in Table 1 which follows.

TABLE 1

Product distribution for the low molecular weight hydrocarbon fraction

Component:	Weight percent
C ₁ -----	41.8
C ₂ -----	15.0
C ₃ -----	17.5
C ₄ -----	15.0
C ₅ + -----	10.7

In addition to the low molecular weight hydrocarbon fraction, a trace of oil is also produced.

As pointed out previously, the process of our invention can be employed using cementite as the carbided material. A number of such embodiments are illustrated in the following examples.

EXAMPLE 2

70.2 parts of substantially completely reduced iron pellets are carbided by passing carbon monoxide over them for about 10 hours at atmospheric pressure, a temperature of from about 570° to about 670° F., and an average carbon monoxide space velocity of about 80. The reduced iron is completely converted to cementite and, in addition, 92.8 percent excess carbon is deposited upon the carbided material. 79.9 parts of carbided material containing 9.7 parts as total carbon of which 5.0 parts are carbide carbon, are prepared in this manner.

Steam is then reacted with the carbided material for about 5 hours at a pressure of about 150 pounds per square inch, a temperature of about 570° F., and an average steam space velocity of about 750. The carbided material is then converted principally to ferroferric oxide and 2.158 parts of the carbon are converted, 0.854 part of the carbon being converted to carbon monoxide and carbon dioxide and 1.304 parts of the carbon forming hydrocarbons having the product distribution shown in Table 2 which follows. It will be noted that the conversion of the carbon based upon total carbon available is 22.2 percent while the conversion based upon the carbon available as carbide is 42.9 percent. In like manner the conversion to hydrocarbons based upon total carbon is 13.4 percent, and the conversion based upon carbon as carbides is 25.9 percent.

TABLE 2

Product distribution for the low molecular weight hydrocarbon fraction

Component:	Weight percent
C ₁ -----	32.2
C ₂ -----	12.8
C ₃ -----	37.1
C ₄ -----	9.6
C ₅ + -----	8.3

In addition to the low molecular weight hydrocarbon fraction, a trace of oil is also produced.

EXAMPLE 3

72.5 parts of substantially completely reduced iron pellets are carbided by passing carbon monoxide over them for about 4.5 hours at atmospheric pressure, at a tem-

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perature of from about 570° to about 670° F., and an average carbon monoxide space velocity of about 135. The reduced iron is converted to cementite and, in addition, 39 percent excess carbon is deposited upon the carbided material. 79.7 parts of carbided material are prepared in this manner, containing 7.22 parts as total carbon of which 5.18 parts are carbide carbon.

The carbided material is reacted with steam introduced for 3 hours at a pressure of about 150 pounds per square inch, at a temperature of about 570° F., and an average steam space velocity of about 750. The carbided material is converted principally to ferroferric oxide and 2.208 parts of carbon are converted. 1.142 parts of carbon form carbon monoxide and carbon dioxide and 1.066 parts form hydrocarbons with the product distribution given below in Table 3. The conversion based upon total carbon is 30.7 percent. The conversion based upon carbon as carbide is 42.6 percent. The conversion to hydrocarbons is 14.8 percent based upon total carbon available and 20.6 percent based upon carbon available as carbide.

TABLE 3

Product distribution for the low molecular weight hydrocarbon fraction

Component:	Weight percent
C ₁ -----	26.2
C ₂ -----	20.9
C ₃ -----	23.3
C ₄ -----	21.9
C ₅ + -----	7.7

In addition to the low molecular weight hydrocarbon fraction, a trace of oil is also produced.

As pointed out previously, preferred results, particularly with reference to the production of heavier hydrocarbons, can be obtained by employing cementite, and particularly cementite which is free from a substantial amount of excess carbon. This is illustrated in the following example in which a carbided material consisting of cementite free of excess carbon is formed by first producing Fe₂C and then converting the Fe₂C to cementite by heating.

EXAMPLE 4

75.0 parts of substantially completely reduced iron pellets are carbided by passing carbon monoxide over them for about 19 hours at atmospheric pressure, a temperature of from about 390° to about 485° F., and an average carbon monoxide space velocity of about 375. In this manner about 71.2 percent of the reduced iron is converted to Fe₂C. As pointed out previously, this is the maximum conversion to Fe₂C which can be obtained under these conditions. The Fe₂C is converted to cementite by heating it at about 842° F. for 24 hours. At the end of this time the conversion is complete and the carbided material consists of substantially 100 percent cementite which is free of all excess carbon. 80.2 parts of product containing 97.9 percent cementite including 5.25 parts total carbon are formed.

Steam is then reacted with the cementite for about 5 hours at a pressure of about 150 pounds per square inch, a temperature of about 570° F., and an average steam space velocity of about 750. The carbided material is then converted principally to ferroferric oxide. 1.452 parts of carbon are converted, 0.647 part or 12.4 percent of the total carbon to carbon monoxide and carbon dioxide, and 0.805 part or 15.3 percent of the total carbon to hydrocarbons having the product distribution shown in Table 4. The total conversion of the total carbon is thus about 27.7 percent. Because the carbided material is substantially 100 percent cementite which is free of all excess carbon, the percent conversion is substantially the same whether based upon total carbon or carbon available as carbide.

TABLE 4

Product distribution for the low molecular weight hydrocarbon fraction

Component:	Weight percent
C ₁ -----	24.5
C ₂ -----	20.6
C ₃ -----	17.8
C ₄ -----	22.9
C ₅ + -----	14.2

In addition to the low molecular weight hydrocarbon fraction a quantity of oil estimated to be about 10 percent by weight of the converted carbon is also produced.

The results obtained in the foregoing examples have indicated that the average space velocity for both the carbon monoxide and steam need not be restricted to narrow limits. In the above examples average carbon monoxide space velocities of from about 80 to about 375 are employed. In general, we prefer to employ average carbon monoxide space velocities within the range of about 50 to about 800, but both lower and higher space velocities can be employed by appropriate adjustment of other conditions of the process.

In like manner in the above examples an average steam space velocity of 750 is employed. Average steam space velocities of from about 200 to about 1000 are usually preferable but lower or higher space velocities can be used by appropriate adjustment of the other process conditions.

In each of the above examples the iron is completely reduced before it is carbided to Fe₂C or cementite. When either the Fe₂C or the cementite is reacted with steam, ferroferric oxide is formed. The ferroferric oxide can be carbided to either Fe₂C or cementite under the temperature conditions stated at a superatmospheric pressure, under vacuum, or at atmospheric pressure, employing an average carbon monoxide space velocity of from about 50 to about 800.

The following is an example of an embodiment of our invention in which ferroferric oxide is employed as the initial starting material to produce gaseous and normally liquid hydrocarbons in good yields. Ferroferric oxide in the form of a fine granular material promoted with 1.5 weight percent potassium carbonate and 1.0 weight percent copper is alternately carbided with carbon monoxide for about 5 hours at atmospheric pressure, a temperature of about 450° F., and an average carbon monoxide space velocity of about 175, and the carbided material which is formed comprising Fe₂C is reacted with steam for about 5 hours at a pressure of about 150 pounds per square inch, a temperature of about 575° F., and an average steam space velocity of about 750.

In another embodiment in which ferroferric oxide is employed as the initial starting material, the ferroferric

oxide in pelleted form promoted with 1.5 weight percent potassium carbonate and 1.0 weight percent copper is alternately carbided for about 5 hours at atmospheric pressure, a temperature of about 575° F., and an average carbon monoxide space velocity of about 150, and the carbided material which is formed comprising cementite is reacted with steam for about 5 hours at a pressure of about 150 pounds per square inch, a temperature of about 575° F., and an average steam space velocity of about 750.

As pointed out previously, the pressure employed in carrying out the process of our invention should be maintained above 100 pounds per square inch and preferably between about 150 to 300 pounds per square inch. Higher pressure can be employed if desired, but the use of such pressures causes a change in the product distribution; for example, with pressures in the range of about 150 to about 200 atmospheres, oxygenated hydrocarbons are produced.

Obviously many modifications and variations of the invention may be made without departing from the spirit and scope thereof, but only such limitations shall be imposed as are indicated in the appended claims.

We claim:

1. A process for producing normally liquid hydrocarbons which comprises reacting iron carbide with a gas consisting of steam at a pressure above about 100 pounds per square inch and an elevated temperature of about 525° to about 650° F.

2. A process for producing normally liquid hydrocarbons which comprises reacting iron carbide with a gas consisting of steam at a pressure of about 150 pounds per square inch and an elevated temperature of about 550° to about 600° F.

3. A process for producing normally liquid hydrocarbons which comprises reacting iron carbide with a gas consisting of steam at a pressure above about 100 pounds per square inch gauge and an elevated temperature of about 550° to about 650° F.

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