

Aug. 7, 1951

I. KIRSHENBAUM ET AL
HYDROCARBON SYNTHESIS PROMOTER

2,563,607

Filed Dec. 1, 1948

5 Sheets-Sheet 1

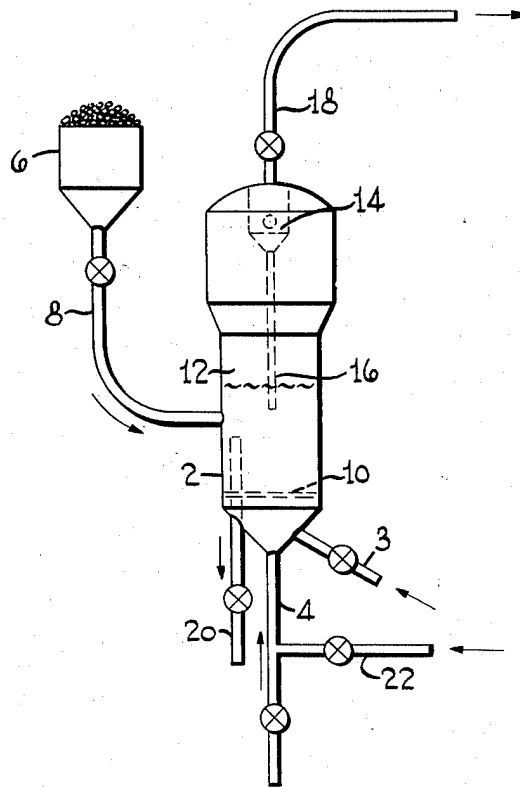


Fig. 1

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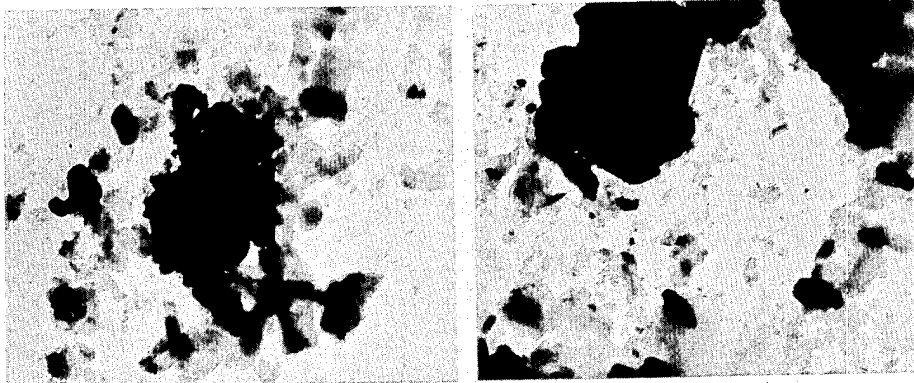
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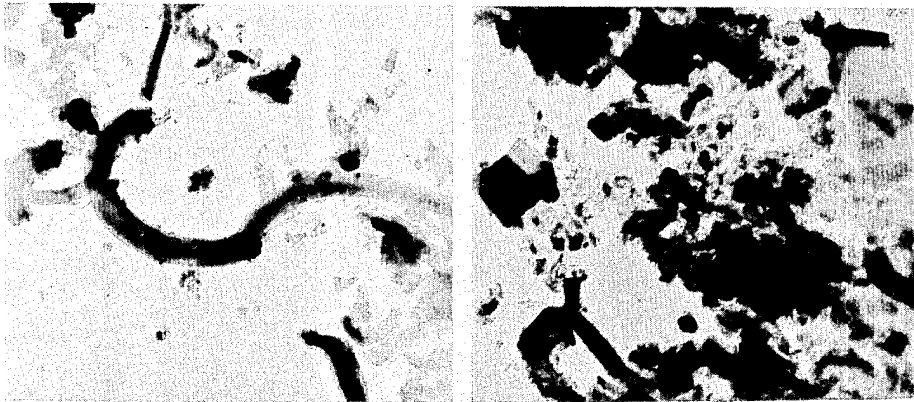
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5 Sheets-Sheet 2

EFFECT ON CUPRENE FORMATION OF C_2H_2 AND O_2
ADDITIONS TO FEED GAS
 $H_2/CO : 1/1$, 60HR. RUNS



1.1% ACETYLENE IN FEED
FIBERS SHORT AND POORLY DEVELOPED



2.2% OXYGEN IN FEED
WELL DEVELOPED FIBERS

— = 1μ

FIG.-2

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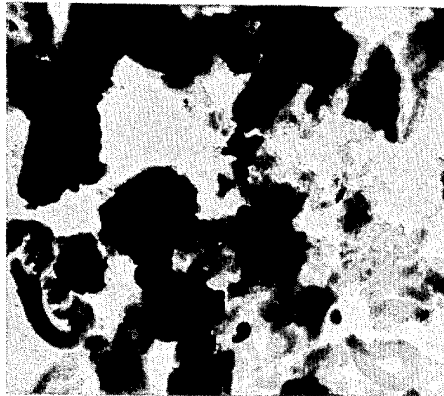
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HYDROCARBON SYNTHESIS PROMOTER

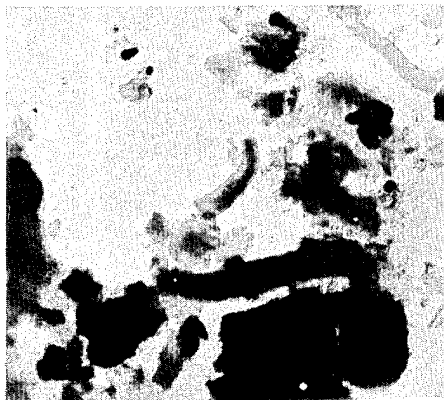
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5 Sheets-Sheet 3

EFFECT ON CUPRENE FORMATION OF C_2H_2 AND O_2
ADDITIONS TO FEED GAS
 $H_2/CO : 1/1, 60 HR. RUNS$



— = 1μ



1.3% ACETYLENE AND 1.4% OXYGEN IN FEED
WELL DEVELOPED FIBERS

FIG.-3

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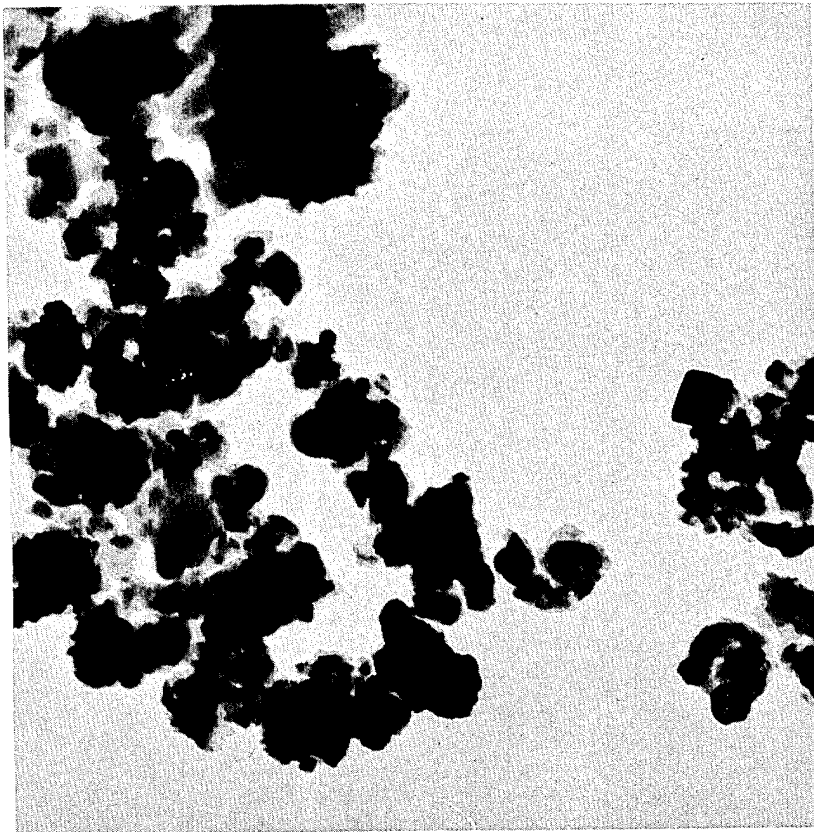
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HYDROCARBON SYNTHESIS PROMOTER

Filed Dec. 1, 1948

5 Sheets-Sheet 4

CUPRENE FORMATION IN PILOT PLANT
HYDROCARBON SYNTHESIS OPERATION
 $H_2/CO : 2/1, 96 \text{ HRS.}$



MANY SHORT FIBERS

FIG. - 4

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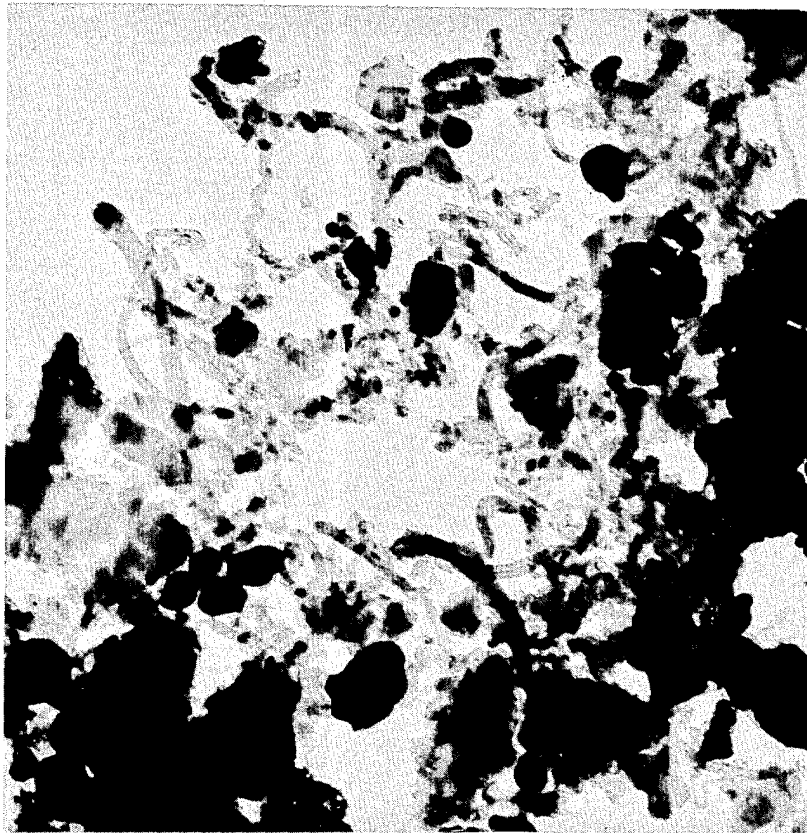
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HYDROCARBON SYNTHESIS PROMOTER

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5 Sheets-Sheet 5

CUPRENE FORMATION IN PILOT PLANT
HYDROCARBON SYNTHESIS OPERATION
 $H_2/CO : 2/1, 290 \text{ HRS.}$



WELL DEVELOPED CUPRENE FIBERS

FIG.-5

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UNITED STATES PATENT OFFICE

2,563,607

HYDROCARBON SYNTHESIS PROMOTER

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Application December 1, 1948, Serial No. 62,914

7 Claims. (Cl. 260-676)

1 The present invention relates to the synthesis of hydrocarbons from carbon oxides and hydrogen in the presence of a suitable catalyst. The invention relates more particularly to a process for obtaining high yields of normally liquid hydrocarbons boiling within the gasoline and gas oil range and concomitantly retarding excessive catalyst fouling and disintegration.

It is known that mixtures of CO and H₂ when brought into intimate contact with suitable catalysts under suitable conditions of temperature and pressure and other variables are converted into hydrocarbons and oxygenated hydrocarbons. It has also been suggested, prior to the present invention, to select reaction conditions of temperature, pressure, contact time, feed gas ratio, etc., as well as the nature of the catalyst as a function of the specific type of product desired. Thus cobalt catalysts have been used at relatively low temperatures of about 350°-450° F. and at relatively low pressures of about 15-150 p. s. i. g. to produce predominantly saturated paraffinic liquids and solid hydrocarbons from which highly valuable Diesel fuel and lubricants, but only low octane motor fuels may be obtained. Iron catalysts in combination with higher temperatures of 450°-650° F. and at higher pressure, up to about 650 p. s. i. g. have been employed where a predominantly unsaturated product is desired from which a valuable motor fuel having relatively high octane rating may be recovered. These iron-type catalysts are usually promoted with alkali metal compounds, such as the carbonates, halides, etc. of sodium or potassium, and generally lower H₂/CO ratios are used with iron catalysts than with the cobalt type.

While it has thus been possible to obtain high octane motor fuels in good yields by this process, it has also been found that operating under conditions that favor good yields of useful (i. e. C₄+ oil) products are accompanied by excessive deposition of carbon and carbonaceous material upon the catalyst. This carbon deposition is a serious problem, particularly when the catalytic operation is carried out by the fluid catalyst technique, which latter, because of better heat distribution, transfer, and control and because of the more intimate mixing and contact of the catalyst with the reactants, is considered far superior to fixed bed processes for effecting the catalytic synthesis of hydrocarbons. However, two problems that arise in conjunction with the fluid solids type of operation when synthesizing hydrocarbons are the fouling of the catalyst by carbon deposition, and the tendency of the catalyst par-

2 ticles to disintegrate, as a result of carbon formation and deposition. Carbon deposition and catalyst disintegration not only cut down product yield through poor fluidization of the catalyst, excessive fines formation and catalyst agglomeration, but may produce conditions requiring shutdown of the plant.

Unfortunately, desirable as it is to keep carbon formation at a low rate and useful product yield high, it has been found hitherto in general, that those factors favoring low rate of carbon formation also tend to keep down the yields of useful synthesis products and, conversely, those operating conditions which favor high yields of C₄+ hydrocarbons also favor formation of excessive amounts of carbon. Thus when the hydrogen partial pressure in the synthesis feed gas is relatively high, say above 200 p. s. i., by raising the ratio of hydrogen in the feed, carbon deposition is held at a low figure, but selectivity to liquid hydrocarbons of the gasoline range is low. Similarly, if the catalyst is an active one, or if the ratio of H₂/H₂+CO+CO₂ is low, the selectivity to useful products is high but the rate of carbon formation is also excessive. Similarly, fresh catalyst is highly reactive, but it also is contaminated with carbonaceous deposits at high rates. Yields of C₄+ product in hydrocarbon synthesis reactions may be approximately classified as follows:

Over 190 cc./cubic meter of CO+H ₂ consumed	-----	Very good
170-190 cc./m. ³ of CO+H ₂ consumed	-----	Good
140-170 cc./m. ³ of CO+H ₂ consumed	-----	Normal
Less than 120 cc./m. ³ of CO+H ₂ consumed	-----	Poor

It is, therefore, the principal object of the present invention to provide an improved process for the conversion of CO and H₂ to form high yields of normally liquid hydrocarbons without forming excessive amounts of carbon during the conversion, and without excessive fragmentation of the catalyst.

Other and more specific objects and advantages of the invention will appear hereinafter.

In the course of investigating means whereby the yields of valuable liquid hydrocarbons may be increased in the hydrocarbon synthesis without the concomitant increase in carbon formation and the undesirable effects associated therewith, in the past several expedients have been tried. Thus previous investigations have found that adding ethylene to the synthesis reactor, using a cobalt catalyst, caused definite increase

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in yield of higher hydrocarbon synthesis product of low octane rating typical of cobalt catalyst. The addition of ethylene to a synthesis reaction mixture in the presence of an iron catalyst, however, was not found to have any particular effect.

The surprising discovery has now been made that the addition of acetylene to the synthesis feed gas to a reactor containing an iron type synthesis catalyst increases substantially the yield of valuable high octane hydrocarbons without the increase in carbon formation usually associated with increases in C_4+ yields. Thus though previous investigators have found the addition of monoolefins to synthesis gas mixtures of CO and H_2 to increase liquid product yields in the synthesis reactions where cobalt was employed as catalyst and to have no effect when iron was employed, the present inventors have found that acetylene gives substantial increases in liquid products when added to synthesis gas in a synthesis reactor employing iron catalysts. Furthermore, under heat treatment it is known that acetylene polymerizes readily to form a solid product, cuprene, which cannot be dissolved by solvents and acts like a carbonaceous deposit. However, when acetylene is added to synthesis gas in accordance with the present invention, not only is the liquid product yield higher than when no acetylene is added, but also the amount of solid carbonaceous material formed and deposited on the catalyst is no greater and in some cases even less, than if no acetylene had been added. Furthermore, it has been found that the presence of a relatively small amount of oxygen impurity in the synthesis gas is conducive to cuprene formation even in the presence of acetylene. Synthesis gas should therefore be pretreated to reduce the oxygen concentration to a low value, for example, to 0.01 to 0.1%.

The process of the present invention may be carried out in any conventional equipment adapted to the fluid catalyst operation. A system suitable for this purpose is shown semi-diagrammatically in the accompanying drawing which is used to describe in greater detail, the operation of the present invention.

Referring now to Figure 1, numeral 2 represents a reactor which is preferably in the form of a vertical cylinder having a lower conical section and an upper expanded section. A synthesis feed gas mixture of hydrogen and carbon monoxide in the ratio of about 0.5-2.0 mols H_2 to 1 mol CO is introduced into reactor 2 through line 4 and flows upward through a screen or grid 10 to effect good gas distribution.

Acetylene from any convenient source, such as a carbide plant, methane cracking plant, or any desired type of acetylene generation unit, is passed into reactor 2 through line 3. The quantity of acetylene in the total synthesis gas feed may be varied over a wide range, for example, from about 4 to about 100 mols H_2+CO per mol C_2H_2 .

It is, of course, desirable to remove sulfur compounds from the synthesis gases prior to introduction into the synthesis reactor, and this may be accomplished by any of the processes well known in the art.

Within reactor 2 a mass of iron catalyst, such as sintered reduced pyrites ash, red iron oxide, ammonia synthesis catalyst (fused reduced high purity magnetite containing a small quantity of alumina and potassium promoter) is maintained in the form of a powder having a particle size

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distribution such that less than 20% of the particles have diameters 0-20 microns and less than 60% of the particles have diameters larger than 80 microns. This catalyst, which is preferably promoted with an alkali metal compound, such as 0.5-1.5% K_2CO_3 , Na_2CO_3 , KF, NaF, etc., may be supplied to reactor 2 from catalyst hopper 8 through line 8.

The linear inlet velocity of the gases to reactor 2 is maintained within the approximate range of 0.3 to 3.0 feet per second, preferably with an upper limit of 1.5 feet per second. Under these conditions the catalyst in reactor 2 assumes the form of a dense, turbulent mass, resembling a boiling liquid, with a more or less well-defined upper level 12, and an apparent density of about 25-75 lbs./cu. ft. depending upon the fluidization conditions, the lower apparent densities being associated with the higher velocities. The amount of synthesis gas and acetylene supplied to reactor 2 is so controlled that about 4 to about 80 normal cubic feet of the gas mixture enters reactor 2 per pound iron catalyst per hour.

Within reactor 2, the total pressure is maintained in the range of 50 to 700 p. s. i. g., preferably 200 to 650 p. s. i. g., and the reaction temperature is controlled by any convenient means, such as by a cooling jacket or coil (not shown) inside or outside reactor 2. A suitable temperature is in the range from about 400° to about 750° F., for example, 550° to 650° F.

When entering the enlarged section of reactor 2, the gas velocity is sufficiently decreased so that the gases will no longer support any substantial quantity of catalyst, and most of the catalyst particles entrained in the gas stream drop back into the fluidized mass.

Volatile reaction products, containing only small quantities of entrained catalyst, are passed through a gas-solids separator 14, such as a cyclone, filter, etc. This removes all but traces of entrained fines, and the catalyst and fines thus removed may be returned through line 16 to the fluidized bed in reactor 2.

Product vapor and gases may be withdrawn through line 18 and recovered through methods well known in the art, such as oil scrubbing, absorption of uncondensable gases on active surfaces, compression, distillation, etc. From time to time catalyst may be withdrawn through line 20 and new or regenerated catalyst added through line 8. Tail gas, comprising unreacted H_2 , CO, C_2H_2 , as well as CO_2 formed in the reactor, is preferably recycled to reactor 2 through line 22. The ratio of recycle tail gas to fresh feed is preferably in the range of 1.5-3.5 volumes tail gas per volume fresh feed.

The embodiment of the invention as shown in the drawing permits of many modifications. Thus instead of pure acetylene, an acetylene-containing gas may be employed as diluent for the synthesis gas feed. Homologs of acetylene may also be employed.

The invention will be further illustrated by the following specific examples.

A series of hydrocarbon laboratory runs was carried out under varying experimental conditions, and the effect of adding acetylene to the synthesis as mixture was compared with results obtained when no acetylene was added under otherwise parallel synthesis conditions. The catalyst employed consisted of 99% Fe_2O_3 (by weight) and 1% KF, and prior to use in the syn-

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thesis reaction, was reduced in a stream of hydrogen at about 900° F.

Effect of C₂H₂ addition to synthesis feed gas

Run.....	1A	1B	2A	2B	3A	3B
Hours on stream.....	15	60	40	40	40	24
Temp., ° F.....	585	550-650	650	650	600	600
Press., p. s. i. g.....	250	250	250	250	250	250
Weight Per Cent C ₂ H ₂ in feed.....	0	1.1	0	1.5	0	1.7
H ₂ /CO ratio in feed.....	0.95	1.1	1.1	1.1	0.85	0.80
Feed rate, v. v./hr.....	200	200	200	200	1,000	1,000
CO conv. Per Cent.....	96.3	97.0	94	93	98	
Yield, C ₄ + products cc./m. ³ H ₂ +CO consumed.....	208	221	169	188	190	217
Carbon selectivity (Per Cent CO conv. to carbon).....	3.18	1.14	2.14	1.91	1.33	1.3
Analysis of hydrocarbon layer:						
Sp. Gr.....				0.771		0.772
Bromine No., c. g. s./cc.....				65.7		58.6
Per Cent C.....				82.0		82.7
Per Cent H.....				13.9		13.4

The above results show that when acetylene is added to synthesis gas in accordance with the present invention, and then passed into a synthesis reactor containing a promoted iron catalyst, substantial increase in valuable liquid (C₄+) product ranging from 6 to 22% or more is obtained, depending upon such variables as reaction temperature, throughput rates, etc. Furthermore, such addition of acetylene does not increase the formation of solid carbonaceous material over that normally formed without the acetylene addition. The hydrocarbon product analysis also indicates that the products obtained with or without acetylene addition are physically and chemically related.

The surprising fact that the addition of acetylene to synthesis gas increases yield, without increasing cuprene formation and therefore, without increasing catalyst disintegration, is dramatically illustrated by the electron photomicrographs show in Figures 2 and 3. In these pictures of iron catalyst which had been used for 60 hours, the large black objects are particles of the iron catalyst, and the small black objects are fragments of disintegrated catalyst. Cuprene appears in the form of fibers. The stability of the cuprene fibers is evident from the fact that they undergo no noticeable change in appearance on heating for 16 hours at 700° F. under a nitrogen atmosphere. In Figures 4 and 5 are shown other electron photomicrographs of iron catalyst which had been used in a hydrocarbon synthesis pilot plant for different periods of time.

With reference to the upper panel of Figure 2, it will be observed that when the feedstock contains acetylene, very few cuprene fibers are formed, and these are short and poorly developed. Similar photomicrographs are obtained when the catalyst has been employed on a feedstock which is substantially free of oxygen. In other words the addition of acetylene, which is the monomer of cuprene, does not increase cuprene formation and catalyst disintegration in hydrocarbon synthesis.

The effect of oxygen in the feedstock is evident from a comparison of the upper panel with the lower panel of Figure 2 and with Figure 3. When oxygen alone, or when both acetylene and oxygen are present, many well developed cuprene fibers are formed. This is also evident from the electron photomicrographs shown in Figures 4 and 5, of catalyst which was operated on a feedstock which had not been pretreated to remove oxygen. It should be noted that the effect of oxygen on

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cuprene formation was not evident from data on total carbonaceous deposits, but became obvious from study of electron photomicrographs. The photomicrographs also give a clue as to the mechanism of catalyst disintegration. In the photomicrograph of Figure 4, and also in the lower panel of Figure 2, small particles of iron are clearly shown imbedded in the cuprene fibers. It would appear that during its formation, cuprene actually tears these bits of iron from the crystal structure of the catalyst particle.

While the foregoing description and exemplary operations have served to illustrate specific applications and results of the invention, other modifications obvious to those skilled in the art are within its scope.

What is claimed is:

1. An improved process for producing valuable liquid hydrocarbons from synthesis gas mixtures containing CO and H₂ in proportions of from about 0.5 to 2 mols of H₂ per mol CO without excessive deposition of solid carbonaceous material which comprises feeding a synthesis gas mixture containing H₂, CO and acetylene from an external source in synthesis proportions into a dense, fluidized bed of finely divided iron-containing catalyst in a reaction zone, maintaining said reaction zone at synthesis conditions of pressure and temperature, contacting the reactants with said catalyst for a sufficient period of time to obtain the desired conversion, and recovering a product containing substantial amounts of olefinic hydrocarbon products boiling in the gasoline range.

2. The process of claim 1 wherein said synthesis gas mixture contains about 1 to 25 volume percent of acetylene.

3. The process of claim 1 wherein said catalyst is promoted with a minor proportion of an alkali metal salt.

4. The process of claim 1 wherein said synthesis temperature is in the range of 550°-650° F.

5. The process of claim 1 wherein said synthesis gas mixture is substantially free of free oxygen.

6. An improved process for producing valuable liquid hydrocarbons from synthesis gas mixtures, comprising CO and H₂ in proportions of from about 0.5 to 2 mols of H₂ per mol CO without excessive deposition of solid carbonaceous material which comprises passing a synthesis gas mixture comprising H₂ and CO in synthesis proportions and containing a minor admixture of oxygen through an oxygen removal zone, substantially removing oxygen from said gas mixture, adding acetylene from an external source to said purified synthesis gas mixture, feeding said mixture into a dense, fluidized bed of finely divided iron containing synthesis catalyst in a reaction zone, maintaining said reaction zone at synthesis conditions of pressure and temperature, contacting the reactants with said catalyst for a sufficient period of time to obtain the desired conversion, and recovering a product containing substantial quantities of olefinic hydrocarbon products boiling in the gasoline range.

7. The process of claim 6 wherein the oxygen content of said synthesis gas prior to conversion in said synthesis zone has been reduced to the range of from about 0.01 to 0.1% by volume.

ISIDOR KIRSHENBAUM.
RICHARD K. GROVER.

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7

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