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(54) LOW PRESSURE HYDROCARBON SYNTHESIS PROCESS
(54) PROCEDE DE SYNTHESE D'HYDROCARBURE A BASSE PRESSION

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1 The present invention relates to the catalytic reaction between carbon monoxide and hydrogen to form valuable liquid hydrocarbons. More particularly, the present invention is concerned with improvements in the reaction based on an improved composition of catalyst employed in the reaction.

 The synthetic production of liquid hydrocarbons from gas mixtures containing various proportions of carbon monoxide and hydrogen is a matter of record and various
10 operating conditions, and numerous catalysts, usually containing a metal of the iron group, have been proposed to promote the desired reactions. For example, to produce substantially saturated hydrocarbons it has been proposed to use catalysts comprising cobalt on an inert carrier at
relatively low pressures of about 1 to 5 atmospheres and at temperatures from 300° to 425°F. whereas in order to produce products containing high proportions of unsaturated
and/or branched chain hydrocarbons it has been found
necessary to use iron catalysts at higher temperatures
20 between 450°-750°F. at higher pressures of 15 to 40 atmospheres.

 In both cases, the reaction is strongly exothermic and the utility of the catalyst declines steadily in the course of the reaction chiefly due to deposition of non-volatile conversion products such as paraffin wax, carbon, and the like on the catalyst.

 The extremely exothermic character and high temperature sensitivity of the synthesis reaction and the relatively rapid catalyst deactivation have led, in recent
30 years, to the application of the fluid solids technique

1 wherein the synthesis gas is contacted with a turbulent bed
of finely divided catalyst fluidized by the gaseous
reactants and products. This technique permits continuous
catalyst replacement and greatly improves heat dissipation
and temperature control.

Most processes for the synthesis of hydrocarbon
involve the step of producing the synthesis gas mixture of
carbon monoxide and hydrogen by partial combustion of coal
or natural gas with an oxidizing gas such as air or oxygen,
10 which synthesis gas is then converted to the hydrocarbons
in a second step. In the usual processes in order to
produce a highly unsaturated hydrocarbon product it is
generally thought desirable as mentioned above to operate
this synthesis reaction at high pressure of about 400 lbs.
per sq. in. using an iron catalyst. This necessitates the
feeding of the synthesis gas to the reactor under high
pressure and usually requires the production of the
synthesis gas under high pressure, which in turn involves
the feeding of the oxidizing gas to the synthesis gas
20 produced under high pressure. This usually necessitates
the use of expensive pure oxygen at high pressure as the
oxidizing gas as it would be uneconomical to utilize air
under high pressure because the recycle requirements
associated with an iron catalyst would result in the
undesirable recirculation of a gas containing an ever-
increasing amount of nitrogen.

For the above reasons, it would be highly desirable
to be able to produce valuable olefinic motor fuel products
by a hydrocarbon synthesis process by the fluid solids
30 technique wherein the synthesis gas could be prepared with

1 air at low pressures instead of with oxygen at high pressures,
and wherein the synthesis itself could be carried out at
moderate instead of at high pressure.

Many attempts have already been made in this
direction using fixed bed processes. Thus it has been
attempted to prepare high octane motor fuel using a thoria
promoted cobalt on silica gel catalyst. However, it was
found that when the variables were adjusted in an effort
to improve the liquid yield and quality of product, the
10 yield of liquid products increases somewhat with pressure
when the temperature is held constant, but the yield of
wax increases also. This is quite undesirable because wax
formation renders it extremely difficult to maintain a
fluidized bed in the reactor. On the other hand, if the
pressure is held constant in the relatively low pressure
areas where cobalt catalyst functions well, that is, in
the region of 15 to about 75 psig., the olefin content of
the product is low, and attempts to increase the
olefinicity by increasing the temperature caused a decrease
20 in liquid product yield and an increase in gas formation.

On the other hand, experience has indicated that
operation with iron catalyst at the lower pressures is
usually accompanied by severe carbonization of the catalyst
as well as formation of wax, both making the maintenance of
a fluid catalyst bed a matter of very great difficulty.

It is now found that hydrocarbon synthesis products
containing high proportions of valuable unsaturated
hydrocarbons can be obtained by contacting a synthesis gas
mixture of carbon monoxide and hydrogen containing consider-
30 able quantities of nitrogen, for example, when prepared by
oxidation of coal or natural gas with air at low pressure

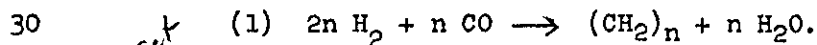
1 by contacting the said gas mixture at relatively low pressures and at elevated temperatures with a finely divided fluidized solid catalyst comprising a mixture of iron and cobalt carried on a silica gel carrier and promoted with thoria or an iron carried on an active carbon support and promoted with an alkali metal compound, for example, potassium carbonate. The invention accordingly comprises a process for the production of hydrocarbon products containing a high proportion of unsaturated hydrocarbons by contacting a synthesis gas mixture of carbon monoxide and hydrogen containing appreciable quantities of nitrogen at a relatively low pressure and at an elevated temperature with a finely divided fluidized solid catalyst comprising a mixture of iron and cobalt carried on a silica gel support and activated with a thorium compound or iron carried on an active carbon support and activated with an alkali metal compound. In general the synthesis reaction is carried out at a pressure between 50 and 100 lbs. per sq. in. guage and preferably between 55 and 75 lbs. per sq. in. guage, and at temperatures between 450 and 650°F., and preferably between 475° and 525°F. in the case of the iron cobalt silica gel catalyst and 550 to 650°F. in the case of the iron active carbon catalyst and with a through-put of from 2 to 20 volumes of synthesis gas per volume of catalyst per hour at a linear velocity of 0.1 to 3 feet per second and preferably between 0.4 and 1.5 feet per second. Furthermore, it is found that the operating range wherein these beneficial effects are realized is a relatively narrow one, and relatively small variations in reaction conditions decrease either the yield

1 or the olefinicity, or increase wax formation.

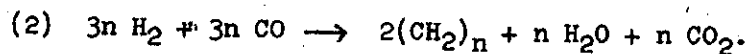
It is found that by operating in the manner described above, it is possible to operate a fluid solids reactor at a moderately low pressure and obtain good yields of olefinic hydrocarbons without serious wax formation from synthesis gas prepared by a process involving oxidation by air instead of by oxygen.

In the synthesis of hydrocarbons from carbon monoxide and hydrogen, as described above wherein the
10 synthesis gas contains large quantities of nitrogen, it is obvious that a once-through operation is most desirable, because otherwise large quantities of inert material would be recycled, markedly decreasing the capacity of the plant and the operation. Such nitrogen is present when the synthesis gas is prepared by partial combustion of natural gas with air at moderate pressures, which is of marked economic advantage over preparing the same by combustion with pure oxygen under pressure. Furthermore, in the
20 synthesis of hydrocarbons from CO and H₂ employing a once-through operation, it is apparent that the optimum consumption ratio of the reactants should be the same as their ratio in the synthesis feed gas.

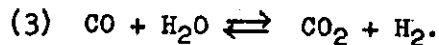
In the production of synthesis gas by partial oxidation with air of methane and natural gas, hydrogen and CO are produced at a 2/1 ratio. When such a gas is used as a feed to the synthesis reactor, the elimination of oxygen in the form of water rather than carbon dioxide is essential for an approximately 2/1 H₂/CO consumption ratio, in accordance with the reaction,



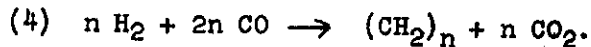
- 1 This is essentially the course of the reaction when cobalt is employed as a synthesis catalyst, and is thus ideally suited for a once-through operation. However, as indicated above and as is well known, cobalt catalyst is not conducive to formation of olefinic hydrocarbons valuable as motor fuel. On the other hand in some cases, when an iron catalyst is employed, the over-all reaction can be more nearly represented by



- 10 The CO_2 that occurs along with the products of the synthesis reaction, as in (2) above, may be a result of the reversible water gas shift reaction



- Thus in the synthesis reaction according to (1) above, the consumption ratio of hydrogen to carbon monoxide is 2/1. However, since some of the water formed in (1) may react with some unconverted CO in accordance with (3), hydrogen is formed and CO is consumed which in effect lowers the H_2/CO consumption ratio. Carried to its limit, the ultimate effect of this reaction would be for all of the H_2O formed to react rapidly and irreversibly with CO in which the net synthesis reaction could be written as



giving an H_2/CO consumption ratio of 0.5/1. From the above it may be seen that, starting with a 2/1 H_2/CO feed gas, the H_2/CO consumption ratio may vary from about 2/1 to almost 0.5/1 depending upon the degree to which the water gas shift reaction takes place.

- During the normal synthesis with an iron catalyst, and iron is considered to be an excellent shift catalyst,
- 30

1 the water gas constants,

$$K = \frac{(CO_2) (H_2)}{(CO) (H_2O)},$$

calculated from the concentrations of the water gas components in the effluent from the reactor are 60-95% of the known water-gas equilibrium constants at temperatures in the range of 550°-650°F. The known values for K at 550°F. and at 650°F. are about 50 and 23 respectively. The low calculated values indicate that the amounts of CO₂ and H₂ present are inadequate to satisfy the water gas shift equilibrium and that the reaction of CO and H₂O is slower than the synthesis reaction.

In such a once-through hydrocarbon synthesis operation at low pressures in the range of about 50 to 100 lbs. per sq. in. guage with fluidized catalyst to prepare high yields of olefinic motor fuel, it is, therefore, highly desirable that the H₂/CO consumption ratio approach as nearly as possible to the ratio in which these two constituents are present in the feed.

20 When employing a cobalt synthesis catalyst in the normal processes the ratio of H₂ to CO consumed is greater than the H₂ to CO ratio in the feed, up to ratios of about 2/1. On the other hand, all previously known modifications of iron synthesis catalysts give H₂ to CO consumption ratios less than the ratio of these constituents in the feed. Now, however, the surprising discovery has been made that catalysts of the compositions defined above give H₂/CO consumption ratios greater than the ratio of these constituents in the feed, thus making the process suitable for a once-
30 through operation with synthesis gas from partial oxidation

1 of natural gas, wherein the H_2/CO ratio is about 2/1.

The invention will best be understood by referring to the accompanying diagrammatic representation of one of the methods of carrying the invention into effect where suitable equipment and flow of material are shown.

Referring now in detail to the drawing, natural gas from any convenient source preheated in preheater 4 is passed to synthesis gas producer vessel 6, which comprises a catalytic oxidation zone. Simultaneously, air is passed
10 through line 18 into compressor 20, wherein it is moderately compressed to about 50-100 psig. and the compressed material is passed through line 22 and preheater 16, wherein it is preheated to about 1200°F., and introduced into synthesis generator plant 6. In generator 6 partial oxidation mainly to CO and H_2 takes place. The temperature in the oxidation zone may be of the order of 2000-2500°F. The lower portion 8 of generator 6 may comprise a catalytic reformer bed, containing a reforming catalyst such as
20 as a result of combustion in the upper part of the generator will reform unreacted methane to produce further quantities of H_2 and CO.

The hot synthesis gases leaving generator 6, which are at a temperature of about 1600°-1800°F. are passed through line 10 and are preferably employed to preheat the incoming natural gas and air in preheaters 4 and 16, respectively, the synthesis gas stream being divided for this purpose to pass through lines 12 and 14, and through lines 25 and 26. The reunited synthesis gas stream in
30 line 27, which has been cooled as indicated to about 450°-

1 600°F., and may be further cooled if desired, is passed to the bottom of hydrocarbon synthesis reactor 28. The latter is preferably in the form of a vertical cylinder with a conical base and an upper expanded section, and has a grid (or screen) 30 located in the lower section to effect good gas distribution.

Within reactor 28, a mass of catalyst is maintained in the form of a finely divided powder having a particle size distribution from about 100-400 mesh, preferably about 10 150 to 200 mesh supplied to the reactor 28 from hopper 34 via line 36.

The synthesis gas mixture, having a molar ratio of H_2/CO of about 2 to 1, flows upwardly through grid 30. The superficial linear velocity of the gas within the reactor is kept within the approximate range of 0.1-3 feet per second, preferably about 0.4-1.5 feet per second so as to maintain the catalyst in the form of a dense, highly turbulent fluidized mass having a well defined upper level 38 and an apparent density of from about 30 to 125 lbs. per 20 cubic foot, depending upon the fluidization conditions.

In accordance with the invention, the pressure within reactor 28 is kept within the approximate limits of 50 to 100 psig., preferably about 55-75 psig. and the temperature is maintained constant within the limits of about 475° to 525°F. Surplus heat from the exothermic reaction may be withdrawn by any conventional means, such as external cooling coil 32.

Only a small portion of the powdered catalyst is carried into the disengaging section of the reactor above 30 level 38, and these catalyst particles are separated from

1 the reaction products in a conventional gas-solids separator, such as cyclone 40 and returned to the dense bed via dip pipe 42. The rate of gas throughput in terms of volume of gas (H_2+CO) per weight of catalyst per hour, or $V/Hr./W$, is in the range of 2 to 20, and is so adjusted as to give the desired conversion without need for any recycle of tail gas.

Product vapor and gases are withdrawn overhead from reactor 28 and are passed through line 44 and condenser 10 46 to liquid products separator 48, wherein liquid products are separated from gases. The liquid products, containing high yields of olefins with little or no oxygenated hydrocarbons may be withdrawn through line 52 for further processing, such as fractionation, cracking of the gas oil fraction, isomerization, polymerization, hydroforming, etc., all in a manner known per se.

The uncondensed gases, comprising lower molecular weight hydrocarbons as well as unreacted synthesis gas and nitrogen are preferably passed through line 50 to a 20 fluidized solids, active carbon adsorption plant, wherein light hydrocarbons may be removed, and recovered by desorption, at the lower pressures of the present operation. This represents a considerably more economical process than the conventional oil absorption of tail gas.

Instead of producing synthesis gas from partial combustion of natural gas or methane by air at low pressures, synthesis gas may also be prepared by the water gas reaction from coal. In such case, depending on how heat is furnished to the process, either by direct combustion 30 of coke or coal within the water gas generator with air or

1 by recycling of hot combustion solids from a burner vessel, the synthesis gas may or may not contain appreciable quantities of nitrogen. However, the ratio of H_2/CO in synthesis gas prepared from coal is about 1/1, and such a synthesis gas may be passed through a shift converter to increase the feed gas ratio from about 1/1 to about 2/1. In such a system, also, a desulfurizing step would be introduced, such as the passing of the synthesis gases through spent synthesis catalyst to remove sulfur.

10 In accordance with the invention the catalyst supplied to the reactor 28 from the hopper 34 is either the cobalt-iron silica gel catalyst or the iron active carbon catalyst above referred to.

The cobalt-iron catalyst which may be used according to the invention preferably contains a total of 10% to 35% by weight of iron and cobalt based on the total weight of the catalyst carried on a silica gel support and preferably contains from 3 to 25% by weight of iron and from 5 to 30% by weight of cobalt in the ratios of 20 from 10 parts of cobalt to 1 part of iron to 1 part of cobalt to 6 parts of iron. The catalyst also contains from 1 to 5% by weight of thoria.

One suitable cobalt-iron catalyst may be prepared in the following manner: Twenty-one wt. percent cobalt, 7 wt. % iron and 4.4 wt. thorium (all as their hydrated nitrate salts) were milled in a Simpson mixer with 67.6% silica (as silica hydrogel containing about 18% solids) and the wet mixture was then passed through a colloid mill. The above composite was dried at about 250°F. and then 30 further heated for 48 hours at 420°F. and for an additional

- 1 5 to 6 hours at 550°F. to complete the decomposition of the nitrates. The resulting dried material was then ground to a suitable size and reduced with hydrogen at 700°F. and atmospheric pressure.

The iron catalysts which may be used according to the invention preferably comprise from 10 to 20% by weight of the total catalyst of reduced iron carried on an active carbon carrier and promoted with not less than 0.4% by weight and not more than 1% by weight, and preferably
 10 between 0.4% and 0.6% by weight of potassium carbonate. The iron is distributed uniformly over the carrier and may be applied by any desired process such as impregnation, thermal decomposition of iron penta carbonyl or the like.

EXAMPLE I

The following example shows the effect of temperature on the activity, selectivity, and unsaturation of the product using the mixed cobalt iron catalyst. For a comparative basis, data obtained under similar reaction conditions for a cobalt catalyst promoted with an alkali
 20 promoter but containing no iron are included. In all cases the pressure was 75 psig., the gas rate 200-400 V/V/Hr. and the H₂/CO ratio 1/1.

Temperature °F.	430	450	500	525	550
<u>Catalyst A</u>					
	25.2% Co				
	2.8% Fe				
	4.4% Th				
	67.6% SiO ₂				
CO Conversion, % Output	41	44	60	--	81
H ₂ Conversion, % Output	82	82	93	--	93
C ₄ + Yield, cc/m ³ H ₂ +CO Cons.	228	221	180	--	128
Bromine No. of Collected Oil	45	48	85	--	97
Product Appearance	Clear	Clear	Clear	--	Clear

1	<u>Catalyst B</u>					
	30% Co					
	1% ThO ₂					
	3% MgO					
	66% SiO ₂					
	2% Na ⁺					
	(*As Na ₂ CO ₃ Based on Co)					
	CO Conversion, % Output	18	30	54	57	74
	H ₂ Conversion, % Output	39	53	85	87	89
10	C ₄ +, cc/m ³ H ₂ +CO Cons.	216	226	187	148	113
	Bromine No. of Collected Oil	34	33	56	54	62
	Product Appearance	Waxy	Waxy	Slightly Waxy	Clear	Clear

The above data show for the iron-cobalt catalyst a steady increase in H₂ and in CO conversion with temperature. Selectivity to valuable C₄+ liquid products was found to decrease with increasing reaction temperature at about the same rate with each of the catalysts. However, the unsaturation of the oil product, as indicated by the bromine number, was appreciably higher in all cases for the iron-cobalt catalyst than for the cobalt catalyst promoted with alkali. The unsaturation was found to improve far more rapidly as the temperature was increased with the former than with the latter catalyst. Thus at about 500°F. operating temperature, when the yields to liquid product were about equivalent in both cases, 180-187 cc C₄+ / m³ of H₂+CO converted, the cobalt-iron catalyst of the invention produced a total oil product having a bromine number of 85, corresponding to a liquid product unsaturation of 59, the gasoline fraction (Initial to 430°F.) of which had an estimated unsaturation of about 66%. Under the same conditions the alkali promoted cobalt catalyst without iron produced a total oil product which had a bromine number of only 56, corresponding to an unsaturation value of 42%. Increasing the operating temperature up to 550°F. with

1 each of these catalysts increased the product bromine numbers in each case, though to a far higher value for the iron-cobalt (97) than for the alkali promoted cobalt (62). Furthermore, the oil product from the iron-cobalt product was clear and much less waxy than that produced at the same temperature with the alkali promoted cobalt catalyst.

EXAMPLE II

To show the effect of variation on the reaction of the cobalt-iron ratio in the cobalt-iron catalyst used according to the invention, the following data were obtained 10 employing a fixed bed operation. The temperature of 500°F. was chosen as a result of the previous example. In each case the catalyst contained 4.4% thorium and 67.6% SiO₂.

	% Cobalt in Catalyst	25.2	21.0	14.0	7.0
	% Iron in Catalyst	2.8	7.0	14.0	21.0
	Pressure, Psig.	-----75-----			
	Temperature, °F.	-----500-----			
	Feed, H ₂ /CO Ratio	-----1.15-----			
	Feed Rate, V/V/Hr.	-----320-----			
20	CO Conversion	64	59	45	41
	H ₂ Conversion	95	92	73	72
	H ₂ /CO Consumption Ratio	1.72	1.79	1.89	1.89
	C ₄ +, cc/m ³ H ₂ +CO Consumed	172	170	205	197
	<u>Olefins in Exit Gas</u>				
	% In C ₂	13	7	6	9
	% In C ₃	68	51	46	57
	% In C ₄	75	72	82	--
	<u>Weathered Product</u>				
	Initial-400°F., Vol.%	71	82	76	77
30	Unset. of Init.-430°F.%	66	64	64	58
	<u>C₄ Product</u>				
	Unsat., %	76	76	73	--
	Butene-2/Butene-1	3.2	4.0	4.0	--
	Water Gas Constant, % of Equilibrium	----Less than 0.1%-----			

From the above data, the following points are noteworthy:

1. The use according to the invention of the cobalt-iron catalyst gives a uniformly high H₂/CO consumption

- 1 ratio despite the variation in iron content and despite use of a low H_2/CO ratio gas. This is consistent with the fact that the calculated water gas constant is apparently less than 0.1% of the equilibrium value, although the amounts of iron present are relatively high. In the case of a promoted iron catalyst under similar reaction conditions, the approach to equilibrium would be in the neighborhood of 50 to 90%.
2. The percent unsaturation of the product is
10 high and is relatively independent of the cobalt-iron ratio when this ratio is 1/1 or higher.
3. Cobalt-iron ratios of 1/1 or less appear to favor higher C_4+ selectivities.
4. The butene-2/butene-1 ratio is high, which is in marked contrast to the low ratios obtained with iron catalysts. This means that since alpha olefins are low, further treating of the product for octane improvement, such as by isomerization, is simplified. This is also true in respect to treatment to convert oxygenated hydrocarbons
20 to olefins; such compounds are found only in negligible quantities in the product from the iron-cobalt catalyst as against an iron catalyst, in the product from which they may be present in amounts equivalent to 2-4% oxygen.

EXAMPLE III

The following example shows the effect when using the iron/active carbon catalyst according to the invention and the effect of varying the promoter content of the catalyst upon the variables of product quality, C_4+ selectivity, catalyst activity, and olefin formation. In
30 all cases, the catalyst contained 14.9% iron supported on

1 an active carbon carrier and the reaction was carried out as a once-through operation at a pressure of 75 psig., a temperature of 600°F. and a feed rate of 200 volumes of synthesis gas per volume of catalyst per hour.

K_2CO_3 , %	0	0.5	2.0	4.0
CO Conversion, %	73	83	77	66
Feed Gas Ratio, H_2/CO	1.15	1.15	1.15	1.15
H_2/CO Consumption Ratio	0.78	0.62	0.55	0.54
Water Gas "K", % of Equil.	33	63	78	91
10 Yield C_4+ , cc/m ³ H_2+CO Cons.	217	215	206	199
% Unsat. in C_3 in Exit gas	41	88	87	83
Collected Oil Product, Appearance	Clear	Slightly Waxy	--Very Waxy--	
Oil Product, Init. - 430°F., Wt. %	90	72	66	58
Est. Unsat. of Init. to 430°F., %	Less than 40	77	76	75

The above data indicate that the catalyst promoted with 0.5% K_2CO_3 , although giving a somewhat lower H_2/CO consumption ratio than the catalyst containing no promoter, 20 gave a product whose unsaturate content was far greater than that of the unpromoted catalyst. Thus, whereas an unpromoted catalyst prepared as above gave a product whose unsaturation was less than 40% (not satisfactory for a motor fuel), the 0.5% K_2CO_3 promoted catalyst showed a product unsaturation of 77%. Furthermore, the last-named catalyst had high selectivity for C_4+ product, good activity for converting CO, and low wax production. Catalysts containing higher quantities of promoter showed 30 considerably higher wax-forming tendencies, lower selectivities, and lower relative percentages of gasoline in the product, as well as substantially lower H_2/CO consumption ratios.

1 EXAMPLE IV

Under the same operating conditions as in Example III catalysts containing 0.1 and 0.3% K_2CO_3 were tested, employing as feed a synthesis gas containing H_2/CO in the ratio of 2.04 to 1 rather than 1.15 to 1.

K_2CO_3 , %	0.1	0.3	0.5
CO Conversion, % Output	94	94	93
H_2/CO Consumption Ratio, Output	1.03	0.85	0.67
Yield, cc. C_4+ /m ³ H_2+CO Consumed	142	205	214
10 <u>Unsats. in Exit Gas, %</u>			
C_2	7	51	77
C_3	31	75	82
<u>Collected Oil Product</u>			
Est. Unsat. of Init. to 430°F., %	11	46	70

Here again it may be seen that even at a slightly lower promoter content the unsaturation of the gasoline product is very low, indicating again the criticality of the promoter content.

20 Other promoters may be used, such as potassium hydroxide, potassium acetate and potassium fluoride. The important consideration is that since the promoter concentration is probably associated with the iron surface, the ratio of promoter content to iron surface is critical. Thus similar catalysts, of different particle size, and therefore of different iron surface area will have a different critical promoter content, depending upon the extent of iron surface area.

30 Thus in accordance with the invention hydrocarbon synthesis operations may be carried out at low pressures to give high yields of unsaturated compounds and minimum

1 quantities of wax. By dispensing with the oxygen unit and operating the synthesis gas generator with air investment costs are substantially decreased from the level where a high pressure type of operation requiring an oxygen unit is employed.

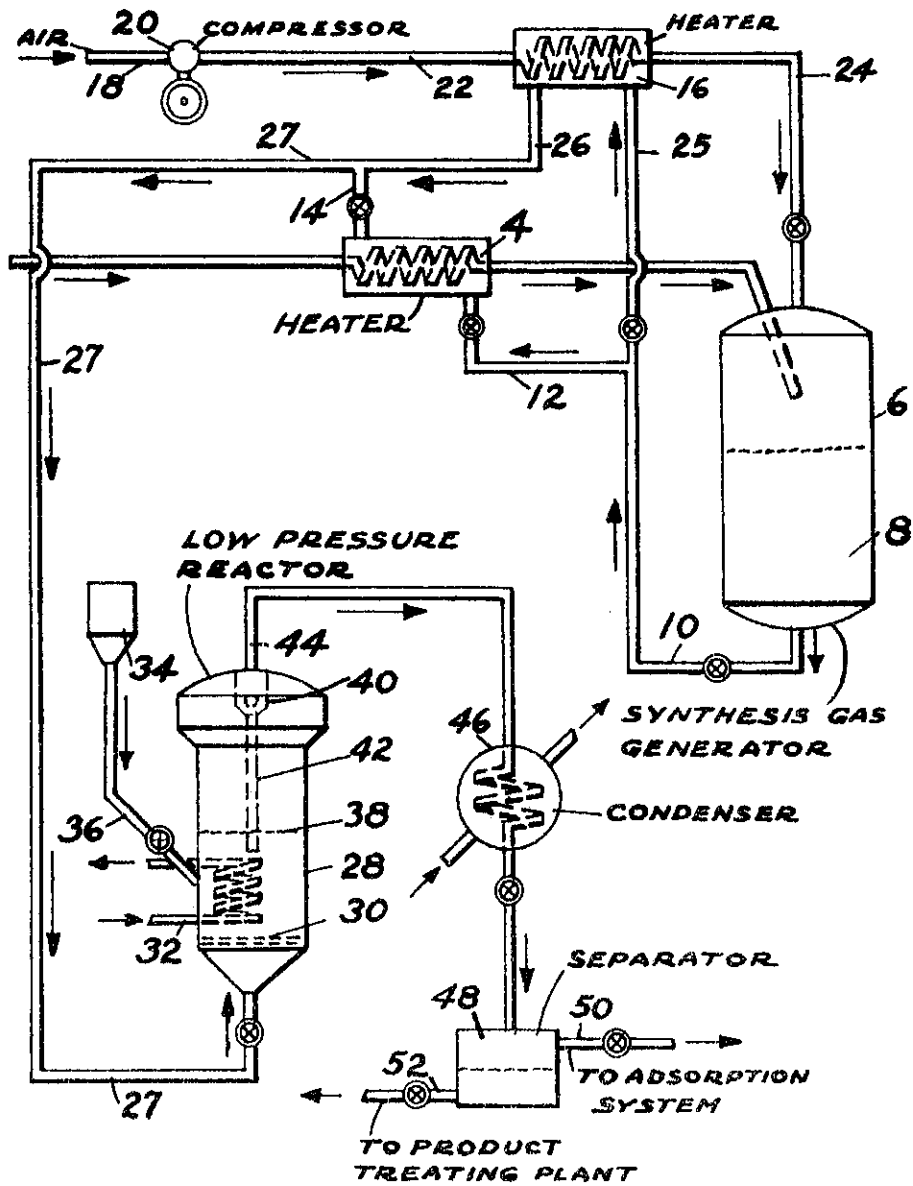
While the foregoing description and examples serve to illustrate specific applications and results of the invention other modifications obvious to those skilled in the art are also within its scope.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. An improved process for converting CO and H₂ to normally liquid hydrocarbons of high olefin content which comprises contacting CO and H₂ in synthesis proportions under synthesis conditions comprising pressures of from about 50 to about 100 p. s. i. g. with a dense turbulent fluidized mass of finely divided synthesis catalyst, said catalyst comprising an activated carbon support carrying as active component iron promoted with not less than 0.4 and not more than 1.0% by weight of the total catalyst, of an alkali metal promoter.
2. The process of claim 1 wherein said iron comprises from 10-20% of the total weight of said catalyst.
3. The process of claim 1 wherein said synthesis conditions include temperatures of from about 550°-650°F. and feed rates of about 2-20 v./hr./w.
4. An improved low-pressure once-through process for preparing high yields of valuable olefinic hydrocarbons from synthesis gas containing appreciable quantities of nitrogen which comprises passing a gas mixture containing H₂ and CO in synthesis proportions diluted with nitrogen into a hydrocarbon synthesis reaction zone, contacting said gaseous mixture with a dense turbulent mass of finely divided synthesis catalyst consisting of an activated carbon support, said support carrying as active component from 10-20% by weight of the total catalyst, of iron promoted with 0.4-1.0% of a potassium compound promoter, maintaining a pressure of about 50-100 p. s. i. g. and a temperature of about 550°-650°F. within said zone, and withdrawing a product containing high yields of liquid olefinic hydrocarbon product.

5. The process of claim 4 wherein said catalyst is promoted with 0.5 weight percent potassium carbonate based on the total weight of catalyst, said catalyst contains 14.9% iron, and reaction conditions within said zone comprise a pressure of about 75 p. s. i. g. and a temperature of about 600° F.

6. The process of converting natural gas to valuable liquid olefinic hydrocarbons in a low pressure once-through operation which comprises oxidizing natural gas with air in an oxidation zone to form synthesis gas containing H₂ and CO in a ratio of about 2/1, and which gas is diluted with nitrogen, passing said gas to a hydrocarbon synthesis zone, contacting said gas with a fluidized catalyst comprising an activated carbon support carrying an iron catalyst promoted with about 0.5 weight percent K₂CO₃ based on the total weight of said catalyst, said iron comprising about 15% by weight of the total catalyst, maintaining a pressure of about 75 p. s. i. g. and a temperature of about 600° F. within said zone, and withdrawing a product containing high yields of liquid olefinic hydrocarbons.



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