THE PATENT OFFICE
LONDON

PATENT SPECIFICATION 651,559

Date of Application and filing Complete Specification: *Aug. 9, 1948.* *No. 20958/48.*

Application made in United States of America on Nov. 28, 1947.

Complete Specification Published: April 4, 1951.

(Under Section 91, sub-sections (2) and (4) of the Patents and Designs Acts, 1907 to 1946, a single Complete Specification was left in respect of this Application and of Application Nos. 20956/48 and 20957/48 and was laid open to inspection on May 30, 1949.)

Index at Acceptance:—**Class 1(i),** F3b2a.

3500

COMPLETE SPECIFICATION.

Hydrocarbon Synthesis.

We, STANDARD OIL DEVELOPMENT COMPANY, a Corporation duly organised and existing under the laws of the State of Delaware, United States of America, having an office at Elizabeth, New Jersey, United States of America, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

This invention relates to the catalytic conversion of carbon oxides with hydrogen to form valuable synthetic products. The invention is more particularly concerned with an improved method of employing and reconditioning finely divided catalysts having a high activity and selectivity for the formation of normally liquid hydrocarbons in the catalytic conversion of carbon monoxide with hydrogen employing the so-called fluid solids technique.

The synthetic production of liquid hydrocarbons from gas mixtures containing various proportions of carbon monoxide and hydrogen is already known and numerous catalysts usually containing an iron group metal, have been described which are specifically active in promoting the desired reactions at certain preferred operating conditions. For example, cobalt supported on an inert carrier is used when relatively low pressures (atmospheric to about 5 atmospheres) and low temperatures (about 375°—425° F.) are applied in the manufacture of a substantially saturated hydrocarbon product while at the higher temperatures (about 450°—750° F.) and higher pressures (about 5—25 atmospheres and higher) required for the production of unsaturated and branched-chain products of high anti-knock value, iron-type catalysts are more suitable.

In both cases, the reaction is strongly exothermic and the utility of the catalyst declines steadily in the course of the reaction due in part at least to the deposition of non-volatile conversion products such as carbon, paraffin wax, 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 years, to the application of the so-called fluid solids technique 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 improved heat dissipation and temperature control.

However, the adaptation of the hydrocarbon synthesis to the fluid solids technique has encountered serious difficulties, particularly with respect to catalyst deposits and their detrimental effects on the fluidization characteristics and mechanical strength of the catalyst.

As stated above, one of the most important modifications of the hydrocarbon synthesis requires the use of iron-type catalysts. These catalysts are the outstanding representatives of a group of catalysts which combine a high synthesizing activity and selectivity toward normally liquid products with a strong tendency to carbonize during the synthesis reaction, that is, to form fixed carbon or coke-like catalyst deposits which can not be readily removed by conventional methods of synthesis catalyst regeneration such as extraction, reduction, or the like.

These carbon deposits, when allowed to accumulate, weaken the catalyst structure which leads to rapid catalyst disintegration, particularly in fluid operation. The reduction of the true density of the catalyst resulting from its high content of low-density carbon coupled with the rapid disintegration of the catalyst particles causes the fluidized catalyst bed to expand, thereby reducing its concentration of catalyst and ultimately resulting in the loss of the catalyst bed because it becomes impossible to hold

[*Price* 2/-]

the catalyst in a dense phase at otherwise similar fluidization conditions. With these changes in fluid bed characteristics, the heat transfer from and throughout the bed decreases markedly, favoring further carbonization and accelerating the deterioration of the fluidity characteristics of the bed.

Prior to the present invention, it has been suggested to reduce the carbon content of the catalyst of this type by withdrawing the carbonized material from the synthesis reactor and subjecting it either to a destructive hydrogenation treatment or to a combustion treatment with free oxygen-containing gases to remove carbon either in the form of volatile hydrogenation products or of carbon oxides. These treatments have various disadvantages. Destructive hydrogenation requires large amounts of expensive high pressure hydrogen. Removal of the carbon by combustion with free oxygen-containing gases may either excessively oxidize the catalyst or lead to undesired physical changes, such as agglomeration due to sintering. Also, the combustion temperatures and oxygen requirements are usually excessive if substantially complete carbon removal is desired.

The present invention overcomes the aforementioned difficulties and affords various additional advantages. These advantages, the nature of the invention and the manner in which it is carried out will be fully understood from the following description thereof read with reference to the accompanying drawings.

In accordance with the present invention, catalyst carbonized in the synthesis of hydrocarbons from CO and H_2 is subjected to an oxidizing treatment with an oxidizing gas at conditions permitting substantially complete removal of the carbonaceous deposit without undesirable effects on the active catalyst component, particularly iron. It has been found that it is possible to effect the oxidation of coke with such oxidizing gases as air, oxygen, steam, carbon dioxide or mixtures of these gases, without oxidizing the iron or even with an appreciable reduction of any iron oxide present in the catalyst.

This invention is based on the discovery that the ultimate state of oxidation of the iron, coke and hydrogen present in the system may be controlled by a suitable control of pressure, temperature and rate and composition of the oxidizing gas. The system may be operated at pressures ranging from close to vacuum to 100 atmospheres or more and temperatures varying from 800°—2000° F., provided temperatures, pressures and gas feed are properly correlated. However, relatively low pressures of, say, about atmospheric and high temperatures of above 1300° F. generally favor the desired reactions.

The reactions encountered in this process may be summarized briefly as follows:

$$C+O_2=CO_2 \quad (1)$$
$$2C+O_2=2\,CO \quad (2)$$
$$FeO+H_2=Fe+H_2O \quad (3)$$
$$H_2O+C=CO+H_2 \quad (4)$$
$$CO+H_2O=CO_2+H_2 \quad (5)$$
$$CO_2+C=2\,CO \quad (6)$$
$$\tfrac{1}{4}\,Fe_3O_4+H_2=\tfrac{3}{4}\,Fe+H_2O \quad (7)$$

At any given temperature and pressure of the system, the ultimate results obtained depend on the total pressure of the carbon oxides and the ratio of partial pressures of carbon dioxide and carbon monoxide present. Whether or not the iron is left unaffected, oxidized, or reduced depends on the partial pressure ratio CO_2/CO within the reacting atmosphere. The fluid technique results in the gas composition throughout the reactor tending to be essentially the same as the exit gas composition. There are different ratios of CO_2/CO at which the state of the iron will not be affected. These ratios are slightly dependent on the temperature but independent of the pressure of the operation. There also exists a certain ratio of carbon dioxide to carbon monoxide partial pressures above which carbon will be oxidized by the gas phase or below which carbon will be deposited from the gas phase. The ratio is dependent on both temperature and carbon oxides partial pressure. Thus, at a given temperature and CO_2/CO ratio, a decrease in the sum of partial pressures of the carbon oxides allows for easier oxidation of carbon and vice versa. For a definite temperature and CO_2/CO ratio there exists a definite partial pressure of carbon monoxide above which carbon will be deposited and below which carbon will be oxidized.

The present invention is based on the discovery of the practical conditions which will permit the treatment of the coked iron catalyst with an oxidizing gas so as to remove the coke deposit but leave the iron unchanged, or even so as to reduce the iron. In effect, the process of the invention consists in an oxidation of the carbonaceous deposit with a predetermined quantity of oxidizing gas under these conditions of temperature and pressure so that the flue gas formed will not burn iron.

The following tabulation shows the partial pressures of carbon monoxide plus carbon dioxide below which our process can be made to operate at different temperatures.

Temperature, °F.	1100	1200	1300	1472
$P_{co}+P_{co_2}$, Atm.	0.132	0.42	1.32	6.14
P_{co_2}/P_{co}	0.84	0.74	0.65	0.52
Minimum P_{co_2}/P_{co}	0.50	0.44	0.36	0.30
Oxide Type	FeO	FeO	FeO	FeO

At these conditions, the ratio P_{co_2}/P_{co} is such that the gas phase is just in equilibrium with solid carbon and also with both Fe and FeO. Practical operation will preferably be conducted at a pressure sufficiently low so that the value of $P_{co}+P_{co_2}$ is lower than indicated for the respective regeneration temperature given in the above tabulation. Under these conditions, the ratio P_{co_2}/P_{co} may be taken from the tabulation at the temperature chosen for operation in which case the iron oxide will remain unaltered but the carbon will tend to be removed. A lower ratio may be chosen in which case some iron will be reduced. The ratio, however, should not be lower than required for coke oxidation. The minimum ratios which must be exceeded for coke oxidation at an operating pressure such that $P_{co}+P_{co_2}$ is, for example, $\frac{1}{2}$ the value indicated are likewise given in the above tabulation.

The ratio of P_{co_2}/P_{co} and the value of $P_{co}+P_{co_2}$ attained, are functions of the relative rates of oxidizing gas to coke and the operation of the process is dependent on proper control of these rates. Perfect control is not necessary, since considerable latitude is possible while still maintaining the desired conditions. For example, if at 1472° F. the combined carbon oxides partial pressure is maintained at 6.14 atmospheres in the reactor outlet, no reaction will occur on either the iron or coke in the system providing the CO_2/CO ratio is held at 0.52. However, if at this temperature the combined carbon oxides partial pressure is reduced to 1 atmosphere and the CO_2/CO ratio is maintained at 0.52, the iron will not be affected while the coke will be oxidized. In other words, at 1 atmosphere partial pressure of the combined carbon oxides, if the CO_2/CO ratio is permitted to go below 0.52 the iron will be reduced while coke will continue to be oxidized unless the CO_2/CO ratio drops to 0.12 at which point no change will occur in the coke. However, if the CO_2/CO ratio is permitted to fall below 0.12, coke will tend to be deposited. At 1472° F., if the combined carbon oxides partial pressure is allowed to rise above 6.14 atmospheres and if the ratio of CO_2/CO is permitted to rise above 0.52 both the coke and the iron will tend to change to the oxidized state.

The conditions of operation for the removal of the carbon from the catalyst without oxidation of the catalyst are that the ratio of the partial pressure of carbon dioxide to the partial pressure of carbon monoxide must not exceed a value given by

$$r=10^{\left(-1.170+\frac{1730}{t+460}\right)}$$

where r represents the ratio of the partial pressures and t is the temperature of operation in degrees Fahrenheit.

The sum of the partial pressures must not exceed the value given by the equation

$$\frac{s}{1+r}=r\times 10^{\left(9.25-\frac{16170}{t+460}\right)}$$

where s is the sum of the partial pressures expressed in atmospheres, and r has the value obtained from the first equation.

Similar results may be obtained when using steam as the oxidizing gas in place of free oxygen or carbon dioxide. Instead of using the combined partial pressures of carbon oxides and the ratio of carbon dioxide to carbon monoxide as the factors controlling the oxidation conditions, the reaction with steam may be governed in the direction of carbon removal without iron oxidation by controlling the steam quantity so as to establish the proper H_2O/H_2 ratio and the proper partial pressure ratio

$$\frac{P_{co}+PH_2}{PH_2O}$$

in the system. In this reaction, carbon oxides will likewise be present in the gas phase and the relationships outlined above also hold in the case of using steam as the oxidizing gas.

A particular advantage in using steam instead of free oxygen in the form of air is the fact that the exit regenerator gases are suitable for use in the hydrocarbon synthesis process since they do not contain nitrogen which would be present had air been used as the oxidizing agent.

Free oxygen, carbon dioxide and steam have been treated above as oxidizing gases substantially equivalent for the purposes of the invention. While this is true as far as the reaction mechanism is concerned which determines the degree of oxidation in the iron-iron oxide-carbon-carbon oxides-hydrogen-steam system, the heat effects of the reactions involved are basically different. The oxidation with free oxygen is strongly exothermic, those with carbon dioxide and steam are endothermic. Oxidation with free oxygen in the form of air, mixtures of air with oxygen, or pure oxygen, requires, therefore, the provision of suitable heat withdrawal means which may have the form of conventional cooling equipment or of a preferably continuous solids cycle from the combustion zone through a cooling zone back to the combustion zone. Oxidation with steam or carbon dioxide, on the other hand, demands the addition of heat which may be accomplished by installing a firetube heating coil, or the like within the reactor so that the reaction may be carried out at any desired temperature.

However, it has also been found that the process of the invention may be carried out substantially adiabatically when steam or carbon dioxide are used as the principal oxidizing gases by the addition of suitable quantities of air or oxygen to the oxidizing gases.

For example, it is possible to control both temperature and selectivity of coke oxidation and/or iron oxidation by the use of proper mixtures of air and steam. The ratio of air to steam required depends on the temperature and pressure of the operation as well as the composition of the coke to be burned in order adiabatically to control the process. However, it may be stated that the decarbonization of an iron catalyst containing in the neighborhood of 15% of carbon and 1% of H_2, without affecting the state of oxidation of the iron, may require about 0.03 lb. mols of air and about 0.01 lb. mols of steam for each pound of catalyst to be regenerated. The temperature in this modification of the process may conveniently be controlled by regulating air preheat, which is most readily accomplished by heat exchange of the air with the exit regenerator gases. The presence of steam, in addition to making the operation adiabatic, has the further advantage of diluting the carbon oxides in the system whereby it is possible to operate the system at higher total pressure at a given temperature than without the steam addition, since the partial pressure of carbon oxide is reduced.

Adiabatic operation of the process may also be accomplished when using carbon dioxide as the principal oxidizing gas, by the addition of free oxygen, for instance in the form of air, to the system in quantities that depend on the quantity and composition of the coke to be removed, in a manner similar to that outlined in connection with the use of steam.

Instead of adding air alone to the steam oxidation system, mixtures of free oxygen, such as air, with gaseous or liquid hydrocarbons or hydrogen may be used in proportions adequate to balance the heat requirements of the system, by the exothermic combustion of the hydrocarbons or hydrogen with the free oxygen added. This modification is particularly beneficial when there is insufficient coke on the carbonized catalyst to supply the required heat for maintaining the desired reactor temperature. Suitable proportions are, for example, 8200 lb./hr. of iron, 11.2% of coke on iron, the coke containing 94.5% C. and 5.5% H_2, a temperature of 1400° F., a maximum pressure of 140 p.s.i.a., and a supply of 26 lb. mols/hr. of CH_4, 52 lb. mols/hr. of O_2, and 81.9 lb. mols/hr. of steam.

A similar procedure may be followed when carbon dioxide is used as the principal oxidizing gas. Thus, it has been found that by charging a mixture of methane and free oxygen containing gas, such as air, to the steam oxidation system either internally or externally from the coke-burning reactor it is possible to operate the system adiabatically. In all cases, there will be a definite ratio of carbon dioxide, free oxygen and hydrocarbon required for adiabatic decarbonization, depending on the type of hydrocarbon used, the amount and composition of the coke to be burned and the temperature and pressure of the operation.

Instead of using a hydrocarbon as described above, hydrogen may be added to the system to render the operation adiabatic. It has been found that this may be accomplished by charging a mixture of hydrogen and oxygen in a ratio of about 2 : 1 along with the steam. The amount of hydrogen required for this type of operation again depends on the temperature and pressure of the operation as well as the composition and quantity of the coke to be burned. In general, the oxygen is fed in a ratio such that it supplies the heat requirement of the system and has the same effect on the system as the steam which it replaces. By way of example, operating conditions suitable for this embodiment of the invention may be given as follows: 8200 lb./hr. of catalyst expressed as iron, 11.2% of coke on iron, the coke containing 94.5% C. and 5.5% H_2, temperature 1400° F., maximum pressure 189 p.s.i.a., supply of about 85.9 lb. mols/hr. of steam, 71.8 lb. mols/hr. of H_2 and 36 lb. mols/hr. of O_2.

Now, it has been further found that the process may be operated at any pressure desired for any given temperature when an inert gas, such as nitrogen, is added to the system in suitable amounts. In this manner, the total pressure of the system may be raised without affecting the ratio and relative partial pressures of the carbon oxides. By the same means it becomes possible to operate at lower temperatures, if it is desired to operate at a definite pressure. For example, when using pure oxygen, the maximum pressure may be, say, about 80 p.s.i.a. to produce 100 mols of inert-free outlet gas. By adding 100 mols of inerts such as nitrogen to the gas feed, the process may be operated at a maximum pressure of about 160 p.s.i.a. Thus, in this case, the maximum allowable pressure is doubled by a dilution of the active gas constituents with an equivalent quantity of inerts.

It will be readily understood that this modification of the invention has significant advantages since it facilitates operation of the catalyst regeneration system at the pressure of the synthesis process and at temperatures more closely approaching those of the synthesis process.

Having set forth its objects and general nature, the invention described above will be best understood from the more detailed description hereinafter in which reference will be made to the accompanying drawings wherein:

Figure 1 is a semi-diagrammatical view of a system suitable for carrying out the regeneration of iron-type synthesis catalyst in an exorthermic or endothermic reaction in accordance with the present invention:

Figure 2 is a similar illustration of a system suitable for the regeneration of the same catalyst in an adiabatic operation: while

Figure 3 illustrates the case of indirect heat supply to the system.

Referring now in detail to Figure 1, the system illustrated therein essentially comprises a synthesis reactor (10) and a catalyst regenerator (30), whose functions and cooperation will be forthwith explained.

In operation, synthesis reactor (10) contains a dense, turbulent, fluidized mass of iron catalyst such as sintered pyrites ash promoted with about 1.5% of potassium carbonate. Synthesis feed gas containing about 0.8—3.0 volumes of H_2 per volume of CO is supplied from line (1) to reactor (10) at a suitable synthesis pressure of 5—50 atmospheres, preferably 20—40 atmospheres. The synthesis temperature may be maintained between the approximate limits of 500°—800° F., preferably between about 550° and 700° F. by conventional methods of heat removal (not shown). Details of the operation of fluid synthesis reactors using iron catalyst are well known and need not be further specified here.

As stated before, carbon deposits form on the catalyst in reactor (10) and in about 100 hours as much as 50 lbs. of carbon may be deposited on each 100 lbs. of catalyst. This will tend to diminish the activity of the catalyst and also cause its physical disintegration so that fines in excessive quantities will be formed. If this condition is not corrected, the density of the catalyst phase will drop rapidly and the entire catalyst will be eventually blown out of reactor (10). The present invention corrects this difficulty by subjecting the carbonized catalyst to a continuous regeneration in regenerator (30) at the conditions of the invention as will appear more clearly hereinafter.

By way of example, it is assumed that 8200 lbs. per hour of catalyst (expressed as weight of pure iron) containing 11.2% coke on iron is to be regenerated without affecting the state of oxidation of the iron. The coke contains 94.5% C., 5.5% H. The carbonized catalyst is withdrawn downwardly through a system of lock hoppers (12) wherein the pressure may be reduced to atmospheric at which the catalyst may be charged through line (15) to regenerator (30) which may have a diameter of about 10—12 ft. and a height of about 25—40 ft. Air is supplied by blower (17) through lines (19) and (21) to the bottom of regenerator (30) which it enters through a distributing means, such as grid (23), at a velocity of about 0.5—5 ft. per second to regenerate and convert the catalyst within regenerator (30) into a dense fluidized mass having an upper level (L_{30}). About 1,620 normal cu. ft. of air per minute is suitable for this purpose at the conditions indicated.

The regeneration reaction is exothermic and about 3.5 million BTU per hour must be removed from the catalyst mass to maintain it at a temperature of about 1400° F. At these conditions, the combined carbon oxides partial pressures equal 0.24 atmospheres and the ratio $\frac{Pco2}{Pco}$ equals 0.58, and the iron will leave the regenerator with the same oxygen concentration as it enters the regenerator.

However, in order to assure a non-oxidizing atmosphere with respect to iron throughout regenerator (30), it is desirable to circulate flue gas from the top of regenerator (30) to the regenerator inlet. For this purpose, the flue gas leaving level (L_{30}) overhead may be passed through a conventional gas-solids separation system (25) which may include cyclones, precipitators and/or filters and from which separated catalyst fines may be returned through line (27) to regenerator (30), or discarded through line (29). The gas now substantially free of entrained solids may be passed through line (31) and a cooling means such as a waste heat exchanger (33) over a recycle blower (35) and line (37) back to air feed line (21). The proportion of gas recycled through line (37) preferably amounts to about 2—8 times the quantity of flue gas produced in regenerator (30). Excess flue gas may be vented through line (39).

In accordance with a preferred embodiment of the invention, the recycle gas is subjected to a partial combustion in an auxiliary burner (40) by the process air supplied through line (19). In this manner, substantially all the oxygen of the air is converted to carbon oxides outside the regenerator, which facilitates the maintenance of the desired oxidation conditions in regenerator (30) so as to avoid undesired oxidation of iron. As a result of the high flue gas recycle ratio, all the oxygen in the air is converted into carbon oxides and water vapor while still maintaining a desirable ratio of CO_2 : CO in the feed gas to regenerator (30). Since, in this case substantially no exothermic reaction takes place in regenerator (30) itself, no cooling of the regenerator is required, the heat needed to support the endothermic reaction in regenerator (30) being generated in burner (40) which is preferably operated at a temperature of about 1800° to 3000° F.

In this manner, the temperature of regenerator (30) may be readily controlled. In cases requiring heat removal from regenerator (30), any additional heat withdrawal means such as cooling coils or jackets (not shown) may be provided. It is preferred, however, to accomplish any necessary additional cooling by means of catalyst circulated from regenerator (30) through a cooling means such as a waste heat exchanger (42) back through line (21) to regenerator (30).

Decarbonized catalyst is withdrawn downwardly through bottom drawoff line (45) and cooler (47) to be cooled to about 400°—600° F. and to be passed via a lock hopper system (49) to synthesis gas feed line (1). The catalyst suspended in the synthesis gas is returned to synthesis reactor (10) for re-use.

The system illustrated by the drawing permits of various modifications. For example, certain iron catalysts tend to sinter under the above described decarbonization conditions, which interferes with a proper fluidization of the catalyst in regenerator (30). In these cases, regenerator (30) may have the form of a rotary kiln to which the oxidizing gas is charged. Iron oxidation may be substantially eliminated by passing solids and gases concurrently through the rotary kiln, because although iron may tend to be oxidized in the feed portion of the kiln, the gas composition in the remaining portion of the kiln is such as will reduce any iron which may have been previously oxidized. Flue gas recycle substantially as described above may be used to suppress iron oxidation in the case of either concurrent or countercurrent flow of catalyst and gases. Heat may be removed by recycling a cooled portion of the flue gases to the kiln.

The regeneration may also be carried out at elevated pressures, if desired, particularly in the presence of inert gases so that pressure reduction on the catalyst flowing from the synthesis reactor to the regenerator may be substantially minimized. For example, at the conditions specified above for the operation of the system of Figure 1, pressures up to about 222 lb. per sq. in. abs. may be used. Operation at higher temperatures permits the use of higher pressures. Either one or both of the lock hopper systems (12) and (49) may be replaced by standpipes or mechanical conveyors, if the prevailing pressure conditions permit.

As a result of the high temperature employed in the regeneration stage, substantial proportions of the alkali metal promoter content of the catalyst may be lost. This promoter may be advantageously replaced at any point of the system after the catalyst has been completely regenerated. For example, a suitable promoter solution such as an aqueous solution of a potassium hydroxide, carbonate or halide may be injected through line (51) into catalyst withdrawal pipe (45). A conventional steam-separating zone (not shown) may then be provided above line (51). Addition of the promoter at this or a similar point rather than in the synthesis reactor is of advantage since the catalyst at this point is free of oil and coke and the promoter may thus penetrate the catalyst much more effectively than if it is added to the catalyst in the synthesis reactor.

It may also be desirable to subject the regenerated catalyst to a carbiding treatment prior to its return to the synthesis stage. This may be advantageously accomplished by contacting the regenerated catalyst, preferably after reduction, with CO-containing gases at relatively low CO-partial pressures, of preferably less than 1 atm. and temperatures of about 500°—800° F. Conditions should be so controlled that the atmosphere in contact with the catalyst is non-oxidizing with respect to iron and its carbides and that about 20—50% of the iron is converted to iron carbides.

Referring now to Figure 2, the system illustrated therein is similar to that of Figure 1, like reference characters identifying like elements. However, the regeneration of the catalyst is carried out adiabatically in the case of Figure 2, a suitable mixture of free oxygen and steam being used as the oxidizing gas.

The carbonized catalyst is transferred from fluid synthesis reactor (10) to regenerator (30) substantially as described before. Air is fed by blower (17) through line (21) and mixed with steam supplied through line (22). The air-steam mixture enters the bottom of regenerator (30) through grid (23), in suitable proportions and in amounts sufficient to maintain a regeneration temperature of about 900° to 1500° F. without the addition or withdrawal of heat and a flue gas composition permitting substantially complete coke removal without affecting the state of oxidation of the iron

For example, when 5,660 lb. per hour of catalyst expressed as iron containing 15.3% of carbon and 0.9% of hydrogen on iron is to be regenerated the air required for regeneration amounts to 169.6 lb. mols per hour and the steam needed to establish the desired heat balance amounts to 53.3 lb. mols per hour.

The air may be preheated to about 200° to 1000° F. in heat exchange with flue gas flowing through lines (31) and (37) and heat exchanger (33). If desired, a portion of the flue gas from line (37) may be recycled to regenerator (30) substantially as described above. The remainder may be vented through line (41). Pressures up to about

210 lb. per sq. in. abs. may be used at the conditions specified above. However, higher pressures may be used at higher temperatures. If the temperatures attain or exceed the sintering temperature of the catalyst, a rotary kiln may replace fluid regenerator (30) substantially as described in connection with Figure 1. Return of decarbonized catalyst and promoter restoration, likewise, may take place in the manner previously described.

In the system of Figure 3, steam alone is used to remove the coke in an endothermic reaction and heat must be supplied to regenerator (30). For this purpose, a bank of fire tube heating coils (55) is arranged within regenerator (30) below level (L_{30}) of the fluidized catalyst mass therein. Steam is supplied through line (22). A combustion mixture of air and gaseous, liquid or powdered solid fuel is fed from lines (57) and (59), respectively, through line (61) to coils (55) wherein combustion takes place at a temperature of about 1500° to 3000° F. to maintain the fluidized catalyst bed at a suitable coke oxidation temperature of about 1100°—1500° F.

The amount of steam supplied is so controlled that conditions non-oxidizing with reference to iron are maintained. Suitable operating conditions may be chosen, for example, as follows: 8200 lb./hr. of catalyst as iron, 11.2% coke on iron, the coke containing 94.5% C and 5.5% H_2, supply of 157.7 lb.mols/hr. of steam, temperature 1400° F., maximum pressure 189 p.s.i.a. At these conditions, about 9,000,000 BTU per hour of heat must be transferred through tubes (55), which requires a supply of about 40 lb.mols/hr. of methane and 380 lb.mols. of air to tubes (55) for heating.

All other steps are similar to those set forth in connection with Figures 1 and 2, like reference characters identifying like elements. The system of Figure 3 may be used in a substantially analogous manner CO_2 alone is employed as the oxidizing gas. When it is desired to supply heat to regenerator (30) by burning a hydrocarbon or hydrogen with free oxygen within reactor (30), suitable mixtures of air with hydrogen and/or hydrocarbons may be supplied through lines (21) and/or (22) in any of the systems illustrated in the drawing. Likewise, an inert gas such as nitrogen may be supplied through these lines whenever high pressure operation or low temperature operation at a definite pressure is desired.

If the oxygen content of the catalyst withdrawn from regenerator (30) through line (45) in any of the systems described is higher than would be desirable for an efficient operation of the hydrocarbon synthesis, the regenerated catalyst may be subjected to a reducing treatment with a reducing gas, preferably hydrogen, under conventional conditions and, if desired, at temperatures and pressures approximating those of the hydrocarbon synthesis.

While iron-type catalysts have been specified by way of example in the preceding description, it will be understood by those skilled in the art that the process of the invention may be applied in a substantially analogous manner to the decarbonization of other spent synthesis catalysts which are associated with carbon, such as other metals, for example nickel, cobalt, molybdenum, manganese, chromium or noble metals, or their oxides, without affecting their state of oxidation. Generally it may be stated that the process of the invention may be successfully applied to carbonized metals or their oxides which stand in about the same or a higher (nobler) position than iron, in the electromotive series. The nobler the metal the broader may be the range of operative ratios of CO_2/CO partial pressures and the lower may be the operating temperatures.

Having now particularly described and ascertained the nature of our said invention and in what manner the same is to be performed, we declare that what we claim is:—

1. A method of removing carbon deposits from finely divided spent catalyst from the catalytic synthesis of hydrocarbons from mixtures of carbon monoxide and hydrogen without substantial oxidation of the said catalyst comprising reacting the said spent catalyst in the fluidized state with an oxidizing gas at a temperature between 800 and 2000° F., preferably above 1000° F., and at a pressure between 0 and 100 atmospheres, preferably at 1 atmosphere, and so adjusting the composition and quantity of the oxidizing gas with reference to the amount of catalyst and the carbonaceous deposit thereon to produce an atmosphere within the regeneration zone containing substantially no free oxygen and containing carbon dioxide and carbon monoxide in such amounts that the ratio of the partial pressure of carbon dioxide to carbon monoxide is equal to or less than the value given by the equation $r=10^{\left(-1.170+\frac{1730}{t+460}\right)}$ where r is the ratio of partial pressures of carbon dioxide to carbon monoxide and t is the temperature in °F., and the sum of the partial pressures of the carbon dioxide and carbon monoxide is less than the value given by the equation

$$S=(1+r)\,r\times10^{\left(9.25-\frac{16170}{t+460}\right)}$$

where S is the sum of the partial pressures of the carbon dioxide and carbon monoxide, and t and r are as above (r having the value obtained from the first equation).

2. A method as claimed in Claim 1 in

which the oxidizing gas is oxygen, air, steam or carbon dioxide.

3. A method as claimed in Claim 1 or 2 in which air or oxygen is used as the oxidizing gas and means are provided to remove the heat of reaction to maintain the temperature at the desired level.

4. A method as claimed in Claim 1 or 2 wherein steam or carbon dioxide is used as the oxidizing gas and means are provided to supply the necessary heat of reaction to maintain the temperature at the desired level.

5. A method as claimed in Claim 4 wherein carbon dioxide or steam is employed as the principal oxidizing agent and sufficient air is added to supply the necessary heat of reaction to make the reaction adiabatic.

6. A method as claimed in Claim 5 in which liquid hydrocarbons or hydrogen are added to the oxidizing gases in quantities sufficient to balance the heat requirements of the system by exothermic reaction with at least part of the free oxygen present.

7. A method as claimed in any of the preceding Claims wherein an inert gas is added to the regeneration zone to enable the same to be operated at a higher pressure.

8. A method as claimed in Claims 1—7 wherein flue gas from the top of the regenerator is recycled to the oxidizing gas inlet of the regeneration zone.

9. A method as claimed in Claim 8 in which the amount of flue gas recycled is from 2—8 times the quantity of flue gas produced in the reaction.

10. A method as claimed in Claims 8 and 9 wherein the flue gas is contacted with the oxidizing gas in a separate burner chamber whereby all the oxygen is converted to carbon oxides or water vapour before passing into the regenerator and the exothermic reaction in the regenerator is avoided and the heat required for the endothermic reaction in the regenerator is produced in the said burner and transferred as sensible heat of the gases entering the regenerator.

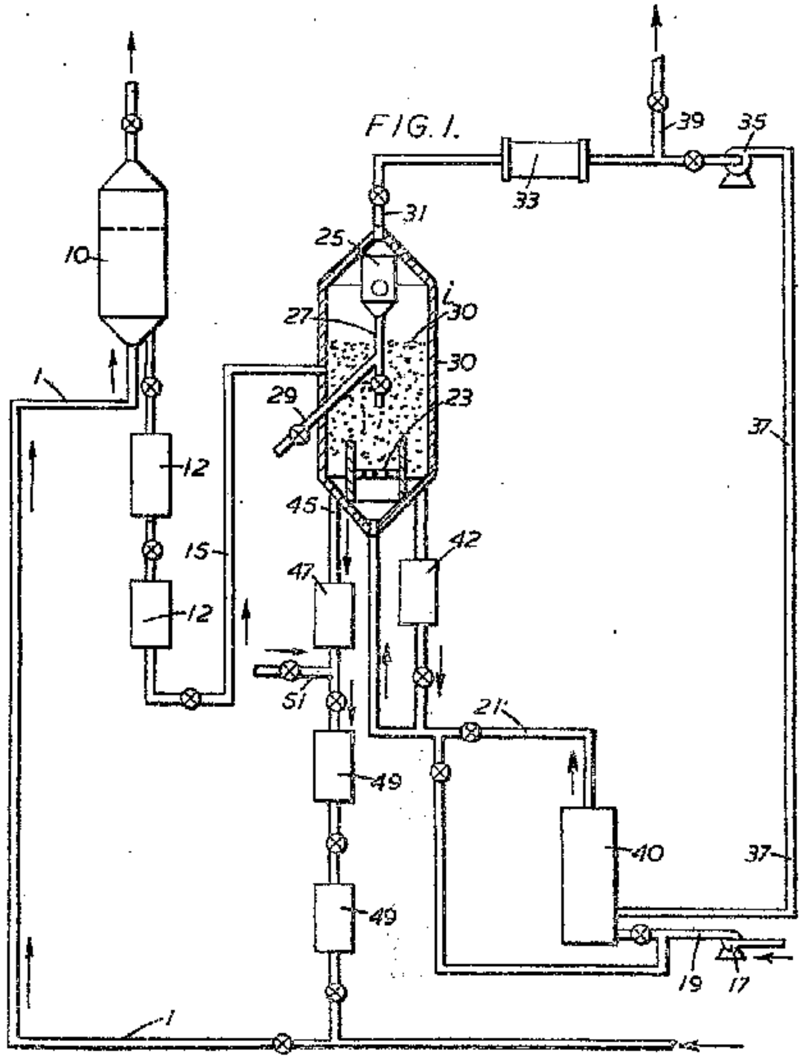
Dated this 9th day of August, 1948.

DAVID T. CROSS,
Brettenham House,
Lancaster Place,
London, W.C.2.
Agent for the Applicants.

Abingdon: Printed for His Majesty's Stationery Office, by Burgess & Son (Abingdon), Ltd.—1951.
Published at The Patent Office, 25, Southampton Buildings, London, W.C.2, from which
copies, price 2*s.* per copy; by post 2*s.* 1*d.* may be obtained.

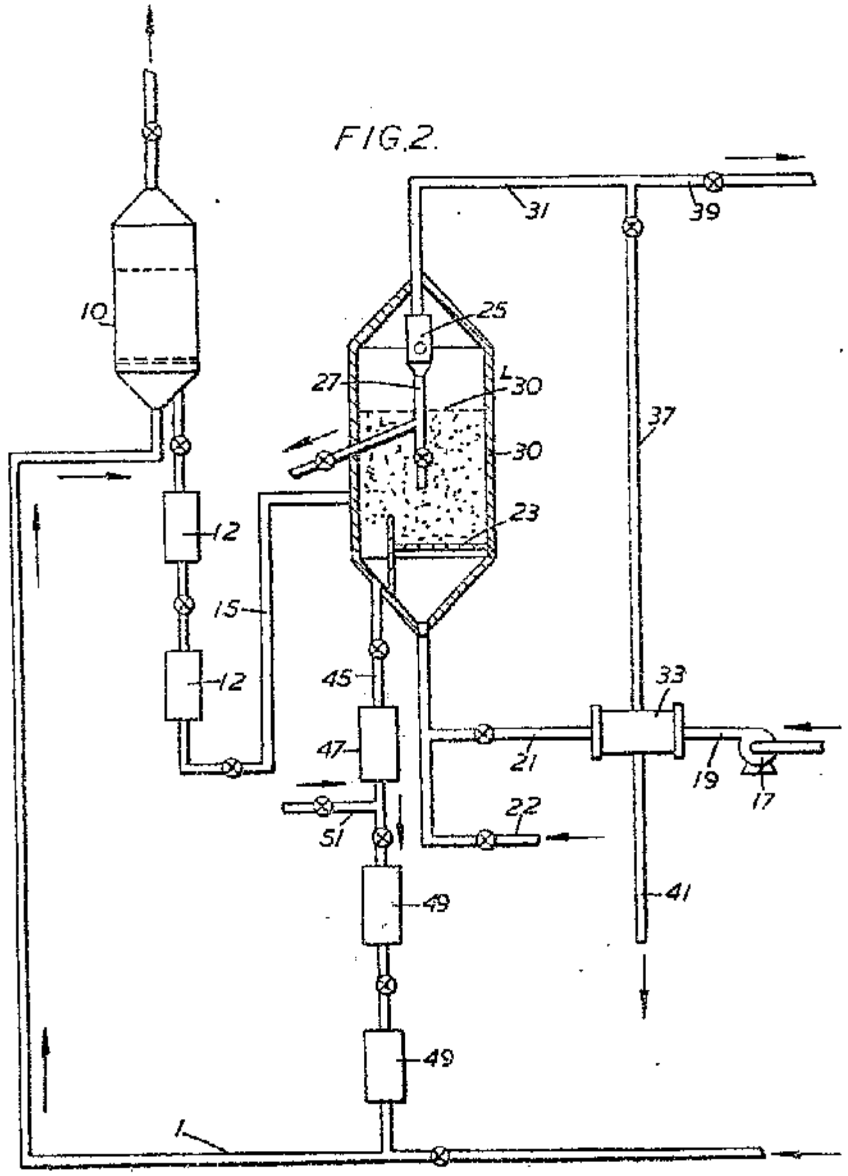
[This Drawing is a reproduction of the Original on a reduced scale.]

FIG. 1.



[This Drawing is a reproduction of the Original on a reduced scale.]

FIG.2.



3 SHEETS

SHEET 2

SHEET 3

FIG.3.

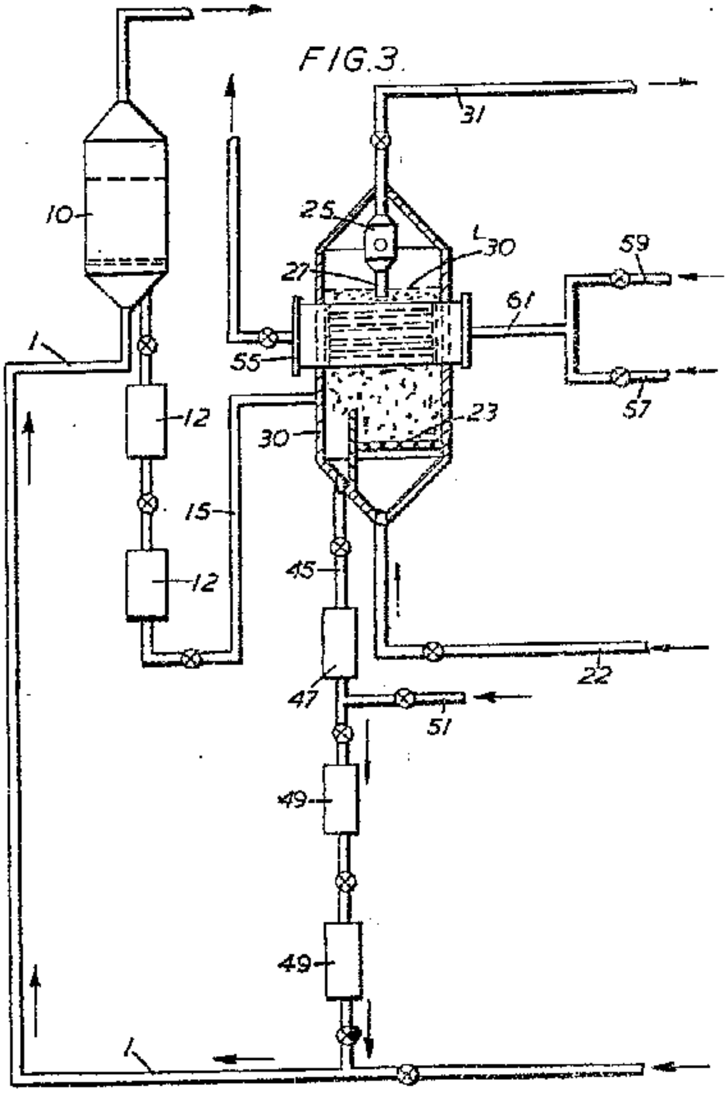


FIG.2.

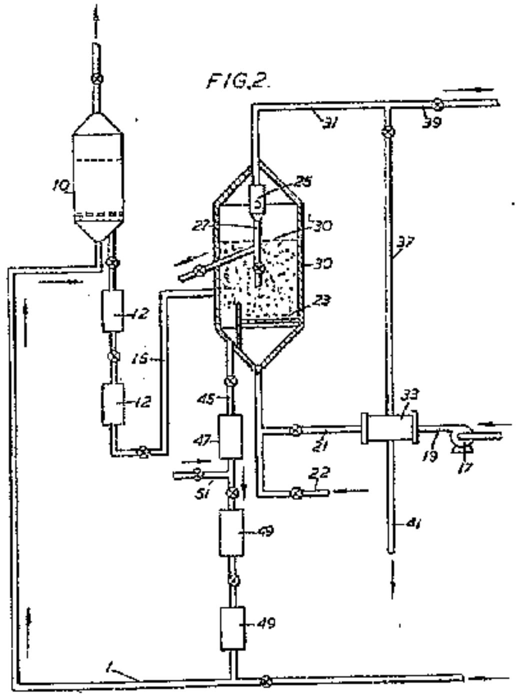
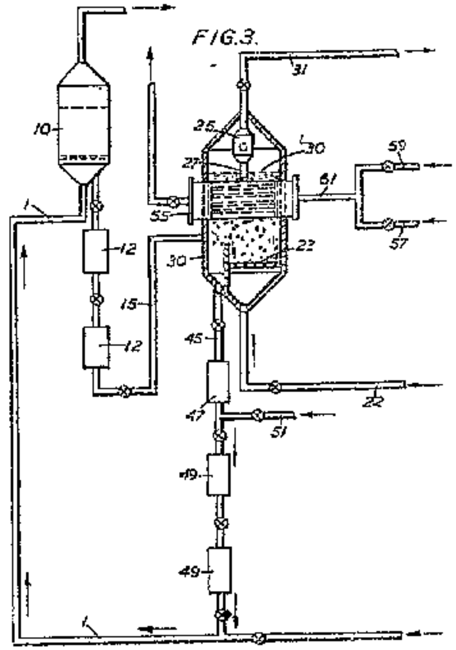


FIG.3.



[This Drawing is a reproduction of the Original on a reduced scale]