



Industry
Canada Industrie
Canada

Canada

strategis.gc.ca

Strategis Index:
[Home](#) [Advanced Search](#) [Simple Search](#) [Help](#)

CIPO  OPIC



Canadian Patents Database

12/19/2001 - 16:41:42

(11) CA 511647

(12) Patent:

(54) REGENERATION OF AN IRON CATALYST WITH CONTROLLED CO₂ : CO RATIOS

(54) REGENERATION D'UN CATALYSEUR DE FER AVEC PROPORTIONS CO₂ : CO REGLEES

(72) Inventor (Country):	HOMER Z. MARTIN (Not Available) IVAN MAYER (Not Available) CHARLES W. TYSON (Not Available)
(73) Assignee (Country):	STANDARD OIL DEVELOPMENT COMPANY
(71) Applicant (Country):	
(74) Agent:	
(45) Filing Date:	Apr. 5, 1955
(22) Filing Office:	
(43) Publication Date:	
(52) IPC Class.:	252/83
(51) Int. Cl.:	N/A

(36) Priority of foreign application: **No**

(30) Application number: **None**

(70) Filing office: **N/A**
 (72) Inventor: **Unknown**

*** Note: Data on abstracts and claims is shown in the official language in which it was submitted.

View or Download Images :

- Cover Page Image
- Abstract Image
- Claims Image
- Disclosures Image

511647

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 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 decrease markedly, favoring further carbonization and accelerating the deterioration of the fluidity characteristics of the bed.

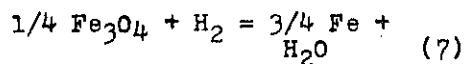
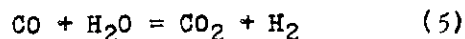
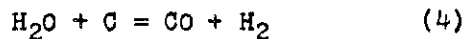
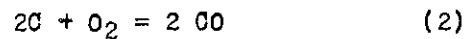
Prior to the present invention, it has been suggested to reduce the carbon content of the catalyst of this type by withdrawing the carbonized material from the synthesis reactor and subjecting it either to a destructive hydrogenation treatment or to a combustion treatment with free oxygen-containing 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, etc. 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 our embodiment of the present invention, catalyst carbonized in the synthesis of hydrocarbons from CO and H₂ 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 embodiment of the 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 about 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 about 1300°F. generally favor the desired reactions.

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



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 or $\text{H}_2\text{O}/\text{H}_2$ 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 or $\text{H}_2\text{O}/\text{H}_2$ 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 embodiment of the 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, $1/2$ 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.

Broadly, these relationships may be expressed by the following equations:

$$r = 10 \left(-1.170 + \frac{1730}{t+460} \right) \dots\dots(1)$$

$$\frac{s}{1+r} = r.10 \left(9.25 - \frac{16170}{t+460} \right) \dots\dots(2)$$

wherein r is the ratio of the partial pressure of CO_2 to that of CO , s is the sum of these partial pressures in atmospheres and t is the temperature of operation in °F. For operation excluding an oxidation of iron during carbon removal, the value of r should be equal to or less than that given by equation (1) but greater than that defined by equation (2). In using equation (2), the temperature t and the sum s must be selected and any value of s which results in a value of r from equation (2), lower than the value of r resulting from equation (1), is satisfactory.

It may be desirable to reduce the oxygen content of the iron catalyst without affecting its carbon content or even with an accompanying increase of its carbon content in the form of free carbon. In these instances, r should be equal to or lower than the value defined by equation (2). Problems like this may occur in connection with synthesis reactions wherein little or no carbon is formed in the synthesis stage. In order to oxidize the iron without burning carbon, the value of r must be greater than that given by equation (1) and the value of s must be at least equal to that given by equation (2) for a value of r greater than that given by

equation (1).

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 $\frac{P_{CO} \times PH_2}{PH_2O}$ 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 reactor 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 been further found that the process of the invention may be carried out substantially adiabatically when suitable mixtures of air and/or oxygen, steam and/or carbon dioxide are used as oxidizing gases under properly controlled conditions.

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 lbs/hr. of iron, 11.2% of coke on iron, the coke containing 94.5% C and 5.5% H₂, a temperature of 1400°F., a maximum pressure of 140 p.s.i.a., and a supply of 26 lb. mols/hr of CH₄, 52 lb. mols/hr. of O₂, 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 lbs./hr. of catalyst expressed as iron, 11.2% of coke on iron, the coke containing 94.5% C and 5.5% H₂, 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 H₂ and 36 lb. mols/hr. of O₂.

It has been shown above that for every temperature there is a definite combined carbon oxides partial pressure

above which, and a definite CO_2/CO ratio below which it is not possible to oxidize coke. 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 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 embodiment of the invention described above will be best understood from the more detailed description hereinafter in which reference will be made to Figs. 1-3 of the accompanying drawings wherein:

Figure I is a semi-diagrammatical view of a system suitable for carrying out the regeneration of iron-type

synthesis catalyst in an exothermic or endothermic reaction in accordance with the present invention;

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

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

Referring now in detail to Figure I, 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 lockhoppers (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 (L₃₀). 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 $\frac{P_{CO_2}}{P_{CO}}$ 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 (L₃₀) 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 $\text{CO}_2:\text{CO}$ 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 reuse.

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 lbs. 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.

Other modifications will appear to those skilled in the art without deviating from the spirit of the invention.

Referring now to Figure II, the system illustrated therein is similar to that of Figure I, like reference characters identifying like elements. However, the regeneration of the catalyst is carried out adiabatically in the case of Figure II, 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 lbs. 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 lbs. 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 III, 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 lbs./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 I and II, like reference characters identifying like elements. The system of Figure III may be used in a substantially analogous manner when 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.

It may also be desirable to carry out the hydrocarbon synthesis in a plurality of fluid type reactors through which the catalyst is passed in series to withdraw catalyst of uniformly highest carbon content rather than of average carbon concentration from the last reactor and the return regenerated catalyst to the first reactor. This method of operation, which is disclosed hereinafter, affords substantial savings in oxidizing gas and solids circulation rate, as will be subsequently shown in greater detail, in connection with Figs. V-VIII.

While synthesis catalysts, such as iron-type catalyst, 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 oxidizable materials which are associated with carbon, such as

other metals, for example nickel, cobalt, molybdenum, manganese, chromium, noble metals, etc. 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.

When operating in the manner previously described, such catalyst fines of undesirably small particle size as may have been formed prior to regeneration may, accumulate and in runs of long duration eventually interfere with an efficient operation of the process unless they are discarded from the catalyst cycle.

The embodiment of the present invention described below overcomes this difficulty and affords various additional advantages.

In accordance with this embodiment of the present invention, catalyst carbonized and disintegrated in the catalytic synthesis of hydrocarbons from CO and H_2 is continuously or intermittently subjected to a combined oxidation and

sintering treatment with a free-oxygen containing gas such as air at temperatures of about 1400°-2000°F. followed by reduction at similar temperatures and grinding to a fluidizable particle size whereupon the catalyst is returned to the synthesis stage. Sintering temperatures in the neighborhood of 1400°F. or thereabove are generally suitable for iron catalysts. The reduction temperature may be the same or slightly lower than the sintering temperature. The catalyst is preferably cooled to about 100° to 200°F. prior to grinding. Since at the high temperatures here involved, substantial proportions of alkali metal promoters may be lost, the cool catalyst is preferably impregnated with a suitable solution of a promoter such as the halides, carbonates or hydroxides of sodium or potassium, prior to its return to the synthesis stage.

For the purpose of reduction, the relatively expensive hydrogen normally used as a reducing agent is replaced by a reducing atmosphere formed on the catalyst undergoing reduction, by contacting the oxidized and sintered catalyst with carbonaceous materials and air and/or steam at temperatures suitable for the reduction of the oxidized catalyst. Coke, coals, fuel oils and fuel gases including methane may be used as carbonaceous materials. In accordance with a preferred embodiment of the invention, sufficient carbon is left on the catalyst during the sintering treatment to react with steam and/or air admitted to the reducing zone so as to form a suitable reducing mixture, if necessary in cooperation with extraneous solid, liquid or gaseous fuel admitted to the

reduction zone. Complete reduction to metal of the catalyst oxidized during the sintering treatment is frequently not required.

From the above absorption of the first embodiment of the invention it follows that at relatively high temperatures of about 1200° to 2000°F. it is possible to produce, by the reaction of steam with coke or other carbonaceous fuels, a gaseous mixture of hydrogen, water vapor, carbon monoxide and carbon dioxide which will be oxidizing with respect to carbon but will tend to reduce iron oxide to metallic iron. For this purpose, the feed ratio of steam to carbonaceous fuel should be so controlled that the values of the volumetric ratio $CO_2:CO$ and the sum of the partial pressures $P_{CO} + P_{CO_2}$ stay below those previously tabulated. These conditions and relationships are fully applicable to the present embodiment of the invention.

Operation in two subsequent sintering and reduction stages affords the advantages of high process flexibility. However, it is noted that satisfactory results may often be secured by treating the catalyst in a single stage at conditions conducive to decarbonization and sintering and simultaneous reduction of iron oxide by charging a mixture of steam, air and fuel, if necessary, to establish the gas composition described in connection with the above table.

Any conventional type of sintering apparatus may be used for the purposes of the invention. Good results may be obtained when the sintering and/or reduction treatment is carried out in rotary kilns with concurrent or countercurrent

flow of catalyst and treating gases. In accordance with a preferred embodiment of the invention, two rotary kilns are used in the first of which the catalyst is sintered and oxidized with countercurrently flowing air, while in the second kiln the catalyst is subjected to reduction with a concurrently flowing reducing gas mixture of the type specified above.

This embodiment of the invention will be best understood from the more detailed description hereinafter in which reference will be made to Fig. IV of the accompanying drawing, which is a semi-diagrammatic illustration of a system suitable for carrying out a preferred modification.

Referring now to Fig. IV, the system illustrated therein essentially comprises a synthesis reactor (410), a sintering reactor (430) and a reduction reactor (440), whose functions and cooperation will be forthwith explained.

In operation, synthesis reactor (410) contains a dense, turbulent, fluidized mass of iron catalyst such as sintered pyrites ash promoted with about 1.5% of potassium carbonate and having an original particle size of about 20-100 microns, preferably 50-100 microns. Synthesis feed gas containing about 0.8-3.0 volumes of H_2 per volume of CO is supplied from line (401) to reactor (410) at a suitable synthesis pressure of 5-50 atm., preferably 20-40 atm. 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 catalysts are well known and need not be further specified here.

As stated before, carbon is deposited on the catalyst in reactor (410) 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 having particle sizes smaller than 20 microns will be formed in excessive quantities. 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 (410). The present embodiment of the invention corrects this difficulty by subjecting the carbonized and partially disintegrated catalyst to an oxidative sintering treatment in reactor (430) followed by a reducing treatment in reactor (440) and by regrinding to the desired size as will appear more clearly hereinafter.

By way of example, it is assumed that 100 lbs. per hour of catalyst expressed as pure iron, containing about 15.5% coke on iron, 6.0% O₂ on iron, and about 40% of fines smaller than 20 microns particle size, is to be decarbonized and restored to its original particle size. The carbonized and partially disintegrated catalyst is withdrawn downwardly through a system of lockhoppers (412) wherein the pressure may be reduced to atmospheric at which the catalyst may be treated in reactors (430) and (440).

After pressure release, the catalyst is conveyed by any suitable conventional mechanical or pneumatic conveying means (414) to a feed hopper (416). The catalyst in hopper (416) may be kept in a readily flowing state by admitting

511647

through line (418) an aerating gas, such as air, flue gas, steam, etc. which may be withdrawn through line (420). From hopper (416) the catalyst is fed by gravity via feeding means (425) to the upper end of reactor (430), which may have the form of a conventional rotary kiln. Simultaneously, air is blown from line (432) into the lower end of reactor (430). The amount of air admitted should be sufficient to heat the catalyst by combustion of coke to a temperature high enough to cause sintering of the catalyst and the formation of larger catalyst agglomerates from the fines present. Reaction temperatures of about 1200°-2000°F. are suitable for this purpose. Thus, reactor (430) may be so operated that an average temperature of about 1900°F. is maintained while about 90% of the carbon is burned off and about 15 to 35% by weight of oxygen is bound by the iron. An amount of about 5,000 to 9,000 standard cu. ft. of air per hour is suitable to establish these conditions in the case of the specific example here involved. If desired, heat may be removed from reactor (430) in any conventional manner, such as use of excess air, recirculation of cooled solids, injection of a water spray, etc. Spent oxidizing gas is removed through line (433), preferably after a suitable gas-solids separation in conventional equipment such as a cyclone separator (not shown) from which separated solids may be returned to reactor (430).

The sintered and oxidized catalyst is supplied at the outlet temperature of reactor (430), i.e. about 1500°-1900°F., from the lower end of reactor (430) to a feeding and mixing means (434) wherein it is mixed with subdivided coke or

511647

a similar carbonaceous fuel supplied from line (436). The mixture of sintered catalyst and fuel enters the upper end of reactor (440) which may likewise be a rotary kiln of suitable dimensions. Simultaneously with the solids feed, a mixture of steam and air is supplied to the upper end of reactor (440) from lines (438) and (439), respectively. The relative amounts of fuel, air and steam are so controlled that an atmosphere reducing with respect to iron oxide is formed within reactor (440) by the conversion of the fuel with steam into CO and H₂ while, at the same time, sufficient heat is generated by the combustion of fuel with air to support the endothermic water gas and reduction reactions. At the conditions of the present example, this may be accomplished by feeding about 15 to 25 lbs. of coke, 1,000 to 1,300 standard cu. ft. of air and 2 to 10 lbs. of steam. These proportions are based on a preheat of the air-steam mixture of about 500°-1500°F. in heat exchange with flue gases from reactor (430) and/or (440).

It will be appreciated that the gas at the inlet of reactor (440) is oxidizing with respect to both iron and coke, since it consists mainly of air and steam. However, in the lower portions of reactor (440) the air, steam and coke will have had opportunity to react and, there, gases reducing with respect to iron will be obtained. The temperature of the solids entering reactor (440) will be in the neighborhood of 1500° to 1900°F. at which the catalyst was removed from reactor (430). The temperature of the outlet gas and solids depends on the fuel, air and steam quantities and preheat.

In any case, the steam, air and coke rates may be so controlled that the desired gas composition is obtained

prior to the discharge of the catalyst from reactor (440). Thus, it may be stated, quite generally, that for a discharge temperature of about 1500°F. these rates should be so controlled that the ratio of CO₂ to CO is less than about 0.5. At 1800°F. this ratio should be less than about 0.4. These conditions may be easily met by varying the quantity of steam charged to the kiln, no matter whether reactor (440) is heated externally or, as described above, operated substantially adiabatically by the admission of controlled amounts of air. The treatment of the catalyst with a CO+H₂ mixture rather than pure H₂ has, at relatively low temperatures within the ranges indicated above, the further advantage of suitably preconditioning the catalyst for the subsequent synthesis reaction, since it has been found that the carbonization tendency of iron catalysts may be substantially reduced by a pretreatment with CO at elevated temperatures conducive to carbide formation.

The sintered, decarbonized and reduced catalyst discharges from the lower end of reactor (440) into a quenching chamber (442) wherein the temperature of the catalyst may be reduced to about 400°-600°F., by heat exchange with catalyst cooled by quench water in vessel (443) and recirculated to chamber (442) through line (445) by any conventional means. Chamber (442) may have the function of, or comprise a conventional gas-solids separator, such as a cyclone. Quench water may be introduced through line (444). The catalyst cooled to about 200°F. passes, by gravity, into a conventional grinding and sizing device (446) from which it discharges at a particle size of about 50-100 microns into lockhopper system (448).

Device (446) may comprise sieving and/or elutriation means suitable for properly sizing the ground catalyst. Particles of undesirably small size may be discarded through line (450) or returned to reactor (430) for resintering.

As a result of the high temperatures employed in reactors (430) and (440), 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 it leaves quenching zone (442). For example, a suitable promoter solution, such as an aqueous solution of a potassium hydroxide, carbonate or halide, may be injected through line (451) into the catalyst leaving grinding device (446). 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.

Properly sized regenerated and reduced catalyst may be passed from lockhoppers (448) at the synthesis pressure to synthesis gas feed line (401) to be returned therein as a dilute suspension of solids-in-gas to synthesis reactor (410) for reuse.

The system illustrated by the drawing permits of various modifications. Reactors (430) and/or (440) may be operated at elevated pressures, if desired, so that pressure reduction on the catalyst may be substantially minimized. Either one or both lockhopper systems (412) and (448) may

be replaced by standpipes or mechanical conveyors, if the pressure conditions permit. Concurrent rather than countercurrent flow of gases and solids may be applied to reactor (430).

As previously indicated, decarbonization, sintering and reduction may also be carried out in a single reactor of the type of reactors (430) and (440), by properly controlling the reaction temperature in combination with the composition of the regenerating atmosphere. For example, this may be accomplished by feeding spent catalyst, air, and steam (coke may be required in addition) to a reactor in concurrent flow, the air and steam being controlled so as to adjust the atmosphere at the kiln outlet.

8 Instead of using rotary kilns as reactors, either one or both of reactors (430) and (440) may be of the type of a Dwight Floyd machine or Herreshoff burner. Other modifications will appear to those skilled in the art without deviating from the spirit of the invention.

In normal fluid synthesis operation, the individual particles making up the fluidized catalyst mass vary widely in carbon content, i.e. the withdrawn catalyst particles fall within the wide range of from carbon-free particles to particles of highest degree of carbonization. When a catalyst mass of this type is subjected to oxidative regeneration at conditions optimum for a catalyst of average carbonization, it will be appreciated that only a relatively small proportion of catalyst particles will be fully benefited by these optimum conditions while the major portion of the particles will be either over- or under-treated.

511647

The embodiment of this invention described below eliminates this drawback and affords various additional advantages.

In accordance with this embodiment, the hydrocarbon synthesis using fluidized iron-type catalysts is carried out in a plurality of conventional fluid-type reactors through which the fluidized catalyst flows in series continuously or intermittently. Catalyst is withdrawn from the last reactor in the direction of catalyst flow, regenerated by a treatment comprising complete combustion of the carbonaceous deposits and usually some oxidation of the iron, and the regenerated catalyst is returned to the first synthesis reactor in the direction of catalyst flow. The synthesis gas may be passed through the synthesis reactors either in series or in parallel. When applying series flow of synthesis gas, it may be advisable to pass the synthesis gas countercurrently to the catalyst flow through the reactors. The advantages of this procedure are as follows:

Assuming that a given coke formation rate occurs in a fluid-type synthesis reactor, the larger the catalyst circulation rate through the regeneration system the lower will be the coke content of the spent catalyst. Large circulation rates of the catalyst are obviously expensive inasmuch as larger transfer means, such as lock hoppers, are required and, what is more important, more air is needed for regeneration since a larger quantity of iron is oxidized. Laboratory work has shown that when the carbon content approaches 30% or there about on iron catalyst, disintegration

tends to become excessive. At concentrations substantially below this percentage, the carbon has little effect either on catalyst disintegration or on catalyst activity.

It will be understood that in a system such as described in which a stream of regenerated catalyst is charged to a fluid type synthesis reactor, not all of the particles of the catalyst will remain in this synthesis reactor for the same length of time. Some will remain for much less than average and some for a time much greater than average. Consequently, in order to operate in such a way that only a small fraction of the catalyst, say about 5%, has less than about 30% carbon it will be necessary to circulate sufficient catalyst to the regeneration system so that the average carbon concentration on the spent catalyst is much less than 30%. It will be observed then that one of the most serious problems encountered here is that of decreasing the catalyst flow rate.

When operating in accordance with this embodiment of the present invention, the catalyst particles withdrawn from the last synthesis reactor in the direction of catalyst flow will have a very nearly uniform carbon content approaching the average carbon content of particles withdrawn from a single reactor synthesis system after a residence time roughly corresponding to the total residence time of the catalyst particles in the plurality of synthesis reactors, provided the regenerated catalyst is returned to the synthesis reactor first in line in the direction of catalyst flow, in accordance with the invention. The more reactors in series the

closer will be the approach of the carbon concentration on each particle to the average. As a result, catalyst circulation between the regeneration and reaction stages may be reduced without increasing the proportion of catalyst particles having a carbon concentration above the disintegration limit. When a sufficient number of stages is used, this proportion may even be substantially reduced. It follows that operation according to the invention permits a substantial reduction in the requirements of oxidizing and reducing gases as well as size of regeneration equipment.

These relationships will be best understood from an inspection of the curves shown in Figures V and VI of the drawing.

Figure V illustrates the effect of catalyst circulation rate and plurality of reaction zones on the residence time distribution of the spent catalyst in the reaction stage, i.e. the percentages of catalyst remaining in the reaction stage for definite minimum times.

Figure VI illustrates the effect of catalyst circulation rate and plurality of reaction zones on percent carbon on spent catalyst, based on the pure iron content of the catalyst, i.e. percentages of catalyst containing definite minimum quantities of carbon.

The curves of Figures I and II are based on a coke production of 975 lbs. per hour and a catalyst hold-up based on iron, of 65 tons. The following comparison may be derived from these curves.

Curve No.	Iron Circulation Rate, Tons Per Hour	No. Stages in Series	% Iron Having More Than 30% C	Ave. % C on Iron	Air Requirements (MSCFH)	Hydrogen Requirements for Catalyst Reduction (MSCFH)
A	2.83	4	8.0	17.25	211	72
B	4.1	1	8.0	11.9	252	105
C	4.1	4	1.5	11.9	252	105

Curves A and B indicate that 8.0% of catalyst is in the disintegration range for both curves, i.e. above 30% C. The 4 stage operation A is at a lower circulation rate. Hence, in operation A less oxygen is consumed by oxidation of the iron associated with the coke, which results in a substantially reduced overall oxygen requirement.

Comparison of curves B and C, which are for the same circulation rate of 4.1 tons per hour, indicates that the same amount of oxygen is required. However, the 4 stage process (c) has only 1.5% of the spent catalyst in the disintegration range (above 30% C) as compared with 8% for curve B.

It has been pointed out heretofore that the oxidative regeneration treatment is preferably carried to a complete decarbonization of the catalyst. This may involve an oxidation of the iron component beyond the degree desirable for an efficient operation of the synthesis stage. The catalyst may also contain an undesirably high oxygen concentration when it leaves the synthesis stage. In these cases, the catalyst, after carbon removal and prior to its return to the synthesis stage, may be reduced at least in part, as indicated in the above table. This separate reduction stage is preferably conducted at an elevated pressure approximating that at which

the synthesis is carried out. Hydrogen is the preferred reducing agent. Water formed during the reduction reaction should be removed from the system, which may be best accomplished by drying the effluent gases from the reduction reactor and recycling the dried gases. This operation is greatly aided by high pressures because the condensation of water is facilitated.

The need of a separate reduction stage may be avoided by so controlling the oxidation conditions in the oxidative regeneration zone that the carbonaceous deposits are removed in the form of carbon oxides either without affecting the state of oxidation of the iron or even with a simultaneous reduction of iron oxide to iron. This may be accomplished by properly correlating the amount and composition of the oxidizing gas with the temperature and pressure of the regeneration zone and the partial pressures of the components of the oxidizing atmosphere in contact with the catalyst, as disclosed above in connection with Fig. I-IV.

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 atmosphere 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.

This embodiment of the invention will be best understood from the more specific description hereinafter in which reference will be made to Figures VII and VIII of the accompanying drawing, wherein:

Figure VII is a semi-diagrammatical illustration of a system suitable for carrying out a preferred embodiment of the invention; and

Figure VIII is a similar illustration of a system involving a separate catalyst reduction stage.

Referring now to Figure VII, the system illustrated therein essentially comprises a series of conventional fluid type synthesis reactors (710a), (710b), (710c) and (710d) and an oxidizer regenerator (730) whose functions and cooperation will be forthwith explained.

In operation, synthesis reactors (710a), (710b), (710c) and (710d) contain 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 (701) through line (703), manifold (705) and line (707) to the various synthesis reactors which are arranged for parallel flow with respect to the gas feed in the case of the present example. As indicated by lines (711), (712) and (713) the catalyst is passed through the synthesis reactors in series from reactor (710a) through (710b) and (710c) to reactor (710d) from which it is withdrawn and returned to reactor (710a) as will appear more clearly herein-

after. Any conventional means for conveying finely divided solids such as aerated standpipes, lockhoppers, mechanical conveyors, etc. (not shown) may be used in a manner known in the art to maintain the desired catalyst flow between the reactors.

The reaction conditions in the synthesis reactors are those known for the conversion of CO and H₂ on fluidized iron catalysts. They may include pressures of about 5-50 atm., preferably 20-40 atm., temperatures of about 500°-800°F., preferably about 550°-700°F., total gas throughputs of about 5 to 500 v/w/hr., preferably about 10 to 50 v/w/hr. and superficial gas velocities of about .3-5.0 ft. per second, preferably about .5-1.5 ft. per second for catalyst particle sizes of about 20-150 microns, predominantly about 50-100 microns. The synthesis gas enters the lower portion of the synthesis reactors through suitable distributing means such as grids (G). Vaporous and gaseous reaction products and unconverted reactants are withdrawn overhead from catalyst levels (L) through lines (714), (715), (716) and (717) to be worked up in a conventional product recovery system (not shown). If desired, tail gas may be recycled to the reactors in conventional ratios of about 1-5 volumes, preferably 1-2 volumes of tail gas per volume of fresh synthesis gas. Other details of the operation of fluid synthesis reactors are well known and need not be further specified here.

As stated before, carbon deposits form on the catalyst in the synthesis reactors and in about 100 hours of catalyst residence time as much as 50% 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 active catalyst will be continually blown out of the synthesis reactors.

As a result of the series flow of catalyst through the synthesis reactors, the carbon content will increase in the direction of catalyst flow and will be lowest in reactor (710a) and highest in reactor (710d) because the catalyst maintained in reactor (710d) has been subjected to carbonization conditions for the maximum time. It is an essential feature of the invention that the catalyst circulation rate through reactors (710a), (710b), (710c) and (710d) is so adjusted that the total catalyst residence time in reactors (710a), (710b), (710c) and (710d) is below that which will cause carbonization sufficient seriously to interfere with proper fluidization in any, and particularly the last one, of the synthesis reactors employed. While this total residence time depends on the specific reaction conditions employed, it may be stated that at a throughput of about 20 v/v/hr. total residence times of about 50 to 700 hrs., preferably 75-200 hrs., which may cause total coke deposits of about 10 to 20% by weight of iron, are suitable for the purposes of the invention at the conditions specified above.

The catalyst residence times within the individual reactors (710a), (710b), (710c) and (710d) may be equal or

unequal fractions of the total catalyst residence time as desired. It is also noted that the reaction conditions in the individual synthesis reactors need not be identical. Allowances may be made for the steadily increasing age and degree of carbonization of the catalyst as it advances through the reactors. This may be compensated for by increasing the temperature in the direction of catalyst flow, for example. If series flow of synthesis gas is employed, the reaction conditions in the successive reactors may be adjusted to the changes in synthesis gas composition in a manner known per se for multi-reactor systems. It is also possible to operate the individual reactors at different conditions to produce products of different character in the individual reactors. The level (L) within any reactor is preferably maintained constant so as not to disturb the synthesis operation. The catalyst flow to, among and from the synthesis reactors may likewise be maintained at a substantially constant average rate.

Fluidized catalyst containing about 10.0 to 20.0% of carbon by weight of iron in substantially uniform distribution over the individual particles is withdrawn downwardly through a system of lockhoppers (720) wherein the pressure may be reduced to atmospheric at which the catalyst may be charged through line (725) to regenerator (730). An oxidizing gas, such as air, is supplied by blower (732) through line (734) to the bottom of regenerator (730) which it enters through a distributing means, such as grid (736), at a velocity of about .5-3 ft. per second to regenerate and convert the catalyst within reactor (730) into a dense

fluidized mass having an upper level (L₃₀). About 25 to 75 normal cu. ft. of air per pound of iron on the catalyst is normally sufficient substantially completely to burn off the carbon from the catalyst, taking into consideration the oxygen consumed by simultaneous iron oxidation. Temperatures of about 900°-1800°F., preferably about 1000° to 1200°F., are suitable.

The regeneration reaction is exothermic and heat must be removed from the catalyst mass to maintain it at the desired temperature. This may be accomplished by a suitable recycle of cooled flue gases, and, if necessary, any additional heat withdrawal means, such as cooling coils or jackets (not shown). It is preferred, however, to employ a catalyst circulation from regenerator (730) downwardly through line (736) to air feed line (734) and through a cooling means, such as waste heat exchanger (738), back to regenerator (730).

The flue gas leaving (L₇₃₀) overhead may be passed through a conventional gas-solids separation system (740) which may include cyclones, precipitators and/or filters and from which separated catalyst fines may be returned through line (742) to regenerator (730) or discarded through line (744). The gas, now substantially free of entrained solids, may be passed through line (746) to a cooling means, such as a waste heat exchanger (748) and line (750) provided with blower (751), back to air feed line (734) as indicated above. Excess flue gas may be vented through line (752).

Catalyst substantially completely decarbonized is withdrawn downwardly through bottom drawoff line (754) and

cooler (756) to be cooled to about 400°-600°F. and to be passed via a lockhopper system (758) to synthesis gas feed line (707). The catalyst suspended in the synthesis gas in line (707) is returned to synthesis reactor (710a) to repeat the cycle.

The system illustrated by Figure VII 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 (730). In these cases, regenerator (730) may have the form of a rotary kiln to which the oxidizing gas is charged. Heat may be removed by recycling a cooled portion of the flue gas to the kiln, or by recycling cooled catalyst to the kiln, or by quenching within the kiln with water. The regeneration may also be carried out at elevated pressures, if desired, so that pressure reduction on the catalyst flowing from reactor (710d) to the regenerator may be substantially minimized or eliminated. Either one or both of the lockhopper systems (720) and (758) may be replaced by standpipes or mechanical conveyors if the prevailing pressure conditions permit.

As a result of the high temperatures employed in regenerator (730), 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 (760) into catalyst withdrawal pipe (754). A conventional steam-separating zone (not shown) may then be provided above

line (760). Addition of the promoter at this or a similar point rather than in the synthesis reactors 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.

Other modifications will appear to those skilled in the art without deviating from the spirit of the invention.

As indicated above, the catalyst withdrawn from regenerator (730) may, as a result of overoxidation in regenerator (730) or of oxidation in the synthesis stage, contain more oxygen than desirable for an efficient operation of the synthesis stage, say more than about 10.0 to 15.0% by weight. In this case, the decarbonized catalyst may be subjected to a separate reduction treatment in equipment of the type illustrated in Figure VIII.

Referring now to Figure VIII the system shown therein comprises a synthesis stage (810) and a regeneration stage (830) of the type illustrated in Figure III, like reference characters being used to identify like elements. The system, particularly the synthesis stage (810), is drawn in a simplified manner, only one reactor being shown as representative of a multi-reactor system of the type described above. The operation of the system of Figure VIII is substantially the same as that of Figure VII up to the point of withdrawing the regenerated catalyst from regenerator (830) through line (854).

Now, instead of cooling and returning the catalyst

to the synthesis stage it is passed to catalyst reducer (870) which is preferably operated at an elevated pressure at least as high as that of the synthesis stage. Pressures of about 400-700 lbs. per sq. in. are generally suitable. The catalyst from line (854) is passed, therefore, through lockhopper system (858) to build up the desired pressure and thence directly to reducer (870). Since the reduction reaction is endothermic, the sensible heat of the decarbonized catalyst may be utilized to advantage in reducer (870) which may be operated at about 400°-1200°F., preferably 700°-1000°F., using hydrogen as the reducing agent.

Reducer (870) is preferably of the fluid type and has a construction similar to that of regenerator (830). Hydrogen, preheated to a temperature sufficiently high to maintain the desired reduction temperature in cooperation with the sensible heat of the catalyst, is supplied from line (872) through grid (874) to the bottom of reducer (870) to reduce and convert the catalyst therein into a dense, turbulent, fluidized mass of solids, substantially as described in connection with regenerator (830). Reducer (870) is so designed as to allow for a catalyst residence time adequate for the desired degree of reduction. The proper amounts of hydrogen to be used depend on the amount of oxygen to be removed from the catalyst and may be readily determined by those skilled in the art for each given set of conditions. Reduced catalyst is withdrawn downwardly through line (876), cooled in cooler (880), enriched, if desired, with promoter supplied through line (878) and

returned through gas feed line (807) to the final reactor of synthesis stage (810), if desired after carbiding, all substantially as described heretofore.

The hydrogen, after contacting the catalyst, passes through a gas-solids separation system, such as cyclone (882) provided with solids return pipe (884), and thence through line (886) to a heat exchanger (888) wherein it gives off some of its heat to a mixture of fresh and recycle hydrogen. The partially cooled spent hydrogen passes on to a cooler (890) wherein it is cooled sufficiently to condense the water which is finally knocked out of the gas in drum (892). The separated water along with suspended catalyst carry-over is returned through line (894) to regenerator (830).

The substantially dry gas is withdrawn from drum (892) through line (896) to which make-up hydrogen may be added through line (898). The resulting gas mixture is passed by recycle booster (900) through line (902) to heat exchanger (888), wherein it picks up heat from the exit hydrogen, and thence through line (904) and recycle heater (906) back to line (872) and reducer (870) at the desired preheat temperature for maintaining the endothermic reaction in reducer (870). Since inert gases will accumulate in the hydrogen recycle system just described, it is desirable to bleed part of these gases from the system. This may be done by way of line (908).

It will be understood that the system of Figure VIII permits of substantially the same modifications as those described with reference to Figure VII.

This embodiment of the invention will be further illus-

trated by the following specific examples.

E X A M P L E I

A multi-reactor hydrocarbon synthesis system designed for a daily production of 6,200 bbl. of gasoline, 565 bbl. of gas oil and 570 bbls. of alcohols and other oxygenated compounds is operated at the conditions given below using reduced pyrites ash promoted with 1.5 potassium carbonate as the catalyst in a fluidized bed.

Synthesis Conditions

Synthesis Gas Quantity, MMSCFD	226.5
Synthesis Gas Composition, Vol. %	
H ₂	60.1
CO	33.6
CO ₂	1.3
N ₂	3.8
H ₂ O	.2
CH ₄	1.0
Total	<u>100.0</u>
No. of Reactors	4
Total Catalyst in Reactors - Tons	65
Average Catalyst Residence Time in Reactors - Hrs.	159.5
Throughput, v/hr./w (H ₂ +CO in Fresh Feed)	72.5
Recycle Ratio (Recycle to Total Fresh Feed)	1.62
Synthesis Reactor Temperature, °F.	650
Synthesis Reactor Pressure, p.s.i.g.	400
CO Conversion, % on Fresh Feed	98.0
H ₂ Conversion, % on Fresh Feed	88.0

At these conditions about 975 bbls. of coke are formed per hour.. The following table compares the condition and results of catalyst regeneration when applying series flow of catalyst in the reactors in accordance with the

invention with those of regeneration when using conventional parallel flow of catalyst, substantially as described in connection with Figures V and VI of the drawing.

<u>Catalyst Regeneration</u>	<u>A</u>	<u>B</u>	<u>C</u>
Catalyst Flow Through Reactors In Series	In Parallel	In Series	
Total Catalyst Circulation Rate, Tons/Hr. of Fe	2.83	4.1	4.1
% Catalyst Having More Than 30% Carbon on Fe	8.0	8.0	1.5
Relative Quantity of Catalyst Disintegrated/Hr.	5.33	5.33	1.0
Average % C on Iron (Carbon and Oxygen Free)	17.25	11.9	11.9
Average % O on Iron (Carbon and Oxygen Free)	5.8	5.8	5.8
Average % O on Regenerated Catalyst	38.6	38.6	38.6
Air For Regeneration, MSCFH	211.0	251.5	251.5
Temperature of Regeneration, °F.	1000	1000	1000
Pressure of Regenerator, P.s.i.g.	5	5	5
Residence Time in Regenerator, Hrs.	25	25	25
Relative Regenerator Hold Up Volume	1.0	1.45	1.45

The above data demonstrate that operation in accordance with the invention permits either a substantial reduction in catalyst circulation, air requirements and equipment size at a given coke content and disintegration of the catalyst (Column A), or a substantial reduction in coke content and disintegration at a given catalyst circulation, air consumption and equipment size (Column C).

EXAMPLE II

In order to illustrate the application of a separate reducing stage in accordance with the invention, a comparison of the conditions and results of the reduction of catalysts decarbonized as indicated in Columns A and B of Example I are summarized in the table given below.

<u>Catalyst Reduction</u>	<u>A</u>	<u>B</u>
	In Series	In Parallel
Catalyst Flow Through Reactors		
Total Catalyst to be Reduced, Tons/hr. of Fe	2.83	4.1
Hydrogen Fresh Feed Composition, % H ₂ Inerts	93.4 6.6	93.4 6.6
Hydrogen Fresh Feed, MSCFH as Hydrogen	72.2	104.6
Hydrogen Recycle Ratio (As Hydrogen)	18.2	18.2
Hydrogen Purge, MSCFH (As Hydrogen)	20.25	29.4
Hydrogen Purge Composition, % H ₂ Inerts	80.0 20.0	80.0 20.0
Temperature, °F.	900	900
Pressure, p.s.i.g.	415	415
Residence Time, Hrs.	2	2
Hydrogen Preheat Temperature, °F.	1000	1000
% O on Catalyst Charged (on Fe)	38.6	38.6
% O on Catalyst After Reduction (on Fe)	1.0	1.0

The above data indicate savings of about 30% in the hydrogen requirement for the case of the present invention (Column A).

While the foregoing description and exemplary operations have served to illustrate specific applications and

511647

results of the invention, other modifications obvious to those skilled in the art are within the scope of the invention. Only such limitations should be imposed on the invention as are indicated in the appended claims.

THE EMBODIMENTS OF THE INVENTION IN WHICH AN EXCLUSIVE PROPERTY OR PRIVILEGE IS CLAIMED ARE DEFINED AS FOLLOWS:

1. A method for removing carbonaceous deposits from an iron catalyst contaminated therewith without substantially increasing the oxygen content of the iron, which comprises oxidizing the contaminated catalyst in a decarbonization zone in an atmosphere containing carbon oxides and essentially no free O₂ at a temperature above about 1000°F. while correlating the partial pressures of CO₂ and CO with the temperature in such a manner that r will not be greater than that defined by the equation

$$r = 10 \left[-1.170 + \frac{1730}{t + 460} \right] \quad (1)$$

but greater than r as defined by the equation

$$r = -1/2 + 1/2 \sqrt{1 + \frac{4s}{9.25 - \frac{16170}{t + 460}}} \quad (2)$$

wherein r is the ratio of the partial pressure of CO₂ to that of CO, s is the sum of these partial pressures in atmospheres and t is said temperature in °F.

2. The process of claim 1 in which said atmosphere comprises steam.

3. The process of claim 1 in which free oxygen and an extraneous combustible material are added to said combustion zone in amounts and proportions adequate to supply by combustion of said material the heat required by said oxidation reaction.

4. The process of claim 3 in which said material is a hydrocarbon.

511647

5. The process of claim 3 in which said material is hydrogen.

6. The process of claim 1 in which an inert gas is added to said decarbonization zone.

7. The process of claim 1 in which gas produced in said decarbonization zone is recycled to said decarbonization in a volume ratio greater than 1 with reference to the net volume of gas leaving the decarbonization zone.

8. The process of claim 7 in which said recycle gas is partly burned prior to its return to said decarbonization zone.

9. The process of claim 1 in which a promoter is added to the decarbonized catalyst.

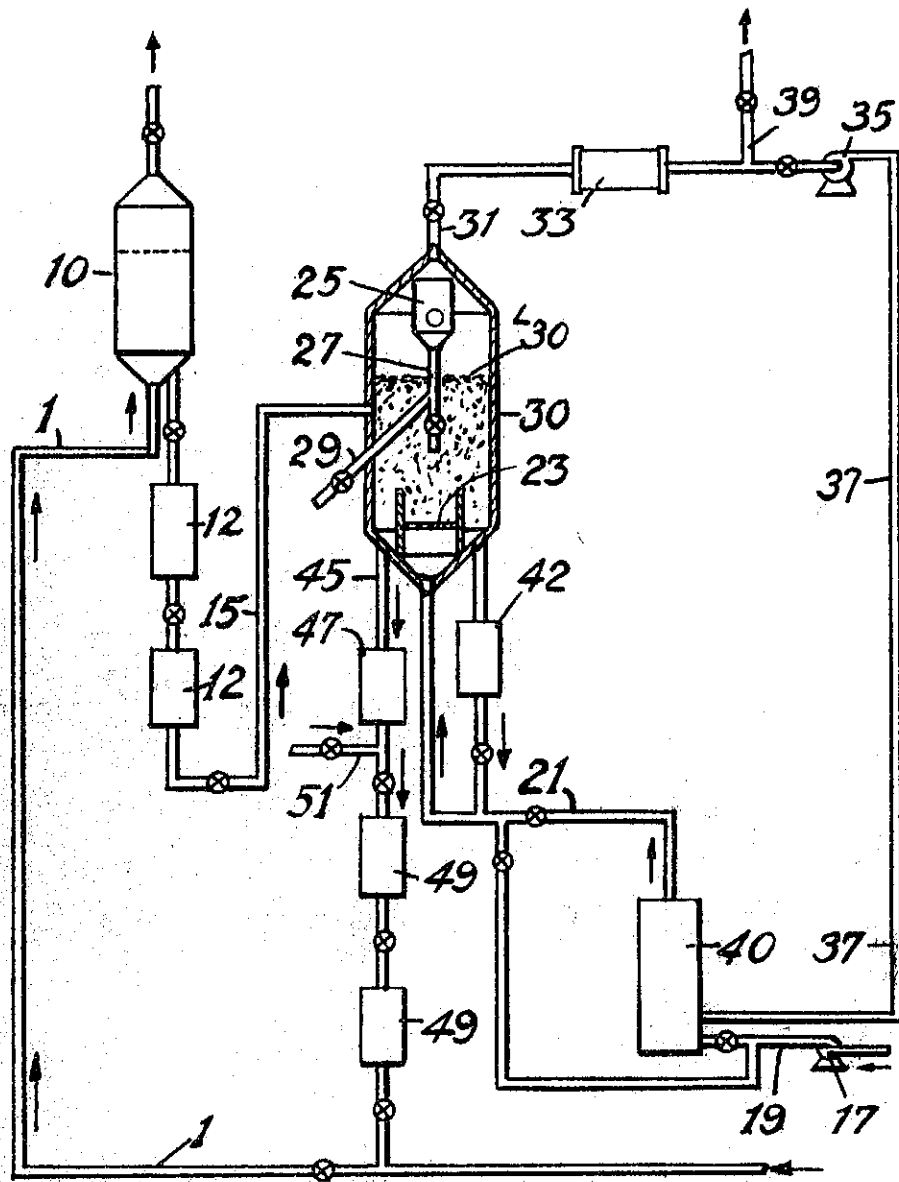


FIG.-I

*Standard Oil
Development Company*

Certified to be the drawings referred to
in the specification hereunto annexed.

Ottawa July 5

1948

Marko Clark

ATTORNEY-5

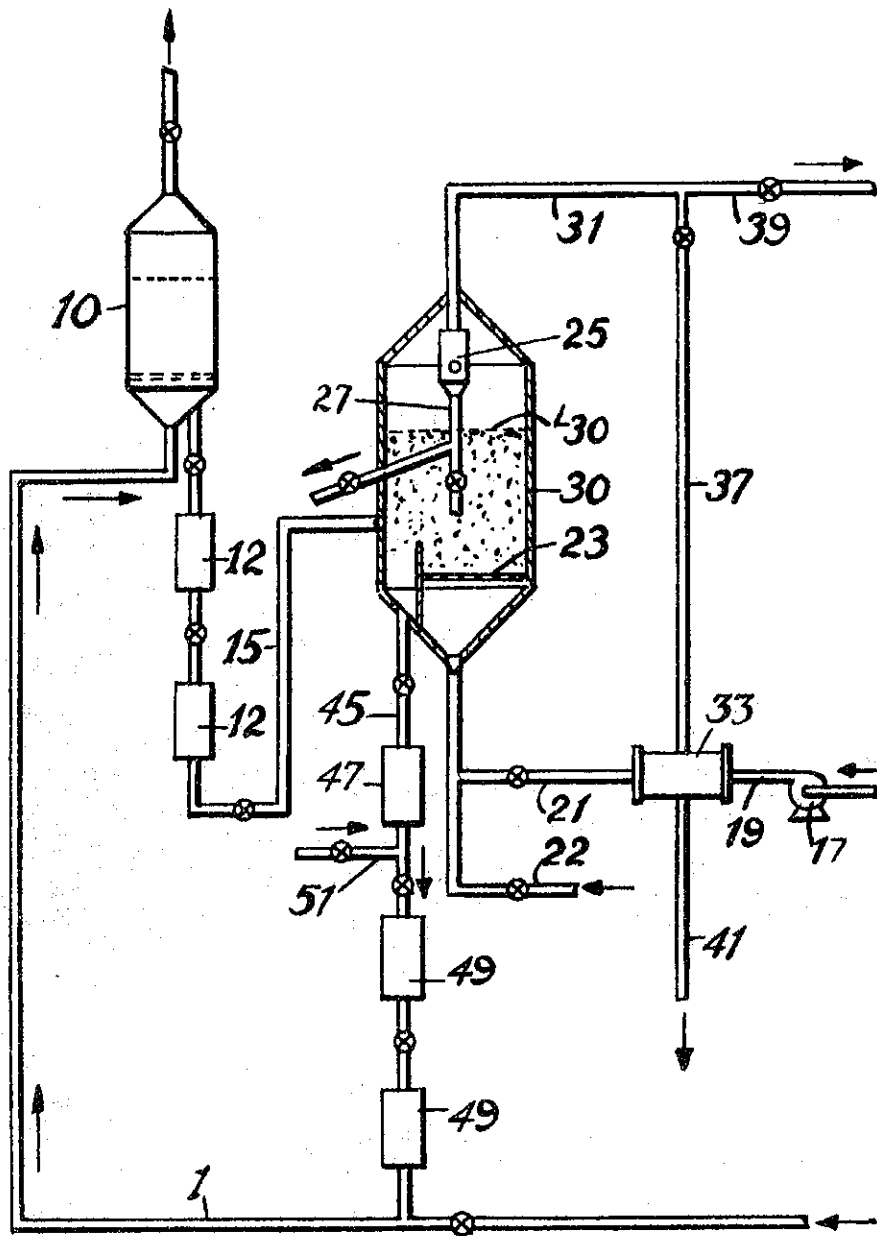


FIG.- II

*Standard Oil
Development Company*

Certified to be the drawings referred to
in the specification hereunto annexed.

Ottawa July 5 1928

Markus Clark

ATTORNEY S

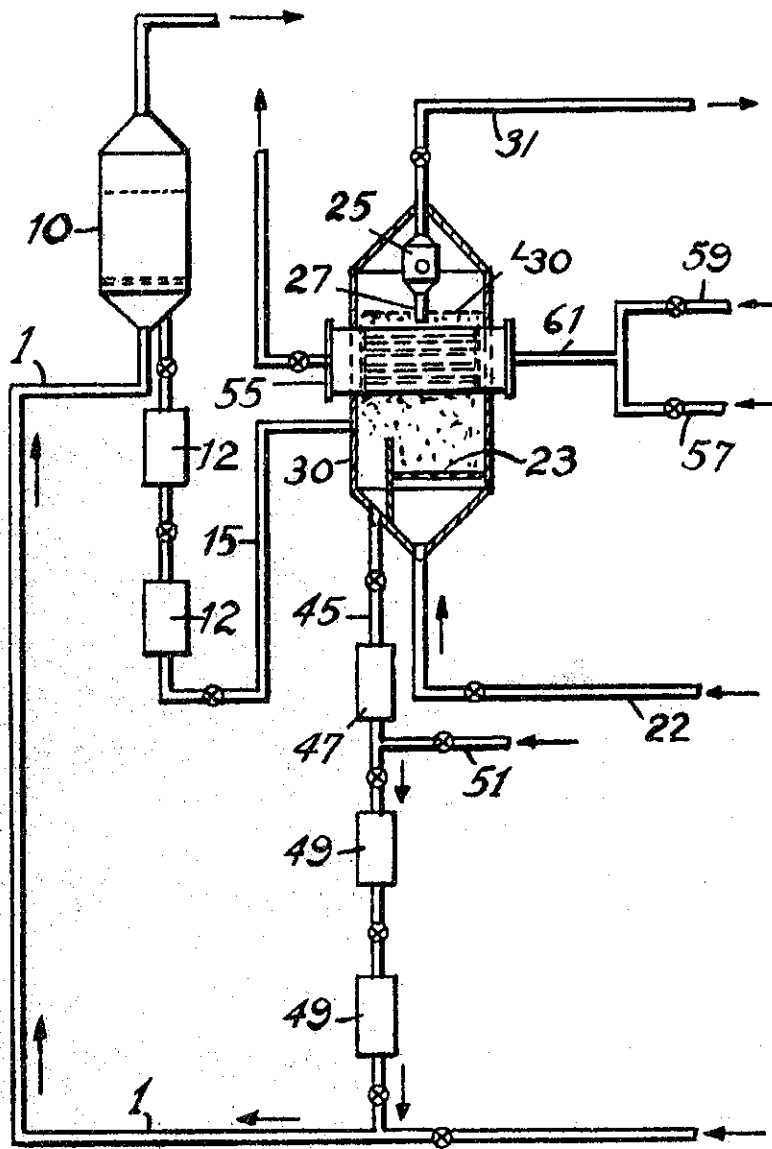


FIG. III

Standard Oil
Development Company

Certified to be the drawings referred to
in the specification hereunto annexed.

Ottawa July 5 1928

Marks & Clerk

ATTORNEY ->

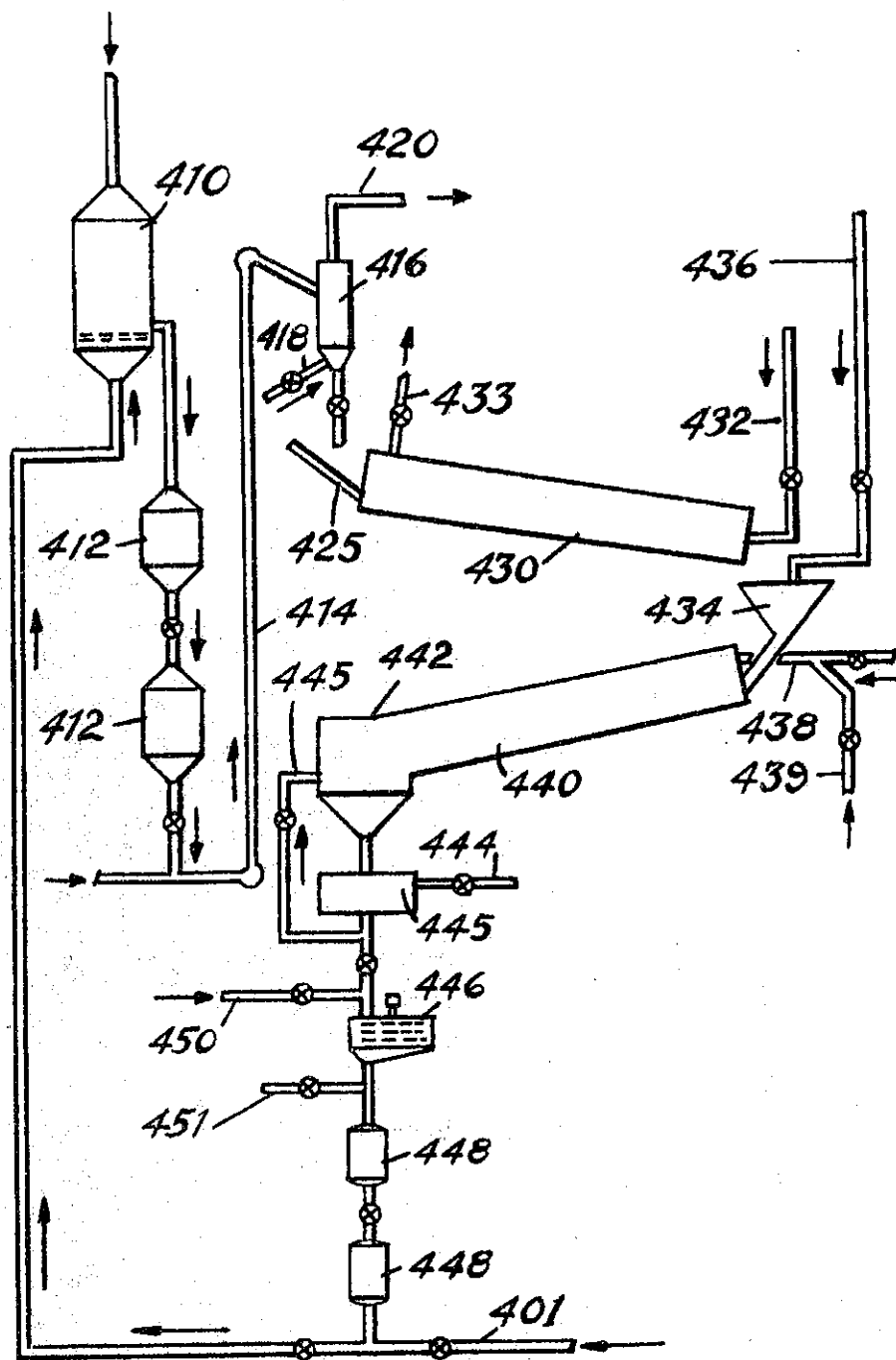


FIG.-IV

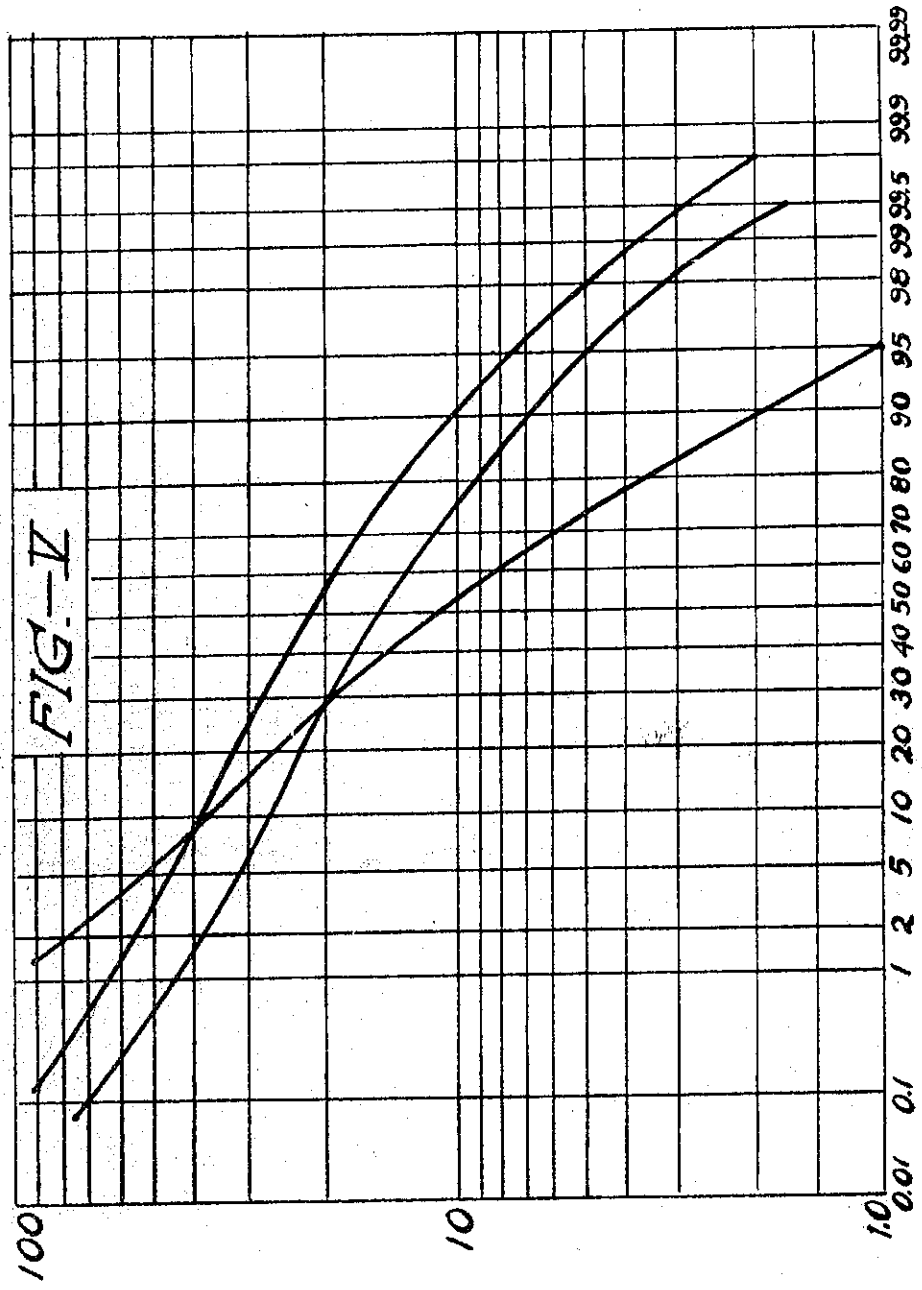
*Standard Oil
Development Company*

Certified to be the drawings referred to
in the specification hereunto annexed.

Ottawa July 5 1928

Marko Clark

ATTORNEY



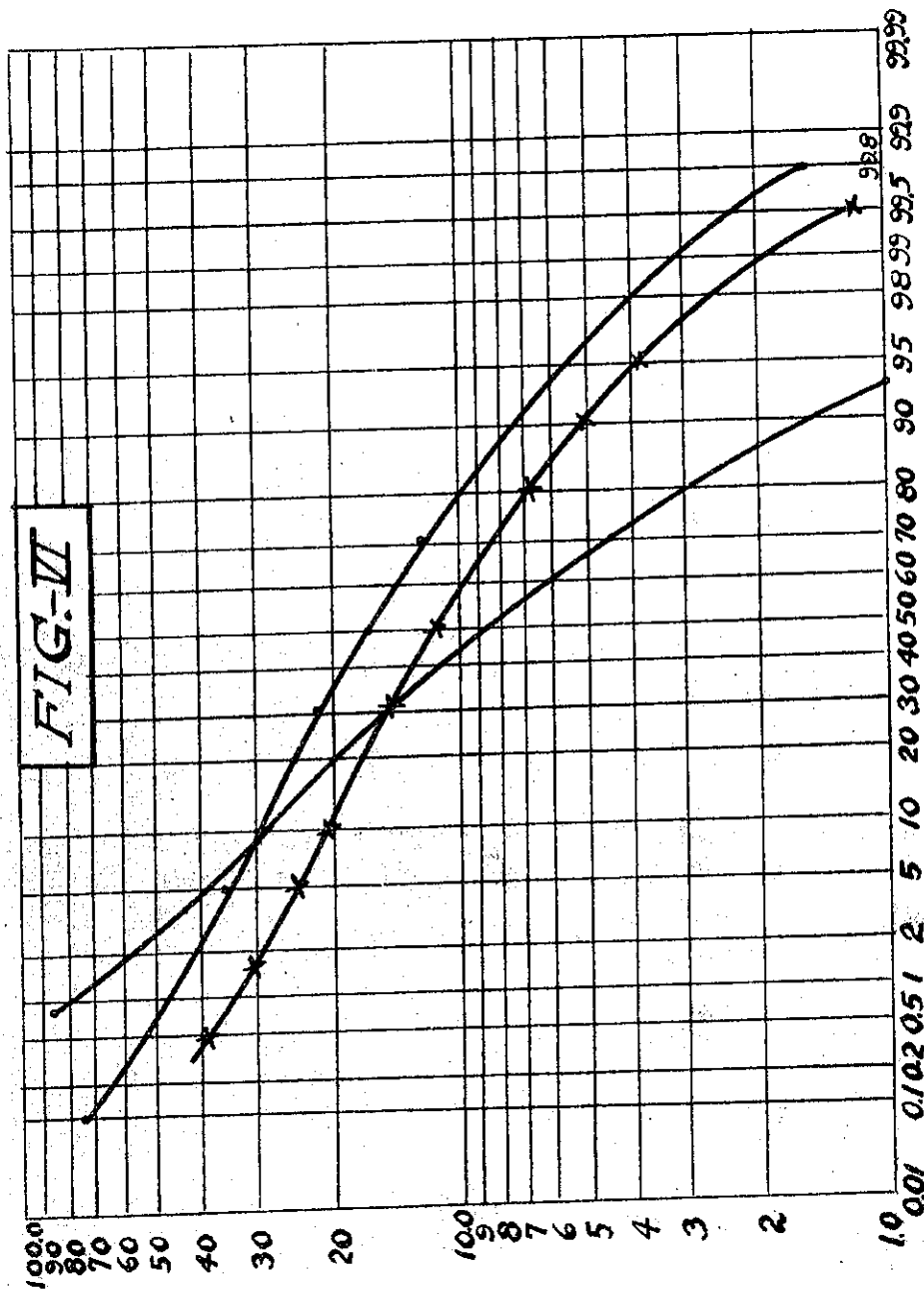
Certified to be the drawings referred to
in the specification hereunto annexed.

Ottawa July 5 19 88

Standard Oil
Development Company

Markus Clark

ATTORNEY &



Certified to be the drawings referred to
in the specification hereunto annexed.

Ottawa July 5 1948

Standard Oil
Development Company
Market Clerk

ATTORNEYS

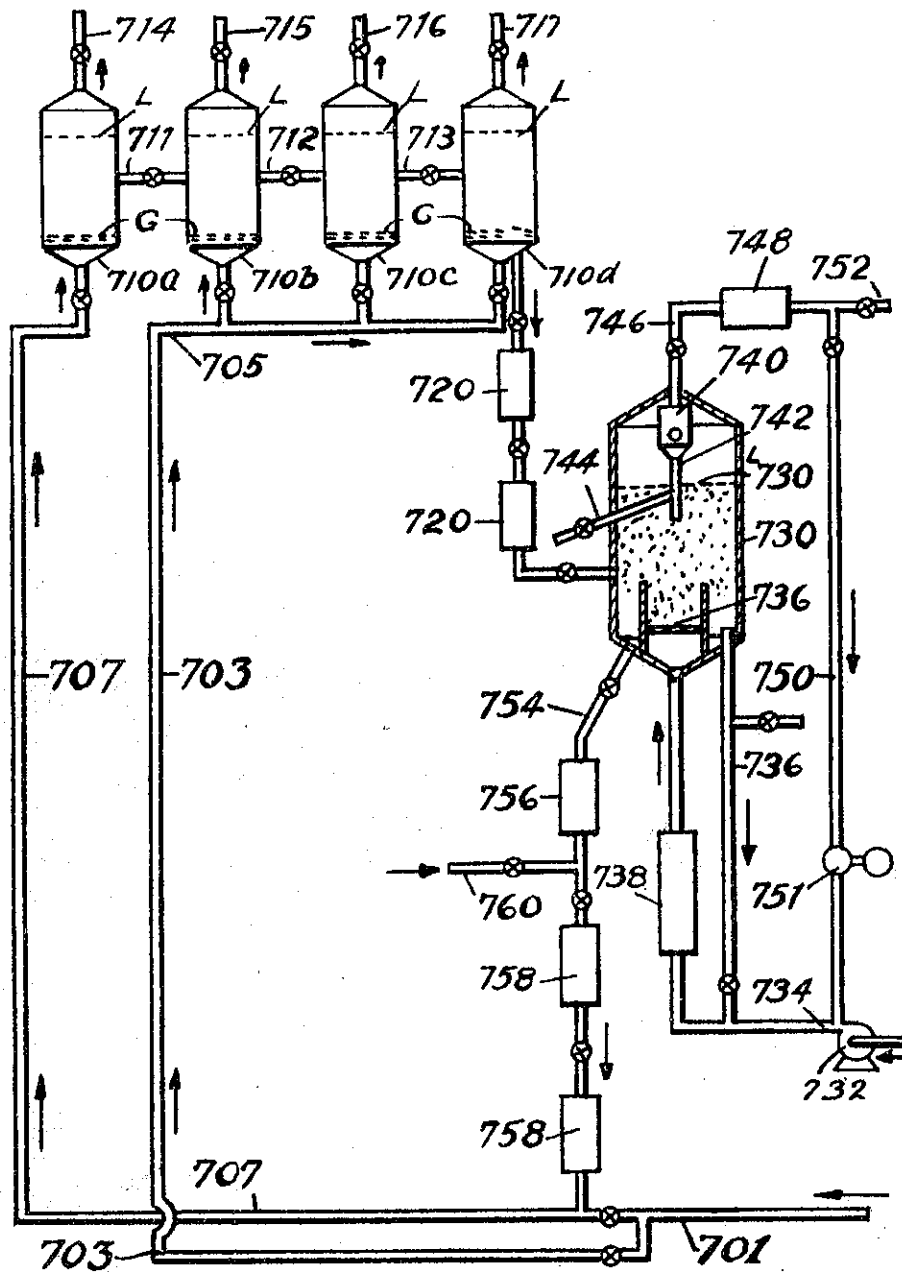


FIG-VII

*Standard Oil
Development Company
Sparks Clerk*

Certified to be the drawings referred to
in the specification hereunto annexed.

Ottawa July 5 1948

ATTORNEY

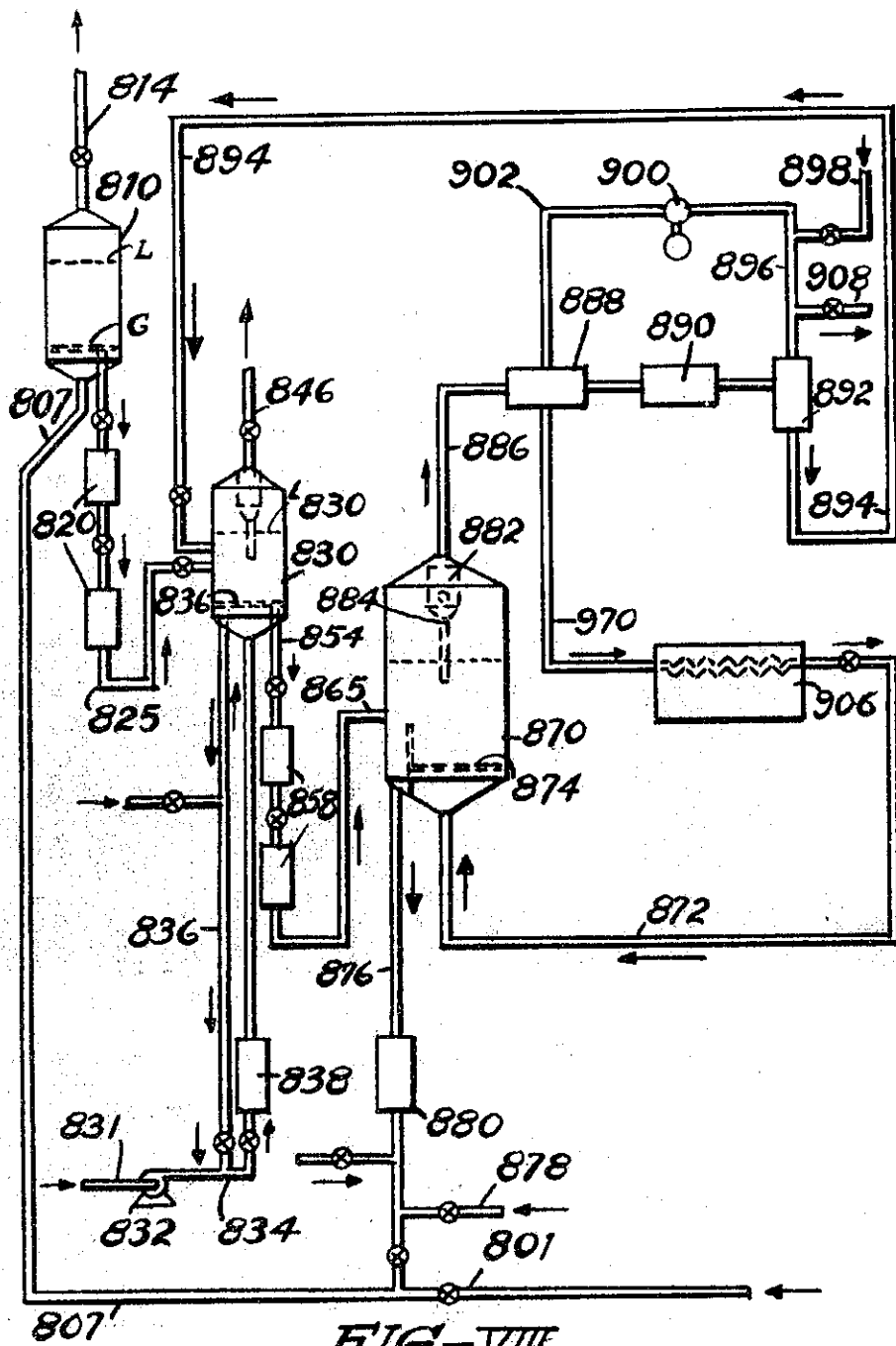


FIG.-VIII

Certified to be the drawings referred to
in the specification hereunto annexed.

Ottawa July 5 1928

Standard Oil
Development Company
Marks & Clark

ATTORNEY