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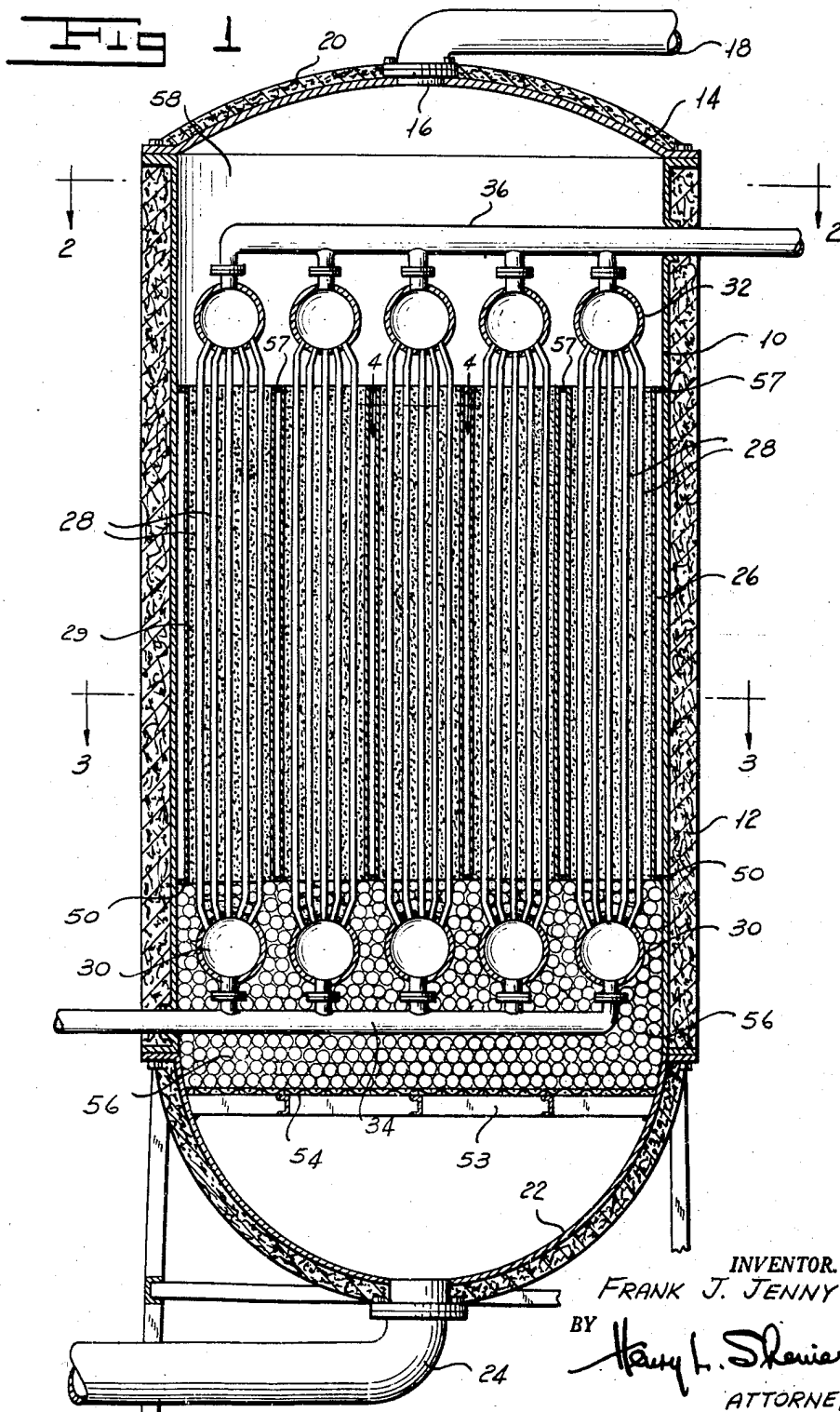
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METHOD AND APPARATUS FOR SYNTHESIZING HYDROCARBONS

Filed Feb. 15, 1954

2 Sheets-Sheet 1



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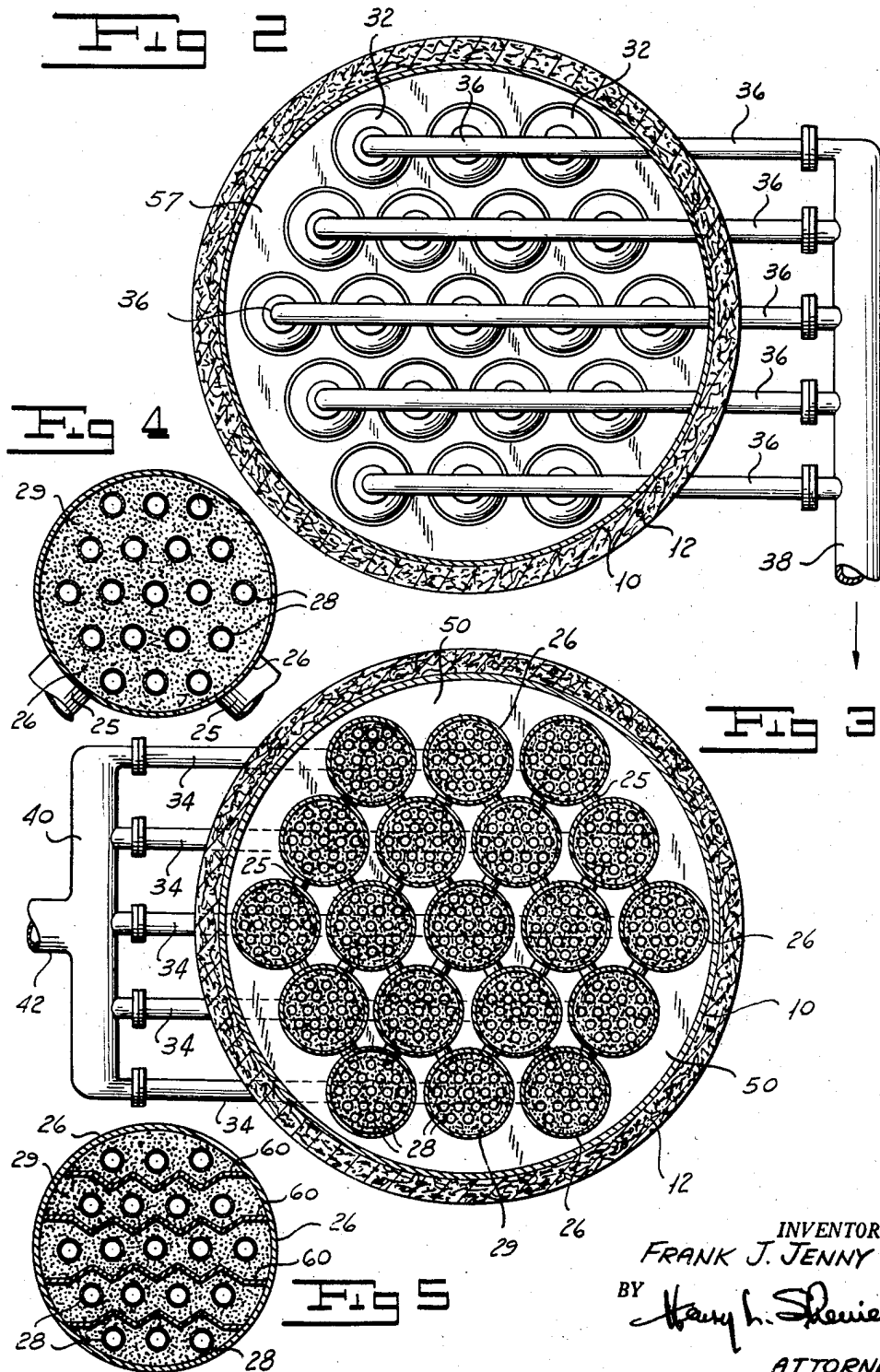
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METHOD AND APPARATUS FOR SYNTHESIZING
HYDROCARBONS

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18 Claims. (Cl. 260-449.6)

My invention relates to a method and apparatus for synthesizing hydrocarbons and more particularly to a method for synthesizing hydrocarbons from a mixture of carbon monoxide and hydrogen and to an improved and novel apparatus for carrying out my method.

The perfection of the internal combustion engine and its wide application at the present time is such that future generations might well refer to our civilization as the "oil age." This vital commodity is necessary for transportation on land, on sea, and in the air. Without it, aircraft, automotive vehicles, oil burning ships, diesel-powered locomotives, tanks, and tractors would be useless. The convenience, comfort and safety of our people depend in large measure on hydrocarbon oil and its immediate products—gasoline, lubricating oil and fuel oil.

The world has been using fossil fuels at a tremendous rate. This rate has been increasing rapidly, in an exponential fashion. The supply of liquid fossil fuels, namely crude oil, appears to be much less than the solid fossil fuels, such as coal. A recent Government Materials Policy Commission report has forecast that by the year 1965 the U. S. economy will incorporate the production of about one million barrels per day of synthetic fuels. In a land of free enterprise, such a high production level of synthetic fuels must necessarily be dependent on the development of an efficient and basically sound process or processes. Such processes will have to compete on a sound economic basis within the well-established framework of the petroleum industry.

The vital importance of liquid hydrocarbon fuels, such as gasoline and diesel oil, has long been recognized by scientists. Franz Fischer and Hans Tropsch worked a number of years in the Fuel Research Laboratories of the Kaiser Wilhelm Institute für Kohlenforschung, Mulheim an der Ruhr, Germany, to develop a process for converting coal into liquid hydrocarbons. They were successful. Their process consisted in generating water gas from the coal, carefully purifying it and then passing it over certain catalysts, as for example, iron or cobalt, with small amounts of thoria, deposited on kieselguhr, at temperatures of between 180° C. and 325° C. at atmospheric pressure. By this means, with careful precautions in gas purification and the exact control of the temperature, about eighty percent of the carbon monoxide was converted to form a mixture of hydrocarbons. It will be observed that the process is essentially a hydrogenization of carbon monoxide.

The optimum temperature ranges were found by German scientists to be 180° C. to 205° C. for iron catalysts, and from 170° C. to 225° C. for ruthenium catalysts. It was further found that nickel catalysts produced best results at atmospheric pressures, cobalt and iron catalysts at pressures of about fifteen atmospheres, while ruthenium catalysts were most efficient at much higher pressures.

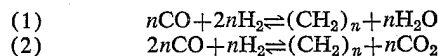
The work of Fischer and Tropsch stemmed from earlier work in 1902 of Sabatier and Senderens, who observed that a reduced nickel catalyst would synthesize methane from a mixture of carbon monoxide and hydro-

2

gen. Fischer and Tropsch found that not only was methane produced but also its homologues. In addition, the synthesis product contained oxygen-bearing compounds, such as alcohols, acids, aldehydes, and ketones. Since the object of the German research at this time was the production of gasoline and motor fuel, Fischer and Tropsch directed their efforts to the discovery of a catalyst which would produce a maximum yield of motor fuel hydrocarbons and a minimum yield of oxygen-bearing compounds.

In April of 1936 a Fischer plant was started for the Braunkohle-Benzin A. G. at Brabag, Ruhrland. This plant was designed to make 150,000 tons of "Kogasin I" and "Kogasin II" (motor spirits) per annum from a mixture of coke water gas and coke oven gas.

The hydrocarbon synthesis by the Fischer-Tropsch process may be represented by the following reactions:



In Equation 1 we have a complete hydrogenation. In Equation 2 we have a partial hydrogenation. Equation 1 is the preferred and predominant one. In actual practice the ratio of H₂ to CO depends in large measure on the composition of the primary fuel from which synthesis gas is derived. With coal this ratio is less than with CH₄. When the value of *n* is from four to twelve inclusive, the mixture of hydrocarbons resulting from the synthesis will be predominantly gasoline.

In England, Imperial Chemical Industries built a plant at Billingham, Co. Durham, for the hydrogenation of bituminous coal by the Fischer-Tropsch synthesis. Similar plants have also been built in Italy.

In the United States it has been recognized that natural gas, which is available in large quantities in Texas and elsewhere, is a most appropriate primary fuel for conversion to synthesis gas and subsequently to synthetic gasoline. Accordingly, a synthesis plant was built by Carthage Hydrocol Inc. at Brownsville, Texas. The plant was designed to produce 7,000 barrels per day of petroleum products plus 300,000 pounds per day of oxygenated hydrocarbons. The plant has never achieved more than an average of about ten percent of its design capacity.

The synthesis reaction is highly exothermic. In Brownsville, for example, the design calls for the removal of approximately three hundred sixty million B. t. u.'s per hour from the synthesis reactors. This heat must be removed under controlled temperature conditions. At high temperatures the synthesis gas, which in the case of Brownsville was obtained from methane by partial oxidation, will revert back to methane. That is, low boiling hydrocarbons will be formed at high temperatures. At lower temperatures heavy, waxy hydrocarbons will be formed. The temperature of the reaction, therefore, is a very critical one and it, in turn, depends upon the type of catalyst. For example, with an iron catalyst activated with sodium carbonate, a temperature range between 500° F. and 700° F., preferably between 600° F. and 675° F., should be maintained to produce gasoline hydrocarbons. Almost any of the hydrogenation catalysts may be employed in the process, but, having determined the type of catalyst one wishes to employ and the optimum temperature at which a maximum yield of the desired hydrocarbons is obtained, this temperature must be carefully maintained. A variation from this temperature will result in obtaining yields of undesired products. A deviation downward in temperature produces heavier, waxy-like products. A deviation upward in temperature will produce lighter, normally gaseous hydrocarbons. With a good fluidized bed, temperature variations will be reduced to a narrow range.

Inasmuch as the reaction is so highly exothermic, there

must be continuous and substantially uniform removal of the heat of reaction if the maximum yield of the desired product is to be obtained. For desirable results the temperature should be maintained within a plus or minus 35° F. of the optimum temperature.

The pressure at which the process is carried on is normally not a critical factor. It is frequently sensitive, however, to the type of catalyst. Pressures from atmospheric pressure to fifty atmospheres or more may be employed. High pressures require stronger equipment structurally in order to withstand increased pressure. Greater volumes of gas may be put through, however, for a given size of apparatus when higher pressures are used. Advantageously, pressures from atmospheric to forty atmospheres may be employed. For nickel catalysts, pressures near atmospheric pressure are preferred. For iron catalysts, we may employ pressures in the vicinity of thirty atmospheres.

The success of a synthesis operation depends on the constant and substantially uniform maintenance of temperature. This, in turn, owing to the highly exothermic nature of the reaction, depends upon the constant, adequate and uniform removal of heat from the reaction zone.

Several methods for the removal of heat have been suggested. One is the recirculation of large volumes of unconverted synthesis gas to the reaction zone. Another method is the recirculation of oil fractions to the reaction zone for the removal of heat through vaporization of these oil fractions. Other methods employ the use of various heat exchange mechanisms. Most of the methods of the prior art are inefficient, costly to build or difficult to maintain, or all of these. The difficulty, it will be observed, is introduced by the necessity of carrying out the reaction in the presence of a catalyst and simultaneously removing large quantities of heat. In catalytic cracking of hydrocarbons, the use of a fluidized catalyst bed is a modern technique, which has proved eminently successful. Carbon and coke deposited on a catalyst reduce the catalytic activity. Owing to the fluidized state of the catalyst, the catalyst may flow as a liquid flows from the reaction zone to the regenerator where the coke is removed by burning. This raises the temperature of the catalyst so that when it is charged back to the reactor the heat of the endothermic cracking reaction may be conveniently supplied.

In the synthesis reaction, however, the problem is quite different owing to the highly exothermic nature of the reaction and the huge quantities of heat released. The heat must be removed immediately at a uniform rate if the substantially constant and critical temperature in the reaction bed is to be maintained. In an actual case, a reduction in the temperature, brought about by a combination of excessive heat removal and reduced catalytic activity, has resulted in the formation of heavy, waxy-like hydrocarbons which have completely clogged the catalytic bed to gas flow. On the other hand, if the temperature is allowed to increase, light, normally gaseous hydrocarbons are formed, representing a substantial economic loss in the reduction of the yield of the desired end products.

It has been demonstrated that the heat released in the synthesis reaction can be effectively removed by the application of fluidized catalyst techniques to the Fischer-Tropsch synthesis. Finely divided catalysts can be suspended as a solid phase and the reactant gases as the suspending or gaseous phase. The fluidizing of pulverized solids imparts to them a physical behavior quite similar to that of a liquid. Finely divided solids, fluidized by gas suspension, will flow. A fluidized catalyst bed, therefore, will act very much the same as a liquid. There will be currents, turbulence, vortexing and circulation. Under these conditions, bundles of heat exchange tubes may be imbedded in the fluidized catalyst. A cooling medium may be circulated through the interior of the tubes. The fluidized catalyst of the bed will circulate around the tubes

in heat exchange relation with the coolant within the tubes. In this manner the exothermic heat of reaction can be readily removed. This theory is generally old but has not proven successful in practice on a commercial scale.

I have discovered that in order to carry on this method effectively on a commercial scale, the catalyst must be maintained at a predetermined, substantially uniform fluidity, that the tube spacing must be uniform, and that the gas flow through the catalyst bed must be unimpeded.

It must be remembered a predetermined linear flow of gas through the fluidized catalytic bed must be maintained in order to fluidize the catalyst. If the linear flow is too low, the fluidity of the fluidized catalyst will become too low, and the circulation of the fluidized catalyst will become too sluggish. If the linear velocity of the gases is too high, the fluidized bed will become too light and the catalyst will become entrained in the outgoing products of the reaction. This will reduce the depth of the catalyst bed and progressively make the situation worse until finally a channel for gas flow will be formed and the reactant gases will bypass the bed by canalization through the fluidized bed, resulting in a loss of fluidity. This results in loss of heat removal and failure of the process. Then, too, any variations in the fluidity of the bed will result in a non-uniform distribution of the gases at the bottom level of the fluidized bed. While such non-uniformity of the gas flow ultimately produces the channelling just referred to, it is to be remembered that the non-uniform flow of gases through the bed will itself reduce the efficiency of the synthesis. The gases will follow the path of least resistance and in so doing will by-pass large segments of heat exchange surface which has been provided to maintain temperature control. Then, too, excessive velocities in local areas of the fluidized bed will result in the excessive surging and cavitation of the finely divided catalyst.

It must be further remembered that as the synthesis gas reacts to form high-boiling hydrocarbons, its volume contracts. The gas flow, however, must be such that the desired fluidity of the bed is maintained. This can be accomplished by recycling an excess of one of the reactant gases to insure that even if the reaction is completed, sufficient gas will remain to give a linear gas velocity which will maintain the upper reaches of the bed in fluidized condition. It is to be observed further that the gas flow is from the bottom of the bed upwardly. As the gases rise and contract in volume, owing to the reaction, the head of the bed decreases so that progressively a relatively smaller rate of gas flow is required to maintain fluidity of the bed. From this it will be seen that we can control the fluidity of the bed under a given set of conditions by adjusting the composition of the synthesis gas. This can be done quite simply by recycling unreacted or end gases.

The heat transfer surface is determined in part by the mean temperature difference between the desired reaction temperature and the coolant. An appropriate cooling agent is water, which will be readily converted into steam, which in turn can be used to furnish power or for other purposes in the plant. An appropriate reaction temperature for an iron-type catalyst, we have seen, is 650° F. An appropriate operating pressure for the generation of process steam is 665 pounds per square inch gauge. This corresponds to a boiling temperature of 500° F. It will be seen, therefore, that the temperature differential under these conditions is 150° F. This figure can be employed to determine the area of heat exchange surface.

Another factor affecting the heat exchange surface to be disposed in the bed is the value of the heat transfer co-efficient which may be designated as U. In a fluidized bed, large values of U are obtainable. This represents one great advantage of a fluidized bed over a fixed bed. The value of U is affected by a number of vari-

ables; such as the density of the fluidized catalyst, which may range from twenty pounds to one hundred pounds per cubic foot; the linear gas velocity through the bed; the operating pressure and the gas recycle ration. The linear velocity of the gas flow through the fluidized bed may vary from about three inches to three feet per second.

Reaction time can be expressed very readily as "space velocity." Normal space velocity may be defined as volume in standard cubic feet per hour of fresh feed synthesis gas per cubic foot of reaction volume. The reciprocal of space velocity is reaction time. The space velocity must be sufficiently low to assure a high percentage conversion of synthesis gas to the desired product but yet sufficiently low to minimize the undesired side reactions. The synthesis reaction may be considered as a combination of hydrogenation of carbon monoxide followed by polymerization reactions. If the reaction time is too long, there will be excessive formation of heavy hydrocarbons owing to undue polymerization of lighter desirable hydrocarbons. If the reaction time is too short, then a large quantity of the synthetic gas will be unreacted. The excessive formation of higher-boiling hydrocarbons, furthermore, increases the tendency toward carbon formation and waxy compounds with ensuing loss in catalyst activity and catalyst density.

Space velocities may vary over wide ranges with fluidized catalytic beds. Space velocities, for example, may lie between 250 and 3,000 standard cubic feet per hour of fresh feed synthesis gas per cubic foot of reaction volume, that is, volume of the reaction zone, with a preferred range between 1,000 and 2,500 cubic feet per hour per cubic foot.

When it has been attempted to apply fluidized techniques to the synthesis of hydrocarbons in the prior art, difficulties were encountered. Yields were low, operating times were short and catalytic activity quickly dropped owing to the formation of heavy, waxy-like hydrocarbons accompanied simultaneously with the formation of normally gaseous hydrocarbons. These phenomena indicated local areas of overheating and local areas of overcooling. Attempts to increase throughput to approach design percentages of conversion resulted in mechanical failures.

One object of my invention is to provide a method and apparatus of synthesizing hydrocarbons from synthesis gas which will have a high on-stream operating efficiency or time efficiency.

Another object of my invention is to provide a method and apparatus for synthesizing hydrocarbons by means of fluidized catalytic beds capable of producing high yields of predetermined end products under economical conditions of operation.

A further object of my invention is to provide a method and apparatus for synthesizing hydrocarbons in which large variation in the pressure head of the fluidized bed owing to surging and turbulence are avoided.

Still another object of my invention is to provide a method and apparatus for synthesizing hydrocarbons from synthesis gas which will provide a uniform gas flow without channelling through the bed.

Still another object of my invention is to provide a method and apparatus for reacting synthesis gas in a fluidized bed having imbedded therein heat exchange tubes for removal of net heat of reaction in which I provide a constant free cross-sectional area for gas flow.

Another object of my invention is to provide a method and apparatus for maintaining a uniform temperature level throughout a fluidized bed.

Still another object of my invention is to provide a method and apparatus for the uniform and constant removal of the exothermic heat of reaction in synthesizing hydrocarbons from a mixture of carbon monoxide and hydrogen by maintaining a substantially constant catalyst fluidity.

Other and further objects of my invention will appear from the following description.

In the accompanying drawings, which form part of the instant specification and which are to be read in conjunction therewith and in which like reference numerals are used to indicate like parts in the various views:

Figure 1 is a sectional view of a reactor capable of carrying out the process of my invention and embodying the apparatus of my invention.

Figure 2 is a sectional view drawn on the line 2—2 of Figure 1.

Figure 3 is a sectional view taken along the line 3—3 of Figure 1.

Figure 4 is a fragmentary sectional view, drawn on an enlarged scale, taken along the line 4—4 of Figure 1.

Figure 5 is a fragmentary sectional view similar to Figure 4 showing a modification.

In general my invention contemplates a novel method and apparatus for synthesizing hydrocarbons from a mixture of carbon monoxide and hydrogen, which I may refer to as "synthesis gas," by means of a fluidized catalytic bed in which I flow the reactant gases at a uniform rate throughout the fluidized bed in a manner to avoid "tidal" or "tornado" effects and canalizing, channelling or "rat-holing." In my process I insure not only uniform gas distribution over the entire cross-sectional area of the fluidized bed, but I insure the maintenance of a substantially uniform temperature throughout the bed or beds. The maintenance of uniform temperature throughout the fluidized bed or beds, whose fluidity is maintained, is accomplished by the uniform and constant removal of the exothermic heat of reaction from the bed or beds. I limit the cross-sectional area of a single bed and I may divide the reaction zone into a plurality of beds through which the reactant gas flows in parallel.

It is to be understood, of course, that by a "fluidized bed" I refer to the use of gas-phase suspensions in which a finely divided catalyst is suspended by the reacting synthesis gas or by mixtures of the reactant gas with other gases or an excess of one of the reactant gases. The fluidized bed is of the "fixed" fluidized bed type and the operation is such that there is relatively little entrainment of the catalyst in the reaction products leaving the bed. The operation is such that with iron-type catalyst conversion in the order of ninety percent may be obtained, with selectivities of C_3+ hydrocarbons above about seventy percent. A suitable catalyst is an alkali-promoted reduced iron oxide ground to particle sizes varying between twenty and two hundred microns in diameter. These promoted catalysts of the iron type include the well known "ammonia synthesis catalysts." As is taught in the art, they are prepared by reducing and conditioning iron oxides which, in turn, may be relatively pure oxides or oxides obtained by roasting certain natural magnetite ores. The alkali metal promoters may be sodium or potassium carbonate and are normally used in amounts of 0.1 to 2% by weight. It is to be understood that these catalysts are well known to the art and do not form any part of my invention per se. Advantageously, the bulk of the catalyst can be of a particle size lying between forty-five and one hundred fifty microns in diameter.

In the prior art where fluidized fixed catalyst beds were attempted to be employed, poor yields were obtained and inordinate amounts of lighter than desired and heavier than desired hydrocarbons were formed. I have discovered that this resulted from lack of uniform removal of the heat of the exothermic reaction. This, in turn, was owing in part to the channelling of gas through the fluidized bed and by variations in the fluidity of the catalyst as well as from non-uniform heat exchange. The latter, in turn, resulted largely from the presence of obstructions to gas flow in the fluidized bed with resulting loss of fluidity.

I have discovered that what may be termed as a pre-

determined "viscosity" of the catalytic bed must be maintained. This viscosity depends in part upon the density of the catalyst and its state of sub-division. These necessarily are determined by the nature of the reaction and the necessity of a fine particle size for practicing the fluidized bed technique. Since viscosity is the reciprocal of fluidity, I may use these terms interchangeably when referring to maintenance of predetermined levels. It will be further appreciated that a predetermined linear velocity of the reactant gases through the bed is necessary if we are to maintain a fluid catalytic bed. Similarly, a predetermined space velocity or reaction time has been determined for us by the nature of the reaction, the temperatures involved and the particular type of catalyst we are employing. Having chosen a catalyst, its density is fixed. Particle size follows from the necessity of providing extensive contact area of the catalyst and the requirement of fluidity for the fixed catalytic bed. With a given density and given particle size, the fluidity of the bed will depend on the linear velocity of the gas flow through the bed. I have pointed out, furthermore, that the gas flow through the fluidized bed must be uniform throughout the cross-sectional area of the bed. The space velocity is dictated by the rate of the reaction for the concentration of the reactants, the temperatures, and the particular catalyst.

According to my invention, in my process, the correct relation of linear velocity and space velocity is critical and must be controlled within certain limits for optimum results. I have found that this critical relationship can be expressed as follows:

$$(3) \quad A_f = K(V_1/V_s)^2$$

in which:

V_1 = linear velocity

V_s = actual space velocity

A_f = free cross-sectional area of the bed

K = a constant

It is to be understood, of course, that linear velocity and actual space velocity are to be expressed in consistent units. It is to be further remembered that the velocities are average values allowing for contraction of gas volume during the reaction. Besides this, the velocities are to be determined on the basis of free cross-sectional area without regard to the fact that a catalyst is present.

I have found that the constant K should lie between .0840 and .0021. A preferred range of K is between .0470 and .0084. It will be observed further that A_f represents the free cross-sectional area of the bed. Since it is necessary to dispose heat exchange means, preferably heat exchange tubes, in the bed, a portion of the cross-sectional area of the reaction chamber will be occupied by such heat exchange tubes. The actual reaction chamber, therefore, will have a larger cross-sectional area than the fluidized bed per se. I have found that the heat exchange means may occupy from four per cent to forty percent of the cross-sectional area of the reaction chamber.

Viewed generally, therefore, my process contemplates reacting synthesis gas at a proper temperature and pressure in a fluidized bed of catalyst in which there is imbedded heat exchange means wherein the free cross-sectional area for gaseous flow may be expressed by Equation 3.

Let us look at a specific case. We determine an average linear velocity of the reactant gases of 1.0 foot per second to insure a proper fluidity for the particular catalyst to be used. The reaction time is such that we determine a space velocity of .06 cubic foot of total gas (including recycle gas) per second per cubic foot of reaction zone. The reaction time is necessary to insure a substantially complete conversion of the reactants to obtain high yields. A value of K within the preferred range equal to .0300 is then selected. The resultant free

area is calculated to be 8.4 square feet per reacting unit. Allowing 12½% of the total area as the space occupied by the heat transfer tubes, the total cross-sectional area is 9.6 square feet per reacting unit. Let us assume further that such a reactor can process 5.3% of the total gas it is desired to treat. It will then be necessary to employ a total of nineteen reacting sub-units, which I arrange for parallel gas flow. This can readily be done by sub-dividing the reactor bed into nineteen sub-areas or components.

It will readily be appreciated that a convenient way of removing heat from a reaction zone is by passing a convenient heat exchange medium, such as water, through tubes imbedded in the reaction zone. It will be seen that we must have a free and unimpeded predetermined cross-sectional area for gas flow. The reaction zone, therefore, must be so constructed and arranged as to permit unimpeded flow of gases.

More particularly referring now to Figure 1, we have seen that we must have a predetermined free cross-sectional area if we are to carry on the synthesis process in a continuous manner and to obtain high yields. This is accomplished in the given example by dividing the catalyst bed into components and arranging the components or sub-beds in parallel with each other. Each of the catalyst sub-beds has the correct cross-sectional area. The number of sub-beds will be such as to give a catalyst bed of sufficient area to accommodate the entire volume of synthesis gases to be reacted. The main casing 10 may be constructed of any appropriate material, such as steel, and of a sufficient strength to withstand the super-atmospheric pressure under which the process is to be conducted. The main casing 10 may be lagged with an appropriate heat insulating material 12 which may be glass fiber insulation or the like. The main casing 10 has secured thereto a cover 14 provided with an opening 16 communicating with a pipe 18 from which the products of reaction in vapor form, together with unreacted gases, are removed. The cover 14 is likewise provided with a heat insulating layer 20. If desired, manholes (not shown) as known in the art may be provided to facilitate the installation or removal for repair or replacement of heat exchange tube bundles or other parts. Similarly, connections (not shown) may be provided for replacement and removal of catalyst, either in cover 14 or elsewhere as desired. The bottom of the casing is enclosed by a bottom closure 22 into which synthesis gas is introduced through pipe 24. This synthesis gas may be preheated if desired. The main casing 10 is subdivided into a plurality of subcasings 26. In the example given above, we determined that nineteen subcasings were necessary and accordingly I have shown nineteen subcasings, and pursuant to the example, each of the subcasings will have an area of 9.6 square feet.

A portion of the cross-sectional area of each sub-casing 26 is occupied by heat exchange tubes 28 which extend from lower headers 30 to upper headers 32. The remainder of each subcasing surrounding the tubes 28 is filled with the finely divided catalyst 29. A plurality of headers 30 are connected by a manifold 34 and a plurality of headers 32 are connected by a manifold 36. As can readily be seen by reference to Figure 3, the subcasings 26 may advantageously be aligned in transverse rows within the main casing 10. This enables me readily to connect the headers by straight manifolds. As can be seen by reference to Figure 2, the five rows of subcasings 26 are provided with tubes terminating in upper headers 32 which are arranged in five rows. These rows are then connected by five manifolds 36. The manifolds 36 communicate with an outlet manifold 38. In a similar fashion, as can be seen by reference to Figure 3, the bottom headers 30 are arranged in five rows. Each of the rows are then connected by a respective manifold 34. The manifolds 34 communicate with a main inlet manifold 40. Water may be introduced to the inlet manifold through a pipe 42 and flow into the inlet

manifold 40 and thence through the bottom manifolds 34 to the headers 30 with which the heat exchange tubes 28 connect. The other ends of the heat exchange tubes communicate with the outlet or steam headers 32 which are connected by sub-manifolds 36. These are, in turn, connected by the outlet steam manifold 38.

The cross-sectional area around the tubes and within the subcasings 26 is the free cross-sectional area of A_f which we obtained, as pointed out above from Equation 3. It is to be understood, of course, that the tubes 28 are evenly spaced within the subcasings 26 so that there will be a substantially uniform rate of heat exchange with the fluid catalyst bed. A bottom baffle 50 seals off the spaces around the outside of the subcasings 26 for the gas inlet area and prevents the reactant gases from short-circuiting or by-passing the individual reaction zones. It will be observed that the baffle 50 constrains the incoming reaction gases to flow upwardly and parallel through the sub-divided composite reaction zone. Each of the sub-reaction zones, that is, the area within the subcasings 26 not occupied by the heat exchange tubes 28, is filled with an appropriate synthesis catalyst 29 in finely divided form. A screen 54 or perforated plate or the like carried by grid 53 supports a plurality of glass or ceramic marbles, Raschig rings or like inert intersticed packing 56. The inlet manifolds 34 and the headers 30 are disposed in the gas inlet space and may be surrounded by the inert packing 56. The interstices between the packing are such as to permit a substantially free flow of the incoming reactant gases to the reaction zone. The glass or ceramic marbles, in turn, however, may support the finely divided catalyst within the reaction zone. If desired, a perforated or apertured plate (not shown) may be interposed between the packing and the catalyst beds. The passage of the incoming gases from the packing material into the reaction zone will fluidize the catalyst. The intersticed packing below the fluidized beds permits an equalization of pressure across the bottom of the fluidized beds. In this manner the reactant gases will be distributed over the entire cross-sectional area of the fluidized bed in an even and uniform manner. When a plurality of fluidized beds in parallel within a large reaction chamber are employed to form the reaction zone, as shown in Figure 1, the intersticed packing permits the reactant gases to be introduced at the same pressure to all of the fluidized beds comprising the composite reaction zone. This construction provides one mode of carrying out my process and provides an uninterrupted and unobstructed free area for gas flow within the fluidized bed or beds.

It will also be observed that the outlet or steam headers 32 are likewise disposed outside of the reaction zone in the space 58 in the main casing 10 above the subcasings 26. A plate 57, similar to baffle plate 50, seals off the space between casings 26 and space 58.

It will be remembered that a fluidized bed of finely divided catalyst behaves physically as a liquid. It will also be recalled that for the parallel flow the linear velocity for each of the parallel fluidized beds should be substantially the same if uniform results are to be obtained from each of the sub-reactors. It is important, therefore, that the level of the fluidized catalyst in each of the subreactors be substantially the same. To accomplish this, I contemplate interconnecting each of the sub-reactor casings within the main housing by ducts or the like so that the level of the fluidized catalyst in each of the hub-reactors will be the same. The cross-connecting ducts in the lower ends of casing 26 which permit fluidized catalysts to flow between adjacent casings 26 can readily be seen in Figure 3.

It will be remembered that as the reaction proceeds, the volume of the reactants contracts since they are being converted from synthesis gas to normally liquid hydrocarbons. It is necessary to maintain a minimum linear velocity of gas flow in order to maintain the bed in

fluidized condition. As pointed out above, a linear velocity from about three inches per second to three feet per second may be employed. It is usually preferred to use a linear velocity of from about six inches to eighteen inches per second. This linear velocity may be maintained by recycling end gas to the fresh gas feed. In practice, recycle ratios between one and two volumes of end gas to one volume of fresh gas may be employed. The handling of excessive recycle gas is generally undesirable and increases the cost of operation. With efficient operation, lower recycle ratios are desirable.

At low recycle ratios the percentage of contraction of the total gas is less than at high ratios. Theoretically this means a lower linear velocity at the upper level of the bed. Referring now to Figure 5, baffles can be advantageous to fluidity by minimizing distortion in gas flow caused by localized excessive contractions. This is accomplished by installing vertical baffles 60 across the inner or subcasings 26.

Let us now consider the application of my invention to a commercial plant, say for example, the Brownsville, Texas, plant of Carthage Hydrocol, which has failed to attain its commercial economic and designed potentialities. The plant was designed to produce 7,000 barrels per day of a liquid product plus 300,000 pounds per day of oxygenated hydrocarbons. We know, of course, that it has never achieved about ten percent of its designed capacity in practice. Two reactors were employed at Brownsville, having a reaction volume of about 5,500 cubic feet, thus giving each of the reactors a volume of 2,750 cubic feet. The reactor diameter was 16.5 feet. This corresponds to a normal space velocity of about 1,800 cubic feet per hour of fresh feed synthesis gas per cubic foot. With a catalyst whose operating fluidized bed density was eighty pounds per cubic foot, the total weight of the catalyst came to 440,000 pounds or 220,000 pounds per reactor. The net exothermic heat of reaction to be removed is approximately 360 million B. t. u.'s per hour or 180 million B. t. u.'s per hour per reactor. The operating pressure employed was thirty atmospheres.

Let us assume a design recycle ratio of 1.5 and let us assume that owing to an exceptionally high conversion, in the order of ninety percent, that there will be an estimated contraction of the fresh feed synthesis gas volume of fifty percent. Under these circumstances, the actual average quantity of gas under reaction conditions is about 220 cubic feet per second per reactor. This corresponds to a space velocity of about .080 reciprocal seconds. In a sixteen and one-half foot diameter vessel, having ninety-two percent of the total area as free area, the superficial average linear velocity of the gas would be 1.13 feet per second. Applying my equation for A_f to these figures, we obtain a K for Brownsville of .975. This value of K, it will be seen, is over eleven times the maximum permissible value of K in accordance with my invention.

It will be understood in the light of my invention why the Brownsville plant of Carthage Hydrocol did not achieve more than approximately an average ten percent of its designed output. The ratio of eleven to one immediately indicates that the cross-sectional areas of the two large reactors should be sub-divided or segmented into twelve or more sub-reactors or sub-areas. Using the nineteen units given in the example above, we can readily subdivide a sixteen and one-half foot diameter reaction vessel into nineteen units, each having an area of 8.55 square feet. Each of these sub-reactor units can be provided with its own heat exchange bundle in accordance with the structure shown in Figure 1. The resultant value of K in such an arrangement would be .022 which is within the optimum range of K.

In an assembly of multiple cell reactors, in accordance with my invention I am enabled readily to provide for

uniform gas distribution and maintain uniform high heat densities for removal of the net heat of reaction. These heat densities range from about 5,000 to 60,000 B. t. u.'s per hour per square foot of heat exchange surface.

In the operation of my process, a synthesis gas can be generated from a carboniferous material by partial oxidation by any appropriate process. The reactor may be brought to temperature by preheating the gases fed to the reactor until the desired reaction temperature of between 500° F. and 700° F. is reached. Alternately, the reactor bed may be brought to temperature by passing a heating medium instead of a cooling medium through the heat exchange tubes. A pressure between ten atmospheres and fifty atmospheres may be employed. This, as pointed out above, will vary depending upon the catalyst. An alkali metal promoted iron catalyst may advantageously be employed. The catalyst should be ground so that the major portion of it is in particle sizes having diameters between forty and one hundred fifty microns. The linear velocity of the reactant gases should lie between three inches and three linear feet per second. A recycle ratio between one volume and two and one-half volumes of end gas per volume of fresh feed gas may be employed. Under optimum conditions, smaller recycle ratios may be achieved. The contact time should be such that the normal space velocity falls between 250 and 3,000 standard cubic feet per hour of fresh feed synthesis gas per cubic foot of catalyst volume. This space velocity is a reciprocal time factor. In order to convert this factor into actual reaction time, the standard gas volume must be converted to actual volume by correcting for temperature, pressure and compressibility factors. Furthermore, the gas volume is the total average volume, allowing for contraction and including recycle gas. I prefer to use actual space velocity based on total average gas volume, corrected for temperature, pressure and compressibility. In applying linear velocity and space velocity to calculate the necessary free cross-sectional area of the fluidized catalytic bed in accordance with my invention, it is to be understood, of course, that both linear velocity and space velocity must be in consistent units, that is, if linear velocity is expressed in feet per second, then space velocity must be expressed in reciprocal seconds rather than reciprocal hours.

It will be observed that owing to the interstices which exist between the ceramic marbles or Raschig rings that there will be a lower pressure drop per linear foot of vertical flow in the region of the pressure equalizing zone below the catalyst bed than there will be through the fluidized catalytic bed. This difference in Δp per foot of vertical flow enables cross flow to occur so that substantially uniform gas flow will occur in all of the parallel reactors comprising the composite reaction zone. The ratio of Δp through the intersticed, inert packing zone or pressure equalizing zone with respect to the Δp per foot of vertical flow through the fluidized bed should be less than 0.9 or greater than 1.11 to insure cross flow. A greater pressure drop through the gas distribution zone can easily be achieved by inserting a small mesh screen or perforated plate (not shown), such as screen 54, on top of the packing at the interface and the bottom of the fluidized bed or beds. The difference in Δp enables a cross flow readily to take place.

It will be seen that I have accomplished the objects of my invention. I have provided a method and apparatus of synthesizing hydrocarbons from synthesis gas which will have a high on-stream operating efficiency. I have provided a method and apparatus for synthesizing hydrocarbons employing a fluidized bed of finely divided catalyst in which surging and turbulence of the bed are avoided by carefully controlling the free cross-sectional area of the bed. I have provided a method for synthesizing hydrocarbons from synthesis gas in which I avoid vortexing or channelling of the reactant gases through

the fluidized bed by controlling the free cross-sectional area of the fluidized bed for gas flow.

By means of my method and apparatus, I am enabled to maintain a predetermined, substantially uniform fluidity and uniform temperature throughout the fluidized bed whereby the exothermic heat of reaction is removed at a constant rate. I have provided a method of synthesizing hydrocarbons from synthesis gas in a fluidized catalytic bed in which the heat of reaction is removed by heat exchange means imbedded in the fluid bed in which the cross-sectional area for gas flow is predetermined and constant. My novel method contemplates dividing the total volume of gas to be reacted into a plurality of confined parallel streams within a single reaction vessel and directing each of the parallel streams simultaneously through fluidized beds of catalytic material while constantly removing the exothermic heat of reaction at a predetermined uniform rate. I have provided a novel apparatus for carrying out the process of my invention in which I manifold in parallel a plurality of fluidized beds of catalytic material in a single housing. Each of the beds has positioned therein heat exchange tubes extending co-axially of the fluidized beds. I have provided novel apparatus for conducting synthesis operations employing a fixed bed of fluidized catalyst in which I use intersticed inert packing or the like below the catalyst bed in which heat exchange means are positioned within the catalyst bed. The packing permits equalization of pressure of and the distribution of the reactants even though headers and other obstructions to flow are present. The obstructions are present on account of the physical necessity of having heat exchange appurtenances. The use of the intersticed packing, which may take the form of an apertured plate (not shown) just below the catalytic bed, permits an unobstructed, constant free area for reactant flow through the fluidized bed owing to the distribution of the reactants uniformly over the bottom level of the catalytic bed.

The correct A_f or free cross-sectional area for a given catalyst is really determinative of the fluidity of the catalytic bed. If the A_f is too large, this bed will be too viscous and there will be tidal or tornado effects, canalizing or channelling, uneven heat transfer with resulting low yield and poor operability. Conversely, if the A_f is too small, the viscosity of the fluidized catalyst becomes so small that there is serious danger that too much of the finely divided catalyst will become entrained and carried out of the bed. Catalysts having higher densities permit the employment of higher linear velocities. There must be a co-relation of the free cross-sectional area of the catalytic bed with the linear velocity and space velocity. The uniform removal of the heat of reaction, the provision of a constant free cross-sectional area for reactant flow, within the confined fluidized bed, and the proper co-relation of the linear velocity and space velocity is readily accomplished by means of my invention.

It will be understood that certain features and subcombinations are of utility and may be employed without reference to other features and subcombinations. This is contemplated by and is within the scope of my claims. It is further obvious that various changes may be made in details within the scope of my claims without departing from the spirit of my invention. It is therefore to be understood that my invention is not to be limited to the specific details shown and described.

Having thus described my invention, what I claim is:
1. A method of synthesizing hydrocarbons from a synthesis gas comprising a mixture of carbon monoxide and hydrogen in the presence of a finely divided catalyst including the steps of passing the synthesis gas upwardly through a confined bed of finely divided catalyst at a linear velocity sufficient to fluidize the same, continuously removing the exothermic heat of reaction by passing a heat exchange medium in a confined stream in heat

exchange relation with the fluidized catalyst, maintaining a predetermined fluidity of the fluidized catalyst by providing a free cross-sectional area of the confined bed for gas flow in accordance with the expression

$$A_f = K(V_1/V_s)^2$$

in which: V_1 is linear velocity of the synthesis gas, V_s is actual space velocity of the synthesis gas, A_f is free cross-sectional area of the confined fluidized catalyst bed and K is a constant lying between .0840 and .0021.

2. A method as in claim 1 in which said free cross-sectional area of the confined fluidized bed lies between 60% and 96% of the total cross-sectional area of the confined bed.

3. A method as in claim 1 in which the linear velocity of the synthesis gas lies between three inches per second and three feet per second.

4. A method as in claim 1 in which the normal space velocity of the synthesis gas lies between 250 cubic feet per hour of fresh feed synthesis gas per cubic foot of reaction volume and 3,000 cubic feet per hour per cubic foot.

5. A method as in claim 1 in which K lies between .0470 and .0084.

6. A method of synthesizing hydrocarbons from a synthesis gas comprising a mixture of carbon monoxide and hydrogen in the presence of a finely divided catalyst including the steps of dividing the synthesis gas into a plurality of confined streams, passing each of the streams of synthesis gas upwardly in parallel through confined beds of finely divided catalyst at a sufficient linear velocity to fluidize the catalyst, continuously removing the exothermic heat of reaction by passing a heat exchange medium in a confined stream in heat exchange relation with the fluidized catalyst in each of the fluidized beds and maintaining the level of the fluidized catalyst in each of the beds substantially the same.

7. A method as in claim 6 including the step of maintaining a predetermined fluidity of the fluidized catalyst in each of the confined beds by providing a free cross-sectional area of each of the confined beds for gas flow in accordance with the expression

$$A_f = K(V_1/V_s)^2$$

in which: V_1 is linear velocity of the synthesis gas, V_s is actual space velocity of the synthesis gas, A_f is free cross-sectional area of the confined fluidized catalyst bed and K is a constant lying between .0840 and .0021.

8. A method as in claim 6 including the step of maintaining a predetermined fluidity of the fluidized catalyst in each of the confined beds by providing a free cross-sectional area of each of the confined beds for gas flow in accordance with the expression.

$$A_f = K(V_1/V_s)^2$$

in which: V_1 is linear velocity of the synthesis gas, V_s is actual space velocity of the synthesis gas, A_f is free cross-sectional area of the confined fluidized catalyst bed and K is a constant lying between .0470 and .0084.

9. Apparatus of character described including in combination a housing, a heat exchange tube positioned within said housing and extending co-axially therewith, finely divided material positioned within said housing and surrounding said heat exchange tube, intersticed inert packing, means for supporting said inert packing within said housing below said material, a header embedded in said housing above said material, said heat exchange tube extending between said headers and communicating therewith, means for introducing a gas into said housing adjacent said inert packing, means for introducing a heat exchange medium to one of said headers, means for removing the heat exchange medium from the other of said headers and means for withdrawing the products of reaction from said housing.

10. Apparatus for the catalytic reaction of gases in a fluidized catalyst bed including in combination a housing, a casing positioned within said housing, a heat exchange tube positioned in said casing and extending co-axially therewith, finely divided catalyst positioned within said casing and surrounding said heat exchange tube, intersticed inert packing, means for supporting said inert packing within said housing below said casing, a header embedded in said inert packing, a second header positioned within said housing above said casing, said heat exchange tube extending between said headers and communicating therewith, means for introducing a gas into said housing adjacent said inert packing, means for introducing a heat exchange medium to one of said headers, means for removing the heat exchange medium from the other of said headers and means for withdrawing the products of reaction from said housing.

11. Apparatus for the catalytic reaction of gases in fluidized catalyst beds including in combination a housing, a plurality of substantially vertically extending casings positioned in said housing, a heat exchange tube positioned in each of said casings and extending substantially co-axially therewith, finely divided catalyst positioned within each of said casings and surrounding respective heat exchange tubes, intersticed inert packing, means for supporting said inert packing within said housing below said casings, a plurality of headers positioned adjacent said inert packing, a corresponding second plurality of headers positioned within said housing above said casings, respective heat exchange tubes extending between respective headers and communicating therewith, means for introducing a gas into said housing adjacent said inert packing, means for introducing a heat exchange medium to one plurality of said headers, means for removing the heat exchange medium from the other plurality of said headers and means for withdrawing the products of reaction from said housing.

12. Apparatus as in claim 11 including in combination baffling means positioned within the housing and extending between the casings whereby to constrain gas from said inert packing to flow through the casings in contact with the finely divided catalyst.

13. Apparatus for the catalytic reaction of gases in fluidized catalyst beds including in combination a housing, a plurality of casings positioned within said housing, the height of said casings being less than the height of said housing whereby to provide a gas inlet space within the housing below said casings and a gas outlet space within the housing above said casings, gas distributing means positioned within said housing below said casings, finely divided catalyst positioned within said casings, means for supporting the catalyst within said casings, a plurality of headers positioned within said housing below said casings, a corresponding plurality of headers positioned within said housing above said casings, a plurality of respective bundles of heat exchange tubes extending between respective headers, means for introducing reactant gases into the housing below said gas distributing means, means for withdrawing the products of reaction from housing above said casings, means for introducing a heat exchange medium to one plurality of said headers and means for withdrawing a heat exchange medium from the other plurality of said headers.

14. Apparatus as in claim 13 in which said gas distributing means comprises intersticed inert packing.

15. Apparatus as in claim 13 in which said gas distributing means comprises intersticed inert packing surrounding said lower headers.

16. Apparatus as in claim 13 including in combination baffling means positioned within the housing and between the casings whereby to constrain gas from said gas distributing means to flow through the casings in contact with the finely divided catalyst.

17. Apparatus as in claim 13 in which each of said casings is provided with vertically extending baffles posi-

15

tioned within the casing and extending between heat exchange tubes.

18. Apparatus for the catalytic reaction of gases in fluidized catalyst beds including in combination a housing, a plurality of substantially vertically extending casings positioned in said housing, a heat exchange tube positioned in each of said casings and extending substantially coaxially therewith, finely divided catalyst positioned within each of said casings and surrounding respective heat exchange tubes, intersticed inert packing, means for supporting said inert packing within said housing below said casings, said heat exchange tubes extending downwardly into said inert packing, means for passing a heat exchange medium through said heat exchange tubes, means for introducing a gas into said housing adjacent said inert packing and means for withdrawing the products of reaction from said housing.

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