PATENT SPECIFICATION

630,950

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COMPLETE SPECIFICATION

Hydrocarbon Synthesis Process

We, Standard Oil Development Company, a corporation duly organized and existing under the laws of the State of Delaware, United States of America, having an office at Elizabeth, New Jersey, United States of America, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

The present invention is concerned with an improved hydrocarbon synthesis process (Fischer Synthesis). The invention is more particularly concerned with a hydrocarbon synthesis process wherein finely subdivided solid particles are employed as a catalyst in a fluidized state. The invention is specifically directed to a process in which the rate of carbon formation and the carbon concentration of the catalyst comprising iron nickel or cobalt is controlled by the addition of steam to the total feed gases entering the reaction zone. Simultaneously and concurrently therewith, the selectivity and yield of the total products is controlled by continuously treating a portion of the catalyst with hydrogen or a gas containing hydrogen and returning the revivified catalyst to the reaction zone.

It is well known in the art to conduct hydrocarbon synthesis reactions by contacting hydrogen and oxides of carbon with catalysts under various temperature and pressure conditions. It has also been proposed to add steam to the feed gases, in order to reduce the partial pressure of the CO and H_2. The catalyst employed is usually iron, cobalt or nickel. The catalysts are utilized either alone or are employed in conjunction with carriers, such as kieselguhr, diatomaceous earth, synthetic gels, silica and alumina. Promoters, such as oxides of chromium, zinc, aluminium, magnesium and the alkali and rare earth metals may be used. These catalysts are employed in either fixed bed or fluid catalyst operations. In the fluid operations the catalyst comprises fine particles having a particle size in the range from 0 to 200 microns and higher. These particles are suspended in a fluid ebullient state by means of upflowing gases, the velocity of which is in the range of from about 0.1 to 5 feet per second and higher.

The temperatures employed in the synthesis reaction vary widely, as for example, in the range from about 300° F. to about 800° F. and are generally in the range from about 350° F. to about 750° F. The pressures likewise, vary considerably and are a function of other operating conditions, such as catalyst employed, activity of the catalyst, character of the feed gases and the temperatures utilized. Pressures in the range from about 1 to 100 and higher atmospheres have been suggested. The character of the feed gases introduced into the synthesis reaction zone depends somewhat on the particular temperatures and pressures, and upon the catalyst employed. For example, when employing an iron catalyst, the mol ratio of hydrogen to carbon monoxide may be from one mol to four mols of hydrogen per mol of carbon monoxide. On the other hand, when a cobalt catalyst is utilized, it is usually the practice to use two mols of hydrogen per mol of carbon monoxide.

In these reactions wherein the feed gases comprising carbon monoxide and hydrogen are contacted with an iron catalyst for the production of hydrocarbons containing more than one carbon atom in the molecule, one problem encountered is that the carbon concentration on the catalyst progressively increases. As the carbon concentration of the catalyst increases, the particles disintegrate and tend to be removed from the reaction zone with the product gases.

A process has now been discovered by which it is possible to control the rate of carbon formation and at the same time to maintain the selectivity of the catalyst at a relatively high efficiency. In accordance with this process, carbon formation that normally occurs during a hydrocarbon synthesis process is minimized by adding steam to the total feed to the reaction zone. Simultaneously the deactivating effect of the steam and resulting loss in catalyst activity is controlled by continuously treating a portion of the catalyst in a separate vessel with hydrogen or with a stream comprising hydrogen. The revivified catalyst is returned to the synthesis reaction zone.

The process of this invention may be more readily understood by referring to the accompanying drawings illustrating embodiments of the same. Figure 1 illustrates an embodiment wherein two separate zones are utilized. Figure 2 illustrates an adaptation of this invention in which two zones are utilized, except that each zone functions during a cycle as the hydrocarbon synthesis reaction zone and as the hydrogenation zone. Figure 3 illustrates a modification of this process wherein a single combination hydrocarbon synthesis reaction zone and a hydration zone is utilized.

Referring specifically to Figure 1, feed gases comprising carbon monoxide and hydrogen are introduced into hydrocarbon synthesis reaction zone (10) by means of line (1). Steam is introduced with fresh feed gases by means of line (2). For the purpose of illustration, it is assumed that reaction zone (10) contains a fluidized catalyst comprising iron. The catalyst is maintained in a fluid condition by means of the upflowing suspending gases. Suitable and known means are provided within reaction zone (10) to remove entrained catalyst particles from the reaction gases as they are removed from zone (10) by means of line (3). Temperature and pressure conditions in reaction zone (10) are adapted to secure the desired synthesis reaction. In accordance with this invention, catalyst particles in a fluidized condition are withdrawn from the bottom of zone (10) by means of line (5) and these particles are introduced into hydrogenation zone (20) through line (9). Prior to introducing the catalyst particles into zone (20), hydrogen is introduced by means of line (6) into the catalyst stream. Suitable compressors and control valves and other necessary means are provided.

The catalyst in zone (20) is subjected to conditions adapted to hydrogenate the same. Temperatures, for example, may vary in the range from about 400° F. to 1100° F., preferably 550° to 1100° F. while the pressures may vary between atmospheric and 750 pounds per square inch preferably 100 to 750 pounds per square inch. After suitable time of contact, the hydrogenated catalyst is withdrawn from zone (20) by means of line (7) and reintroduced into zone (10) along with the fresh feed in line (4). Unused hydrogen is removed overhead from zone (20) by means of line (8). These gases may be combined with gases removed from the synthesis zone (10) but are preferably passed to a separation zone (30) by means of line (31). Uncondensed gases are removed overhead from separation zone (30) by means of line (32) and may be withdrawn from the system. However, it is preferred to recycle these gases to zone (20) by means of line (33). Hydrogenated condensate separated in zone (30) may be withdrawn from the system by means of line (34) and handled in any manner desirable.

The reaction products removed overhead from synthesis reaction zone (10) by means of line (3) are preferably cooled in cooling zone (21) and introduced into separation zone (40). Uncondensed gases are removed overhead from zone (40) and may be removed from the system by means of line (41). A portion of these gases, however, is preferably recycled to zone (10) by means of lines (42) and (4). Under certain conditions, a portion of these gases may be recycled to a hydrogenation zone (20) by means of lines (42) and (9). The liquid product in separation zone (40) is removed from the system by means of line (43) and may be handled and further processed in any manner desirable.

Referring specifically to Figure 2, fresh feed gases and steam are introduced into the system by means of lines (51) and (52). Reaction zones (60) and (70) function alternately as the hydrocarbon synthesis reaction zone and as the hydrogenation zone. When reaction zone (60) is functioning as a hydrocarbon synthesis reaction zone, zone (70) is functioning as the hydrogenation zone. For the purpose of description it is assumed that zone (60) is functioning as the hydrocarbon synthesis reaction zone. The fresh feed gases comprising carbon monoxide and hydrogen are introduced into the bottom of zone (60) by means of line (53). These gases flow upwardly through a bed of catalyst which may be either fixed or fluidized within zone (60). For the purpose of description it is assumed that the catalyst comprises iron and that the temperature and pressure conditions in zone (60) are adapted to secure the desired hydrocarbon synthesis reaction. After a sufficient time of contact, synthesis products are removed from zone (60) by means of line (54) and passed to a product recovery system. During this cycle, hydrogen is introduced into the bottom of zone (70) by means of lines (55) and (56). Temperature and pressure conditions in hydrogenation zone (70) are adapted to secure the desired hydrogenation of the catalyst. The gases are removed from zone (70) by means of line (57) and are preferably recycled to the bottom of zone (70).

When the carbon concentration of the catalyst in zone (60) has reached a predetermined critical amount, the fresh feed synthesis gases are introduced into the bottom of zone (70) by means of line (71). The synthesis product is removed overhead from zone (70) by means of line (72) and passed to the product recovery system. Hydrogen is introduced into the bottom of zone (60) by means of lines (55) and (73). The reaction gases from zone (60) are removed by means of line (74) and are preferably recycled as heretofore described. Suitable valves and other control means are provided for securing this type of cycle operation.

Referring specifically to Figure 3, synthesis gases comprising carbon monoxide and hydrogen are introduced into the system by means of line (81); steam is introduced through line (82). These gases are introduced into an intermediate point of reaction zone (100). The gases flow upwardly through reaction zone (100) and contact a fluidized bed of a catalyst comprising iron. Synthesis products are removed overhead from zone (100) by means of line (83) and passed to a product recovery system. Hydrogen is introduced into the bottom of zone (100 by means of line (84) The temperature in the hydrogenation or bottom portion of zone (100) is adapted to secure the desired hydrogenation of the catalyst. On the other hand, the temperature in the upper synthesis portion of zone (100) is adapted to secure the desired hydrocarbon synthesis reaction. Hydrogen is introduced into the system by means of line (85) while recycle gases from the product recovery system may be introduced by means of line (86).

This invention generally comprises employing steam in a hydrocarbon synthesis reaction with the fresh feed gases and simultaneously hydrogenating a portion of the catalyst. The invention is particularly applicable to a synthesis reaction utilizing iron. By operating in this manner, the rate of carbon deposition on the catalyst is controlled while, at the same time, the selectivity of the catalyst is maintained at a relatively high efficiency.

This invention may be employed in hydrocarbon synthesis reactions wherein the temperature varies in the range from about 500° to about 750° F., and wherein the pressures are in the ranges from atmospheric to 750 pounds per square inch. The amount of hydrogen and carbon monoxide employed per pound of catalyst may vary in the range from about 3 to 200, measured in cubic feet per hour at standard conditions. The recycle to fresh feed may vary from 0 to 10 and the mols of hydrogen employed per mol of carbon monoxide may range from 0.5 to 2.0 and above. Varying amounts of steam may likewise be employed but the percentage is preferably in the range from about 1 to 20 mol per cent. of steam in the total feed.

The hydrogenation conditions used may likewise vary appreciably. The temperature may range from about 400° F. to 1100° F. and the pressure range from atmospheric to 750 pounds per square inch. The amount of hydrogen measured in cubic feet per hour per pound of catalyst may vary from about 3 to 200. The amount of hydrogen in the treating stream is preferably in the range from 10 to 100 per cent. The residence time also may vary appreciably.

The process of this invention may be more readily understood by the following examples illustrating the same.

EXAMPLE 1.

Feed gases comprising carbon monoxide and hydrogen were treated with an iron catalyst at a temperature of 650° F. and at 400 pounds pressure. The results of the various operations were as follows:

Operation	Carbon*	Mol. % Water	Selectivity C_4**
A	8	4.0	—
B	6	4.3	133
C	6	3.9	158
D	46	0.1	—
E	10	1.7	—

From these operations it is apparent that the addition of water with the feed gases appreciably decreased the rate of carbon formation.

EXAMPLE 2.

Operations similar to those described in Example 1 were conducted with the following results:

Operation	Carbon*	Mol. % Water	Selectivity C_4**
F	2.8	4.1	161
G	6.0	3.0	
H	36.0	1.6	189

Example 3.

Additional runs were made under the conditions specified in Example 1 with the following results:

Operation	Carbon*	Mol. % Water	Selectivity C_4**
I	78	0.2	199
J	23	0.7	214
K	26	0.7	

* Pounds of carbon per 100 pounds of iron per 100 hours.

** The cubic centimeters of hydrocarbons having four carbon atoms in the molecule and higher boiling constituents produced per cubic meter of hydrogen and carbon monoxide consumed.

From the above data as shown in Examples 1, 2 and 3 it is apparent that although the addition of water materially decreases the rate of carbon formation, the addition of water impairs the selectivity of the catalyst

Example 4.

Two operations were made under the conditions and with the results as listed in the following table:

Operation	L	M
Temperature °F.	655	651
Pressure lbs./sq. in.	235	398
Recycle/fresh feed	1.9	1.8
Total Feed Composition		
H_2	43.8	35.9
CO	14.8	13.6
CO_2	23.1	30.6
H_2O	0.2	3.1
H_2+CO Conversion	85	93
Yields		
C_3+**	236	245
C_4+**	199	203
Water Soluble Oxygenated Compounds	23	42
Carbon Formation Rate, lbs. Carbon per 100 lbs. Iron per 100 Hours	78	6

** The cubic centimeters of hydrocarbons having three or four carbon atoms in the molecule and higher boiling constituents produced per cubic meter of hydrogen and carbon monoxide consumed.

Substantially the same ultimate yields of hydrocarbons are obtained during both operations. Products of water soluble oxygenated compounds were higher in the operation in which water was added.

Example 5.

Two operations were conducted employing the conditions and with results as shown in the table.

Operation	N	O
Temperature, °F.	651	653
Pressure, Psig.	407	400
(1) Feed Rate	13.6	17.7
Recycle/Fresh Feed	5.0	4.3
H_2CO in Fresh Feed	2.07	2.11
Mol. % Water in Total Feed	5.0	4.0
H_2+CO Conversion, %	75	90
Yields, cc/m^3 of H_2+CO Conc.		
C_3+**	201	226
C_4+**	135	178
Carbon Formation Rate, lbs. Carbon per 100 lbs. Iron per 100 hours	6	6

(1) Standard Cubic Feet per Hour of H_2+CO fed per lb. of CO free catalyst.

** The cubic centimeters of hydrocarbons having three or four carbon atoms in the molecule and higher boiling constituents produced per cubic meter of hydrogen and carbon monoxide consumed.

In operation "O" the catalyst was hydrogenated in accordance with this invention, while in operation "N" the catalyst was not hydrogenated. It is readily apparent that although the addition of water controlled the rate of carbon formation in both operations, it is necessary to hydrogate in accordance with this invention if the selectivity of the catalyst is to be maintained at a high efficiency.

In Specification No. 618,068 which, although not public at the date of the present Application, is of earlier date, there is claimed a Fischer synthesis process using a fluidised catalyst, wherein a higher weight ratio of catalyst to reactant gas than can be obtained with a reactant gas alone is maintained by supplementing the reactant gas with a sufficient quantity of steam, and separating the said steam from the product by condensation.

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

1. An improved Fischer synthesis, employing an iron, nickel or cobalt catalyst, wherein the feed gases are diluted with steam, and a portion of the catalyst is continuously led from the synthesis zone to a hydrogenation zone in which it is reduced in the presence of hydrogen and returned to the synthesis zone.

2. A process according to Claim 1, wherein the hydrogenation zone is an extension of the synthesis zone, and the catalyst can flow freely between the two zones.

3. A process according to Claim 1, wherein the hydrogenation and synthesis zones are separate and catalyst is continuously passed from the synthesis to the hydrogenation zone and *vice versa*.

4. A process according to any of the preceding claims, wherein the catalyst is maintained in a fluidised state.

5. A process according to Claim 2, wherein the catalyst is maintained as a dense fluidised bed in an elongated vertical reaction zone, the upper part of which serves as the synthesis zone and the lower part as the hydrogenation zone.

6. A process according to Claim 5, wherein the hydrogenation zone is of smaller cross-sectional area and capacity than the synthesis zone.

7. A process according to any of the preceding claims, wherein the temperature in the hydrogenation zone is from 400° to 1100° F., preferably 550° to 1100° F., and the pressure from atmospheric to 750 lbs. per sq. in., preferably 100 to 750 lbs. per sq. in.

8. A process according to any of the preceding claims, in which the amount of steam used is from 1 to 20 mol. per cent. of the total feed.

Dated this 12th day of August, 1947.

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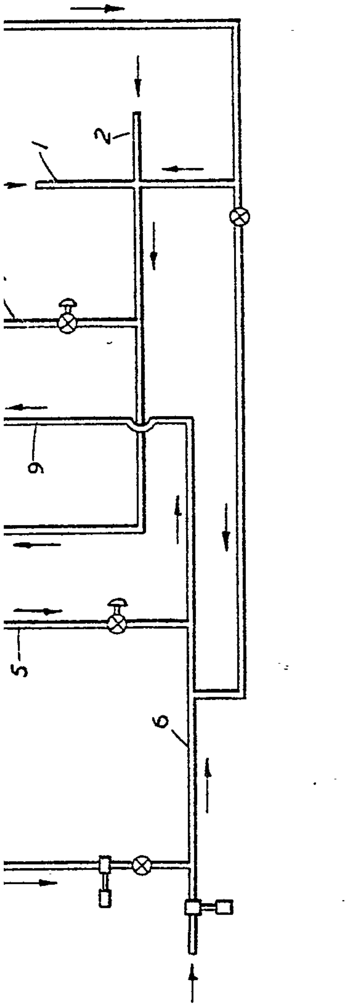

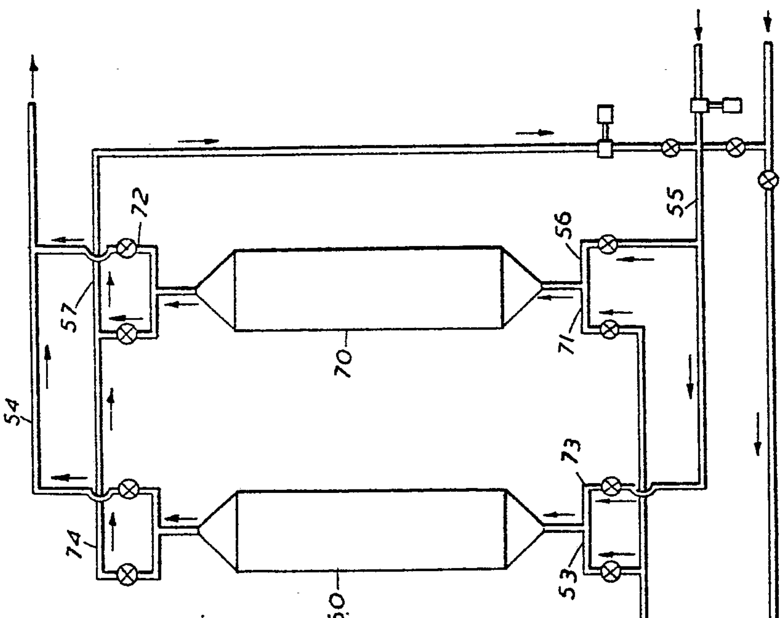

FIG. 2.

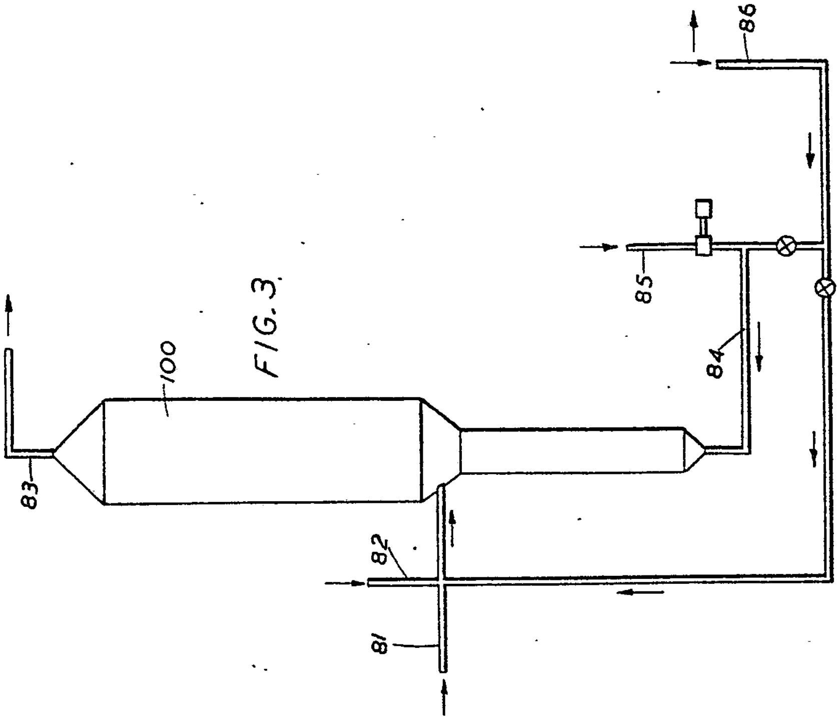

FIG. 3.

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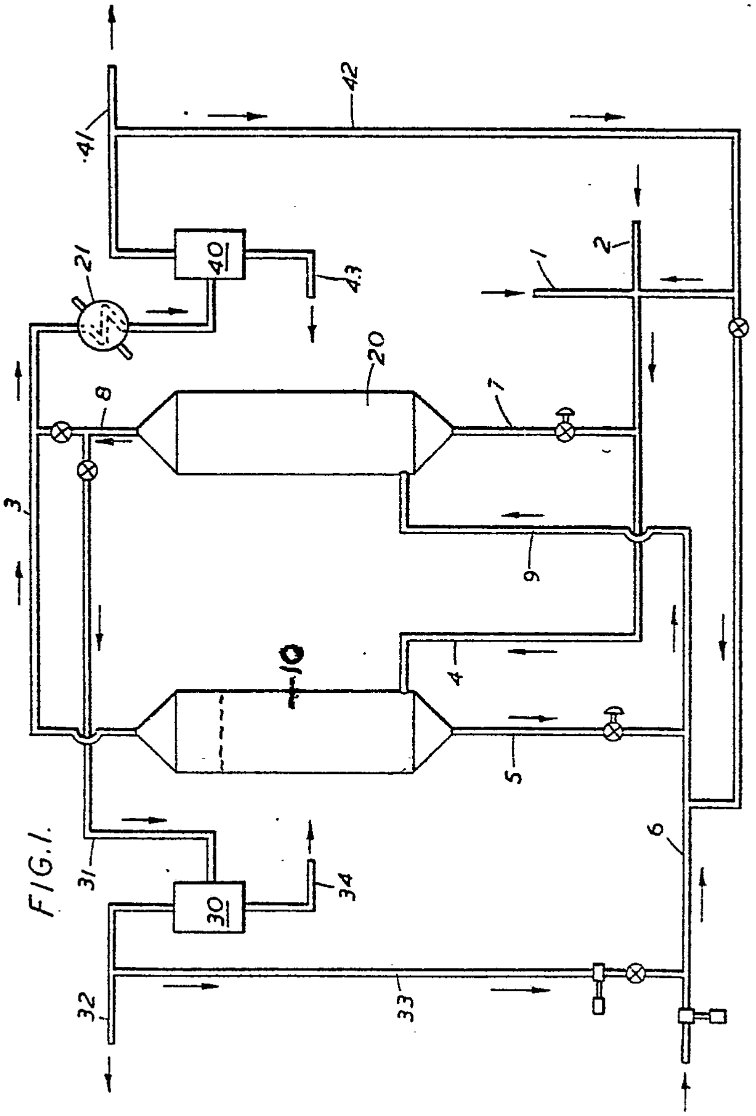

FIG. 1.

SHEET 1

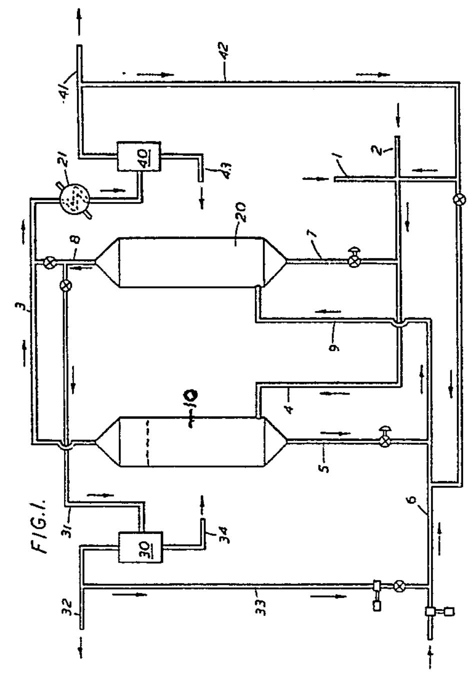

FIG. 1.

SHEET 2

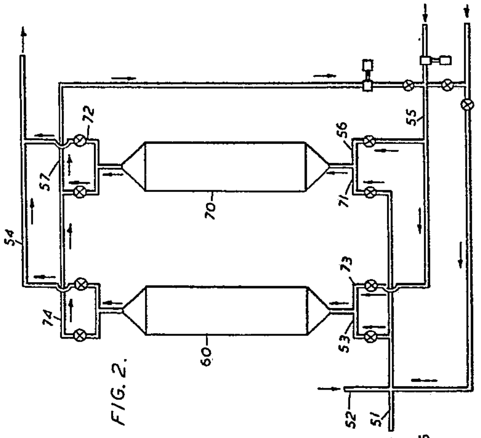

FIG. 2.

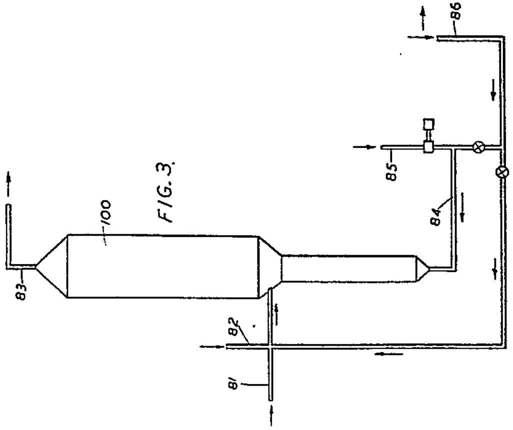

FIG. 3.

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