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(54) HYDROCARBON SYNTHESIS

(54) SYNTHESE D'HYDROCARBURES

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1   This invention relates to the catalytic conversion
of the oxides of carbon with hydrogen to form valuable synthetic
products, and more particularly to the synthesis reaction of
hydrogen with carbon monoxide in the presence of iron base
catalysts.

The invention will be fully understood from the
subsequent detailed description wherein reference will be made
to the accompanying drawing.

It is well known in the art that oxides of carbon
10 may be reacted with hydrogen in the presence of suitable
catalysts at temperatures between about 380°F. and about 800°F.
and at pressures varying from atmospheric to about 100 atmospheres
and higher to prepare hydrocarbons and oxygenated organic
compounds. The temperatures and pressures employed depend mainly
upon the catalyst employed, the character of the feed and the
final products desired. Compositions containing either iron,
cobalt, or nickel with minor amounts of promoter substances
such as compounds of the alkali and rare earth metals are
employed as catalysts alone or associated with carriers such as
20 alumina, silica or silicates, carbon, magnesia etc.

The synthesis reaction is now widely effected in the
presence of a fluidized catalyst, that is, the synthesis gas is
contacted with the catalyst in a finely divided state fluidized by
the upflowing gasiform reactants and reaction products to form a
dense turbulent mass similar in many respects to a boiling liquid.
This technique affords important advantages with respect to
temperature control and continuity of operation.

Catalyst masses containing iron in major amounts are
widely used in the synthesis reaction to produce a predominantly
30 unsaturated product from which valuable motor fuels of high

1   straight run octane number and substantial amounts of oxygenated

products may be recovered. These iron base catalysts are usually

prepared by the reduction of a variety of natural and synthetic

iron oxides; or by the decomposition of iron carbonyls; or the

heating of an iron salt such as ferrous oxalate. The final

catalyst usually consists substantially of reduced iron. Iron

base catalysts have also been obtained from such sources as

magnetite, mill scale or pyrites ash by suitable treatments

including reduction. Magnetite may be obtained from natural

10 deposits while mill scale is a by-product from steel industry

and pyrites ash is a by-product from the sulfuric acid industry.

All are substantially pure iron oxide.

     The activities of these iron base catalysts are

usually enhanced by the addition of compounds of alkali metals

or the oxides of zinc, aluminum, magnesium, manganese and the

rare earth metals in amounts between about 0.5 and 10% by weight

of the iron. These compounds may be added to the iron base by

simple impregnation followed by drying at 300° to 400°F., or

followed by sintering at 1600° to 2200°F. The promoter compounds

20 also may be added to the iron base while it is maintained in a

molten condition.

     For use as a fluidized catalyst, the particle sizes

of iron-type catalysts usually vary from about 1 micron to 200

microns and higher and preferably in the range from about 10

microns to 100 microns. With such particle sizes, the catalyst

bed can be satisfactorily fluidized; that is, the catalyst, the

reacting gases and reaction vapors form a pseudo-liquid of

aerated catalyst particles, the high turbulence of which permits

the maintenance of relatively uniform temperatures throughout

30 the catalyst mass and which exhibits the hydrostatic and

1 hydrodynamic characteristics of a liquid.

Prior to the present invention, the fluid-type synthesis process employing iron-type catalysts has been used mainly for the production of high-octane motor fuels while all other reaction products including higher boiling hydrocarbons such as fuel oils, lubricating oils or waxes were of lesser importance. Actually, hydrocarbons of the gasoline and gas oil range constitute invariably by far the major proportion of the liquid product from conventional iron-catalysed synthesis

10 processes chiefly due to the fact that the high temperatures and pressures required for satisfactory conversion on iron catalyst are unfavorable to the formation of high-molecular weight compounds. When products of a substantially higher molecular weight were desired in more significant yields, it had been necessary heretofore to use different catalysts, particularly cobalt-type catalysts, whose application is associated with milder temperature and pressure conditions. The market demand for the various hydrocarbon products varies greatly within relatively short times and depending on location.

20 However, it is hardly feasible to follow every change in market demand by a change in the catalyst used, because this would require a complete redesign of equipment and operation. There is therefore a strong need for a simple means adapted to change the molecular weight distribution of the hydrocarbon product of the iron-catalyzed synthesis process. The present invention fills this need.

It is therefore the principal object of the present invention to provide an improved process for the catalytic production of valuable synthetic products from CO and H_2, which

30 is more flexible with respect to the molecular weight of the products formed.

1   A more specific object of the invention is to
provide an improved process of the type specified which employs
iron catalysts in the fluidized state.

      Other objects and advantages will appear hereinafter.

      It has been found that the molecular weight of the
synthetic products formed in the catalytic conversion of CO with
H_2 on fluidized iron catalysts depends to a large extent on the
oxygen content of the catalyst. More specifically, it has been
found that the molecular weight of the synthesis products

10 increases substantially when the oxygen content of the catalyst
increases, until large proportions of waxy materials are formed.
Based on this discovery the present invention provides for a
control of the oxygen content of iron synthesis catalysts in
accordance with the desired molecular weight or wax content of
the synthetic product.

      Unreduced iron catalyst which usually is substantially
Fe_3O_4 or Fe_2O_3 has an oxygen content of about 38-43%, based on
pure iron. Theoretically, therefore, highest yields of wax-like
and other high molecular weight products should be obtainable

20 when using unreduced catalyst and this has been found to be
actually the case. However, it has been found that oxygen contents
of this magnitude seriously interfere with a proper operation, and
particularly with proper fluid operation of the synthesis process.
The cause of these difficulties is believed to be excessive
formation of products of highest molecular weight which at the
temperatures (500°-700°F.) and pressures (150-750 psig.) required
for the iron-catalyzed synthesis are deposited on the catalyst.
These wax deposits cause agglomeration of the catalyst particles
to aggregates which cease to be fluidizable at the reaction

30 conditions.

1   This effect is demonstrated by the experimental data

reported in Table I below which presents a summary of three fluid

synthesis runs carried out at an H_2:CO ratio of about 2:1 and

with an iron oxide base catalyst promoted with 1.5% of K_2O.

Table I

Catalyst Preparation	Reduced	Unreduced	Unreduced
% O_2 on Cat., Fe Basis	5	39.6	39.6
Pressure, Psig.	400	400	400
Catalyst Temperature, Specified, °F.	650	650	650
Catalyst, Temperature, Max. Range, °F.	650-655	650-743	650-783
Feed, V/V/Hr.	1350	1330	1250
Duration of Run, Hrs.	387	38	45

It will be seen that in the run using reduced catalyst the maximum

temperature range throughout the catalyst mass was only 5°F. for

a duration of about 400 hours while the runs using unreduced

catalyst had to be discontinued after less than 50 hours when

20   the temperature range over the catalyst bed approached or exceeded

100°F. as a result of poor fluidization.

In accordance with the present invention, therefore,

the oxygen content of the catalyst mass is maintained somewhere

between complete reduction and complete oxidation. A broad

operation range is an oxygen content of up to about 35%, based on

pure iron, within which specific values may be selected depending

on the amount and molecular weight of high molecular weight

products desired. More specifically, it may be stated that

satisfactory yields of waxy materials may be obtained at oxygen

30   contents of the catalyst of about 10-30%, based on pure iron,

without affecting the fluid characteristics of the catalyst mass.

In accordance with one embodiment of the invention

the oxygen content of the catalyst is controlled by the addition

of controlled amounts of fresh unreduced fluidizable iron

catalyst to a fluidized mass of substantially reduced iron

1 catalyst in synthesis operation.

Between about 2% to 10% of catalyst inventory per
day of unreduced iron oxide catalyst may be added to a hydro-
carbon synthesis reactor containing reduced or partially
reduced iron catalyst depending on the desired molecular weight
of the product. The addition of iron oxide catalyst in these
amounts to a bed of substantially reduced iron catalyst avoids
the operating difficulties caused by the formation of excessive
quantities of high boiling hydrocarbons and the resulting proper
10 fluidization conditions. The actual total oxygen content of
the catalyst mass is greater than the equivalent of oxygen
added with the unreduced catalyst, because the initially reduced
catalyst is likewise oxidized at the synthesis conditions until
it reaches an equilibrium content of about 5-20% of oxygen,
based on pure iron. Thus this embodiment of the invention
provides for the introduction of unreduced iron base catalysts
in desirable incremental quantities to the hydrocarbon synthesis
reactor depending upon the molecular weight of the hydrocarbons
in the oil that it is desired to obtain, upon the level of
20 conversion it is desired to maintain, and upon the desired level
of the fluidized catalyst in the reactor.

In some types of operation there may be an expansion
of catalyst volume because of carbon deposition and catalyst
fragmentation. In accordance with the embodiment of the present
invention just described any desired volume of catalyst in the
reactor and substantially any carbon concentration on the
catalyst such as between about 15% to about 25% by weight of the
reduced catalyst may be maintained by withdrawing, continuously
or periodically, appropriate quantities of used catalyst from
30 the upper portion of the bed where the particle size is smallest

1 and the carbon concentration on the catalyst is greatest and
adding controlled quantities of unreduced catalyst. Since un-
reduced catalyst has a tendency to become partially reduced
under operation conditions, an equilibrium state between re-
duced and unreduced catalytic material containing oxygen in an
amount between about 10% and 30% by weight of the reduced catalyst
may thus be maintained by control of the withdrawal of the used
catalyst and introduction of the unreduced catalyst. The
molecular weight of the hydrocarbon product may be controlled
10 in this manner.

Example I

The following data illustrate the effect of intro-
duction of unreduced catalyst into the system in accordance with
this embodiment of the invention.

TABLE II

Conditions

Temperature, °F.		650
Pressure, psig		400
Throughput, v/v/hr		3500
H2:CO Ratio		2/1
Linear Velocity		0.37 ft/sec.

Catalyst

Type		Iron oxide base
Unreduced O2-content		39% based on Fe
Average Particle size		90 microns

Hours	Catalyst Started	Catalyst Added	Pour Point of Collected Oil, °F.	Oil Recovered cc/m³ of Feed	C4+ Yield cc/m³ of H2 + CO Consumed
22-45	Reduced (638 g.)		-60	100	188
70-93			-60	93	185
115-138		Unreduced (168g.)	+5	116	202
182-193		Unreduced (168g.)	+30	116	190
218-229		Unreduced (168g.)	+55	94	175
230-253			+40	107	191
254-277			-5	103	190

1 Catalyst amounting to about 40% of the expanded catalyst volume

was withdrawn at Hour 93 and Hour 158 from an upper portion of

the reactor.

Example 2

Given in Table III are results that were obtained in

another run which was made with the catalyst of Example 1 under

substantially the same conditions as were employed in Table II

but _without_ addition of unreduced catalyst.

TABLE III

10 Conditions

Temperature, °F.	650
Pressure, psig	400
Throughput, v/v/hr	1360
H_2/CO Ratio	2/1
Linear Velocity, ft/sec.	0.37

Catalyst

Type	Iron Oxide Base
O_2 content after reduction	5% based on Fe
20 Average Particle Size	96 microns

Vol. Yields, Vol. % of C_4+		% Unsatis.	Res.O.N.+2cc TEL
Excess C_4	15.0	75	
Gasoline	62.4		82.0
400°F. + Bottoms	22.6		

The presence of a high percentage of gasoline and a relatively

low percentage of 400°F. bottoms which cooperate to establish a

pour point of the total oil are recovered of the order of -60,

demonstrates the fact that the completely reduced catalyst was

not conducive to the formation of wax-type constituents.

30 From these data it will be seen that the addition of

unreduced catalyst causes an increase in the molecular weight

of the product since three additions of unreduced catalyst in-

creased the pour point from -60 to +55°F. However, when the

addition of unreduced catalyst was discontinued, the material

became less waxy indicating that the tendency to form high

molecular weight material is a transient condition when unreduced

catalyst is added.

It is evident, therefore that the molecular weight of the reaction product oan be controlled by the addition of unreduced catalyst to the hydrocarbon synthesis reactor.

In accordance with a further embodiment of the invention the oxygen content of the iron catalyst, and with it the molecular weight of the synthetic product, is controlled by periodic hydrogenation and/or oxidation of the catalyst in situ or in separate treating equipment. Depending on the desired molecular weight of the reaction product and the equilibrium
10 oxygen content of the iron oatalyst at the prevailing synthesis conditions the synthesis gas supply may be periodically replaced by the supply of a more strongly oxidizing gas such as air, CO_2, steam and/or oxygen or of a more strongly reducing gas such as pure hydrogen or a gas mixture richer in hydrogen than the synthesis gas used. Similar treatments may be carried out in separate treating zones, without interrupting the synthesis reaction, by periodically or continuously circulating suitable proportions of the fluidized catalyst from the synthesis reactor to the treating zone and back to the synthesis reactor in a
20 manner well known in the art of fluid solids handling.

Suitable catalyst oxidation conditions include treating with steam alone or with steam-air mixtures containing 1 to 10% O_2 at 0-750 psig., 500-750°F. and velocities from 0.3 to 1.5 ft./sec. specific conditions depending on the degree of oxidation desired and the nature of the catalyst. Hydrogenation may be carried out quite generally at 0-750 psig., 650°-1100°F. and 0.3 to 1.5 ft./sec. with pure H_2 or with gases rich in H_2 depending on the desired oxygen content of the catalyst and the nature of the catalyst.

30 The oxygen content of the catalyst may be also controlled in situ without interrupting the synthesis reaction, by altering the nature of the entering feed to give a more oxidizing or more reducing atmosphere in the reactor. The oxidizing activity of the feed may be conveniently increased by addition of extraneous

1   steam with the total feed, or by decreasing the ratio of $H_2/CO+CO_2$

in the feed, and decreased by increasing the ratio of $H_2/CO+CO_2$

in the feed.

Example 3

Another run was conducted as follows:

Conditions
Temperature, °F.	650
Pressure, psig.	400
Throughput, v/v/hr.	3500
H_2/CO ratio	2/1
Linear Velocity, Ft./sec.	0.4-0.6

Catalyst
Type	Iron Oxide Base
O_2 Content After Reduction	< 5% based on Fe
Average Particle Size	70 microns

The run was interrupted after 359, hours no appreciable amounts

of wax having been formed to this point. During the interruption

of the run no precautions were taken to avoid oxidation of the

catalyst. When this catalyst was placed back on stream at the

20 same conditions appreciable wax formation was observed in sus-

pension in the hydrocarbon product and temperatures indicated

poor fluidization.

Thereafter the catalyst was reduced in situ with hydro-

gen at 700°-750°F. and 400 psig. pressure for 26 hours. When

the reduced catalyst was placed back on stream at the conditions

specified above, the hydrocarbon product collected did not show

any evidence of suspended wax.

The advantages of the invention and preferred means for

securing the same will now be further explained with reference to

30 the accompanying drawing in which

Figure 1 is a graphical illustration of the relationship

between oxygen content of the catalyst and wax formation in the

reactor; and

Figure 2 is a semidiagrammatical view of equipment

suitable to carry out the preferred embodiments of the invention.

Referring now to Figure 1 the curve shown therein represents an evaluation of various fluid type synthesis runs carried out at substantially identical conditions except for the oxygen content of the catalyst. The essential reaction conditions are given in the legend of Figure 1. The catalysts used were as follows:

"NH$_3$ Synthesis Catalyst" (Runs 1 and 2) is a fused high purity magnetite promoted with about 1.5% of K$_2$O and about 3% of alumina, and initially reduced by treating with H$_2$ at 250 psig. and 725°F. to an oxygen content of <5%.

"NH$_3$ Synthesis Catalyst, Precarbided" (Run 3) is the "NH$_3$ Synthesis Catalyst" first reduced as above and then subjected to a treatment with an 8/1 H$_2$/CO gas mixture at 623°F. and atmospheric pressure in fluid operation for 8 hours.

"1.5% K$_2$CO$_3$ Resintered Pyrites" (Runs 4 and 5) is a sintered iron pyrites ash resintered with air in the presence of about 5% of coke and 1.5% of K$_2$CO$_3$ at about 2200°-2500°F. and initially reduced as indicated above to an oxygen content of <5%.

The oxygen content of the catalyst used for the correlation with the wax formation was determined by analysis of samples withdrawn during the runs. The same procedure was used to determine the wax formation on the catalyst.

It will be seen from the curve that wax formation increases rapidly as the oxygen content increases, substantially alike for all three catalysts tested. Wax formation may therefore be readily controlled by controlling the oxygen content of the catalyst under otherwise equal conditions.

Referring now to Figure 2 of the drawing, reference numeral 10 indicates a reaction vessel wherein a mixture of

hydrogen and carbon monoxide admitted through line (12) is
brought into contact with a finely divided catalyst mass (16)
in a fluidized condition. The catalyst is initially added to
the system through line (18) from hopper (20). Catalyst may
also be added through line (22) from hopper (24). Vessel (10)
is provided with a catalyst withdrawal line (26) and a gas
distributing means, such as a grid (14). One or more gas-solid
separating units such as cyclone separator (30) with dip pipe
(32) may be arranged in the top of vessel (10). Cyclone
10   separator (30) is connected to a discharge line (28).

The hydrogen and carbon monoxide supplied through
line (12) and grid (14) pass upwardly through the catalyst (16)
at a linear velocity of between about 0.2 to 5 ft. per second and,
preferably, from about 0.2 to 1.5 ft. per second to convert the
finely divided catalyst into a dense suspension of catalyst
resembling a boiling liquid in appearance and behavior. The
particle size distribution of the catalyst may be between about
1 micron and 500 microns and, preferably, as follows: 0-20μ
= 20-30%, 80+μ =30-40%. The density of the fluidized mass may
20   be from about 30 to 150 pounds per cubic foot depending upon
the amount of the catalyst in the vessel (10), the average
particle size and the gas velocity. The fluidized mass maintains
a general level (L) in the reactor some distance from the top
of the vessel. Small quantities of catalyst fines are carried
overhead. The density of the phase above level (L) may be about
0.1 to 0.2 pound per cubic foot. The catalyst material is
preferably metallic iron promoted with a minor amount of a
potassium compound such as from about 0.3% to 1.5% potassium
carbonate. Material of this type may be initially added to
30   reaction vessel (10) through line (18) from hopper (20).

1 After the reaction has proceeded for some time, a portion of
the catalyst may be withdrawn through line (26) and a corresponding
quantity of catalyst added through line (22) from hopper (24).
The catalyst supplied through line (22) is fresh unreduced
catalyst prepared from an iron oxide.

The reaction conditions in vessel (10) may be as
follows:

	Broad Range	Preferred Range
Temperature, °F.	500-750	625-725
10 Pressure psig.	100-750	400-600
Linear Velocity, Ft./sec	0.2-5.0	0.4-1.5
Fluidized Catalyst Density Lbs./Cu.Ft.	10-100	20-60
Feed rate, Cu.Ft.H_2+ CO/Hr./Lb. of Catalyst	5-90	10-40

The heat generated by the reaction may be absorbed
by any conventional cooling means not shown.

At the conditions specified a dilute suspension of
catalyst fines entrained in gasiform products passes into the
upper portion of reaction vessel (10) above level (L) and enters
20 cyclone separator (30). Catalyst separated in cyclone separator
(30) may be returned to the fluidized mass (16) through dip pipe
(32). The gases and vapors separated in cyclone (30) pass
overhead through line (28) to a product recovery unit (34). In
the product recovery unit (34) the reaction product is separated
into a water layer and a plurality of fractions such as the
normally gaseous material largely consisting of normally gaseous
hydrocarbons, unreacted hydrogen and carbon monoxide, a naphtha
fraction boiling usually up to about 400°F. and higher boiling
fractions varying from gas oils to solid waxes, in a manner
30 known per se.

In accordance with the invention, a balance may be

1   maintained between the catalyst withdrawal through line (26)

and the addition of unreduced catalyst through line (22). By

the control of this withdrawal and addition, the nature of the

reaction product recovered in unit (34) may be determined with

respect to the relative proportion of hydrocarbons boiling up

to about 400°F. to those boiling above 400°F.

Similar results may be obtained by periodically

admitting an oxidizing gas through line (12), in place of the

addition of fresh unreduced catalyst through line (22), in the

10 manner previously described. For example, air or air mixed with

a diluent may be admitted at intervals of about 24 to 100 hours

for about 1 to 5 hours at the flow conditions of the run while

maintaining temperatures of about 625° to 725°F. and pressures

of about 400 to 600 psig. in reactor (10).

When it is desired to reoxidize the catalyst without

interrupting the synthesis reaction, catalyst continuously or

periodically withdrawn through line (26) may be passed through

line (36) to a separate oxidizing vessel (38) which may have a

construction similar to that of reactor (10). Air may be

20 supplied through line (40) at conditions similar to those of

the in-situ oxidation described above. Reoxidized catalyst may

be withdrawn through line (42) from the bottom of vessel (38),

mixed with fresh or spent synthesis gas supplied through line

(44) and then returned through line (46) as a dilute solids-in-

gas suspension to reactor (10) under the pseudohydrostatic

pressure of the fluidized mass in vessel (38). It will be

understood that vessel (38) may also be used as a reducing

zone using hydrogen at reducing conditions, in a generally

analogous manner.

30   Other modifications of the system illustrated in the

drawing may appear to those skilled in the art without departing from the spirit of the invention.

The preceding description and exemplary operations have served to illustrate the invention, but are not intended to limit 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. The process of increasing the content of high
molecular weight hydrocarbon in the total liquid product
synthesized from a gas mixture of hydrogen and carbon monoxide
which comprises passing said gas mixture at a temperature of
between about 625 and 725°F. and a pressure of between about
400 to 600 pounds per square inch in contact with a catalyst
consisting of a major amount of metallic iron and iron oxides
promoted with a minor amount of a potassium compound, said
conditions corresponding to a normal equilibrium content of
between about 5% and 20% of oxygen based on total iron in
the catalyst while producing a yield of total C_4+ product
overhead of at least about 175 cc. per cubic meter of H_2+CO
consumed at a synthesis gas H_2 to CO feed ratio of between
about 1:1 and 2:1, said product containing normally an amount
of high molecular weight material insufficient to raise the
pour point of the total product above about 0° F., raising the
oxygen concentration of said catalyst to a value above said
normal equilibrium value, within the range of about 20% to 35%
by weight of 0 based on total Fe, and maintaining said increased
oxygen content continuously for an extended period of time to
produce a total C_4+ product containing an increased amount of
high molecular weight products over that normally obtained
at said operating conditions.

2. The process according to claim 1 in which said
synthesis reaction is started with a fluidized mass of substantially
reduced catalyst, and in which fresh unreduced iron oxide catalyst
is added continually to said reduced catalyst during the course
of said reaction in amounts sufficient to maintain the oxygen
content of the total catalyst at a value above said equilibrium
range.

A

3. The process of claim 2 in which about 2 to 10% of fresh unreduced iron oxide catalyst, based on catalyst inventory, is added per day.

4. The process according to claim 1 in which the total catalyst in the reaction zone is kept thoroughly mixed in the form of a turbulent fluid bed, an aliquot portion of said total catalyst is continually withdrawn from said fluid bed and allowed to oxidize spontaneously in an oxygen containing gas, controlling the oxygen content of said latter gas to avoid overheating of the catalyst, returning said reoxidized catalyst to the reactor, and controlling the rate of said catalyst withdrawal and its return after reoxidation to supply an amount of iron oxide sufficient to maintain the total oxygen content of the catalyst in the reactor at said level substantially above the normal 5-20% equilibrium oxygen content.

Hydrocarbon Synthesis Laboratory Fluid Units
Wt.% O₂ On Catalyst Versus Wt.% Wax on Catalyst
Scrubbed Feed, 650° F., 400 PSIG., 2 Recycle

H₂/CO F. Feed				
2/1	1.5/1	RUN NO		
O	●	1	NH₃	Synthesis Catalyst
Δ		2	NH₃	Synthesis Catalyst
▽		3	NH₃	Synthesis Catalyst Precarbided
	■	4	1.5% K₂CO₃	Resintered Pyrites
◇	◆	5	1.5% K₂CO₃	Resintered Pyrites

Graph: vertical axis "WT.% O₂ On C+O Free Catalyst" from 5 to 30; horizontal axis "WT.% Wax On C+O Free Catalyst" from 5 to 35.
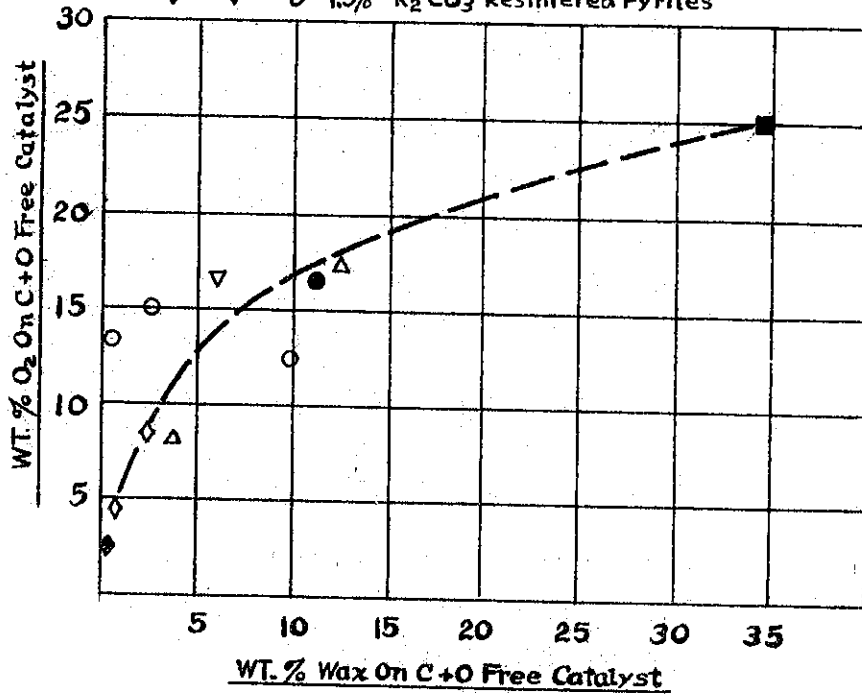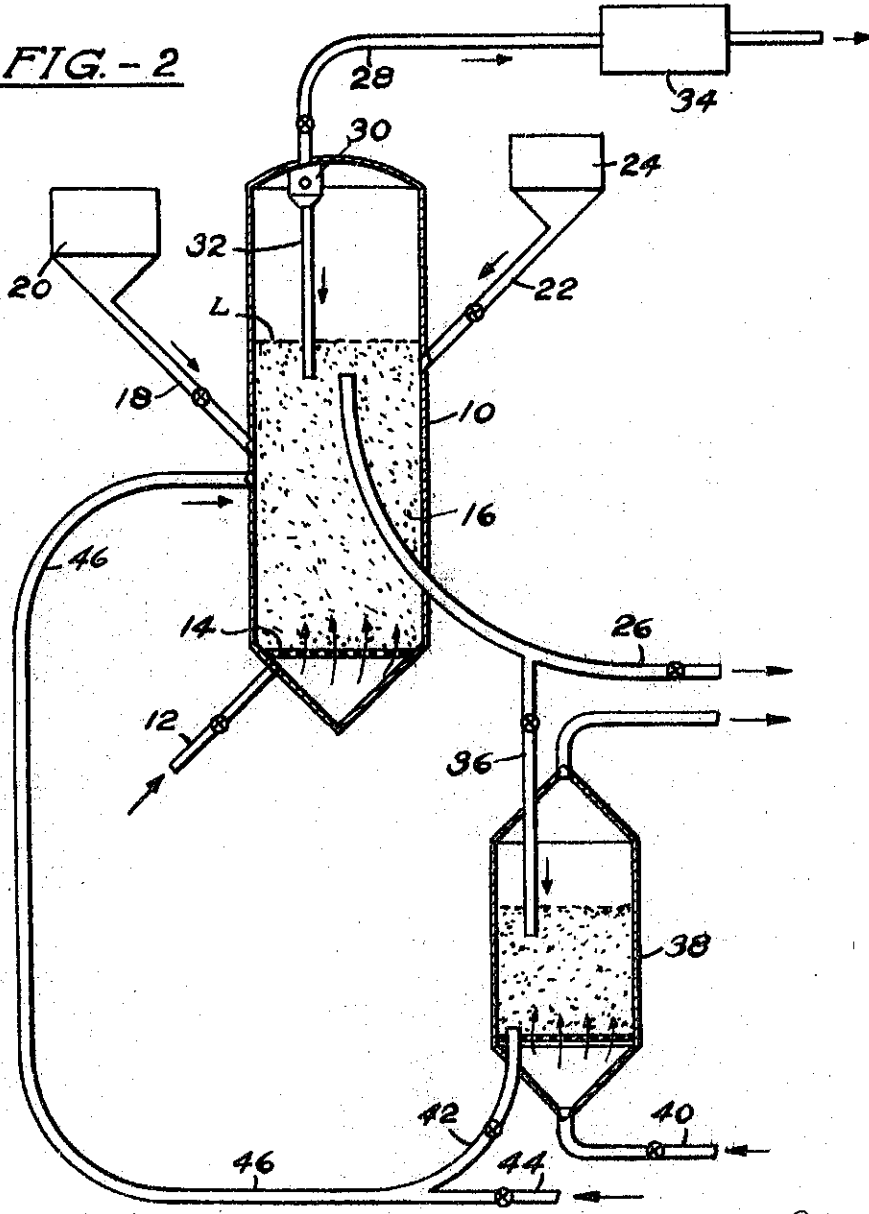
FIG.-1

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FIG.-2

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