PATENT SPECIFICATION

655,827

Index at acceptance:—Class 2(iii), B1(g: i).

PROVISIONAL SPECIFICATION

Improved Hydrocarbon Synthesis

20 containing various proportions of hydrogen and carbon oxides, particularly carbon monoxide, both in fixed bed as well as in dense phase fluid catalyst operation is well known in the art. The 25 character and quality of the synthesis product depends largely on the temperatures, pressures, H_2 : CO ratios of the feed gas and the nature of the catalyst used, the latter being usually an iron group metal 30 catalyst promoted with such promoters as various alkali metal compounds, rare earth metal oxides, magnesia, alumina, etc. in amounts of about 0.5—10%. Thus cobalt catalysts promoted with thoria 35 and/or magnesia have been used at relatively low pressures of about 15—75 psig. and relatively low temperatures of about 350° to 450° F. and high H_2 : CO ratio of 2 or more to produce a substanti- 40 ally saturated hydrocarbon material from which valuable diesel fuels, lubricating oils, and waxes may be obtained. Iron-type catalysts, usually promoted with a suitable alkali metal compound, such as 45 carbonates, halides, etc. of potassium or sodium may be used in combination with relatively high pressures up to 600 to 700 psig. and temperatures of 450° to 750°

mixing and contact of the catalyst with the reactants, is considered far superior to fixed bed processes for effecting the 70 catalytic synthesis of hydrocarbons. However, two problems that arise in conjunction with the fluid solids type of operation are the fouling and consequent inactivation of the catalyst by formation 75 and deposition of waxy materials and the tendency of catalyst particles to agglomerate as a result of the wax formation and deposition. Wax deposition due to catalyst inactivation not only cuts down 80 product yield but causes poor fluidization of the catalyst, poor temperature control, agglomeration and conditions requiring shut down of the plant.

The present invention is particularly 85 concerned with the removal of waxy material from a catalyst used in the synthesis of hydrocarbons in a fluid solids type operation.

As stated above, one of the principal 90 problems in the application of the fluid catalyst technique to the synthesis of hydrocarbons from CO and H_2 has been the accumulation of wax or heavy oil on the catalyst. In the fixed bed operation 100 this was not a serious problem; because

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Improved Hydrocarbon Synthesis

We, STANDARD OIL DEVELOPMENT COMPANY, a Corporation duly organized and existing under the laws of the State of Delaware, United States of America, of
5 Elizabeth, New Jersey, United States of America, do hereby declare the nature of this invention to be as follows:—

The present invention relates to the synthesis of hydrocarbons from carbon
10 oxides and hydrogen in the presence of a suitable iron catalyst. This invention relates more particularly to the treatment of a powdered catalyst associated with an oily hydrocarbonaceous and waxy
15 material, wherein the catalyst is cleansed and valuable oily and waxy materials are recovered.

The synthesis of hydrocarbons and other valuable products from gas mixtures
20 containing various proportions of hydrogen and carbon oxides, particularly carbon monoxide, both in fixed bed as well as in dense phase fluid catalyst operation is well known in the art. The
25 character and quality of the synthesis product depends largely on the temperatures, pressures, H_2:CO ratios of the feed gas and the nature of the catalyst used, the latter being usually an iron group metal
30 catalyst promoted with such promoters as various alkali metal compounds, rare earth metal oxides, magnesia, alumina, etc. in amounts of about 0.5—10%. Thus cobalt catalysts promoted with thoria
35 and/or magnesia have been used at relatively low pressures of about 15—75 psig. and relatively low temperatures of about 350° to 450° F. and high H_2:CO ratio of 2 or more to produce a substanti-
40 ally saturated hydrocarbon material from which valuable diesel fuels, lubricating oils, and waxes may be obtained. Iron-type catalysts, usually promoted with a suitable alkali metal compound, such as
45 carbonates, halides. etc. of potassium or sodium may be used in combination with relatively high pressures up to 600 to 700 psig. and temperatures of 450° to 750°

F., and lower H_2:CO ratios generally not
50 above 2, to produce predominantly unsaturated material from which large proportions of high octane motor fuels may be recovered.

While it has thus been possible to
55 obtain high octane motor fuels in good yields by this process, it has also been found that operations under conditions that favor good yields of useful (i.e., C_4+oil products are accompanied by ex-
60 cessive deposition of carbon and carbonaceous material upon the catalyst. This carbon deposition is a serious problem, both when the catalytic operation is carried out by the fixed bed and the fluid
65 catalyst technique, which latter, because of better heat distribution, transfer and control and because of the more intimate mixing and contact of the catalyst with the reactants, is considered far superior
70 to fixed bed processes for effecting the catalytic synthesis of hydrocarbons. However, two problems that arise in conjunction with the fluid solids type of operation are the fouling and consequent in-
75 activation of the catalyst by formation and deposition of waxy materials and the tendency of catalyst particles to agglomerate as a result of the wax formation and deposition. Wax deposition due to
80 catalyst inactivation not only cuts down product yield but causes poor fluidization of the catalyst, poor temperature control, agglomeration and conditions requiring shut down of the plant.

The present invention is particularly
85 concerned with the removal of waxy material from a catalyst used in the synthesis of hydrocarbons in a fluid solids type operation.

As stated above, one of the principal
90 problems in the application of the fluid catalyst technique to the synthesis of hydrocarbons from CO and H_2 has been the accumulation of wax or heavy oil on the catalyst. In the fixed bed operation
100 this was not a serious problem; because

of the downflow, the wax drains off the catalyst, and wax could be allowed to collect to the extent of 100 to 150% by weight of catalyst before activity of the
5 catalyst was seriously impaired, and consequently wax removal was required only at infrequent intervals such as every 30 or 60 days. Also, particle motion was not important. However, in the fluid type of
10 operation the accumulation of wax on the catalyst interferes with proper fluidization of the catalyst long before the wax content of the catalyst is sufficient to interfere seriously with the activity there-
15 of. One of the ways wherein wax interferes with fluidization is by accumulation on any relatively cold walls. Fine catalyst particles make contact with this wax, are wetted thereby, and the result-
20 ing agglomerate falls into the reactor and causes poor fluidization and/or coking and caking. Thus it has been found, for example, in a fluid type operation that only about 20 to 25 weight percent of wax
25 can be tolerated on the catalyst before it causes sticking together of the catalyst particles, thus preventing proper aeration and fluidization which are essential for the operation of the fluid type process.
30 It has been proposed to remove catalyst from the reactor and to treat it with a solvent to remove the materials contained therein. Not only is this an expensive operation, but it is impossible to remove
35 completely the deposit from the catalyst by solvent extraction. It is also possible to burn the deposit from the catalyst, but in this case the catalyst must be reduced before re-employment and it fre-
40 quently suffers deterioration during the cycle. Beside the association of the catalyst within the synthesis reactor with heavy oil and waxy materials, another part of the catalyst is also closely associ-
45 ated with heavy oil in the catalyst recovery system. When upflowing synthesis gas is contacted with a dense bed of turbulent fluidized catalyst particles, the product stream comprising reaction pro-
50 ducts, unreacted gases and catalyst fines generally pass in the upper section of the reactor through a gas-solids separator, such as a cyclone, wherein the greater part of the catalyst fines and entrained
55 catalyst particles is removed from the gas stream and returned to the catalyst dense bed. However, a minor portion of the catalyst is not removed by this means, and to prevent such catalyst fines that
60 remain suspended in the vapors leaving the gas-solids separator from contaminating the liquid product, it is customary to contact the product vapors with a circulating oil stream to scrub out the re-
65 maining catalyst from the product

stream. The resultant slurry is then settled or concentrated by some conventional means, such as thickening, and the thickened material usually discarded.

As a result therefore, of the formation 70 of waxy deposits on synthesis catalyst within the reactor and of the product vapor scrubbing process wherein catalyst is scrubbed out of hydrocarbon synthesis product vapors, there is lost not only 75 catalyst but also a significant proportion of product oil—i.e., that associated with the catalyst within and without the reactor.

It is therefore, the main object of the 80 present invention to separate oily or waxy material from finely divided hydrocarbon synthesis catalyst, simultaneously purifying the latter and recovering valuable oil material. 85

Another object of the invention is to recover a high quality diesel oil from the hydrocarbon synthesis process.

Other and further objects of the invention will appear from the following 90 more detailed description.

The catalyst from the two sources, the reactor and the recovery system is mixed as a slurry with high-boiling (400+ °F.) synthesis product in a reactor and sub- 95 jected to low pressure hydrogenation. This operation consists of passing the slurry with hydrogen through a reactor at pressures in the order of 50 to 750 psi. and temperatures of about 500° to 800° 100 F.

Not only are the olefinic constituents of the oil phase of the slurry hydrogenated and oxygenated materials converted so that an excellent diesel oil in the order 105 of 60 to 70 cetane number is obtained, but also the heavy oil and the wax are removed from the catalyst. Furthermore, the catalyst is also partially reduced in case it was oxidized in the reactor. Under 110 the conditions specified, the hydrocarbon synthesis catalyst itself acts as the hydrogenation catalyst and no other catalyst need be added for the desired reaction. Inasmuch as a hydrogen manufacturing 115 plant is almost invariably a part of a synthesis plant to reduce the feed catalyst, such plant is readily adaptable to furnish the hydrogen for use in accordance with the present invention. 120

Having set forth the general nature, advantages, and objects of the invention, the latter will best be understood from the more detailed description hereinafter in which reference will be made to the 125 accompanying drawing which is a diagrammatic representation of a system suitable to carry out a preferred embodiment of the invention.

Referring now in detail to the accom- 130

panying drawing, 2 is a reactor prefer-
ably in the form of a vertical cylinder
with a conical base and an upper ex-
panded section, having a screen or grid 4
5 located in the lower section to effect good
gas distribution, and a catalyst with-
drawal line 6 extending through grid 4.
A synthesis gas feed mixture of H₂ and
CO in synthesis proportions, that is, a
10 mol ratio of H₂ to CO of about 0.7 to 1.8
to 1, is introduced into the reactor
through line 8 and flows upwardly through
grid 4.

Within reactor 2 a mass of powdered
15 iron catalyst, such as alkali metal pro-
moted sintered reduced pyrites ash is
maintained in the form of a dense fluid-
ized bed, having particle size distribution
such that less than 10% of these par-
20 ticles have diameters 0—20 microns, and
all of the material is finer than 100 mesh.
This catalyst may be supplied to reactor
2 through line 10 from catalyst hopper
12. The linear velocity of the gases with-
25 in reactor 2 is within the approximate
range of 0.3 to 1.5 feet per second, and
under these circumstances the catalyst
assumes the form of a dense, turbulent
mass, having a well-defined upper level
30 and an "aerated" density of about 30—
150 lbs./cu.ft. depending upon fluidiza-
tion conditions. The pressure within the
reactor may vary from about 250 to 750
psig., and the reaction temperature,
35 which may be controlled with the aid of
cooling coils (not shown) located in the
dense phase of the catalyst bed, is kept
uniform at about 450°—750° F.

The catalyst is preferably promoted
40 with about 0.3 to 1.5% of an alkali metal
salt, such as K₂CO₃, Na₂CO₃, KF, etc.
Higher concentrations, particularly in
the presence of catalyst fines in the 0—20
micron range favor formation of high
45 boiling and waxy materials. Further-
more, even when the total promoter con-
tent on the catalyst is within the above
range, the presence of high concentra-
tions of 0—20 micron fines is undesirable
50 from a wax forming point of view be-
cause the finer catalyst usually contains
the highest concentration of promoter
which has been found to increase wax
accumulation. Also, fines are usually
55 more highly oxidized than coarser cata-
lyst, and a catalyst oxygen content above
about 15% definitely promotes formation
of wax deposits.

When entering the enlarged section of
60 reactor 2 the gas velocity is sufficiently
decreased so that the gases no longer sup-
port any substantial quantity of catalyst,
and most of the coarser particles entrained
in the gas drop back into the fluidized
65 mass.

The volatile reaction product contain-
ing as well varying quantities of entrained
catalyst fines and also finely divided
organic iron compounds are withdrawn
through a gas-solids separator, such as 70
cyclone 14 equipped with dip pipe 16.
The bulk of the entrained catalyst fines is
removed in the cyclone and returned to
the fluidized bed via dip pipe 16.

The reaction products and the remain- 75
ing catalyst fines, etc, and undesirable
synthesis product contaminants, such as
entrained iron salts of fatty acids are
passed from the top of reactor 2 through
line 17 and may be partially condensed in 80
cooler 18. The reaction products and cata-
lyst fines are then passed into oil scrubber
20 wherein the remaining entrained cata-
lyst powder is removed by circulating
product oil in a manner known *per se*. The 85
temperature within scrubber 20 is pre-
ferably above 175—250° F. so that lighter
and lower boilng vapors are not substanti-
ally scrubbed out by the oil. The over-
head vapors and gases from scrubber 20, 90
comprising tail gas and reaction products
uncondensed in cooler 18 and scrubber 20
are then passed through line 22 to cooler
24 and partial condenser 26. The latter
are operated at such temperatures that 95
reaction products boiling above 400° F.
are substantially condensed in 26 but
lighter reaction products pass overhead
a vapor through line 28, are substantially
cooled in cooler 30 and pass to separator 100
32 wherein normally condensible synthesis
products are withdrawn and sent via line
34 to the liquid products recovery system.
Non-condensible tail gas from 32 is re-
moved overhead through line 36, a por- 105
tion sent back as recycle to reactor 2 via
line 38, and the balance withdrawn
through line 40, used in the plant as
desired, such as fuel, recycle to gas
generator, etc. 110

The condensate in separator 26, com-
prising oily synthesis products boiling
above 400° F. is withdrawn through line
42, and, as required, sent as scrubbing
oil to catalyst scrubber 20 via line 44. A 115
portion of the condensate from 26 may
be sent to the liquid products recovery
system.

A liquid stream comprising scrubbing
oil, scrubbed catalyst fines, and other 120
condensed, scrubbed, or entrained reac-
tion products, such as organic iron salts
is withdrawn from oil scrubber 20 and
passed through line 46 to slurry mixing
tank 48, preferably equipped with means 125
of mechanical agitation.

Returning now to reactor 2, a stream
of catalyst is intermittently or con-
tinuously withdrawn from the dense bed
through catalyst withdrawal line 6, which 130

may be provided with aeration taps 50 to aid in the moving of the catalyst through the line. Catalyst is preferably withdrawn from reactor 2 as wax accumulates, 5 evidenced by decrease in fluidizability, and is passed to slurry mixing tank 48. Catalyst and liquid stream from 20 are preferably so proportioned that the resulting slurry has a composition of about 10 1—3 lbs. catalyst per gallon of oil.

The catalyst-oil slurry is now pumped through slurry pump 52 and line 54 to hydrogenation reactor 56. This is a reactor of conventional design, which may 15 be packed with non-catalytic material, such as Raschig rings, pumice, activated carbon, etc. to aid in the mutual contacting of liquids, gases, and finely-divided catalytic solids. Because of the nature 20 of the synthesis catalyst, no extraneous hydrogenation catalyst need be added to reactor 56. Hydrogen from any convenient source, as from the hydrogen manufacturing plant commonly associ- 25 ated with a synthesis plant is supplied to reactor 56 through line 58. Reactor 56 is under pressure of about 50 to 750 psi., preferably 300 to 500 psi., and a temperature of about 500°—800° F. Under 30 these conditions not only are the oxygenated organic compounds present in the $400+°$ F. products comprising the slurry reduced, and the olefinic constituents saturated, but also the waxy constituents 35 deposited on the synthesis catalyst are removed partly by solution in the slurry oil, and partly by being broken down to smaller molecular fragments as a result of the hydrogenation. Also, organic iron 40 salts coming overhead with the fines are reduced during the hydrogenation and thus an increase in product yield is realized. Furthermore, any oxidized synthesis catalyst is partially reduced. As 45 pointed out above, this is of great advantage, because oxidized synthesis catalyst favors wax formation.

Hydrogen may be withdrawn from reactor 56 and at least in part recycled 50 through lines 55 and 63, and 65. Recycle hydrogen rates in the order of 2000—10,000 cubic feet/barrel of oil are advantageously employed and the liquid throughout through reactor 56 is about 1 55 to 5 liquid volumes per volume reactor per hour.

Also withdrawn overhead through line 55 are volatile decomposition products resulting from the hydrogenation reactor, 60 such as volatile hydrocarbons, water, etc.

The overhead exit stream from 56 and withdrawn through line 55 may advantageously pass through cooler 57 and separator 61, wherein normally condensible material is cooled and separates out 65 as a liquid. This liquid, comprising lower molecular weight hydrocarbons, water, etc. may be sent to its own liquid products separating and fractionation system through line 65. 70

After the desired conversion in reactor 56, a slurry containing now cleaned reduced catalyst and saturated oil with little or no oxygen content is withdrawn from 56 through line 60 and is pumped 75 to filter 62, which may be of any conventional type, such as a rotary press, plate and frame, etc. for removing solids from liquids. The liquid product from filter 62 may be withdrawn through line 69 and 80 may be further processed if necessary. Even without further processing it is suitable for use as a diesel fuel, having high cetane values of from 60—70.

Catalyst from which the bulk of adher- 85 ing oil has been removed during the filtration process and which is substantially free of wax is withdrawn from filter 62, and is conveyed by any suitable means, such as conveyors, lock hoppers, etc., 90 through line 64 to catalyst hopper 12, for reuse in the system.

By the term "wax" there is considered here those deposits on catalyst which are soluble in benzene and which 95 are substantially composed of hydrogen and carbon only.

If the quantity of fines in the slurry is such that, when composited with the dewaxed catalyst, it amounts to more than 100 about 10% of the total, the filtered material is preferably passed through a classification zone 66, such as a screen or other means of classification known in the art, to remove the fines prior to returning 105 catalyst to hopper 12.

The invention admits of numerous modifications apparent to those skilled in the art. Thus mention has not been made of various accessory equipment which 110 normally would be used in a commercial plant. Thus in the interest of good heat economy, various heat exchangers and economizers would be employed to utilize whatever heat is available in the most 115 efficient manner and, in order to control the process, pumps, compressors, flow meters, etc, would be included in the equipment.

Dated this 22nd day of November, 1948.

COMPLETE SPECIFICATION

Improved Hydrocarbon Synthesis

We, STANDARD OIL DEVELOPMENT COM-
PANY, a Corporation duly organized and
existing under the laws of the State of
Delaware, United States of America, hav-
ing an office at Elizabeth, New Jersey,
United States of America, do hereby de-
clare the nature of this invention and in
what manner the same is to be performed,
to be particularly described and ascer-
tained in and by the following state-
ment:—

The present invention relates to the
synthesis of hydrocarbons from carbon
oxides and hydrogen in the presence of
a suitable iron catalyst. This invention
relates more particularly to the treatment
of a powdered catalyst associated with an
oily hydrocarbonaceous and waxy
material, wherein the catalyst is cleansed
and valuable oily and waxy materials are
recovered.

The synthesis of hydrocarbons and
other valuable products from gas mix-
tures containing various proportions of
hydrogen and carbon oxides, particularly
carbon monoxide, both in fixed bed as
well as in dense phase fluid catalyst opera-
tion is well known in the art. The char-
acter and quality of the synthesis pro-
duct depends largely on the temperatures,
pressure, $H_2:CO$ ratios of the feed gas
and the nature of the catalyst used, the
latter being usually an iron group metal
catalyst promoted with such promoters as
various alkali metal compounds, rare
earth metal oxides, magnesia, alumina,
etc. in amounts of about 0.5—10%. Thus
cobalt catalysts promoted with thoria
and/or magnesia have been used at rela-
tively low pressures of about 15—75 psig.
and relatively low temperatures of about
350° to 450° F., and high $H_2:CO$ ratio of
2 or more to produce a substantially satur-
ated hydrocarbon material from which
valuable diesel fuels, lubricating oils, and
waxes may be obtained. Iron-type cata-
lysts, usually promoted with a suitable
alkali metal compound, such as carbon-
ates, halides, etc. of potassium or sodium
may be used in combination with rela-
tively high pressures up to 600 to 700
psig. and temperatures of 450° to 750°
F., and lower $H_2:CO$ ratios generally not
above 2. to produce predominantly
unsaturated material from which large
proportions of high octane motor fuels
may be recovered.

While it has thus been possible to
obtain high octane motor fuels in good
yields by this process, it has also been
found that operations under conditions
that favor good yields of useful (i.e.,
C_4+ oil) products are accompanied by ex-
cessive deposition of carbon and carbon-
aceous material upon the catalyst. This
carbon deposition is a serious problem,
both when the catalytic operation is
carried out by the fixed bed and the fluid
catalyst technique, which latter, because
of better heat distribution, transfer and
control and because of the more intimate
mixing and contact of the catalyst with
the reactants, is considered far superior
to fixed bed processes for effecting the
catalytic synthesis of hydrocarbons. How-
ever, two problems that arise in conjunc-
tion with the fluid solids type of opera-
tion are the fouling and consequent in-
activation of the catalyst by formation
and deposition of waxy materials and the
tendency of catalyst particles to agglo-
merate as a result of the wax formation
and deposition. Wax deposition due to
catalyst inactivation not only cuts down
product yield but causes poor fluidization
of the catalyst, poor temperature control,
agglomeration and conditions requiring
shut down of the plant.

The present invention is particularly
concerned with the removal of waxy
material from a catalyst used in the
synthesis of hydrocarbons in a fluid solids
type operation.

As stated above, one of the principal
problems in the application of the fluid
catalyst technique to the synthesis of
hydrocarbons from CO and H_2 has been
the accumulation of wax or heavy oil on
the catalyst. In the fixed bed operation
this was not a serious problem; because
of the downflow, the wax drains off the
catalyst, and wax could be allowed to
collect to the extent of 100 to 150% by
weight of catalyst before activity of the
catalyst was seriously impaired, and con-
sequently wax removal was required only
at infrequent intervals such as every 30
or 60 days. Also, particle motion was
not important. However, in the fluid
type of operation the accumulation of
wax on the catalyst interferes with proper
fluidization of the catalyst long before the
wax content of the catalyst is sufficient to
interfere seriously with the activity there-
of. One of the ways wherein wax inter-
feres with fluidization is by accumulation
on any relatively cold walls. Fine cata-
lyst particles make contact with this wax,

are wetted thereby, and the resulting agglomerate falls into the reactor and causes poor fluidization and/or coking and caking. Thus it has been found, for example, in a fluid type operation that only about 20 to 25 weight percent of wax can be tolerated on the catalyst before it causes sticking together of the catalyst particles, thus preventing proper aeration and fluidization which are essential for the operation of the fluid type process.

It has been proposed to remove catalyst from the reactor and to treat it with a solvent to remove the materials contained therein. Not only is this an expensive operation, but it is impossible to remove completely the deposit from the catalyst by solvent extraction. It is also possible to burn the deposit from the catalyst, but in this case the catalyst must be reduced before re-employment and it frequently suffers deterioration during the cycle. Beside the association of the catalyst within the synthesis reactor with heavy oil and waxy materials, another part of the catalyst is also closely associated with heavy oil in the catalyst recovery system. When upflowing synthesis gas is contacted with a dense bed of turbulent fluidized catalyst particles, the product stream comprising reaction products, unreacted gases and catalyst fines generally pass in the upper section of the reactor through a gas-solids separator, such as a cyclone, wherein the greater part of the catalyst fines and entrained catalyst particles is removed from the gas stream and returned to the catalyst dense bed. However, a minor portion of the catalyst is not removed by this means, and to prevent such catalyst fines that remain suspended in the vapors leaving the gas-solids separator from contaminating the liquid product, it is customary to contact the product vapors with a circulating oil stream to scrub out the remaining catalyst from the product stream. The resultant slurry is then settled or concentrated by some conventional means, such as thickening, and the thickened material usually discarded.

As a result therefore, of the formation of waxy deposits on synthesis catalyst within the reactor and of the product vapor scrubbing process wherein catalyst is scrubbed out of hydrocarbon synthesis product vapors, there is lost not only catalyst but also a significant proportion of product oil—i.e., that associated with the catalyst within and without the reactor.

It is, therefore, the main object of the present invention to separate oily or waxy material from finely divided hydrocarbon synthesis catalyst, simultaneously purifying the latter and recovering valuable oily material.

Another object of the invention is to recover a high quality diesel oil from the hydrocarbon synthesis process.

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

In the preferred embodiment the catalyst from the two sources, the reactor and the recovery system is mixed as a slurry with high-boiling (400 +° F.) synthesis product in a reactor and subjected to low pressure hydrogenation. This operation consists of passing the slurry with hydrogen through a reactor at pressures in the order of 50 to 750 psi. and temperatures of about 500° to 800° F.

It is known to regenerate or revivify spent Fischer synthesis catalyst by reduction with hydrogen, e.g. as a fluidised bed, in the course of which waxy contaminants are partially removed. Such proposals are limited to the treatment of the catalyst as such, however, and differ from the process of the present invention in which a slurry of catalyst in oil is hydrogenated, so giving excellent wax removal together with the production of an improved oil fraction.

Not only are the olefinic constituents of the oil phase of the slurry hydrogenated and oxygenated materials converted so that an excellent diesel oil in the order of 60 to 70 cetane number is obtained, but also the heavy oil and the wax are removed from the catalyst. Furthermore, the catalyst is also partially reduced in case it was oxidized in the reactor. Under the conditions specified, the hydrocarbon synthesis catalyst itself acts as the hydrogenation catalyst and no other catalyst need be added for the desired reaction. Inasmuch as a hydrogen manufacturing plant is almost invariably a part of a synthesis plant to reduce the feed catalyst, such plant is readily adaptable to furnish the hydrogen for use in accordance with the present invention.

Having set forth the general nature, advantages, and objects of the invention, the latter will best be understood from the more detailed description hereinafter in which reference will be made to the drawing accompanying the Provisional Specification which is a diagrammatic representation of a system suitable to carry out a preferred embodiment of the invention.

Referring now in detail to the drawing, 2 is a reactor preferably in the form of a vertical cylinder with a conical base and an upper expanded section, having a screen or grid 4 located in the lower section to effect good gas distribution, and a catalyst withdrawal line 6 extending through grid 4. A synthesis gas feed

mixture of H_2 and CO in synthesis proportions, that is, a mol ratio of H_2 to CO of between 0.7 and 1.8 to 1, is introduced into the reactor through line 8 and flows upwardly through grid 4.

Within reactor 2 a mass of powdered iron catalyst, such as alkali metal promoted sintered reduced pyrites ash is maintained in the form of a dense fluidized bed, having particle size distribution such that less than 10% of these particles have diameters 0—20 microns, and all of the material is finer than 100 mesh. This catalyst may be supplied to reactor 2 through line 10 from catalyst hopper 12. The linear velocity of the gases within reactor 2 is within the approximate range of 0.3 to 1.5 feet per second, and under these circumstances the catalyst assumes the form of a dense, turbulent mass, having a well-defined upper level and an "aerated" density of about 30—150 lbs./cu.ft. depending upon fluidization conditions. The pressure within the reactor may vary from about 250 to 750 psig., and the reaction temperature, which may be controlled with the aid of cooling coils (not shown) located in the dense phase of the catalyst bed, is kept uniform at about 450°—750° F.

The catalyst is preferably promoted with about 0.3 to 1.5% by weight of an alkali metal salt, such as K_2CO_3, Na_2CO_3 or KF. Higher concentrations, particularly in the presence of catalyst fines in the 0—20 micron range favor formation of high boiling and waxy materials. Furthermore, even when the total promoter content on the catalyst is within the above range, the presence of high concentrations of 0—20 micron fines is undesirable from a wax forming point of view because the finer catalyst usually contains the highest concentration of promoter which has been found to increase wax accumulation. Also fines are usually more highly oxidized than coarser catalyst, and a catalyst oxygen content above about 15% definitely promotes formation of wax deposits.

When entering the enlarged section of reactor 2 the gas velocity is sufficiently decreased so that the gases no longer support any substantial quantity of catalyst, and most of the coarser particles entrained in the gas drop back into the fluidized mass.

The volatile reaction products containing as well varying quantities of entrained catalyst fines and also finely divided organic iron compounds are withdrawn through a gas-solids separator, such as cyclone 14 equipped with dip pipe 16. The bulk of the entrained catalyst fines is removed in the cyclone and re-

turned to the fluidized bed via dip pipe 16.

The reaction products and the remaining catalyst fines, and undesirable synthesis product contaminants, such as entrained iron salts of fatty acids are passed from the top of reactor 2 through line 17 and may be partially condensed in cooler 18. The reaction products and catalyst fines are then passed into oil scrubber 20 wherein the remaining entrained catalyst powder is removed by circulating product oil in a manner known per se. The temperature within scrubber 20 is preferably above 175—250° F. so that lighter and lower boiling vapors are not substantially scrubbed out by the oil. The overhead vapors and gases from scrubber 20, comprising tail gas and reaction products uncondensed in cooler 18 and scrubber 20 are then passed through line 22 to cooler 24 and partial condenser 26. The latter are operated at such temperatures that reaction products boiling above 400° F. are substantially condensed in condenser 26 but lighter reaction products pass overhead as vapor through line 28, are substantially cooled in cooler 30 and pass to separator 32 wherein normally condensible synthesis products are withdrawn and sent via line 34 to the liquid products recovery system. Non-condensible tail gas from separator 32 is removed overhead through line 36, a portion sent back as recycle to reactor 2 via line 38, and the balance withdrawn through line 40, used in the plant as desired, such as fuel, recycle to gas generator, etc.

The condensate in separator 26, comprising oily synthesis products boiling above 400° F. is withdrawn through line 42, and, as required, sent as scrubbing oil to catalyst scrubber 20 via line 44. A portion of the condensate from condenser 26 may be sent to the liquid products recovery system.

A liquid stream comprising scrubbing oil, scrubbed catalyst fines, and other condensed, scrubbed, or entrained reaction products, such as organic iron salts is withdrawn from oil scrubber 20 and passed through line 46 to slurry mixing tank 48, preferably equipped with means of mechanical agitation.

Returning now to reactor 2, a stream of catalyst is intermittently or continuously withdrawn from the dense bed through catalyst withdrawal line 6, which may be provided with aeration taps 50 to aid in the moving of the catalyst through the line. Catalyst is preferably withdrawn from reactor 2 as wax accumulates, evidenced by decrease in fluidizability, and is passed to slurry mixing tank 48. Catalyst and liquid stream from

scrubber 20 are preferably so proportioned that the resulting slurry has a composition of about 1—3 lbs. catalyst per gallon of oil.

5 The catalyst-oil slurry is now pumped through slurry pump 52 and line 54 to hydrogenation reactor 56. This is a reactor of conventional design, which may be packed with non-catalytic material,
10 such as Raschig rings, pumice or activated carbon, to aid in the mutual contacting of liquids, gases, and finely-divided catalytic solids. Because of the nature of the synthesis catalyst, no ex-
15 traneous hydrogenation catalyst need be added to reactor 56. Hydrogen from any convenient source, as from the hydrogen manufacturing plant commonly associated with a synthesis plant is supplied to
20 reactor 56 through line 58. Reactor 56 is under pressure of about 50 to 750 psi., preferably 300 to 500 psi., and a temperature of about 500°—800° F. Under these conditions not only are the oxy-
25 genated organic compounds present in the 400+° F. products comprising the slurry reduced, and the olefinic constituents saturated, but also the waxy constituents deposited on the synthesis catalyst are re-
30 moved partly by solution in the slurry oil, and partly by being broken down to smaller molecular fragments as a result of the hydrogenation. Also, organic iron salts coming overhead with the fines are
35 reduced during the hydrogenation and thus an increase in product yield is realized. Furthermore, any oxidized synthesis catalyst is partially reduced. As pointed out above, this is of great advan-
40 tage, because oxidized synthesis catalyst favors wax formation.

Hydrogen may be withdrawn from reactor 56 and at least in part recycled through lines 55 and 63, and 65. Recycle
45 hydrogen rates in the order of 2000—10,000 cubic feet/barrel of oil are advantageously employed, and the liquid throughput through reactor 56 is about 1 to 5 liquid volumes per volume reactor
50 per hour.

Also withdrawn overhead through line 55 are volatile decomposition products resulting from the hydrogenation reactor, such as volatile hydrocarbons and water.
55 The overhead exit stream from 56 and withdrawn through line 55 may advantageously pass through cooler 57 and separator 61, wherein normally condensible material is cooled and separates out
60 as a liquid. This liquid, comprising lower molecular weight hydrocarbons, water, etc. may be sent to its own liquid products separating and fractionation system through line 65.
65 After the desired conversion in reactor

56, a slurry containing now cleaned reduced catalyst and saturated oil with little or no oxygen content is withdrawn from 56 through line 60 and is pumped
70 to filter 62, which may be of any conventional type, such as a rotary press, plate and frame, etc. for removing solids from liquids. The liquid product from filter 62 may be withdrawn through line 69 and
75 may be further processed if necessary. Even without further processing it is suitable for use as a diesel fuel, having high cetane values of from 60—70.

Catalyst from which the bulk of
80 adhering oil has been removed during the filtration process and which is substantially free of wax is withdrawn from filter 62, and is conveyed by any suitable means such as conveyors, lock hoppers, etc.,
85 through line 64 to catalyst hopper 12, for reuse in the system.

By the term "wax" there is considered here those deposits on catalyst which are soluble in benzene and which
90 are substantially composed of hydrogen and carbon only.

If the quantity of fines in the slurry is such that, when composited with the dewaxed catalyst, it amounts to more
95 than about 10% of the total, the filtered material is preferably passed through a classification zone 66, such as a screen or other means of classification known in the art, to remove the fines prior to re-
100 turning catalyst to hopper 12.

The invention admits of numerous modifications apparent to those skilled in the art. Thus mention has not been made of various accessory equipment which
105 normally would be used in a commercial plant. Thus in the interest of good heat economy, various heat exchangers and economizers would be employed to utilize whatever heat is available in the most
110 efficient manner and, in order to control the process, pumps, compressors, flow meters, etc., would be included in the equipment.

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

1. A Fischer synthesis process using a
120 dense fluidised iron catalyst, in which the catalyst becomes contaminated with waxy material formed during the synthesis, wherein a portion of the catalyst is continuously or intermittently with-
125 drawn from the synthesis zone and mixed with a liquid hydrocarbon fraction boiling in the gas oil range to form a slurry which is hydrogenated in a hydrogenation zone, partly reduced and dewaxed cata-
130 lyst and hydrogenated slurry oil being

recovered from the hydrogenation zone, and the catalyst, after separation from the hydrogenated slurry oil, recycled to the synthesis zone.

2. A process as claimed in Claim 1, wherein the said liquid hydrocarbon fraction boiling in the gas oil range is recovered from the synthesis products.

3. A process according to Claim 1 or Claim 2, wherein volatile products containing entrained catalyst are withdrawn from the top of the synthesis zone and passed overhead to a scrubbing zone where the catalyst particles are removed with said liquid hydrocarbon fraction,

and the light slurry so formed is mixed with the waxy catalyst withdrawn from the bottom of the synthesis zone and passed to the hydrogenation zone.
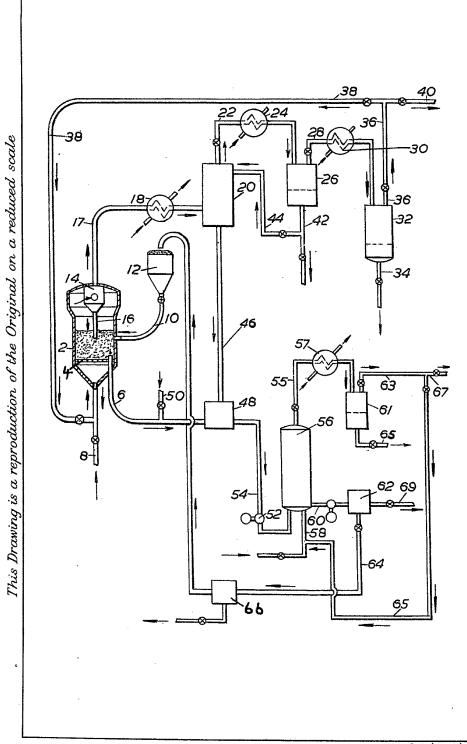
4. A process according to any of the preceding claims, wherein the pressure in the hydrogenation zone is between 50 and 750, preferably 300 to 500 lbs. per sq.in., and the temperature between 500 and 800° F.

5. A Fischer synthesis process as described with reference to the accompanying drawing.

Dated this 12th day of October, 1949.

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