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COMPLETE SPECIFICATION

Process for the Catalytic Hydrogenation of Carbon Monoxide

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The invention relates to a process for the catalytic hydrogenation of carbon monoxide.

The catalytic hydrogenation of carbon monoxide is well known. In such a process, a synthesis gas containing carbon monoxide for example, a synthesis gas containing carbon monoxide and hydrogen is contacted under synthesis conditions of temperature and pressure with a catalyst effective for the hydrogenation of carbon monoxide. The synthesis products obtained, which may, for example, consist predominantly of hydrocarbons or of hydrocarbons and oxygen-containing organic compounds, are then recovered. The several synthesis conditions, including the various catalysts which may be used, the preparation of the catalysts, the composition of the synthesis gas, the synthesis conditions of temperature and pressure, and the like, are well known and have been repeatedly described in the literature.

It is known, in the catalytic hydrogenation of carbon monoxide, to recycle a portion of the gas leaving the synthesis reactor back to the reactor for conversion, after more or less extensive separation of the synthesis products from such recycle gas and after admixture with fresh synthesis gas. It is also known in "recycle syntheses" of this kind to remove the carbon dioxide from the gas which is to be recycled, since the carbon dioxide effects an undesirable dilution of the synthesis gases. By removing carbon dioxide from the recycle gas, the rate of conversion can be increased. This method of operation, however, has the disadvantage that large quantities of gas must be treated by means of liquids effective for the absorption of the carbon dioxide.

It is an object of the invention to obtain high rates of conversion in the catalytic hydrogenation of carbon monoxide with recycling of exit gas from the synthesis reactor.

It has now been found, according to the invention, that high conversion rates may be obtained in the catalytic hydrogenation of carbon monoxide with catalysts by means of which CO_2 is formed as a by-product of the synthesis and with the known recycling of exit gas from the synthesis reactor, if the gas to be recycled is divided into two streams, one of which is returned to the synthesis reactor without removal therefrom of its content of carbon dioxide, whilst the carbon dioxide is removed as far as possible from the other stream which is then combined with the incoming fresh synthesis gas.

The part-stream of exit gases from the reactor which is recycled without removal therefrom of its content of carbon dioxide is recycled after condensation of the synthesis products but prior to the final oil scrubbing, low temperature cooling or active carbon treatment, and is hereinafter referred to as "recycle gas I", whilst the other part-stream which is recycled after separation of the synthesis products and the removal of carbon dioxide, is hereinafter referred to as "recycle gas II".

1—4 volumes of recycle gas I may be used per volume of fresh synthesis gas, whilst as much as 1.5 volumes of recycle gas II freed from carbon dioxide are used per volume of fresh synthesis gas. Recycle gas II is preferably used in an amount of 0.3—0.9 volumes per volume of fresh synthesis gas. The carbon dioxide contained in recycle gas II is removed as far as possible, at least to a residual content of 1—3% by volume by washing the gas with water under pressure or with suitable absorbing solutions.

Two methods of operation according to the invention are illustrated in the flow diagrams shown in Figures 1 and 2 of the accompanying drawings.

In the method illustrated in Figure 1, fresh synthesis gas is passed through conduit 1 to a synthesis reactor 2. The composition of the synthesis gas, construction of the synthesis reactor, the catalyst contained therein, and all of the synthesis conditions of temperature, pressure, throughput, and the like, are well known in the art. Any carbon monoxide and hydrogen-containing gas which is suitable for the catalytic hydrogenation of carbon monoxide may be used as synthesis gas for the process of the invention. Of particular advantage is the use of gases which are, for example, obtained by pressure gasification of carbonaceous materials with the use of oxygen. Gases which have been produced by the cracking of hydrocarbons may also be used.

Any operational method known for the catalytic hydrogenation of carbon monoxide may be used for catalytically reacting these synthesis gases. It is possible to operate with fixed-bed catalysts with fluidized catalysts, with catalysts, which are suspended in liquids, or with catalysts which are moved continuously downwardly through the synthesis zone.

The hydrogen to carbon monoxide ratio in the synthesis gas may vary within wide limits; thus it is possible to use synthesis gases which contain from 0.7 to 3 volumes of hydrogen per volume of carbon monoxide. The temperature used in the synthesis zone may lie between 170° C. and 350° C., the preferred temperature range being 200°—280° C. The gas pressure in the synthesis zone may lie between 5 and 100 kg./sq. cm. and is preferably within the range 10—40 kg./sq. cm.

After passage through the synthesis reactor 2, the hot exit gas from the reactor is passed via conduit 3 through a heat exchanger 4 of known construction and thereafter condensation of the synthesis products is effected in known manner in a condenser 5. After passage through the condenser 5, a part (recycle gas I) of the effluent gas from the synthesis reactor is recycled via conduits 6 and 7 through the heat exchanger 4, where it is heated by heat-exchange with the hot exit gas from the reactor, and thereafter passed back for admixture with the fresh synthesis gas stream fed into the synthesis reactor 2 through the conduit 1. The remainder of the gas from the condenser 5 passes to an oil scrubbing unit 8 or similar device which is suitable for the separation of the synthesis products still present therein. The gas is withdrawn from the unit 8 through a conduit 9 and a part of the gas is withdrawn from the system as tail gas through a conduit 10. The remainder of the gas, constituting recycle gas II, is passed to a carbon dioxide scrubbing unit 11 of known construction, wherein the carbon dioxide is removed by scrubbing with a known absorbing solution or with water under pressure. After passage through the carbon dioxide scrubber, the recycle gas II which is practically free from carbon dioxide, is recycled through conduit 12 for admixture with the fresh synthesis gas being fed to the synthesis reactor through conduit 1. The two gas streams, recycle gas I and recycle gas II, are conveyed in known manner by recycle compressors 13 and 14 in lines 7 and 12.

In the flow diagram shown in Figure 2, wherein the same reference numerals, with the addition of the suffix *a*, designate the same parts of the plant as in Figure 1, the recycle gas II in conduit 12*a*, which has been extensively freed from its carbon dioxide content, is admixed with the cold, fresh synthesis gas in conduit 1*a*, and this mixture is admixed with the recycle gas I being recycled through conduit 7*a* disposed before the oil scrubbing unit 8*a*. The combined gases are then passed through the heat exchanger 4*a* in indirect heat exchange contact with the hot exit gases from the synthesis reactor 2*a*.

The usual forms of apparatus which are used on an industrial scale and which are known *per se*, may be used for carrying out the process of the invention. The synthesis reactors used may be tubular reactors in which the catalysts is disposed in the tubes, or lamellar reactors in which the catalyst is disposed between walls of sheet metal through which cooling tubes pass at right angles thereto. If the catalyst is provided in tubes, the outer walls of the tubes are cooled by cooling media. The fixed-bed catalysts may also be disposed between vertical tubes with the cooling media flowing through the interior of the tubes. For carrying out the process of the invention with a fluidized bed of catalyst, the apparatus usual in the art are used.

The separation of the synthesis products is effected in a manner known in the hydrogenation of carbon monoxide. High boiling synthesis products may be separated directly in the liquid form upon leaving the synthesis reactor. Further synthesis products are subsequently separated from the gases in the liquid state in a heat exchanger at 90°—120° C. and in a gas cooler, downstream of the heat exchanger at 20° C. to 45° C. The last C_3—C_4 hydrocarbons still contained in the exit gases may be separated by means of a scrubbing liquid, for example, in an oil scrubbing unit, or in an absorption unit, such, for example, as an active carbon unit.

The invention is illustrated by the following example:—

EXAMPLE

Use was made of a catalyst which contained 100 parts by weight Fe, 25 parts by weight Cu, 5 parts by weight K_2O and 25 parts by weight SiO_2. This catalyst had been reduced for 80 minutes at 180° C. with hydrogen at a gas flow velocity of 1.5 cm./second in such a manner that 25% of the iron was present in the metallic form, and the catalyst was used in synthesis in a known kind of tubular reactor. The synthesis gas temperature was

220° C. and the gas pressure was 20 atmospheres. The H_2:CO ratio in the fresh synthesis gas was 1.68. The quantity of tail gas removed from the cycle was about 15% based on the volume of fresh synthesis gas, and the CO + H_2 conversion was 89.0%.

The composition of the individual gas streams was as follows:—

	Volume %					
	CO_2	C_nH_m	CO	H_2	CH_4	N_2
Fresh gas	1.8	—	35.9	60.5	—	1.8
Gas entering the reactor	8.5	0.5	24.5	48.9	8.4	9.2
Gas recirculated after CO_2 scrubbing unit	0.1	0.6	23.6	50.3	11.4	14.0
Mixture of CO_2—free recycle gas and fresh synthesis gas	1.4	0.2	32.7	57.6	3.3	4.8
Tail gas	12.0	0.2	22.0	46.1	8.1	11.6

The flow of the individual gas streams was as illustrated in Figure 2. The synthesis products were passed in gaseous form from the synthesis reactor *2a* into the heat exchanger *4a* where they were cooled to about 120° C. by indirect heat exchange with the feed gas. The cooled synthesis products then passed to the condenser *5a* wherein they were further cooled to about 35° C. by indirect heat exchange with water. The liquefied products were removed from the condenser *5a* and part of the residual CO_2—containing gas was recycled through line *7a* as recycle gas I. The remainder of the residual gas was then passed through the oil scrubbing unit *8a* and the exit gas from the unit *8a* was divided into two streams, one stream being removed from the system through the line *10a* and the other stream being passed through the CO_2—scrubber *11a* and then recycled, as recycle gas II, for admixture with the fresh synthesis gas fed in through the line *1a* and with recycle gas I.

The tail gas (recycle gas I) recycled through conduit *7a* constituted about 250% by volume of the fresh synthesis gas, whilst the volume of the CO_2—free gas (recycle gas II) recycled through conduit *12a* was about 30% of that of the fresh feed gas. The gas removed from the system through conduit *10a* constituted about 15% by volume of the fresh synthesis gas.

The composition of the synthesis product was as follows:—

5% of oxygen-containing organic compounds;
14% of C_2—C_4 hydrocarbons;
16% of a benzine fraction (boiling range 30°—180° C.);
16% of a diesel oil fraction (boiling range 180°—320° C.);
20% of a hydrocarbon fraction boiling in the range 320°—460° C.
29% of a hydrocarbon fraction boiling above 460° C.

Thus 49% of the total synthesis product had a boiling point of not less than 320° C.

By the process in accordance with the invention, there occurs no change in the loading of the catalyst and, as indicated by the figures given above, a conversion of as high as 90% or more is obtained.

What we claim is:—

1. A process for the synthesis of hydrocarbons by the hydrogenation of carbon monoxide in the presence of a catalyst which yields carbon dioxide as a by-product of the synthesis, which comprises recycling a part of the exit gases from the synthesis reactor, dividing the recycled gas into two streams, recycling one of the streams without removing therefrom its content of carbon dioxide, and removing the carbon dioxide from the other stream before recycling it to the reactor.

2. A process according to Claim 1, in which the recycled stream from which the carbon dioxide is removed is mixed with incoming fresh synthesis gas and the mixture is added to the gas stream recycled without carbon dioxide removal, the whole mixture being passed in heat exchange with the exit gases from the synthesis reactor before being fed into the reactor.

3. A process according to Claim 1 or Claim 2, in which that stream from which the carbon dioxide has not been removed, is recycled to the synthesis without separating therefrom the low boiling hydrocarbons still contained therein.

4. A process according to any one of Claims 1 to 3, in which that stream from which the carbon dioxide is removed, is treated for the removal of its content of low boiling synthesis products prior to the removal of its content of carbon dioxide.

5. A process according to Claim 4, in which the low boiling synthesis products are removed from the gas stream by scrubbing the gas with oil, or subjecting the gas to a low temperature treatment or to a treatment with active carbon.

6. A process for the catalytic hydrogenation of carbon monoxide, substantially as hereinbefore described.

7. A process for the catalytic hydrogenation of carbon monoxide, substantially as hereinbefore described with reference to Figure 1 or Figure 2.

8. A process for the catalytic hydrogenation of carbon monoxide, substantially as hereinbefore described with reference to the example.

9. Hydrocarbons and oxygen-containing organic compounds whenever obtained by the process claimed in any preceding claim.

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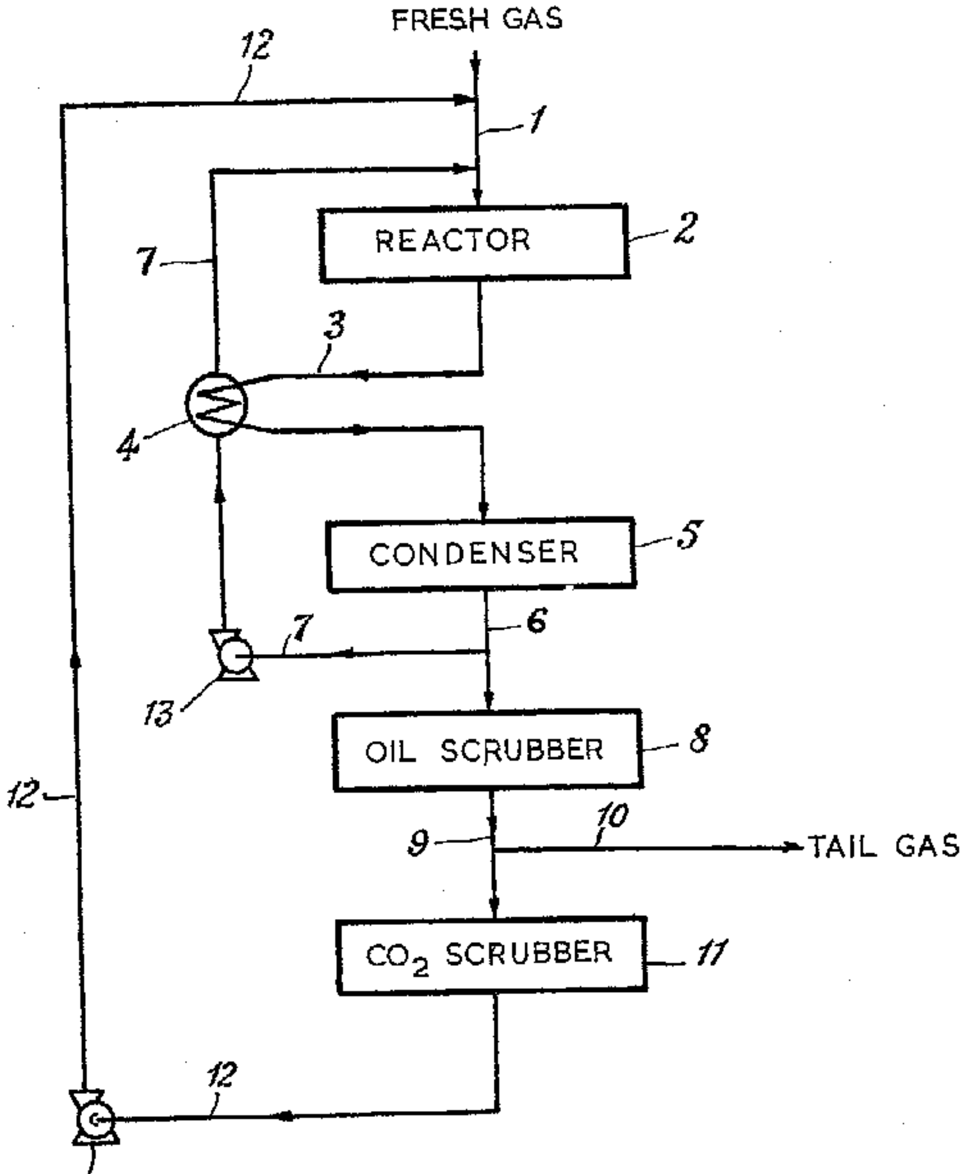
FRESH GAS
12
1
REACTOR
2
7
3
4
CONDENSER
5
6
7
13
OIL SCRUBBER
8
12
9
10
TAIL GAS
CO2 SCRUBBER
11
12
14

Fig. 1

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2 SHEETS *This drawing is a reproduction of the Original on a reduced scale*
Sheets 1 & 2

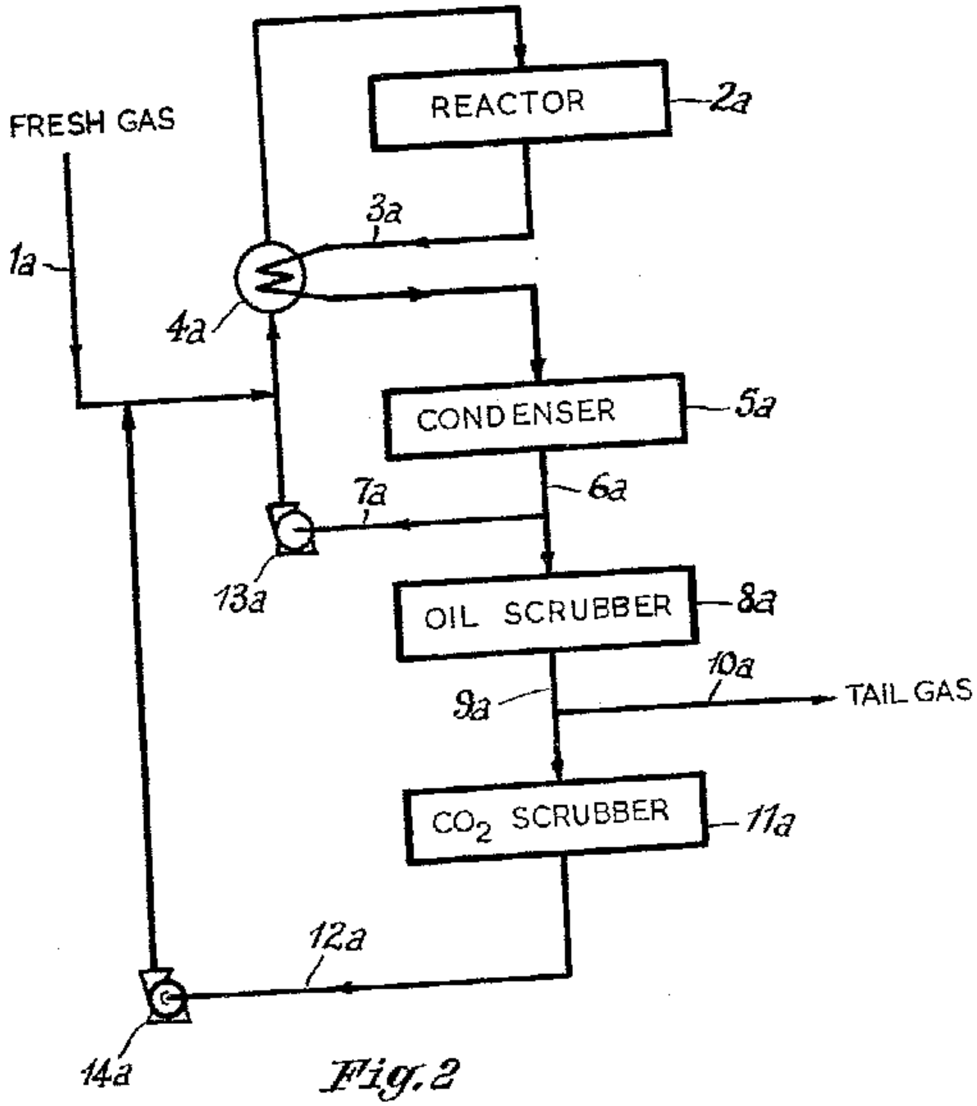

Fig. 2

AIL GAS

780377 COMPLETE SPECIFICATION
2 SHEETS This drawing is a reproduction of the Original on a reduced scale
Sheets 1 & 2

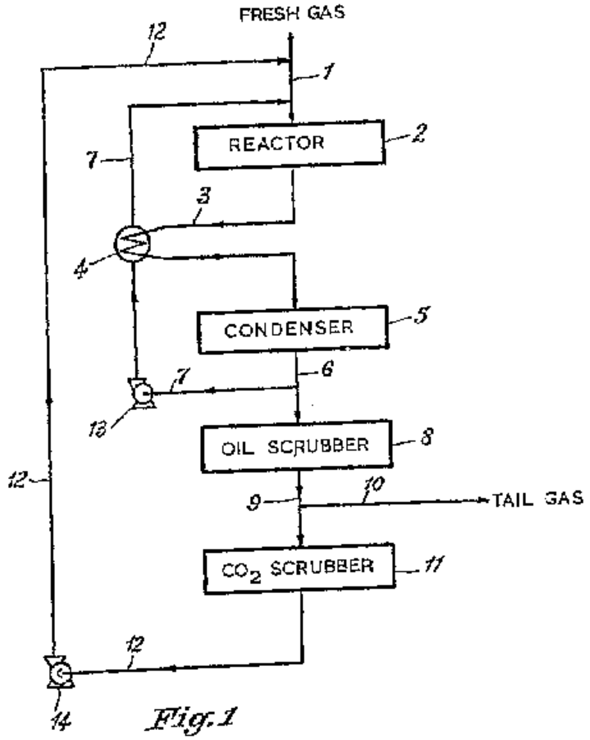

Fig.1

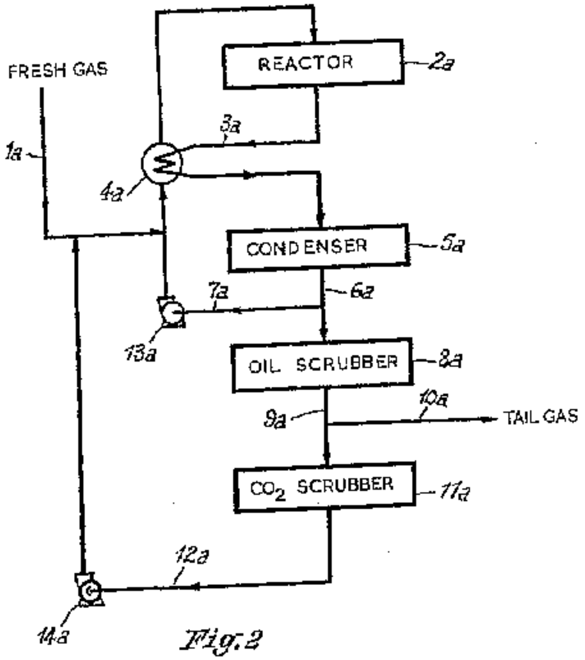

Fig.2