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(54) IMPROVEMENTS RELATING TO FISCHER TROPSCH HYDROCARBON SYNTHESIS

(71) We, SOUTH AFRICAN COAL, OIL AND GAS CORPORATION LIMITED, of Klasie Havenga Road, Sasolburg, O.F.S., Republic of South Africa, a South African Corporation, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to a method for controlling, in the catalytic Fischer-Tropsch synthesis of hydrocarbons from gases comprising hydrogen, carbon monoxide and CO_2 in the presence of an iron catalyst, the relative yields of low molecular weight, predominantly gaseous, aliphatic hydrocarbons to higher molecular weight hydrocarbons which comprises selecting a catalyst having a basicity compatible with the attainment of a desired relative yield.

A big advantage of using iron instead of for example, nickel as a catalyst, is the relative cheapness of iron

In such synthesis it is desirable to be able to control the selectivity of the synthesis process in respect of the relative yields of low molecular weight (predominantly gaseous) and higher molecular weight (predominantly liquid) hydrocarbons, depending on the desired end use of the synthesis product.

It was previously known that with iron catalysts such selectivity is predominantly controlled by two factors: the basicity of the catalyst and the gas composition. The basicity is controlled by the promoter content of the catalyst and depends on the amount of group I alkali metal in the form of basic compounds, e.g. K_2O, Na_2O and the like per unit of effective surface area of the catalyst, the effective basicity being also influenced by other promoters, e.g. silica. Generally speaking, the lower the basicity, the higher is the selectivity for high yields of low molecular weight hydrocarbons, in particular methane. With regard to gas composition, it was previously believed that the ratio of $H_2O:CO$ controls the selectivity of iron catalysts in respect of relative yields of low molecular weight to higher molecular weight hydrocarbons. This is true at comparatively low temperatures, in particular at temperatures up to about 250°C, which is about the upper limit conventionally used in the past.

However, it was now found desirable to raise the reactor temperature in order to increase the conversion rates (a pre-requisite for the attainment, for example of product gases of high heat value). It was surprisingly discovered that at such higher temperatures the influence of H_2O/CO ratio ceases to be the controlling factor (besides catalyst basicity), and that from a certain temperature onwards (which is easily determinable for a given catalyst) the dominating factor controlling the selectivity of iron catalysts in respect of relative yields of higher and lower molecular weight hydrocarbons, is the partial pressure of CO_2 (as distinct from the relative ratio of CO_2 to the remaining gas components).

It is an object of the invention to utilise the above important discovery so as to enable the person skilled in the art to manipulate the said selectivity in a desired sense mainly by adjusting in a given system the partial pressure of CO_2.

The present invention is based inter alia on the surprising discovery that at temperatures above 250°C, and even more so from 280°C onwards, the relative yields of methane (and other gaseous hydrocarbons) on the one hand and of liquid hydrocarbons on the other hand can be controlled sensitively by appropriate adjustment of the partial pressure of CO_2 provided the basicity of the catalyst is not in excess of and preferably below that of a pure iron catalyst promoted only with K_2O in an amount of $0.001\ g\ K_2O/m^2$ of effective surface area of the catalyst. By conventional standards this is a very low basicity.

Accordingly there is provided in accordance with the present invention a method for controlling the relative yields of low molecular weight, predominantly gaseous, aliphatic hydrocarbons and higher molecular weight hydrocarbons in the catalytic Fischer-Tropsch synthesis of hydrocarbons from feed gases comprising hydrogen, carbon monoxide and carbon dioxide in the presence of an iron catalyst, said method comprising reacting said feed gases in a reactor in the presence of a catalyst having a basicity equal to that of a Fischer-Tropsch catalyst consisting essentially of iron and not more than 0.001 g K_2O/m^2 of effective surface area of the catalyst, the K_2O being evenly distributed on the surface of the catalyst and at a temperature in excess of 250°C, and either

(a) adapted to suppress the formation of methane and other gaseous hydrocarbons in favour of the production of higher molecular weight products, in that the catalyst basicity as above defined corresponds to from 0.005 to 0.001 g K_2O/m^2 and the partial pressure of CO_2 measured in the reactor near the feed inlet exceeds 4 kg/cm² but is maintained below 7 kg/cm²; or

(b) adapted to favour the formation of methane and other gaseous hydrocarbons and to suppress the formation of higher molecular weight products, in that the catalyst basicity as above defined corresponds to from zero to 0.005 g K_2O/m^2 and the partial pressure of CO_2 measured in the reactor near the feed inlet is in excess of zero and up to 3 kg/cm².

Preferably a synthesis process including the above method is carried out at a total reactor pressure above 32 kg/cm² and between 280°C and 450°C.

Conventionally fixed bed Fischer-Tropsch reactors are usually operated at pressures up to about 27 kg/cm² whereas moving fluidized catalyst reactors are operated at pressures up to about 20 kg/cm². In the present process it is preferred to operate from pressures of 32 kg/cm² upwards, even in the case of a moving fluidized catalyst reactor, more particularly up to 70 kg/cm², say in the range of 35 to 70 kg/cm². Surprisingly such higher pressures result in a lower rate of carbon build-up.

These pressures are particularly preferred in the context of guiding the selectivity towards a suppression of the formation of methane. In that context a practical upper limit for the partial pressure of CO_2 would be 7 kg/cm², more preferably 6 kg/cm².

However, there now exists a considerable demand for gas of high heat value, that is to say, gas having a comparatively high content of low molecular weight hydrocarbons, and in particular of methane, and for the selective attainment of such a product an iron-type catalyst having either no alkali content at all, or a comparatively low basicity is selected and the partial pressure of CO_2 is adjusted to a low value. (It should be appreciated that in practice the partial pressure of CO_2 can never be zero because of the formation of carbon dioxide by reaction between carbon monoxide and water).

In practice it may nevertheless be desirable to control the synthesis in such a manner that also a reasonably high yield of liquid hydrocarbons, in particular naphtha is obtained, which by fractionation of the reaction products can be recovered as a further desirable product. The present invention enables the person skilled in the art to exercise improved control over the yields of such products.

Because of the commercial importance of being able to produce selectively gases of high heat value, that aspect of the invention will be stressed particularly in the further description of the invention.

In the present context, a high selectivity is particularly one in which the relative yield of hydrocarbons between of from 1 to 4 carbon atoms, both inclusive, exceeds 25%, more particularly 30%, and wherein the relative yield of methane is preferably at least 15%, more particularly at least 20%.

A practical approach would be to first select a convenient temperature and catalyst basicity and then decide on the partial pressure of CO_2 which is sufficiently low for the attainment of a desired degree of methane selectivity. The final adjustment is possible by simple experiment.

An alternative approach would be to decide on a convenient temperature at which the partial pressure of CO_2 has a greater influence on the selectivity than the H_2/CO ratio, adjusting the partial pressure of CO_2 in the feed gas to a value not exceeding 3 kg/cm², preferably not exceeding 2 kg/cm², more preferably from 0.4 to 1 kg/cm², and then determine by simple experiment in accordance with the principles herein taught the composition of the iron catalyst of which the basicity is sufficiently low for the attainment of the desired selectivity.

Within the preferred meaning of "high selectivity" as explained further above a catalyst as aforesaid, composed of iron and containing 0.0007 g K_2O per square meter of effective surface area of the iron, would necessitate maintaining the partial pressure of CO_2 as near as possible to the practical minimum, as well as carrying out the synthesis at a temperature of about 500°C which is normally too high a temperature for a process of this type. For operating at lower, more convenient temperatures, a correspondingly lower basicity (in practice equivalent to not more than 0.0005 g K_2O/m^2) must be employed for attaining the same selectivity as will be explained more fully further below. Generally speaking, it is preferred to carry out the process between

280°C and 450°C, more preferably between 280 and 400°C, more conveniently still between 300 and 360°C, the optimum temperature range from various practical points of view at present being considered to be between 305 and 330°C or at an average of about 320°C.

From the above and other data herein disclosed it can be determined that the preferred process for attaining a high methane selectivity is carried out at a temperature not less than $t_{min}(°C) = 250 + 35 \times 10^4a$, wherein a is the basicity of the catalyst, expressed as g K_2O/m^2 of effective catalyst surface area, being the amount of K_2O which when well distributed as the only promoter in a pure iron catalyst, will produce that particular basicity.

In order within the most preferred temperature range to still be able to attain at least 20% methane in the synthesis product within the practical limits of low partial pressures of CO_2, it is preferred to select a cataylst of which the basicity does not exceed that of an iron catalyst as aforesaid containing 0.0001 g K_2O per m² of effective surface area. Such comparatively low basicity can have the additional advantage, particularly within the preferred temperature range to facilitate the maintenance of a low rate of carbon deposition on the catalyst (other factors being favourable).

At the preferred temperature of about 320°C, the maximum partial pressure of CO_2 at which a high selectivity for low hydrocarbons, in particular methane, is attainable by appropriately lowering the basicity of the catayst, is apprximately 2 kg/cm². This maximum will increase slightly at higher temperatures, although the temperature dependency of that maximum is comparatively low.

For the aforesaid definitions of basicity, a substantially pure iron catalyst, promoted only with the respective amounts of K_2O, fused and ground in the normal manner, was taken as a standard for comparison. As will be readily understood by the person skilled in the art, the basicity of such catalysts can be varied in a variety of manners to achieve degrees of basicity which are empirically comparable with a given concentration of K_2O in pure iron catalyst (normally obtained from millscale). Thus for example, more Na_2O must be employed to achieve the same degree of basicity as a given amount of K_2O. Even high concentrations of lithium oxide achieve a comparatively low increase only in basicity for the purposes of the present invention. On the other hand, the effect of small additions of caesium oxide or rubidium oxide is comparatively greater than that of the same amount of K_2O. Acid components, such as SiO_2 or TiO_2 result in a lowering of the basicity.

Structural promoters such as magnesium oxide, aluminium oxide, calcium oxide, titanium oxide, chromium oxide (Cr_2O_3) and MnO have the effect of increasing the effective surface area of the catalyst, and accordingly lowering the basicity per unit of effective surface area.

In addition the overall activity of the catalyst can be adjusted in manners known per se by the judicious addition of group 8 (e.g. cobalt, nickel, platinum) and group 1B (e.g. copper) elements.

In principle the present invention is not limited to any particular type of synthesis reactor. However, because the process is carried out at comparatively high temperatures, it is preferred to carry out the process in those types of reactors which facilitate thermal control. More particularly, it is preferred to carry out the process with the catalyst maintained in an expanded condition by gas flowing therethrough, either in a dilute phase expanded condition, i.e. a gas-entrained condition or in a dense phase fluidized condition, i.e. either a moving or stationary fluidized bed. If it is desired to operate under fixed catalyst bed conditions, it is preferred to employ what is known as a diluted fixed bed.

Contrary to what would have been expected from the literature, it was found that within the temperature range to which the present invention relates, the rate of carbon deposition on iron catalysts was not simply dependent on the ratio H_2/CO or on the partial pressure of H_2O alone. Instead it was found to be dependent on both the actual partial pressures of carbon monoxide and of hydrogen, with hydrogen having the greater influence, more particularly to be proportional to $p_{CO}/p^3_{H_2}$.

This discovery forms the basis of a copending application 40928/73 (Serial No. 1439007) of even date, entitled "Improvements in Fischer-Tropsch Synthesis", which by reference thereto is to be considered as part of the present disclosure.

In the context of the present invention this principle is preferably applied in that in the context of selecting the total pressure in the reactor, the basicity of the catalyst and the partial pressure of CO_2, the overall composition of the reactor gas in the feed gas entry region is set so that $(P_{CO}/p^3_{H_2}) \times 10^5$ numerically does not exceed

$$\frac{b}{4}(13 - a \times 10^4),$$

wherein p_{CO} and p_{H_2} are the partial pressures of carbon monoxide and hydrogen respectively expressed in kg/cm², a represents the basicity of the catalyst, expressed as g K_2O/m^2 of effective catalyst surface area, being the amount of K_2O which when well distributed as the only promoter in a pure iron catalyst, will produce that particular basicity, and b is the acceptable rate of carbon deposition expressed as a g carbon per 100 g catalyst per day, the reactor temperature being between 300 and 340°C, an appropriate temperature correction being made in the above relationship when operating at temperatures outside that range. Preferably, in particular in the case of moving fluidized catalysts, b is taken as 4. This is so because it was found that a rate of carbon build-up of 4 g C/100 g catalyst/day is readily tolerated.

From the above relationship it is apparent that the rate of carbon deposition also depends (apart from temperature) on the basicity of the catalyst which should preferably be less than 0.0005 g K_2O/m^2 of effective surface area (as explained further above) more particularly less than 0.0002. However, it is also found that at very low basicities the rate of carbon build-up increases again. Accordingly, in order to achieve a low carbon deposition rate as well as a high selectivity for low hydrocarbons, in particular for methane, the preferred basicity is between 0.00005 and 0.0002, more particularly about 0.0001 g K_2O/m^2 effective surface area of catalyst.

For a given partial pressure of carbon monoxide it is also possible in accordance with the present teachings to decrease the rate of carbon deposition by only increasing the partial pressure of hydrogen. Surprisingly the partial pressure of carbon dioxide which has a decided influence on the composition of the synthesis products has virtually no influence on the rate of carbon formation.

It will be readily understood by those skilled in the art that the performance the present process does not depend entirely on the gas composition in the feed gas, but on the composition of the gas throughout its passage through the reactor, the partial pressure of carbon monoxide undergoes a very substantial change from the feed end to the outlet end of the reactor, the partial pressures of hydrogen and of carbon dioxide change less substantially. Also, in known types of reactors, the general patterns of these changes are substantially similar. Accordingly, it is possible from a practical point of view to define the parameters of the process in accordance with the invention with reference to the composition of the partial pressure of the components in the entry region of the synthesis feed gas.

Even though (as far as the gas composition is concerned) the partial pressure of carbon dioxide is the dominant factor, it alone does not control the selectivity, but to a lesser extent the partial pressures of the remaining gases (e.g. H_2O, CO, H_2) also influence the selectivity. As the water gas shift reaction is in equilibrium over iron catalysts at high temperature, these partial pressures are not independent parameters. Increasing the partial pressure of carbon dioxide automatically results in a decrease in the partial pressure of hydrogen and in an increase in the partial pressures of carbon monoxide and water vapour. In spite of this interdependence it is possible to control the selectivity for low hydrocarbons by controlling the partial pressure of carbon dioxide in the feed gas.

In the following the invention will be further described by way of example. The examples should be read in conjunction with the aforegoing more general description of the invention.

The accompanying drawing illustrates a typical relationship of methane selectivity plotted against partial pressure of CO_2 at different catalyst basicities.

Example 1.

One fluidized iron reactor.

The effect of the inlet CO_2 pressure on the methane selectivity is demonstrated in the drawing for three iron catalysts at different levels of basicity. While the reactor temperature was maintained at 320° the other reactor conditions such as feed gas composition, reactor pressure and fresh-feed to recycle-feed ratios were varied over wide ranges. As can be seen the lower the basicity of the catalyst the more pronounced the influence of the carbon dioxide partial pressure. For catalysts of higher basicity the CH_4 selectivity is much lower and the effect of CO_2 becomes progressively less. From the above it is clear that if maximum methane (and hence minimum oil) selectivity is desired catalysts of low basicity should be used at low partial pressures of CO_2.

In the present example graph (a) was obtained with a pure iron catalyst obtained from millscale, containing no basic promoter at all. Graph (b) was obtained with the same catalyst but promoted with some K_2O, corresponding to 0.0005 g K_2O per m^2 of effective surface area (a medium basicity catalyst). Graph (c) was obtained with the same catalyst, but containing more K_2O, equivalent to 0.0010 g K_2O/m^2, i.e. a high basicity catalyst.

If the CH_4 selectivities from the above experimental data are plotted against the H_2/CO ratio within the reactor a wide scatter is obtained indicating that the *ratio* does not play an important role in the product selectivity.

From the above studies it was also established that there is a definite relation between the methane selectivity and the other hydrocarbon gases, e.g. as the CH_4 selectivity increases both the ethane and propane selectivities first increase, pass through a maximum and then decrease while the liquid oil selectivity progressively decreases. On a carbon atom basis, for instance, when the C_1 selectivity is 50%, the C_2 is 12%, the C_3 11% and the liquid oil is 2%.

Example 2.

Using the catalyst (b) of the previous example at 320°C, and constant feed compositions and recycle ratios and the same reactor as in Example 1, syntheses were carried out at different total pressures, thereby increasing the partial pressures of the feed gas components with the following results:

TABLE 1

Total Pressure kg/cm^2	Reactor Inlet					Carbon Deposition rate*	CH_4 Selectivity %
	H_2/CO ratio	p_{H_2} $\frac{kg}{cm^2}$	p_{CO} $\frac{kg}{cm^2}$	p_{CO_2} $\frac{kg}{cm^2}$	$p_{CO}/p^3_{H_2}$ $\times 10^3$		
9.62	4.6	3.94	0.91	1.12	15	17	26
13.14	4.3	5.27	1.19	1.55	7.5	9	19
18.4	4.6	7.45	1.62	1.90	3.9	4	15
21.9	5.0	9.85	1.97	2.11	2.1	2.6	11

*g carbon/100 g Fe per 100 h.

From the above table it can be seen that in spite of the tendency of the H_2/CO ratio within the reactor to increase, the CH_4 selectivity actually decreases which correlates with the increase in CO_2 partial pressure.

Note that in spite of the increasing CO partial pressure the rate of carbon laydown decreases which indicates that the p_{co} alone certainly does not control carbon deposition.

The increase in partial pressure of H_2 clearly more than compensates for the increase in CO pressure. Furthermore it can be seen that the carbon deposition rate bears no relation with the H_2/CO ratio.

The above experiments were carried out with a moving fluidized catalyst.

The beneficial effect of higher pressures (i.e. lower $p_{co}/p^3_{H_2}$ values) on the rate of carbon deposition is clearly apparent. The lower the value of this parameter the lower the carbon deposition. From the above it thus emerges that contrary to literature expectations a low H_2 to CO ratio gas can be used without excessive carbon laydown if the reaction is carried out at high pressures. An additional advantage of higher pressures is the known fact that the rate of hydrogenation of carbon monoxide to hydrocarbons is higher.

To further illustrate that the hydrogen pressure is important not only the CO pressure in controlling carbon laydown the data in table 2 is presented.

TABLE 2

Reactor Inlet					Carbon deposition rate*	CH_4 Selectivity %
p_{H_2} kg/cm^2	p_{CO} kg/cm^2	p_{CO_2} kg/cm^2	$\frac{H_2}{CO}$ ratio	$\frac{p_{CO}}{3} \times 10^3$ p_{H_2}		
6.12	1.83	1.27	3.3	8.3	7.5	18
7.25	1.76	0.91	4.1	4.6	5.6	19
10.1	1.69	0.70	6.0	1.6	2.0	22

* g carbon/100 g catalyst per 100 h.

In these runs the CO partial pressures were very similar while the H_2 and CO_2 pressures were varied. With increasing hydrogen pressure the carbon deposition clearly decreased. Lowering p_{co_2} resulted in improved methane selectivity.

That the CO_2 pressure does not influence the rate of carbon formation is illustrated in the data in table 3 where the CO and H_2 pressures were kept virtually constant while the CO_2 pressure was varied. The partial pressure of CO_2 had a noticeable effect on methane selectivity, however, the lowest partial pressure of CO_2 resulting in the highest percentage methane in the tailgas. The data illustrate the link of CH_4 selectivity with CO_2 pressure rather than with the H_2/CO ratio.

TABLE 3

p_{H_2} kg/cm²	p_{CO} kg/cm²	p_{CO_2} kg/cm²	$\frac{H_2}{CO}$	$\frac{p_{CO}}{p_{H_2}^{3}} \times 10^3$	Carbon Deposition rate*	CH_4 Selectivity %
7.25	1.67	0.91	4.1	4.6	5.6	19
7.45	1.62	1.90	4.6	3.9	4.2	15
7.53	1.62	2.46	4.6	3.8	4.2	10
7.66	1.76	4.36	4.4	3.9	5.1	8

*g carbon/100 g catalyst per 100 h.

The results given in table 4 show that there is no real relation between the H_2/CO ratio and either the carbon deposition rate or the CH_4 selectivity. The ratio H_2:CO was kept approximately constant in these tests but both carbon deposition and methane selectivity varied markedly.

TABLE 4

H_2/CO	p_{H_2} kg/cm²	p_{CO} kg/cm²	p_{CO_2} kg/cm²	$\frac{p_{CO}}{p_{H_2}^{3}} \times 10^3$	Carbon deposition rate*	CH_4 Selectivity %
4.6	7.46	1.62	1.90	3.9	4.2	15
4.2	7.10	1.69	2.81	4.7	4.2	9
4.6	5.56	1.27	1.41	6.7	10	23
4.3	3.94	0.91	1.13	15	17	26

* g carbon/100 g catalyst per 100 h.

The results of this example also demonstrate that the basicity of 0.0005 g K_2O/m^2 of the catalyst is about the upper limit for attaining a reasonably high methane selectivity. Such a high basicity is therefore only recommended is besides methane a reasonably high yield of higher hydrocarbons is also desired.

The knowledge revealed by examples 1 and 2 can be applied over a wide range of conditions so that the desired products can be maximised and the carbon deposition can be minimised. To maximise higher molecular weight hydrocarbon production for instance, catalysts of high basicity should be used and the maximum gas pressures should be used to maximise the CO_2 partial pressure and to minimise the value of the parameter $p_{co}/p_{H_2}{}^{3}$

thus minimising the carbon deposition rate. To maximise methane production on the other hand, catalysts of low basicity should be used, high gas pressures should be used (to lower the value of $p_{co}/p^3_{H_2}$) but at the same time the partial pressure of CO_2 should be minimised. The simultaneous minimisation of $p_{co}/p^3_{H_2}$ and of P_{CO_2} is not normally possible and so a compromise has normally to be made between these two opposing factors.

Example 3.

Two fluidized iron reactors in series.

The first reactor operates at 320°C and at a pressure of 21.5 kg/cm². The tail gas of this reactor together with the required amount of CO_2 (taken from an upstream shift reactor) is fed to the second higher pressure reactor to obtain the desired conversion.

The composition of the fresh feed to the first reactor depends on the desired C_4+ selectivity. The results of three cases are illustrated in table 5.

TABLE 5

Case	H_2/CC ratio fresh feed	CO+CO_2 conversion %	Total Feed				Selectivity (C Basis)					Tail Gas Comp. %					
			P_{CO_2} kg/cm²	P_{CO} kg/cm²	P_{H_2} kg/cm²	$\frac{P_{CO}}{P^3_{H_2}} \times 10^3$	CH_4	C_2	C_3	C_4–C_6	Liq. Oil	H_2	CO	CO_2	C_1	C_2	C_3
a	4.8	98	0.05	0.84	12.5	0.4	71	14	8	7	0	53	0.1	0.4	41	2.6	0.9
b	3.3	92	0.49	1.27	9.9	1.3	55	16	10	16	2	39	0.7	3.4	46	4.2	1.5
c	2.8	84	0.91	2.60	10.6	2.2	42	17	13	23	5	35	0.4	8.8	44	4.5	2.1

Say the raw gas produced by the coal gasifiers has a H_2/CO ratio of *ca* 2.0. The higher the ratio of the feed gas to the first reactor the greater the amount of gas which has to be shifted and also because of the higher H_2 content of the tail gas of the first reactor, the more the work which has to be done in the second reactor. The higher the ratio of the feed gas the higher the methane selectivity (because of the lower CO_2 pressure) and the lower the rate of carbon depositions (because of the lower value of $p_{co}/p^3_{H_2}$).

The required amount of CO_2 is added to the tail gas from the first reactor, the mixture is pressurized to a higher pressure and fed to the second reactor. The results for the case in which the fresh feed to the first reactor had a H_2/CO ratio of 3.3 (case b in table 5) is illustrated in table 6. The second reactor operated at 38 kg/cm² with a fresh feed to recycle ratio of 2.0.

TABLE 6

Total Feed					C_4 Scrubbed Tail Gas							
					Anal. %							
p_{CO_2} kg/cm²	p_{CO} kg/cm²	p_{H_2} kg/cm²	$\frac{p_{CO}}{p_{H_2}^3} \times 10^3$	$CO+CO_2$ Conversion %	H_2	CO	CO_2	CH_4	C_2	C_3	N_2 + A	Joule/Nm³
0.56	0.42	7.87	0.9	93	17.1	0.1	0.7	69.5	6.6	2.5	3.5	3.91×10^6

Example 4.

One high pressure reactor.

From the experience gained (e.g. see table 5) it is clear that with a feed gas of H_2/CO ratio in the vicinity of 2.9 a scrubbed tail gas having a heating value in excess of 3.6×10^6 Joule/Nm³ could be obtained at high conversion levels. The high required conversion, however, results in low hydrogen partial pressures within the reactor (i.e. high values of $p_{CO}/p_{H_2}^3$) and consequently high carbon laydown results. If the total reactor pressure is increased, however, the value of the parameter $p_{CO}/p_{H_2}^3$ can be decreased to a satisfactory level.

Table 7 illustrates two cases the first operating with a feed gas of H_2/CO ratio of 2.9 and the second with a 3.06 ratio gas.

TABLE 7

H_2/CO Ratio of feed	$CO+CO_2$ Conversion %	Recycle to fresh feed ratio	Reactor pressure kg/cm^2	Total Feed				Selectivity % (C basis)		C_4+ Scrubbed tail gas							Joule/Nm^3
										Analysis (Vol. %)							
				P_{CO_2} kg/cm^2	P_{CO} kg/cm^2	P_{H_2} kg/cm^2	$\frac{P_{CO}}{P_{H_2}^2} \times 10^3$	CH_4	C_4+	H_2	CO	CO_2	CH_4	C_2	C_3	N_2 + A	
2.90	96	2.0	38.6	0.77	2.82	12.5	1.9	47	24	18.8	0.1	2.5	68.1	5.3	2.3	2.9	3.80×10^6
3.06	97.5	2.0	38.6	0.42	2.67	12.7	1.3	57	18	17.4	0.1	1.3	72.0	4.6	1.7	2.9	3.84×10^6

Even lower H_2/CO ratio feed gases than the above might be used if the recycle stream of the reactor is scrubbed to remove CO_2 from it. This amounts to simultaneously using the reactor as a shift reactor and could eliminate the need of an upstream shift reactor.

Example 5.

One reactor coupled to a hydrogen separator.

With reference to the runs illustrated in table 5 it can be seen that if the excess hydrogen were selectively removed from the tail gas, a product gas of high calorific value would result. The required separation techniques are well established processes, e.g. the scrubbing train could commence with CO_2 removal and end with the cryogenic separation into hydrogen-rich and hydrogen-poor gas streams. The hydrogen-rich stream can be recycled to the reactors as part of the fresh feed.

The higher the H_2/CO ratio of the combined fresh feed to the reactor the lower the C_4+ production but the higher the amount of gasification gas that needs be shifted upstream and the higher the amount of hydrogen from the cryogenic separator that has to be recycled (i.e. the larger the cryogenic unit). Once again the choice will depend on the required amount of C_4+ hydrocarbons.

The knowledge revealed in Examples 3 to 5, can be utilised in many ways to produce a gas of high heating value. The examples given or for the purposes of illustration and do not limit the scope of application of the invention. Local economics and conditions, (e.g. how much hydrocarbon heavier than propane is desired) will dictate which of the many possibilities is the most suitable. In the examples discussed the "product" gas contains only inerts (e.g. N_2 and A), methane, hydrogen, CO, CO_2, C_2 and C_3 hyrocarbons.

Hydrocarbons heavier than C_3 are scrubbed out and termed "heavier hydrocarbons". The "heavier hydrocarbons" may be fractionated and sold as petrochemicals or petrochemical precursors; used as fuel oil (e.g. raising steam for the gasifiers); recharged to the gasifiers (i.e. reconverted to synthesis gas); catalytically steam reformed to CH_4, CO and H_2 and the gas either blended into the product gas or recycled to the reactors; or catalytically hydrocracked to CH_4 and recycled. Similarly the water produced in the reactors could be discarded; recycled to the gasifiers; or catalytically treated to hydrocrack any dissolved oxygenated hydrocarbons to methane. Alternatively the dissolved oxygenated hydrocarbons could be extracted and sold.

WHAT WE CLAIM IS:—

1. A method of controlling the relative yields of low molecular weight, predominantly gaseous, aliphatic hydrocarbons and higher molecular weight hydrocarbons in the catalytic Fischer-Tropsch synthesis of hydrocarbons from feed gases comprising hydrogen, carbon monoxide and carbon dioxide in the presence of an iron catalyst, said method comprising reacting said feed gases in a reactor in the presence of a catalyst having a basicity equal to that of a Fischer-Tropsch catalyst consisting essentially of iron and not more than 0.001 g K_2O/m^2 of effective surface area of the catalyst, the K_2O being evenly distributed on the surface of the catalyst and at a temperature in excess of 250°C, and either
   a) adapted to suppress the formation of methane and other gaseous hydrocarbons in favour of the production of higher molecular weight products in that the catalyst basicity as above defined corresponds to from 0.005 to 0.001 g K_2O/m^2 and the partial pressure of CO_2 measured in the reactor near the feed inlet exceeds 4 kg/cm² but is maintained below 7 kg/cm²; or
   b) adapted to favour the formation of methane and other gaseous hydrocarbons and to suppress the formation of higher molecular weight products in that the catalyst basicity as above defined corresponds to from zero to 0.0005 g K_2O/m^2 and the partial pressure of CO_2 measured in the reactor near the feed inlet is in excess of zero and up to 3 kg/cm².

2. Synthesis process including the method as claimed in claim 1 carried out at a total reactor pressure above 32 kg/cm² and between 280°C and 450°C.

3. Synthesis process as claimed in claim 2 carried out at a total reactor pressure between 35 and 70 kg/cm².

4. Synthesis process as claimed in any one of claims 1 to 3 carried out under the conditions of paragraph a) of claim 1.

5. Synthesis process as claimed in any one of claims 1 to 3 carried out under the conditions of paragraph b) of claim 1.

6. Process according to claim 5 carried out at a temperature not less than $t_{min}(°C)=250+35\times10^4a$, wherein a is the basicity of the catalyst, expressed as g K_2O/m^2 of effective catalyst surface area, being the amount of K_2O which when well distributed as the only promoter in a pure iron catalyst, will produce that particular basicity.

7. Process according to claim 5 for achieving a methane selectivity of at least 20% which comprises carrying out the synthesis at between 280 and 400°C, and with a catalyst of which the basicity is between zero and 0.0001, expressed as g K_2O/m^2 of effective catalyst surface area, being the amount of K_2O which when well distributed as the only promoter in a pure iron catalyst, will produce that particular basicity.

8. Process according to any one of claims 5 to 7 wherein the upper partial pressure of CO_2 is set to at the most 2 kg/cm² at the gas feed end of the reactor.

9. Process according to claim 8, wherein said partial pressure is from 0.4 to 1 kg/cm².

10. Process according to any one of claims 1 to 7 carried out at a temperature of from 300 to 360°C.

11. Process according to claim 10 carried out at a temperature of from 305 to 330°C.

12. Process according to any one of claims 1 to 11, carried out with the catalyst maintained in an expanded condition by gas flowing therethrough.

13. Process according to claim 12, wherein the catalyst is maintained in a gas-entrained condition.

14. Process according to claim 12, wherein the catalyst is maintained in a fluidized bed condition.

15. Process according to claim 14, wherein the catalyst is maintained in a moving fluidized bed condition.

16. Processs according to any one of claims 5 to 15 carried out in two reactors in series, of which the down stream reactor operates at the higher pressure of the two, additional CO_2 being fed with the tail gas of the first reactor into the second, higher pressure reactor.

17. Process according to any one of claims 1 to 16 wherein in the context of selecting the total pressure in the reactor, the basicity of the catalyst and the partial pressure of CO_2, the overall composition of the reactor gas in the feed gas entry region is set so that $(p_{CO}/p^3_{H_2})\times10^3$ numerically does not exceed

$$\frac{b}{4}(13-a\times10^4),$$

wherein p_{CO} and p_{H_2} are the partial pressures of carbon monoxide and hydrogen respectively expressed in kg/cm^2, a represents the basicity of the catalyst, expressed as g K_2O/m^2 of effective catalyst surface area, being the amount of K_2O which when well distributed as the only promoter in a pure iron catalyst, will produce that particular basicity, and b is the acceptable rate of carbon deposition expressed as g carbon per 100 g catalyst per day, the reactor temperature being between 300 and 340°C, or an appropriate temperature correction being made in the above relationship when operating at temperatures outside that range.

18. Process according to claim 17 wherein the temperature of the reactor is between 300 and 340°C.

19. Process according to claims 17 or 18 wherein b is taken as 4.

20. A method as claimed in claim 1 substantially as hereinbefore described.

21. A process as claimed in claim 5, substantially as hereinbefore described.

22. Fischer-Tropsch synthesis wherein the methane selectivity is enhanced substantially as described in any one of the aforegoing examples.

23. Fischer-Tropsch synthesis products whenever obtained by a method or process claimed in any one of claims 1 to 22.

24. High thermal value gas whenever produced substantially as hereinbefore described.

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1 SHEET *This drawing is a reproduction of the Original on a reduced scale*