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(57) Abstract

Hydrocarbons are produced by contacting a gaseous mixture comprising carbon monoxide, hydrogen and at least one unsaturated hydrocarbon, the unsaturated hydrocarbon being present in an amount less than 50% molar, with a Fischer-Tropsch catalyst under Fischer-Tropsch conditions.

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FISCHER-TROPSCH CONVERSION OF SYNTHESIS GAS TO HYDROCARBONS

The present invention relates generally to a process for converting gaseous mixtures containing carbon monoxide and hydrogen into hydrocarbons by contact with Fischer-Tropsch catalysts. More particularly, the present invention relates to a process for the conversion of carbon monoxide, hydrogen and unsaturated hydrocarbons, for example alkenes, to hydrocarbons by contact with Fischer-Tropsch (FT) catalysts. Within the context of the present application the term "Fischer-Tropsch catalyst" includes related catalysts of the type generally referred to as "iso synthesis catalysts" and derivatives thereof.

The Fischer-Tropsch (F-T) synthesis originated in Germany in the 1920's, reached its zenith in Germany during World War II as a supplier principally of motor fuels and now survives only in South Africa in combination with a coal gasification process at the Sasol works. Immediately following World War II, most industrial nations were involved in F-T research but interest began to decline with the advent of cheap oil and gas. In recent years however interest in the F-T process has revived and considerable research has been directed towards the development of new and improved catalysts. As a consequence, the range of catalytically active F-T metal components has been extended beyond iron and cobalt, the basis of the original catalysts.

A demand exists for a Fischer-Tropsch process for converting synthesis gas to produce high yields of liquid hydrocarbon products, at the same time minimising the production of C_1 products and maximising the total carbon conversion and productivity and in particular the conversion and productivity to C_3 or greater hydrocarbons.

We have found that this demand can be to some extent met by the provision in the synthesis gas feed to a Fischer-Tropsch process of a defined proportion of at least one unsaturated hydrocarbon, particularly if the Fischer-Tropsch catalyst incorporates a solid acidic component.

Processes in which mixtures of synthesis gas and unsaturated hydrocarbons are reacted over a catalyst are known in the art.

Thus, for example, USP-A-2,606,939 describes the conversion of olefinic feedstock containing carbon monoxide and hydrogen, the olefin being present in an amount greater than 60 per cent, preferably greater than 70% by volume, by polymerisation/hydropolymerisation over a promoted iron catalyst to higher olefinic hydrocarbons. This represents a disclosure of an olefin conversion process, as opposed to a synthesis gas conversion process.

USP-A-4.547,525 published after the priority date claimed for the subject application on an application claiming an earlier priority date discloses that methane production in Fischer-Tropsch hydrocarbon synthesis reactions is reduced by adding one or more olefins to the hydrogen and carbon monoxide gas feed. Little effect on the extent of carbon monoxide conversion was observed. Not disclosed is the use of a solid acidic component in the catalyst.

Accordingly, the present invention comprises a process for the production of a hydrocarbon product which process comprises contacting a gaseous mixture comprising carbon monoxide, hydrogen and at least one unsaturated hydrocarbon, the unsaturated hydrocarbon being present in an amount less than 50% molar, with a Fischer-Tropsch catalyst under Fischer-Tropsch reaction conditions.

The unsaturated hydrocarbon may suitably be either an alkene or an alkyne or a mixture thereof. A suitable alkene is ethylene and a suitable alkyne is acetylene. Suitably the unsaturated hydrocarbon may be present in an amount of at least 1% molar, preferably at least 2% molar, and up to 40% molar in the gaseous mixture comprising the feed to the process.

F-T catalysts generally comprise one or more metals of Group VIII of the Periodic Table, optionally on a suitable support. Suitable metals include for example iron, cobalt, nickel, molybdenum, tungsten, rhenium, ruthenium, palladium, rhodium, osmium, iridium and platinum, preferably iron, cobalt or ruthenium. The metal may suitably be in the form of the elemental metal, an oxide or a sulphide. The catalyst may suitably include a promoter which may be an alkali metal, an alkaline earth metal or a rare earth metal. Examples of suitable promoters include the hydroxide, oxide or salt of lithium, sodium, potassium, rubidium; cesium, magnesium, calcium, strontium, barium and thorium. The support may be, for example, alumina, carbon, silica, zirconia, titania, magnesia, ceria or mixtures thereof. Iso-synthesis catalysts generally comprise non-reducible oxides, for example thoria, zirconia, alumina, ceria, and gallia. Conventional techniques, such as for example, impregnation, may be used for the preparation of such catalysts.

It is preferred to incorporate into the F-T catalyst, suitably either by way of a support or as an intimate admixture therewith, a solid acidic component. Suitable acidic components include for example, silica/alumina, layered clays, pillared layered clays, and crystalline tectometallosilicate, for example gallosilicate and aluminosilicate zeolites. Preferred are crystalline gallosilicate and aluminosilicate zeolites having a high silica content (silica to alumina molar ratio greater than 12:1), suitably in the hydrogen form. An example of a suitable zeolite is an MFI-type zeolite, for example ZSM-5 as described and claimed in US Patent No. 3,702,886. The hydrogen form of a crystalline aluminosilicate zeolite may suitably be prepared by techniques well-known in the zeolite art.

Examples of catalysts suitable for use in the process of the present invention include (i) an oxide of zinc, gallium or indium and at least one other metal, together with a porous crystalline tectometallosilicate as described in our European patent application publication No. EP-A-0124999, for example a thoria/gallia/MFI-type crystalline aluminosilicate zeolite, (ii) a composition comprising ruthenium/ceria as described in our published European application No. 169743, preferably in combination with an MFI-type crystalline aluminosilicate zeolite and (iii) an iron/crystalline acidic aluminosilicate zeolite catalyst as described, for example, in USP-A-4,298,695.

In one embodiment of the present invention, the mixture of carbon monoxide and hydrogen and the olefinic hydrocarbon are derived from separate sources and are subsequently combined in the presence of the F-T catalyst. Mixtures of gases principally comprising carbon monoxide and hydrogen, possibly containing also carbon dioxide, nitrogen and methane for example are generally referred to in the art as synthesis gas. Synthesis gas may in theory be obtained from any carbonaceous source, of which coal, natural gas and high molecular weight hydrocarbon residues may be mentioned as examples. Thus, the synthesis gas may suitably be obtained by the gasification of coal using technology well-known in the art, for example the gasifier process developed by Lurgi Kohle und Mineraloeltechnik GmbH. Alternatively, the synthesis gas may be obtained by the steam reforming of hydrocarbon feeds, for example sulphur-free natural gas or paraffinic naphtha, in the presence or absence of a reforming catalyst. In another alternative, synthesis gas may be produced by partial oxidation of a hydrocarbon feed, wherein the hydrocarbon feed is introduced into an oxidation zone maintained in a fuel rich mode, in the absence of a catalyst and the presence or absence of steam. Catalytic autothermal reforming of hydrocarbon liquids, i.e. partial oxidation in the presence of added steam, may also be used to produce the synthesis gas necessary for the performance of the invention.

An example of a suitable method of preparing synthesis gas is described in our copending European application publication No. 164864 which provides a process for the production of synthesis gas in which (a) a saturated hydrocarbon and an oxygen containing gas having a ratio of hydrocarbon to oxygen of greater than the stoichiometric ratio for complete combustion are introduced into a bed of particulate material, the bed comprising material which is catalytically active for partial oxidation and/or steam reforming reactions, (b) the upward flow rate of the hydrocarbon/oxygen containing gas stream being sufficiently large to cause a spouting action of the bed material, (c) the hydrocarbon and oxygen reacting together and (d) the products of the reaction being withdrawn.

The unsaturated hydrocarbon may be substantially pure or may be present in a mixture with other materials, for example hydrogen and paraffinic hydrocarbons, in a petroleum refinery fraction or other fraction. A suitable fraction rich in unsaturated hydrocarbons is for example the product derived from thermal cracking of C_2 to C_4 alkanes or other petroleum fractions such as naphtha.

The olefinic hydrocarbon may be combined with the synthesis gas feed to a reactor containing an F-T catalyst or may be fed separately to such a reactor.

According to a preferred embodiment of the process of the present invention, in a first step there is formed a gaseous mixture comprising carbon monoxide, hydrogen and at least one unsaturated hydrocarbon and in a second step the mixture formed in the first step is converted to a product comprising hydrocarbons by contact with a Fischer-Tropsch catalyst under Fischer-Tropsch conditions.

An advantage of operating the process in this manner is that the total carbon converted per pass can be greatly increased as compared with making the carbon monoxide/hydrogen separately and converting that over an F-T catalyst. Furthermore, certain catalysts show a synergistic effect i.e. the CO conversion is increased in the presence of the unsaturated hydrocarbon and/or the proportion of CO_2 and methane produced are reduced.

The first step wherein there is formed a gaseous mixture comprising carbon monoxide, hydrogen and at least one unsaturated hydrocarbon may be performed in a variety of ways. It may, for example, be formed by the partial oxidation/cracking of one or more gaseous hydrocarbons or readily vapourisable hydrocarbons. One suitable method involves the partial oxidation of gaseous or vapourised hydrocarbons with oxygen by preheating the reactants together or separately, supplying the mixture to a reaction chamber, reacting them in a flame and rapidly cooling the reaction gases, as described in British Patent No. 835,676 for example.

A particularly preferred method is described in our pending published European application No. 163385 which provides a process for the production of synthesis gas and higher hydrocarbons in which (a) a saturated hydrocarbon and an oxygen containing gas having a ratio of hydrocarbon to oxygen of greater than the stoichiometric ratio for complete combustion are introduced into a bed of an inert particulate material, (b) the upward flow rate of the hydrocarbon/oxygen containing gas stream being sufficiently large to fluidise or to produce a spouting action of the bed material whereby at least a part of the particulate material is thrown up above the bed surface and subsequently falls back into the bed, (c) the hydrocarbon and oxygen containing gas being ignited and reacted together and (d) the products of the reaction being withdrawn.

Yet another method is described in our copending published European application publication No. 178853 which provides a process for the production of synthesis gas and/or higher hydrocarbon in which (a) a saturated hydrocarbon and an oxygen containing gas having a ratio of hydrocarbon to oxygen of greater than the stoichiometric ratio for complete combustion are introduced together with hydrogen into a bed of particulate material (b) the upward flow rate of the gases being sufficiently large to cause a spouting action of the bed material above the slumped level of the bed (c) the hydrocarbon, oxygen and hydrogen reacting together and (d) the products of the reaction being withdrawn.

Other methods of performing the first step to provide a feedstock comprising carbon monoxide, hydrogen and at least one unsaturated hydrocarbon will be readily apparent to those skilled in the art.

It is preferred that the gaseous mixture produced in the first step of the process be transferred without substantial intermediate treatment directly to the second step. However, in certain circumstances it may be desirable to subject the gaseous mixture formed in the first step to, for example, an intermediate step in which water is removed from the gaseous mixture and/or an intermediate step in which alkynes present in the gaseous mixture are selectively hydrogenated to alkenes.

Typical Fischer-Tropsch reaction conditions are a temperature in the range from 150 to 500°C, preferably from 175 to 450°C and a pressure in the range from 10 to 200 bars, preferably from 20 to 100 bars. The optimum reaction conditions will vary from catalyst to catalyst but will generally be within the aforesaid ranges.

The process is preferably operated on a continuous basis.

The nature of the hydrocarbon product will depend amongst other factors on the particular F-T catalyst selected, the specific reaction conditions employed and upon the particular composition of the gaseous mixture fed to the F-T catalyst.

The invention will now be further illustrated by way of example only and with reference to the accompanying drawing.

(A) PRODUCTION OF CO, H_2, UNSATURATED HYDROCARBON MIXTURE

The drawing shows a schematic layout of a reactor and ancillary equipment.

The reactor 1 takes the form of a lagged elongate quartz column 2 having a conical base portion 3, the angle of the cone from the vertical being 20°. The base portion of the reactor contains a slumped bed 4 of particulate material having a particle size of the order 1-1.5 mm diameter. The particulate materials were crushed firebrick, silicon carbide, quartz and zirconia. The base of the column is adapted to receive a nozzle 5 for the introduction of reactants. The nozzle outlet may be adjusted vertically within the bed of particulate material. The upper portion 6 of the reactor is open to form an outlet for withdrawal of the product gases. A line 10 enables samples of the products to be withdrawn from the product gas stream.

The nozzle 5 is connectable to a supply of air 7 or other oxygen containing gas under appropriate pressure and to a supply of methane 8. A suitable supply may comprise cylinders of hydrocarbon e.g. methane, and air or oxygen linked to the nozzle through a mixer and gas pressure and flow rate measuring devices such as manometers and rotameters (not shown).

The reactor may also have an additional nozzle or nozzles for supplying further methane or other hydrocarbon to the bed (not shown in the drawing). The reactor 1 is lagged with a suitable insulating material 9.

A number of techniques may be used for start up of the reactor. In the present example, the ignition source was a gas burner (not shown) located at the outlet portion 6 of the column.

During start up of the reactor, a pre-mixed gas stream of hydrocarbon and air was passed under pressure to the nozzle 5 in the base portion 3 of the column. The velocity of the gas stream was sufficient to cause a fountain 11 of bed particles in the freeboard above the bed.

The gas stream used was very fuel rich and consequently the gas mixture was ignited by the gas burner and a flame stabilised at the exit of the reactor. The air flowrate was increased, bringing the mixture closer to stoichiometric, until the flame began to move slowly back down the reactor. A flame was stabilised at the surface of the slumped bed and the fuel flowrate reduced slightly to obtain a near stoichiometric mixture. When the bed temperatures had equilibrated, the fuel flowrate was increased and a low flowrate of oxygen was added to the bed. The air flowrate was then reduced and both the fuel and the oxygen increased to maintain the stable flame and the spouting action of the bed. This procedure was repeated until the feed composition was entirely fuel and oxygen. The total feed mixture was always maintained on the rich side of stoichiometric close to or beyond the rich limit of flammability. At atmospheric pressure, the rich limit of flammability corresponds to a methane/oxygen mole ratio of 1.5.

The constituents and composition of the reactant gases were ascertained by means of conventional techniques. This procedure was repeated for a number of fuel rich hydrocarbon/oxygen reactant compositions and different particulate bed materials. The products obtained from the reaction may include carbon monoxide and hydrogen (synthesis gas), acetylene, and ethylene.

Table 1 shows results for the reaction of methane and oxygen in a reactor using various bed materials. The bed materials generally had particle size of 1 to 1.5 mm diameter and were crushed firebrick, quartz and silicon carbide. The increased carbon molar selectivities to C_2 and higher hydrocarbons is shown for all the bed materials for fuel rich conditions as the feed composition is made increasingly fuel rich up to and beyond the rich limit of flammability.

Table 2 shows results for the reaction of methane and air in a reactor. The bed material used was zirconia spheres of the order 1-1.2 mms diameter. The carbon molar selectivities and feed conversions achieved are similar to those obtained with oxygen.

Calculations have shown that the residence time of the reactant gases in the hot zone is desirably less than 1 millisecond in order to avoid an undesirably high degree of cracking of the products to soot or other compounds. It may be possible to use longer residence times at low or atmospheric pressures.

Alternatively a lower velocity of the gas stream may be used so as to cause fluidisation of the bed material and/or surface bubbling of the bed material. The fluidisation and/or bubbling is sufficient to cause the particulate material to be thrown up into the freeboard, the material returning to the bed. The bubbling may also be associated with total fluidisation of the bed.

Table 3 shows results obtained in a fluidised bed reactor with a methane/oxygen feed. The bed comprised 0.25-0.85 mm particles of zirconia. The reactant gases were fed to the reactor through a distributor plate at a sufficient velocity to attain turbulent fluidisation with bed material thrown randomly into the gas phase or freeboard above the bed.

Experiments with fuel rich mixtures close to or beyond the limit of flammability using conventional fluidised bed operation at one bar pressure and with an inert bed material generally resulted in flame lift off or instability. At the onset of surface bubbling (or localised spouting) a more stable combustion regime ensued and partial oxidation with production of CO/H_2 and C_2's resulted. This effect persisted into the complete spouting regime. It is believed that the stable combustion of mixtures close to or beyond the limit of flammability results from the countercurrent heat transfer between the descending hot particulate material and the ascending gases thereby enabling pre-heat of incoming feed gases.

As the pressure of operation is increased the upper limit of flammability widens. Thus, the need for particulate heat recirculation for stable combustion is greater at lower operating pressures than at higher operating pressures. However by application of the present invention the limit of flammability can be further extended at increased pressures by particulate heat recirculation in a similar way as at atmospheric pressure.

Table 1

Conversion of methane and oxygen using various bed materials

Run No.	Feed inlet gas composition (% mole)			Total Flowrate (1/min)	Feed (CH_4/O_2) (Mole ratio)	% Conversion of CH_4 feed	Exit dry gas composition (% mole)								Carbon Molar Selectivity to C_2 and higher hydrocarbons (%)	Bed Material
	O_2	CH_4	N_2				N_2	H_2	CO	CO_2	CH_4	C_2's	C_3-C_6	aromatic		
1	32.9	63.7	3.4	10.7	1.93	70.9	3.6	42.0	23.3	3.3	18.7	8.7	0.2	0.1	36.2	Firebrick
2	43.8	53.4	2.8	11.0	1.22	90.3	2.9	48.6	35.1	5.0	5.1	3.2	0.01	0.04	13.2	"
3	51.3	46.2	2.5	11.3	0.90	99.4	3.2	47.0	37.2	12.2	0.3	0.1	0	0.01	0.3	"
4	38.2	58.9	2.9	16.0	1.54	87.1	2.8	51.9	26.7	2.5	7.2	7.6	0.2	0.13	38.3	"
5	36.2	59.2	4.6	23.1	1.64	82.3	4.6	49.9	23.3	3.1	10.6	8.1	0.1	0.23	36.8	"
6	36.6	59.4	4.0	23.1	1.62	91.8	3.4	55.4	26.4	3.4	4.1	7.1	0	0.16	33.6	Quartz
7	36.5	59.2	4.4	23.5	1.62	90.6	4.0	52.7	26.4	3.3	5.1	8.1	0.1	0.18	36.2	Silicon carbide

Table 2

Conversion of methane and air using zirconia bed material

Total Flow Rate (litres/min)	Feed Ratio (CH_4/O_2)	% Conversion of CH_4 feed	% Carbon Molar Selectivity				Bed Temperature (°C)	Product Gas H_2/CO (Mole Ratio)
			C_2+	CO	CO_2	soot		
45	1.18	92	27	63	10	0	1040	1.6
33	1.23	89	27	61	11	1	1065	1.6

Table 3

Conversion of methane and oxygen in a fluidised bed reactor using zirconia bed material

Gas Hourly Space Velocity (bar $^{-1}$)	Feed Ratio (CH_4/O_2)	% Conversion of CH_4 feed	% Carbon Molar Selectivity			Bed Temperature (°C)	Product Gas H_2/CO (Mole Ratio)
			C_2+	CO	CO_2		
25300	1.54	67	33	58	8	1050	1.1
19000	1.70	85	40	46	10	1000	2.1

(B) CONVERSION OF CO, H_2 AND UNSATURATED HYDROCARBON MIXTURE

Comparison Test 1

A tubular reactor was loaded with 10mls of a ThO_2/Ga_2O_3/H-MFI zeolite catalyst (bound with silica) which had previously been run for 20 hours with a syngas feed at about 400°C. Feed gas (syngas comprising 65% volume hydrogen and 35% carbon monoxide designated feed gas X) was fed to the reactor at a gas hourly space velocity (GHSV) of 2,000 h^{-1}. The reactor was heated externally to maintain an average bed temperature of 400°C at a pressure of 50 barg. The reaction products were analysed by gas chromatography. The conditions and results are summarised in Table 4.

This is not an example according to the invention because an unsaturated hydrocarbon was not present.

Example 1

Following comparison Test 1, a feed stream Y containing hydrogen 57% volume, carbon monoxide 33.5% and ethylene 9.5% (i.e. simulating in composition the product as produced in A) was fed to the reactor under essentially identical conditions. The conditions and results are summarised in Table 4.

The presence of ethylene in the feed clearly has a synergistic effect:- ethylene is converted completely while carbon monoxide conversion is increased and overall carbon conversion is increased. Methane and carbon dioxide selectivities are reduced. The net result is a five fold increase in productivity of C_3 and higher hydrocarbons.

Comparison Test 2

A reactor was charged with 10mls of a $Ru/K/CeO_2$ catalyst. Feed gas X (cf Comp Test 1) was passed over the catalyst at 40 bar, 2500 GHSV, while the maximum bed temperature was maintained at 331°C. Results are given in Table 4.

This is not an example according to the invention because of the absence of an unsaturated hydrocarbon.

Example 2

Ethylene containing syngas (Feed gas Y of Example 1) was substituted for the syngas feed (X) over the catalyst of Comparison

Test 2. The results are shown in Table 4. Under identical conditions there is a significant increase in C_3+ productivity due to the addition of ethylene, and a reduction in methane and carbon dioxide selectivities. However ethylene conversion is relatively low over this catalyst.

Comparison Test 3

The reactor was charged with a physical mixture of $Ru/K/CeO_2$ (6mls) and silica bound zeolite (H-MFI) (4mls). Feed gas X (cf Comp. Test 1) was fed to the reactor at 40 bar, 2500 GHSV, 370°C. Results are shown in Table 4.

This is not an example according to the invention because of the absence of unsaturated hydrocarbon.

Example 3

Feed gas Y (cf Example 1) was substituted for Feed gas X in Comparison Test 3 and the reaction products over the catalyst used in Comparison Test 3 were analysed. Results in Table 4 show that there is a greater improvement in C_3+ productivity in this example where an acidic zeolite has been incorporated into the catalyst bed and a greater increase in total carbon conversion. Ethylene conversion is considerably higher while at the same time, selectivity to C_3+ hydrocarbons is improved.

Comparison Test 4

The procedure of Comparison Test 1 was repeated except that instead of the ThO_2/GaO_2O_3/H-MFI zeolite catalyst there was used a magnetite/H-MFI catalyst. The reaction conditions and the results obtained are given in Table 4.

This is not an example according to the invention because of the absence of an unsaturated hydrocarbon in the feed.

Example 4

Comparison Test 4 was repeated except that instead of feed gas X there was used feed gas Y.

The results are given in Table 4.

From the above results it is clear that olefin conversion is maximised in the presence of an acidic (zeolite) component.

Table 4

Example	Catalyst	Feed	GHSV	Pressure (barg)	Temp (°C)	Conversion %			Carbon molar selectivity			Productivity of C_3+ (g/1/h)	Yield of C_3+ %
						CO	C_2H_4	Total carbon	CH_4	CO_2	C_3 hydrocarbons		
Comp.Test 1	TCM	X	2,000	50	400^1	32	-	32	7.1	36	53	62	17
1	TCM	Y	2,000	50	400^1	43	100	64	2.1	11	74	319	47
Comp.Test 2	Ru/K/CeO_2	X	2,500	40	331^2	55	-	55	8.6	8.3	77	215	42
2	Ru/K/CeO_2	Y	2,500	40	331^2	60	23	46	6.3	6.2	75	279	45
Comp.Test 3	Ru/K/CeO_2/H-MFI	X	2,500	40	370^2	54	-	54	16	14	66	198	36
3	Ru/K/CeO_2/H-MFI	Y	2,500	40	370^2	50	84	62	7.4	8	72	348	45
Comp.Test 4	Magnetite/H-MFI	X	2,500	20	325^2	98	-	98	8.4	32	54	274	52
4	Magnetite/H-MFI	Y	2,500	20	326^2	75	40	75	6.2	31	59	339	44

Note: 1. Average bed temperature
2. Maximum bed temperature

Feed: X 65% H_2, 35% CO
Y 57% H_2, 33.5% CO, 9.5% C_2H_4

Claims:

1 A process for the production of a hydrocarbon product which process comprises contacting a gaseous mixture comprising carbon monoxide, hydrogen and at least one unsaturated hydrocarbon, the unsaturated hydrocarbon being present in an amount less than 50% molar, with a Fischer-Tropsch catalyst under Fischer-Tropsch reaction conditions.

2 A process according to claim 1 wherein the amount of unsaturated hydrocarbon is in the range from 1 to 40% molar.

3 A process according to either claim 1 or claim 2 wherein the unsaturated hydrocarbon is ethylene.

4 A process according to any one of the preceding claims wherein the Fischer-Tropsch catalyst is one or more metals of Group VIII of the Periodic Table of the Elements in the form of the elemental metal, an oxide or a sulphide.

5 A process according to claim 4 wherein the Group VIII metal is either iron, cobalt or ruthenium.

6 A process according to either claim 4 or claim 5 wherein the catalyst is supported on either alumina, carbon, silica, zirconia, titania, magnesia, ceria or gallia.

7 A process according to any one of the preceding claims wherein the catalyst incorporates a solid acidic component.

8 A process according to claim 7 wherein the solid acidic component is a crystalline aluminosilicate or gallosilicate zeolite having a silica to alumina molar ratio greater than 12:1.

9 A process according to claim 8 wherein the zeolite is in the hydrogen form.

10 A process according to claim 1 wherein the Fischer-Tropsch catalyst is an oxide of either zinc, gallium or iridium and at least one other metal together with a porous crystalline tectometallosilicate.

11 A process according to claim 1 wherein the Fischer-Tropsch catalyst is a composition comprising ruthenium and ceria.

12 A process according to claim 11 wherein the ruthenium and ceria are combined with an MFI-type crystalline aluminosilicate zeolite.

13 A process according to claim 1 wherein the Fischer-Tropsch catalyst is an iron/crystalline acidic aluminosilicate zeolite.

14 A process according to any one of the preceding claims wherein the synthesis gas is obtained by a process in which (a) a saturated hydrocarbon and an oxygen-containing gas having a ratio of hydrocarbon to oxygen of greater than the stoichiometric ratio for complete combustion are introduced into a bed of particulate material, the bed comprising material which is catalytically active for partial oxidation and/or steam reforming reactions, (b) the upward flow rate of the hydrocarbon/oxygen containing gas stream being sufficiently large to cause a spouting action of the bed material, (c) the hydrocarbon and oxygen reacting together, and (d) the products of the reaction being withdrawn.

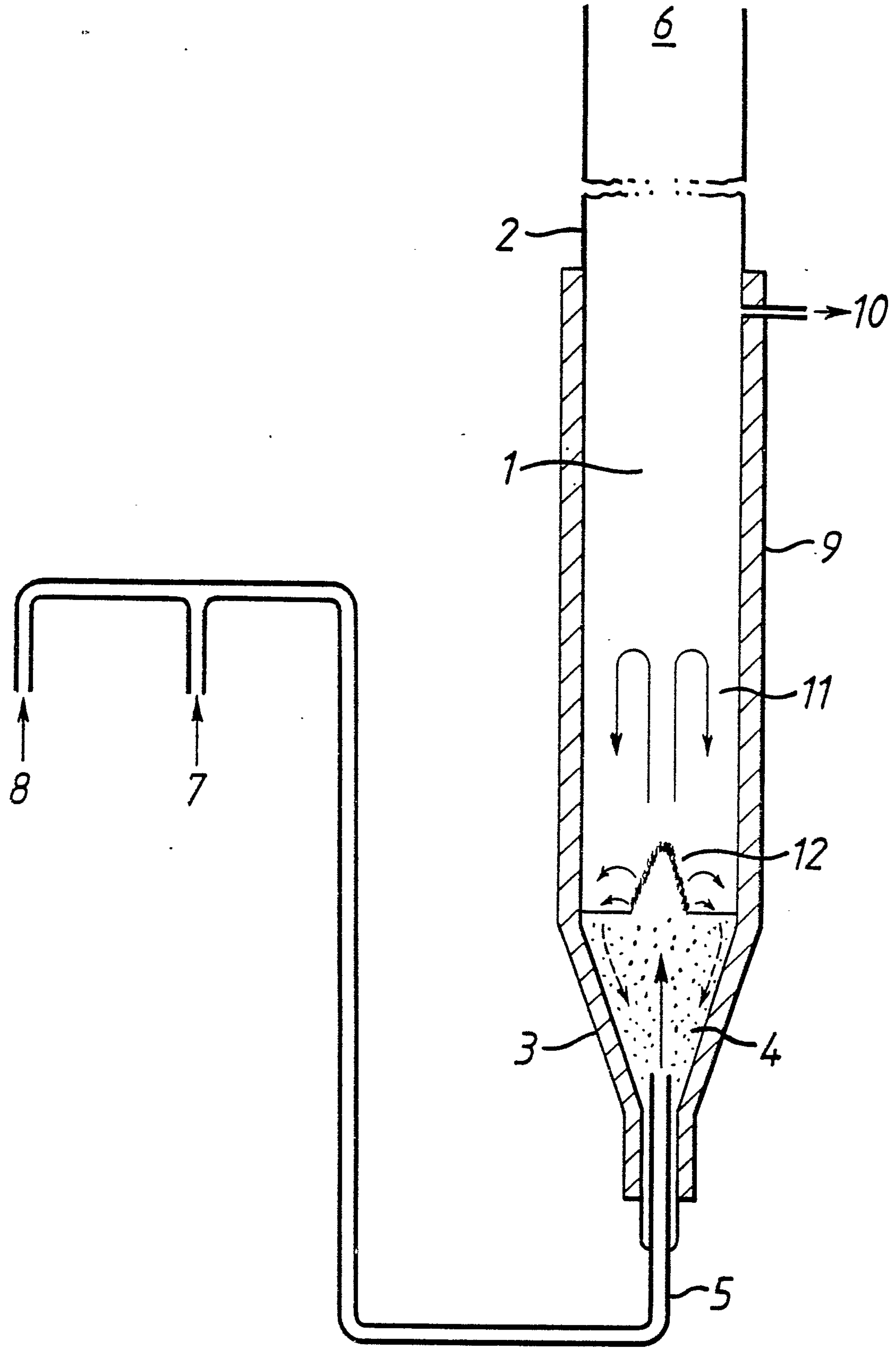
15 A process according to any one of claims 1 to 13 wherein a gaseous mixture comprising carbon monoxide, hydrogen and at least one unsaturated hydrocarbon is formed in a first step and the mixture formed in the first step is converted to a product comprising hydrocarbons in a second step.

16 A process according to claim 15 wherein the gaseous mixture is obtained by partial oxidation/cracking of one or more gaseous hydrocarbons or readily vapourisable hydrocarbons.

17 A process according to claim 16 wherein the gaseous mixture is obtained by a process in which (a) a saturated hydrocarbon and an oxygen containing gas having a ratio of hydrocarbon to oxygen of greater than the stoichiometric ratio for complete combustion are introduced into a bed of an inert particulate material, (b) the upward flow rate of the hydrocarbon/oxygen containing gas stream being sufficiently large to fluidise or to produce a spouting action of the bed material whereby at least a part of the particulate material is thrown up above the bed surface and subsequently falls back into the bed, (c) the hydrocarbon and oxygen containing gas being ignited and reacted together, and (d) the products of the reaction being withdrawn.

18 A process according to claim 16 wherein the gaseous mixture is obtained by a process in which (a) a saturated hydrocarbon and an oxygen containing gas having a ratio of hydrocarbon to oxygen of greater than the stoichiometric ratio for complete combustion are introduced together with hydrogen into a bed or particulate material, (b) the upward flow rate of the gases being sufficiently large to cause a spouting action of the bed material above the slumped level of the bed, (c) the hydrocarbon, oxygen and hydrogen reacting together, and (d) the products of the reaction being withdrawn.

19 A process according to any one of claims 16 to 18 wherein alkynes present in the gaseous mixture are selectively hydrogenated to olefins.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INTERNATIONAL SEARCH REPORT

International Application No PCT/GB 86/00183

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symools apply, indicate all) [6]

According to International Patent Classification (IPC) or to both National Classification and IPC

IPC^4: C 07 C 1/06; C 01 B 3/30

II. FIELDS SEARCHED

Minimum Documentation Searched [7]

Classification System	Classification Symbols
IPC^4	C 07 C 1/00

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched [8]

III. DOCUMENTS CONSIDERED TO BE RELEVANT [9]

Category [*]	Citation of Document, [11] with indication, where appropriate, of the relevant passages [12]	Relevant to Claim No. [13]
X	DE, C, 896792 (RUHRCHEMIE) 16 November 1953 see the entire document --	1-6
X	US, A, 2253607 (G.A. BOYD et al.) 26 August 1941 see pages 3,4; claims --	1,4-6,14-18
X	US, A, 2497761 (A. CLARCK) 14 February 1950 see claims --	1
P,X	US, A, 4547525 (KIM) 15 October 1985 see the entire document (cited in the application) --	1-6
X	EP, A, 0124999 (B.P.) 14 November 1984 see claims (cited inthe application) --	10
P,X	EP, A, 0164864 (B.P.) 18 December 1985 see claims (cited in the application) & JP, A, 60239301; & WO, A, 85/05094;	14-18 ./.

* Special categories of cited documents: [10]

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search 4th June 1986	Date of Mailing of this International Search Report 16 JUL 1986
International Searching Authority EUROPEAN PATENT OFFICE	Signature of Authorized Officer M. VAN MOL

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)

Category *	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No
	& AU, A, 41792/85 ------	

ANNEX TO THE INTERNATIONAL SEARCH REPORT ON

INTERNATIONAL APPLICATION NO. PCT/GB 86/00183 (SA 12730)

This Annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on 26/06/86

The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
DE-C- 896792		None	
US-A- 2253607		None	
US-A- 2497761		None	
US-A- 4547525	15/10/85	None	
EP-A- 0124999	14/11/84	AU-A- 2647184	11/10/84
		JP-A- 59196744	08/11/84
		US-A- 4543347	24/09/85
		CA-A- 1204099	06/05/86
EP-A- 0164864	18/12/85	JP-A- 60239301	28/11/85
		WO-A- 8505094	21/11/85
		AU-A- 4179285	07/11/85