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(54) **Hydrocarbon synthesis**

(57) This Invention relates to hydrocarbon synthesis and particularly to the production of gasoline with a range of C_5 to C_{12}.

In particular the invention relates to a process for synthesising hydrocarbons in the C_5 - C_{12} range from a mixture of hydrogen and carbon monoxide gases, comprising contacting the said mixture with a supported ruthenium catalyst wherein the said mixture is at a temperature within the temperature range of (500 to 550)°K and wherein the outlet partial pressure of carbon monoxide is not less than 0.8 atmospheres in the temperature range (500 to 525)°K and not less than 3.0 in the temperature range (525-550)°K.

Fig.4. Example 2
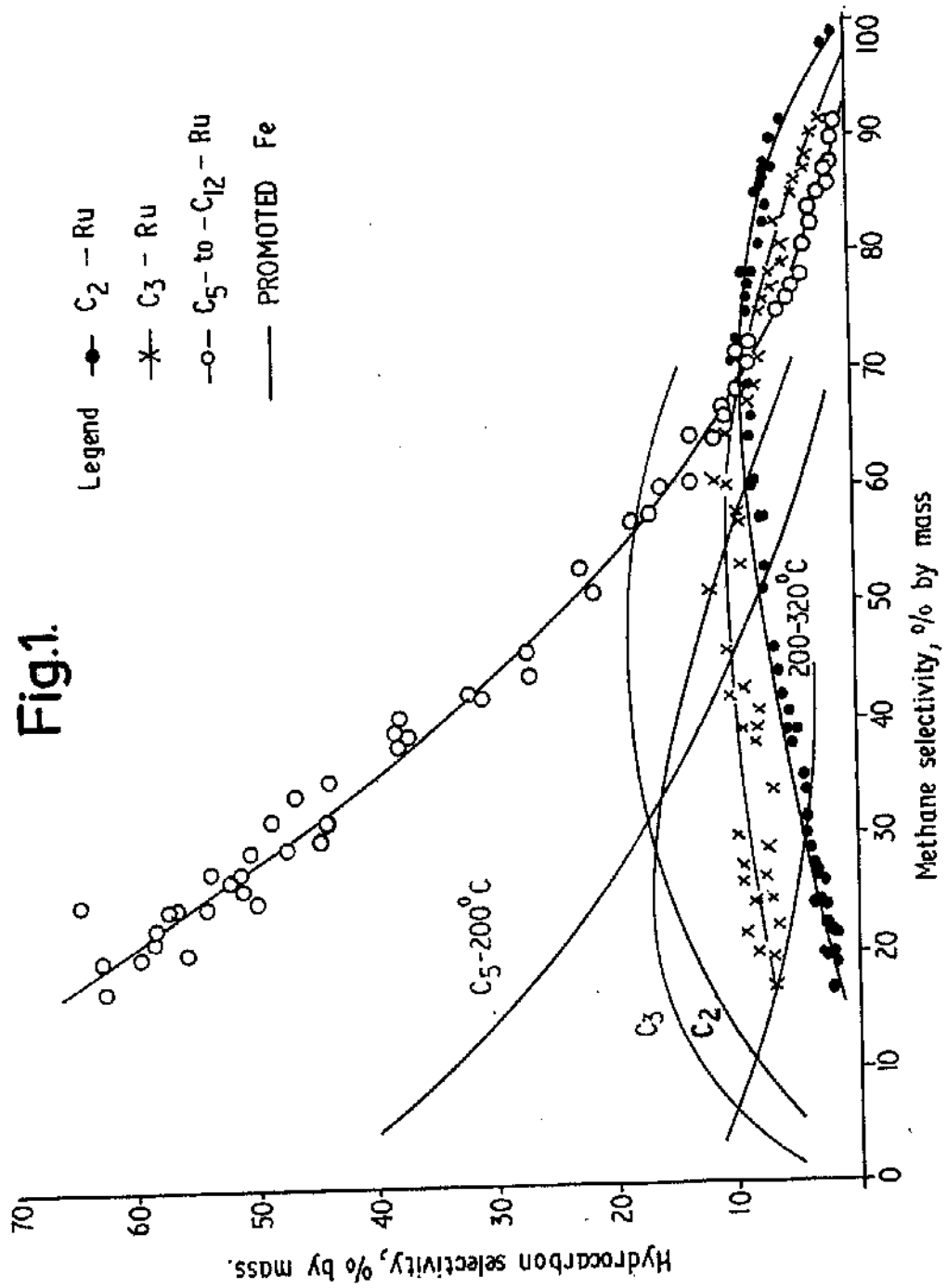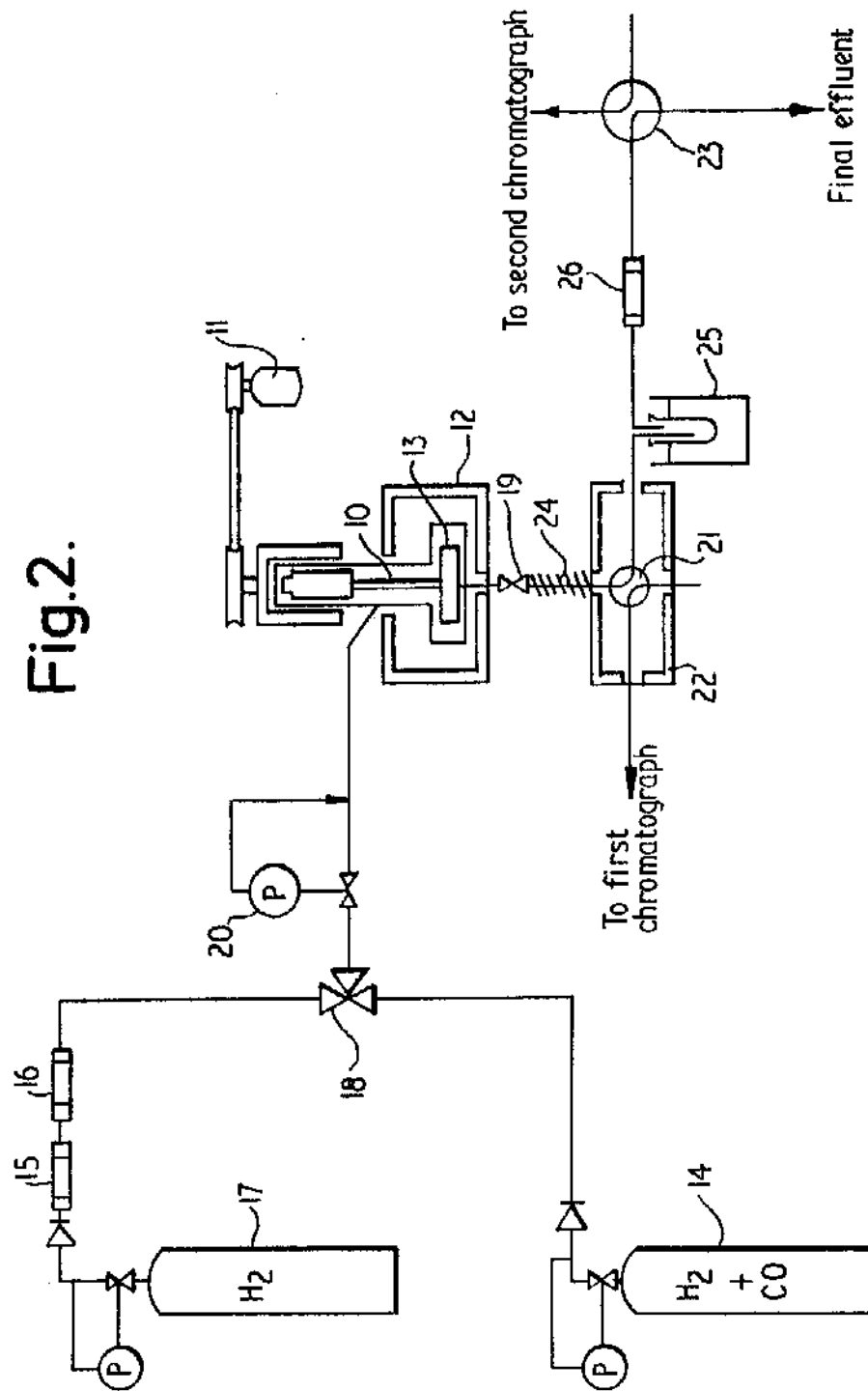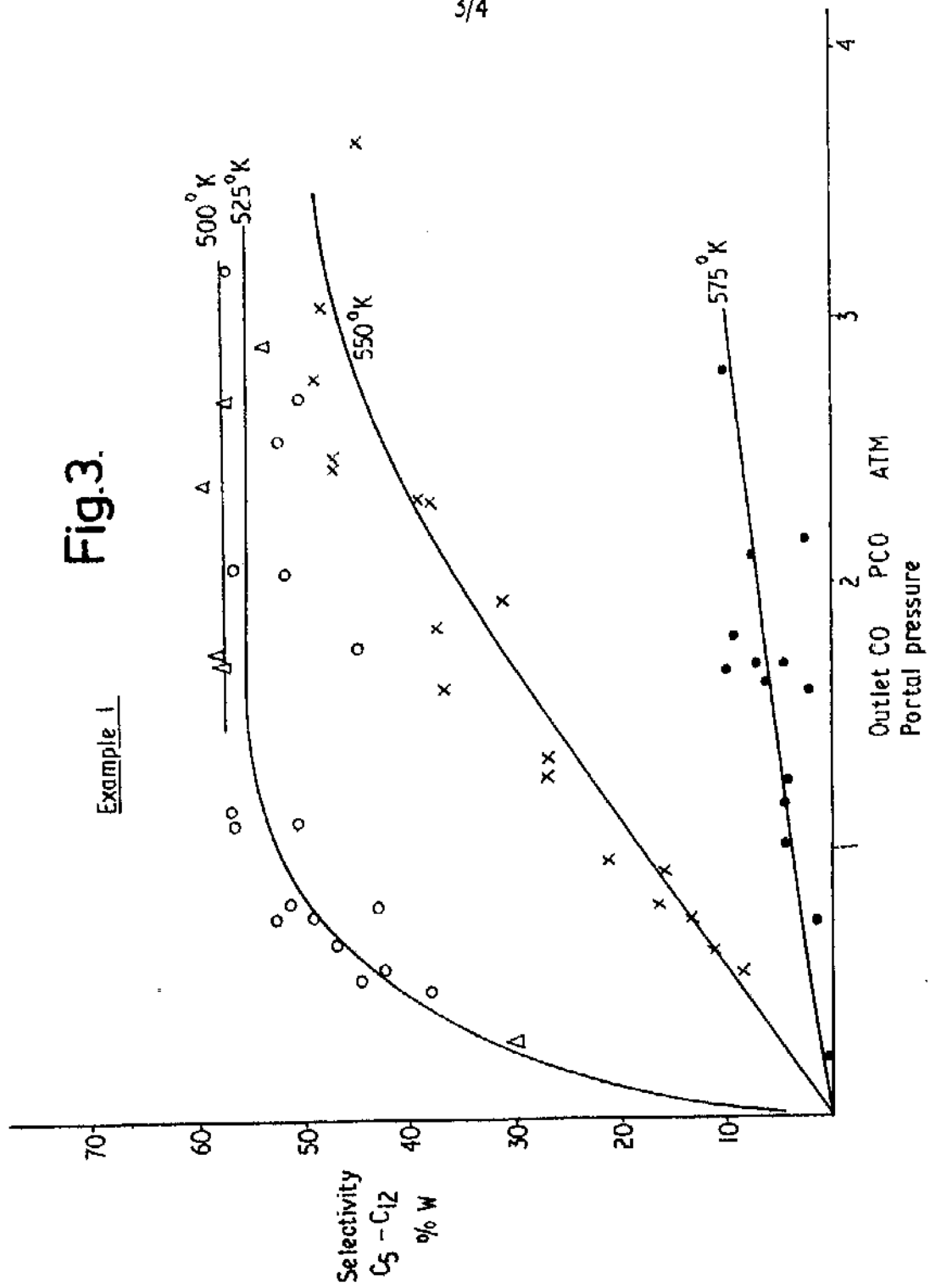
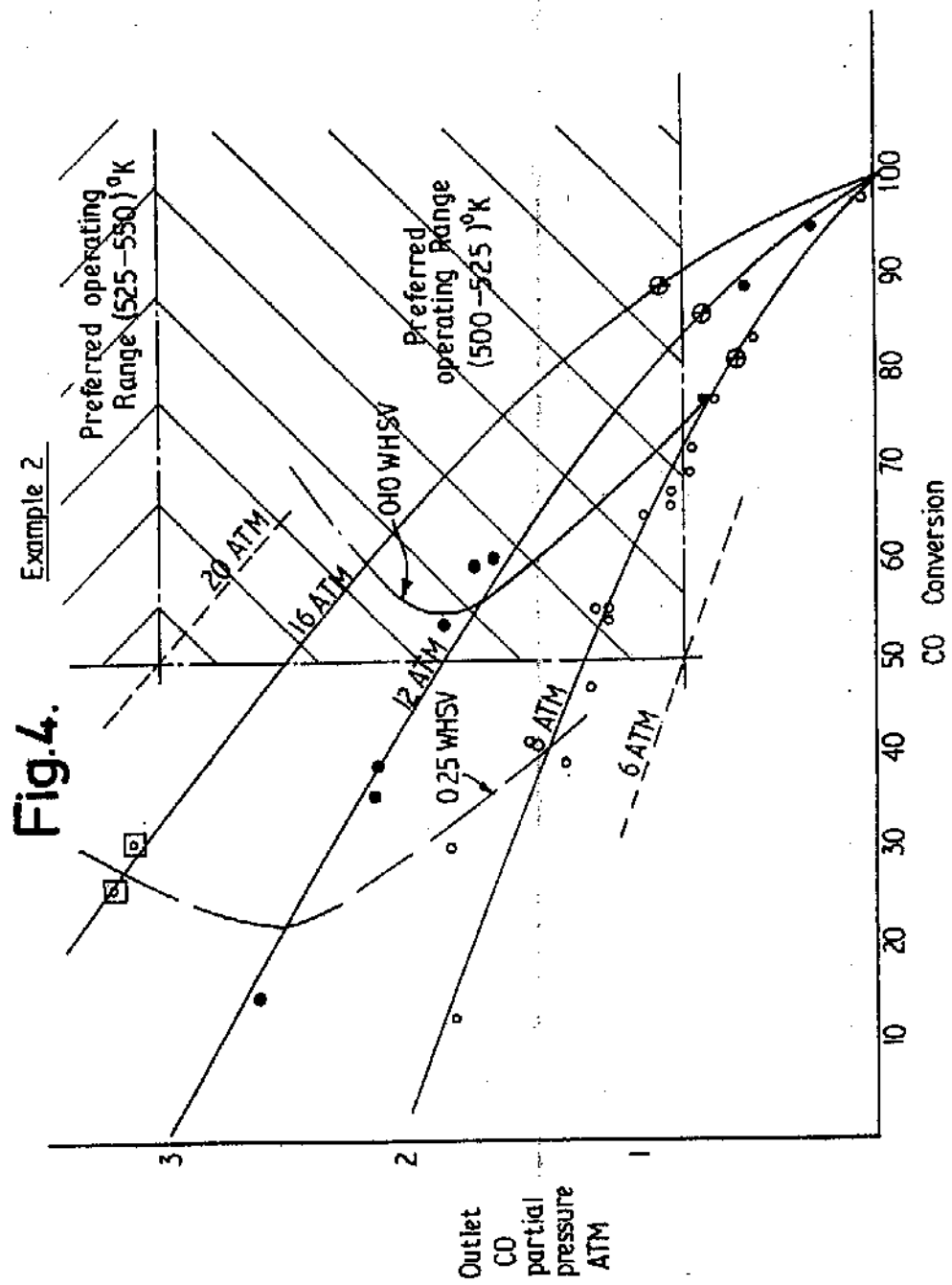Fig.1.

Fig.2.

Fig.3.

Example 1

Fig. 4.

Example 2

Preferred operating Range (525-550)°K

Preferred operating Range (500-525)°K

0.10 WHSV

0.25 WHSV

20 ATM

16 ATM

12 ATM

8 ATM

6 ATM

Outlet CO partial pressure ATM

CO Conversion
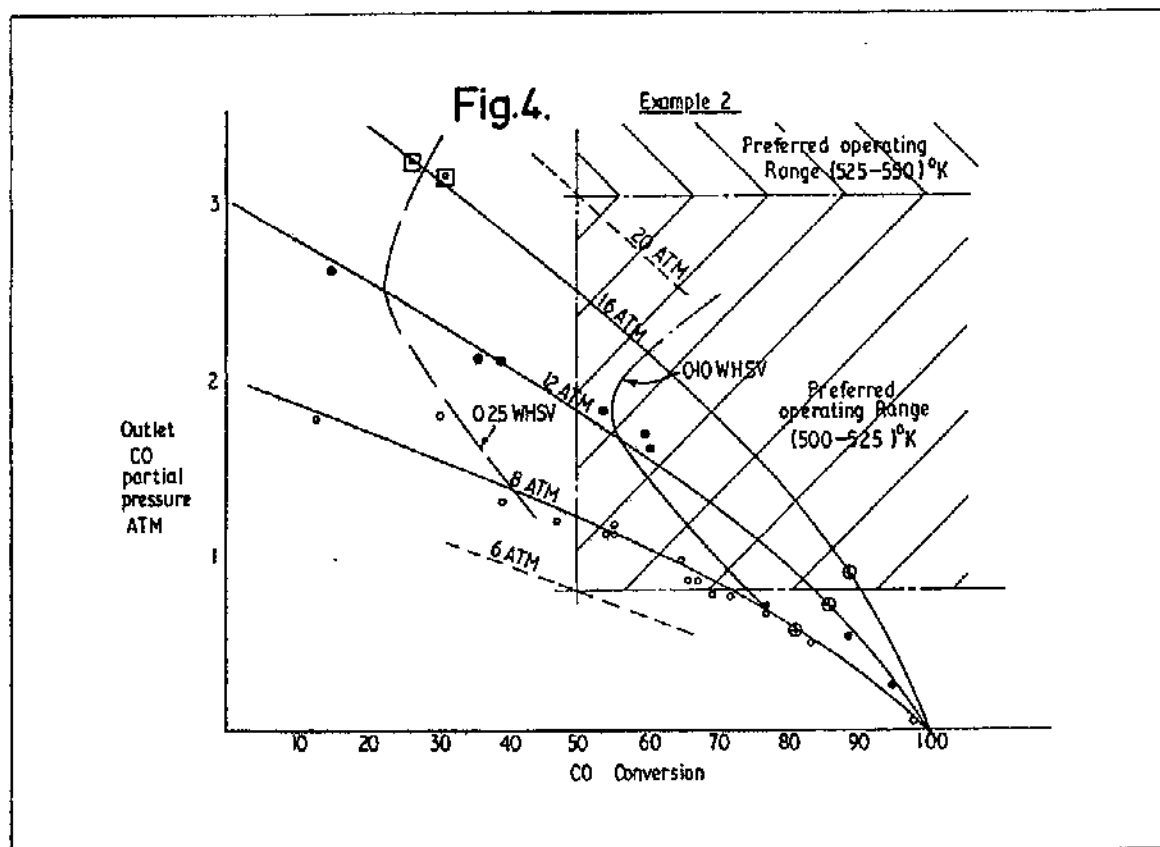
SPECIFICATION

Hydrocarbon synthesis

5 This invention relates to hydrocarbon synthesis.

So-called "synthesis" gas produced from coal has been used for the synthesis of hydrocarbons on a commercial scale in the Fischer-Tropsch process. In the currently used process the synthesis gas, composed of hydrogen and carbon monoxide, is passed over iron catalysts.

With presently used commercial catalysts it is not possible to limit hydrocarbon synthesis to a desirable
10 product range, e.g. the hydrocarbons within the gasoline range. The products produced comprise the whole   10
spectrum from methane to waxes.

Ruthenium is known as a catalyst in hydrogenation reactions, but has not been used commercially in the Fischer-Tropsch process because of its relatively high cost compared with iron catalysts.

The present invention is based on the discovery that with the use of ruthenium catalysts, it is possible to
15 obtain a product mix which favours the gasoline range of hydrocarbons. From a practical point of view   15
ruthenium also now is more attractive due to the development of new techniques for the preparation of relatively cheap supported catalysts which contain low concentrations of ruthenium, e.g. of the order of 0.5 per cent by mass.

By comparison with the promoted iron catalysts used commercially ruthenium would appear to be
20 intrinsically more selective, for gasoline range hydrocarbons. Thus Figure 1 shows a comparison of   20
published data for the iron catalyst with that which we have obtained using a ruthenium catalyst. It is seen that for a given methane selectivity, the yield of gasoline (i.e. C_5 - C_{12}) is much higher and the maximum yield of gasoline possible is also mlch higher. Curves in Figure 1 wihtout individually plotted points refer to promoted Fe catalyst as reported in the literature (M.E.Dry I and EC, Prod. Res. & Dev. vol 15 No. 4 p 283
25 (1976))   25

According to this invention a process for synthesising hydrocarbons in the C_5 to C_{12} range from a mixutre of hydrogen and carbon monoxide gases comprises contacting the said mixture with a supprted ruthenium catalyst such that the said mixture is at a temperature within the range 500° to 550°K and such that the outlet partial pressure of carbon monoxide is not less than 0.8 atmosphere (in the 500° to 525°K temperature range)
30 and not less than 3.0 in the 525° to 550°K temperature range,   30

Controlling the reaction in this way has been found to give unexpectedly high yields of the gasoline fraction with minimum quantities of the less desirable dry gas and heavy wax fractions.

Preferably the weight hourly space velocity based on the mass of the supported catalyst is within the range 0.1 to 0.25 hr^{-1}. Space velocity is defined as mass flow rate of reactant gas per unit time per unit mass of the
35 catalyst. The outlet partial pressure of carbon monoxide is the product of the total reactor pressure and the   35
fraction by volume of carbon monixide remaining in the gaseous reaction products existing from the reactor,

The supported ruthenium catalyst preferably takes the form of 0.5% by weight ruthenium metal deposited upon the external surface of 3 x 3 mm cylindrical pellets of gamma alumina and to a depth of 200 - 300µm. However in a fluidised bed reactor a powdered catalyst (100 - 200 B.S.mesh) is preferred and for this purpose
40 the above described pellets may be crushed.   40

Description of Apparatus:

Figure 2 is a schematic drawing of the apparatus used an of the flow diagram used to product hydrocarbons.

45 The reactor used was a stirred gas-solid reactor 10 driven by a motor 11 through a magnetic coupling. The   45
reactor was housed in an oven 12. Gas enters the reactor above the catalyst 13 and is withdrawn from below so that there is a net downward flow of gas away from the bearing surfaces, thus preventing accumulation of fines and reaction products.

The catalyst used in these examples was 0.5% by weight ruthenium on gamma-alumina in the form of
50 approximately 3 x 3 mm cylindrical pellets with the ruthenium impregnated only on the outer shell of each   50
pellet. The main gas supply to the reactor is from cylinder 14 containing premixed synthesis gas. A cylinder 17 supplied hydrogen gas to feed through a de-oxo unit 15 and a drier 16. A threeway valve 18 controls the gas feed to the reactor. A needle valve 19 controls the rate of gas flow into the reactor 10. A pressure regulator 20 is preset to produce the reactor operating pressure required. A thermocouple not shown
55 embedded in the reactor wall is used to control the temperature of oven 12.   55

A system consisting of two separate gas chromatographs was devised of which one measures the complete product spectrum and the other measures only the CH_4, CO and C_2's (which was noramlly very low) after the removal of water and hydrocarbons above C_2. These analyses, together with a measure of the flow rate of the final effluent stream (CH_4, CO, C_2 and H_2) yield the flow rate of the total product stream
60 directly from the reactor.   60

Each experiment utilised a fresh charge of catalyst taken from the same container obtained from the supplier. This charge was reduced for 12 hours with flowing hydrogen at a rate of 10 ml/min at a temperature of 673 K. After switching over to synthesis gas for reaction, samples of the product stream were analysed periodically in order to establish deactivation within the reactor. The selectivities of the hydrocarbons
65 (considering the total hydrocarbon fraction only) was found to be practically the same over both the initial   65

rapid deactivation period and a subsequent slow deactivation period. The product distributions and selectivities reported below were obained from analysis of samples taken at a time when the deactivation rate was very small.

Selectivity is defined as percentage weight of carbon in converted carbon monoxide found in the given
5 product.   5

Example 1   Selectivities to Gasoline
This example illustrates the fundamental essence of this discovery. From a large number of runs covering a temperature range 500K to 600K, reactor pressure range 8 to 16 atmospheres and weight hourly space
10 velocity 0.1 - 1.0 (hour)$^{-1}$ it was found that very high selectivities to gasoline (C_6 - C_{12}) were obtained if, for a   10
given temperature, the minimum outlet CO partial pressure were greater than a specified value. These results are shown in Figure 3. These show that independent of total pressure and space velocity, high selectivities are obtained at 525 K if and only if the minimum (i.e. outlet(CO partial pressure is greater than 0.8 atmosphere. Relatively high selectivities are obtained at the higher temperature of 550K if, and only if, the
15 minimum CO partial pressure is greater than 3 atmospheres. Conversely at 575 K good selectivities could not   15
be obtained.

Example 2
High conversion selectivities are not in themselves sufficient to ensure economically high yields. High
20 conversions of carbon monoxide are also necessary and desirable in their own right. The requirement set   20
out above imposes severe limitations upon the preferred operating conditions. Figure 4 illustrates this point. The conversion of carbon monoxide is related to the outlet CO partial pressure in the manner shown. Normally it is desirable to have a CO conversion in excess of 50%. Shown in Figure 4 are the ranges according to the present invention defined by this 50% conversion limit and the minimum CO partial
25 pressure discussed in example 1.   25
As is readily apparent a total pressure in excess of 6 atmospheres is required at a temperature of 500 - 525 K and a temperature of 525 - 550 K would imply a total pressure in excess of 20 atmosphers.
Also shown in Figure 4 are the weight hourly space velocities required at 525 K to obtain the indicated conversions at the different pressures. Typical conditions as a preferred embodiment can be deduced from
30 this Figure. For example, at 525 K 8 atmospheres and a 3 : 1 H2/CO ratio, space velocities should be held   30
within the range WHSV = 0.12 - 0.20 (hour)$^{-1}$

Examples 3 - 6 (Table 1)
These illustrate actual examples falling within the preferred ranges given in Example 2. Table 1 shows
35 typical run conditions and the product yield structure which results.   35

Examples 7 - 9 (Table 1)
These illustrate examples following outside the present invention.
In Example 7 the outlet partial pressure is too low primarily because the WHSV is too low.
40 In Example 8 the outlet partial CO pressure of 1.63 atmospheres is too low (i.e. below 3) for the operating   40
temperature of 545.
In Example 9 the outlet CO partial pressure of 1-84 atmospheres is too low for the operating temperature of 573 K.

TABLE 1

	according to invention				comparative examples		
Example No.	3	4	5	6	7	8	9
H_2/CO	3	3	3	3	3	3	3
Total pressure atm.	8	8	8	8	8	10	12
Temperature K	525	525	525	525	523	545	573
WHSV hr^{-1}	0.15	0.18	0.19	0.14	0.11	0.44	0.53
CO Conversion	54.5	55.4	57	69.5	77.4	52.1	54.0
Minimum CO Partial Press.Atms.	1.1	1.1	1.1	0.8	0.66	1.63	1.84
Selectivities							
%w of Hydrocarbon Products							
C_1	29.1	24.2	24.3	26.9	33.7	38.9	71.7
C_2	3.8	3.2	3.3	4.2	4.4	5.8	8.7
C_3	6.9	7.3	7.9	7.3	6.8	7.6	4.4
C_4	9.6	8.5	8.1	8.2	8.3	10.6	6.3
$C_5 - C_{12}$	50.6	56.8	56.5	53.4	46.8	37.1	8.9

CLAIMS

1. A process for synthesising hydrocarbons in the $C_5 - C_{12}$ range from a mixture of hydrogen and carbon monoxide gases comprising contacting the said mixture with a supported ruthenium catalyst wherein the said mixture is at a temperature within the temperature range of (500 to 550)°K and wherein the outlet partial pressure of carbon monoxide is not less than 0.8 atmospheres in the temperature range (500 to 525)°K and not less than 3.0 atmospheres in the temperature range (525-550)°K.

2. A process according to Claim 1 wherein the ruthenium is in the form of ruthenium metal.

3. A process according to Claim 2 wherein the ruthenium metal catalyst is carried on a particulate support.

4. A process according to Claim 3 wherein the particulate support is made from γ alumina.

5. A process according to Claim 4 wherein the support is in the form of 3 x 3 mm clyindrical pellets.

6. A process according to Claim 4 wherein the support is in powder form having a powder size falling within the range 100 - 200 B.S. mesh.

7. A process according to any one of claims 2 to 6 wherein the ruthenium metal is deposited in an amount up to 0.5 wt % and to a depth of 200 - 300 μm on the support.

8. A process according to any preceding claim wherein the reactant gas is synthesis gas.

9. A process according to claim 1 wherein the ratio of H_2 : CO in the reactant gas is within the ratio of between 2 : 1 and 4 : 1.

10. A process according to Claim 9 wherein the said ratio of H_2 : CO is 3 : 1.

11. A process according to Claim 1 wherein the space velocity of reactant gas considered as the mass flow rate of reactant gas per unit time, per unit mass of catalyst falls within the range of 0.10 to 0.25.

12. A process according to Claim 11 wherein the said space velocity is within the range 0.12 to 0.20.