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(54) Title: CATALYTIC PROCESS FOR THE PRODUCTION OF HYDROCARBONS

(57) Abstract

Single-stage catalytic conversion of a gas mixture, having a molar ratio of hydrogen to carbon monoxide greater than 1,9, to hydrocarbons boiling in the gasoline or diesel range, is achieved using three catalysts in admixture. The first is a Fischer-Tropsch catalyst with catalytic activity for the conversion of H₂ and CO into hydrocarbons. The second is a methanol conversion catalyst with catalytic activity for the conversion of methanol into hydrocarbons, such as a crystalline aluminosilicate zeolite or crystalline silicate. Finally, the third is a methanol synthesis catalyst with catalytic activity for both the water-gas shift reaction and methanol synthesis. This combination of catalysts provides high carbon conversion of CO to hydrocarbons, and a high yield of liquid products.

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"CATALYTIC PROCESS FOR THE PRODUCTION OF HYDROCARBONS"

Field of the Invention

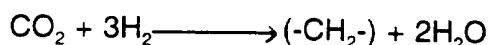
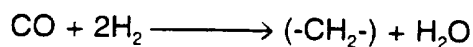
The present invention relates to a catalytic process for the production of hydrocarbons from hydrogen and carbon monoxide.

BACKGROUND OF THE INVENTION

Applicant sought a method for the once-through direct single stage conversion of synthesis or reformer gas to high quality synthetic fuel, to achieve a high yield of hydrocarbons, i.e. a high carbon conversion from CO to hydrocarbons. Synthesis gas has a highly variable H₂ to CO molar ratio of about 2. Synthesis gas from coke or coal generally has a low H₂ to CO ratio, generally less than about 1.0. Synthesis gas from methane typically has a H₂/CO ratio greater than 1.9, usually in the range of 2.0 - 3.0. Reformer gas typically has a H₂ to CO molar ratio of about 3.

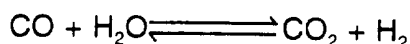
Dwyer et al U.S. patent 4,172,843 discloses a process for single stage catalytic conversion of synthesis gas to hydrocarbon mixtures. This process makes use of two catalysts. The catalysts used are a Fischer-Tropsch catalyst and a methanol conversion catalyst. Dwyer attained a 33% yield using this method.

Fischer-Tropsch catalysts contain one or more metal components from Group VIII of the periodic Table, such as iron, cobalt, nickel, rhodium and ruthenium. Typical Fischer-Tropsch catalysts are potassium promoted fused iron oxide catalysts. These have activity for the conversion of hydrogen and carbon monoxide or carbon dioxide to hydrocarbons, according to the following reactions:

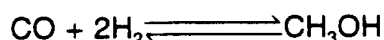


However, the product yielded by a Fischer-Tropsch catalyst alone includes a mixture of carbon dioxide, water, alcohols, and hydrocarbons, due to a number of side reactions, more specifically:

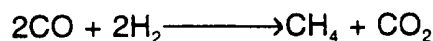
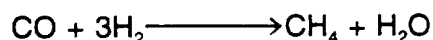
- the water-gas shift reaction:



- the methanol synthesis reaction:



- and the formation of methane, by a number of reactions:

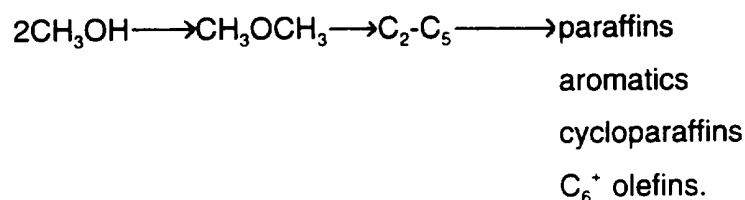


Also, the hydrocarbons produced by a Fischer-Tropsch catalyst alone are of poor quality, containing waxy paraffins which are unsuitable for use in gasoline.

The water-gas shift (WGS) side reaction is of particular significance, since it can lead to high carbon losses, due to the formation of CO_2 . This is a reversible exothermic reaction - low temperatures (less than 350°C) favour forward CO conversion to CO_2 , whereas higher temperatures favour the reverse. The water-gas shift reaction changes the oxygen-containing by-products from H_2O to CO_2 , and alters the usage ratio of hydrogen and carbon monoxide in the Fischer-Tropsch synthesis. It has also been shown to occur in parallel with the methanol synthesis reaction starting with CO_2 (Amenomiya, Y. Applied Catalysis, 30, 57-68, 1987).

Dwyer found that if a Fischer-Tropsch catalyst was combined with a methanol conversion catalyst, a better quality product was obtained.

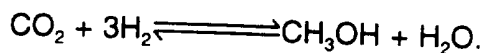
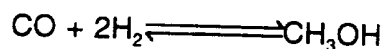
A methanol conversion catalyst, such as crystalline zeolite, has activity for the conversion of methanol into hydrocarbons, according to the following reaction:



Dwyer's combination of a Fischer-Tropsch catalyst and a crystalline zeolite gives a high quality hydrocarbon product. However, there is poor conversion of carbon and a poor yield of 33%. Further, because of the exothermicity of both the Fischer-Tropsch and methanol conversion reactions, Dwyer used a diluent to control and dissipate the heat. The diluent took up half the reaction space and so was not economical.

Another process in the prior art involved combining a methanol conversion catalyst, as described above, with a methanol synthesis catalyst. For example, see Nara, A. et al, Mitsubishi Heavy Industries Ltd. Technical Review Vol. 24 No. 1 (Feb. 1987).

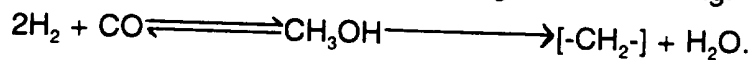
A methanol synthesis catalyst contains one or more metal components with activity for the conversion of hydrogen and carbon monoxide or carbon dioxide into methanol, according to the following reactions:



Typical examples of a methanol synthesis catalysts include Cu/ZnO/Cr₂O₃ and Cu/ZnO/Al₂O₃.

However, methanol synthesis catalysts also are good water-gas shift reaction catalysts.

The combination of methanol synthesis and methanol conversion catalysts produces hydrocarbons according to the following:



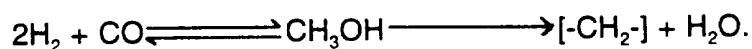
However, the useful product yield is low. Large amounts of methane are formed, and carbon is lost to CO₂ due to the water-gas shift reaction.

It should be noted that Dwyer's process of Fischer-Tropsch plus methanol conversion catalysts is favoured by temperatures of 250 to 350°C. Conversely, the combination of methanol synthesis and methanol conversion catalysts is favoured by temperatures greater than 350°C. As these two catalyst combinations are effective at different temperature ranges, it would be expected that they would be incompatible. Further, as the conversion of CO to CO₂ by the water-gas shift reaction as promoted by the methanol synthesis catalyst is favoured at temperatures less than 350°C, it would be expected that if these two systems were combined at the lower temperature, the losses to CO₂ would increase in the presence of the methanol synthesis catalyst. Thus it would be expected that if the two systems were combined, carbon losses would be severe. This result is illustrated by Canadian Patents 1,111,073 and 1,111,074 issued to Shell Canada Limited.

The Shell patents were based on a feedstock from the gasification

1 of coal, which yields a H₂/CO molar ratio of about 0.5. The claims in Shell were
2 specifically limited to feedstock with H₂/CO less than 1.

3 In the Shell patents, conversion of the H₂ and CO to hydrocarbons
4 using the combination of a Fischer-Tropsch catalyst plus a methanol conversion
5 catalyst was desired. However, this combination produces hydrocarbons, as
6 noted above, according to the following reaction:



8 This requires a H₂/CO molar ratio of 2. Thus the Shell system was deficient in
9 hydrogen. To overcome this problem a methanol synthesis catalyst was added
10 and the feedstream was modified to include water in order to produce hydrogen
11 according to the water gas shift reaction. In addition to producing the needed
12 H₂, this of course led to very high carbon losses to CO₂. Shell taught utilization
13 of the methanol synthesis catalyst only to the extent necessary to produce H₂ for
14 the hydrocarbon synthesis, as any further production would just increase carbon
15 losses to no purpose. Therefore, it follows from the Shell teachings that a
16 methanol synthesis catalyst should not be used in a system where hydrogen is
17 not deficient.

18 This point is made by Anderson in his review paper (Anderson,
19 J.R., Methane to Higher Hydrocarbons, Applied Catalysis, 47, p. 183, 1989):

20 "The formation of H₂ as a primary reaction product means that the
21 possibility exists for the water-gas shift reaction in the reactor.
22 Thus catalysts (e.g. iron) with good activity for the water-gas shift
23 will tend to generate CO₂ rather than water, and simultaneously
24 remove CO and generate H₂. This is a desirable situation when,
25 as with coal-derived synthesis gas, the initial H₂/CO ratio is low".

26 SUMMARY OF THE INVENTION

27 Applicant analyzed the prior art and sought a method to improve
28 on the low hydrocarbon yield obtained from the Dwyer process, which uses
29 Fischer-Tropsch plus methanol conversion catalysts. It should be noted that both
30 Dwyer and Applicant utilize a feedstock which is not deficient in hydrogen.

31 In the development of the invention, Applicant added a methanol
32 synthesis catalyst to the Dwyer system, contrary to the teachings of the prior art.
33 Applicant based this addition on his theory of how this catalyst would work in

1 combination with the others. This theory contended:

- 2 - that under conditions of H_2/CO molar ratio greater than
3 about 1.9, the reverse water-gas shift reaction will
4 predominate, so carbon losses to CO_2 will be reduced;
- 5 - that the endothermic nature of the reverse water-gas shift
6 reaction will help dissipate the heat from the exothermic
7 reactions assisted by the Fischer-Tropsch and methanol
8 conversion catalysts, thus making use of diluent
9 unnecessary;
- 10 - that the formation of methanol by the methanol synthesis
11 catalyst will help the reactions of the other two catalysts
12 along, and absorb heat;
- 13 - some CO_2 formed by the Fischer Tropsch catalyst will be
14 removed by reaction with hydrogen over the methanol
15 synthesis catalyst; and
- 16 - that due to these factors, the yield of useful liquid
17 hydrocarbons will improve.

18 When tested, Applicant found that this combination of three catalysts in
19 admixture in one bed at one temperature was indeed effective, when applied to
20 a feedstock having a H_2/CO molar ratio greater than about 1.9. Improved yields
21 of hydrocarbons were efficiently obtained.

22 Therefore, according to the present invention, a gas mixture
23 feedstock containing a H_2/CO molar ratio greater than 1.9 is reacted in the
24 presence of three catalysts in admixture: Fischer-Tropsch, methanol conversion,
25 and methanol synthesis catalysts. Preferably, the H_2/CO ratio ranges from 2.0
26 to 2.5; more preferably, from 1.9 to 2.1.

27 The temperature at which the process may be carried out
28 preferably will fall in the range from 220 to 360°C. However, temperatures from
29 200 to 400°C are also contemplated.

30 Elevated pressure at conventional levels is desirable to increase the
31 efficiency of the reactions. The process may be carried at pressures falling in
32 the range from 100 psig to 1000 psig, however pressures from 50 psig to 2000

1 psig are also contemplated.

2 This process has surprisingly been shown to be effective in
3 producing a high quality hydrocarbon product boiling in the gasoline range when
4 conducted at higher than normal pressures (greater than 200 psig and preferably
5 greater than about 500 psig) and lower than normal temperatures (less than
6 240°C). Recently, high pressure natural gas-steam reforming processes have
7 been demonstrated . For instance, ICI has developed the LCM (Leading
8 Concept Methanol Process) to produce synthesis gas at 600 psig or higher.
9 Thus, the process of this invention can be operated from such LCM reactor
10 without an intermediate gas comparison step to realize energy savings from heat
11 losses and compression costs.

12 Each of the three components of the catalyst mixture are well
13 known in the art. The Fischer-Tropsch catalyst used is preferably a promoted
14 fused iron oxide (preferably potassium promoted). The methanol conversion
15 catalyst is preferably either a crystalline aluminosilicate zeolite, or a crystalline
16 silicate. The methanol synthesis catalyst is preferably an oxide of one or more
17 of zinc, copper, iron, chromium and aluminum and may be free of, or may
18 contain promoters.

19 It is contemplated that the three catalysts may be provided in
20 different ratios, in order to adjust the composition of the product. For example,
21 if a higher paraffin content is desired, the relative proportion of the Fischer-
22 Tropsch catalyst should be increased. Conversely, if a higher aromatic content
23 is desired, the relative proportion of the methanol conversion or methanol
24 synthesis catalysts should be increased. In this way the final product
25 composition may be manipulated to meet regulatory or other requirements.

26 BRIEF DESCRIPTION OF THE DRAWINGS

27 Figure 1 is a schematic flow diagram of the experimental circuit
28 used in Example 1 to illustrate the process of the present invention;

29 Figure 2 is a schematic flow diagram of a second experimental
30 circuit used in Example 2 to compare the performance of the trifunctional catalyst
31 of the present invention with bifunctional catalyst mixtures; and

Figure 3 is a graph plotting the weight percent liquid hydrocarbons against carbon number for the trifunctional catalyst of the present invention (Run 3.3) and a bifunctional catalyst (Run 3.8).

DESCRIPTION OF THE PREFERRED EMBODIMENT

Each of the catalyst components of the catalyst mixture used in the process of this invention are well known in the art.

Fischer Tropsch catalysts are those having catalytic activity for converting hydrogen and carbon monoxide reactants into hydrocarbons. Such catalysts are described, for instance in U.S. Patent 4,639,431, U.S. Patent 4,595,702, U.S. Patent 4,361,503 and U.K. Patent 506,064. Such catalysts typically include zinc, iron, cobalt, ruthenium, rhodium or osmium. With the exception of ruthenium, such catalysts typically include chemical and structural promoters such as copper, manganese, chromia, alumina, the alkaline earths, the rare earths and alkali, e.g. carbonates of the Group IA of the periodic table. Particular preferred FT catalysts for the process of the present invention include iron or cobalt. Potassium is the preferred promotor with iron, to reduce methane production. Potassium promoted iron catalysts are classical known FT catalysts generally recognized as being illustrative of the group of FT catalysts.

Methanol conversion catalysts have catalytic activity for the conversion of oxygenated hydrocarbons such as methanol into hydrocarbons. Such catalysts are typically crystalline aluminosilicate zeolites or crystalline silicates. In particular, the zeolite ZSM-5 is a classical known catalyst illustrative of the group of methanol conversion catalysts. Such catalysts are disclosed, for example, in U.S. Patents 4,260,841; 4,269,783; and 4,292,410.

Methanol synthesis catalysts are those having catalytic activity for the watergas shift reaction and the methanol synthesis reaction. Typical examples are oxides of one or more of zinc, copper, iron chromium and aluminum. Particularly preferred are zinc and/or copper methanol synthesis catalysts which may contain chromia and/or alumina. Methanol synthesis catalysts are described in the literature, for instance in U.S. Patents 4,292,410 and 4,096,163.

1 The three catalyst components are utilized in intimate admixture in
2 the process of this invention. The mixture may be used as a powder or slurry,
3 or it may be pelletized prior to or following admixture, as is known in the prior art.
4 Prior to use, the catalyst mixture is preferably reduced to remove a substantial
5 portion of the oxides. Reduction can be accomplished by contacting the catalyst
6 mixture with hydrogen at an elevated temperature and pressure. The
7 temperature should be controlled to avoid substantial agglomeration.

8 The feedstock to the process is one having a H_2/CO molar ratio
9 greater than 1.9 and preferably at least 2.0. Synthesis gas and reformer gases
10 are exemplary.

11 The synthesis gas is contacted with the catalyst admixture at
12 elevated pressure and temperature in a pressure reactor. A shell and tube style
13 reactor bed is exemplary of a suitable reactor. Such reactors utilize top down
14 gas flow with heat transfer fluid being circulated around the tubes to remove the
15 heat of reaction. The pressure and temperature conditions are generally
16 mutually dependent and also vary with the particular feedstock and catalysts.
17 While pressures of 50 to 2000 psig are possible, more preferably the pressure
18 will be in the range of 100 to 1000 psig. Temperatures of 200 to 400°C are
19 possible, the more preferable range being 220 to 360°C. At about 200 psig, a
20 temperature range of about 315 - 350°C is preferred.

21 At pressures higher than typically used in the art (i.e. greater than
22 200 psig), the temperature can be dropped below the normal temperature limits
23 in the art (i.e. below 240°C) with the result that a high quality hydrocarbon
24 product boiling in the gasoline range is produced. At about 500 psig a
25 temperature range of 220-240°C is preferred. Below this temperature range, the
26 activity of the iron FT catalyst may drop off, although other catalysts such as a
27 cobalt FT catalyst could operate at a lower temperature.

28 The process is preferably practised in a single reactor, that is the
29 feed gases are passed over the three catalysts in intimate admixture in one
30 reactor. Single or multiple fixed beds, or fluidized beds, may be used. Recycle
31 to improve efficiency may be used.

32 The process is further illustrated by the following non-limiting

examples.

Examples

Catalysts

The following catalysts were used in the examples:

A. FISCHER-TROPSCH CATALYSTS (FT)

CATALYST A1 Promoted iron catalyst G-84B obtained from United Catalysts Inc. United Catalysts Inc. reports the nominal content of G-84B to be Fe_2O_3 88%, K_2CO_3 10% and Cr_2O_3 2%.

CATALYST A2 Promoted iron catalyst C-73 containing Al_2O_3 2-3%, K_2O 0.5-0.8%, and CaO 2-3%, also obtained from United Catalysts Inc.

B. METHANOL CONVERSION CATALYSTS

CATALYSTS B1, B2 ZSM-5 type zeolite was prepared using the method described by Chen et al in U.S. Patent 4,112,056 as modified. ZSM-5 is a synthetic zeolite characterized by parallel straight channels interlocking with zig-zag channels. Two catalysts were prepared with compositions given below. By analysis, the two catalysts had $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios of 67.6 and 45.2 and the crystal structure was verified by comparison of the x-ray diffraction patterns against standard ZSM-5 obtained from Mobil (below).

	<u>B1</u>	<u>B2</u>
Si	42.6	36.2
Al	0.714	0.907
Na	0.234	0.680
SiO_2	91.2	77.5
Al_2O_3	1.35	1.72
Na_2O	0.315	0.917
$\text{SiO}_2/\text{Al}_2\text{O}_3$	67.6	45.2

CATALYST B3 Zeolite catalyst silicalite S-115 $\text{SiO}_2 > 99\%$ obtained from Union Carbide Catalysts.

CATALYST B4 ZSM-5 zeolite catalyst obtained from Mobil Research and Development Corporation.

C. METHANOL SYNTHESIS CATALYSTS (MS or WGS)

CATALYST C1 Proprietary Shell Commercial Methanol Synthesis (MS) Catalyst - approximately 40% CuO, 50% ZnO, 10% Al₂O₃ with several trace elements. Product designation MS-51-2.

CATALYST C2 MS catalyst C-79 obtained from United Catalysts Inc. This is a low temperature Cu/Zn catalyst.

CATALYST C3 United Catalysts Inc. C61-1 MS Catalyst. United Catalysts Inc. reports the content of C61-1 catalyst to be CuO 33 +/-3% by weight, ZnO 65 +/-3.0% Al₂O₃ 2% maximum, S 0.04% maximum, Na 0.10% maximum, Cl 0.01% maximum. Bulk density 85 +/-5 lbs/cu ft., surface area 30-60 m²/g, pore volume 0.25-0.35 cc/g.

4. INERT FILLER

CATALYST D1 Carborundum.

EXAMPLE 1

EXPERIMENTAL DETAILS

The flow diagram of the experimental circuit 10 used in this example is shown in Figure 1. The feed gas streams (H₂, N₂, CO) were fed through filters 12, mass flow controllers 14 and check valves 16 into line 18. The mass flow controllers were Matheson Model 8100 series. The gas mixture was introduced into the pressurized reactor 20 containing the catalyst or diluent. The reactor 20 was housed in furnace 22. Temperature probes 24, 26 monitored catalyst and furnace temperatures respectively. Inlet pressure to the reactor was monitored by pressure meter 28 in line 18. Products leaving the reactor 20 were passed through a +15°C trap 30 and two -75°C traps 32 in the outlet line 34. Pressure was maintained at 200 psig by back pressure regulator 36 in the outlet line 34, as monitored by the pressure meter 38. The outlet gases were fed to a gas chromatograph (GC) 40 through a flowmeter 42. Gases were vented from

the GC through vent 44. Data from the GC was analyzed by a data system 46 to measure (a) total hydrocarbon and (b) mixture of hydrocarbons C1 to C3 and CO₂. The liquid trapped in trap 30 was analyzed using PONA. PONA is a conventional analytical method for describing the paraffinic, olefinic, naphthenic and aromatic components of a predominantly hydrocarbon mixture. Products were also analyzed by GC-MS to separate the components (GC) and then identify the components by mass spectrometry. Gas samples were analyzed throughout each experiment at intervals of 12 minutes.

CATALYST PREPARATION

The G-84B (A1) and MS51-2(C1) catalysts were 14-25 mesh size. The ZSM-5 (B1 and B3) catalysts were fine crystalline powders. In each run, a total of 4 cm³ of catalysts or diluent was loaded into the reactor. The catalyst mixture was pre-treated for each run (to reduce the catalysts) with a flow of H₂ at 200°C and 200 psig for a minimum period of 18 hours. The catalyst combinations and process conditions employed are shown in Table 1 and further described hereinbelow.

EXAMPLE 1(a)

This example illustrates one preferred embodiment of Applicant's invention. Three catalysts were used together - G-84B(A1), ZSM-5(B1), and MS 51-2(C1). All tests were conducted at GHSV 900, and 200 psig at 335°C. The H₂/CO ratio of the feed gas was varied. Results in Table 1 show that CO conversion was excellent over H₂/CO ratios from 1.5 to 3.0. C₅+ yield was best for H₂/CO = 2.5 but was also good at lower ratios. The product slate featured high paraffin content and low aromatic content. For all the tests in Example 1, the oxygenate production was below 2% yield.

EXAMPLE 1(b)

Tests were conducted at H₂/CO = 2.0 GHSV = 900 and pressure = 200 psig but at lower and higher temperatures than in example 1(a). At both

1 290°C and 380°C CO conversion was considerably lower, as was C₅₊ yield. The
2 process conditions are further optimized in further examples. The high-
3 temperature test (380°C) produced high wax levels and the highest aromatic
4 product level (20% of liquid product).

5 **EXAMPLE 1(c)**

6 In this example of the invention, the relative amounts of FT and
7 methanol conversion catalyst were varied, while holding GHSV at 900, pressure
8 at 200 psig and temperature 335°C. A higher level of FT catalyst relative to
9 methanol conversion catalyst gave rise to lower C₅₊ yield.

10 **EXAMPLE 1(d)**

11 In this example the methanol conversion catalyst was changed from
12 a zeolite to silicalite and two ratios with the FT catalyst were tested. Excellent
13 C₅₊ yields were obtained at GHSV 900, pressure 200 psig and temperature 335
14 °C. This example illustrates that product slate can be altered by the choice of
15 methanol conversion catalyst, silicalite produces a high-aromatic hydrocarbon
16 product (16.62%) in comparison with ZSM-5 (12.10%).

17 **EXAMPLE 1(e)**

18 To determine the commercial value of hydrocarbon liquids produced
19 in Example 1, hydrocarbon liquids run from 90-05 (Example 1(a) with ZSM-5)
20 and 91-11 (Example 1(d) with silicalite) were subjected to PONA analysis and
21 octane numbers were calculated. Results in Table 2 show both hydrocarbon
22 liquid products to have a high energy value and excellent utility as a fuel
23 feedstock. The Research Octane Numbers were equal to, or better than, typical
24 light straight run gasoline.

TABLE 1. PARAMETRIC TESTS OF TRIPLE CATALYSTS AT LOW PRESSURE (200 PSIG)

RUN NUMBER	CATALYST VOLUME RATIOS			CATALYST BED TEMPERATURE °C	FEED GAS VOLUMETRIC RATIO H ₂ /CO	CO CONVERSION %	C ₅₊ YIELD
	A1	B3	B1 C1				
Example 1(a)							
90-01	1	0	4 5	335	1.5	96	21
90-05	1	0	4 5	335	2	93	20
90-02	1	0	4 5	335	2.5	96	32
90-03	1	0	4 5	335	3	85	11
Example 1(b)							
91-06	1	0	4 5	290	2	70	9
91-07	1	0	4 5	380	2	80	14
Example 1(c)							
91-08	2	0	3 5	335	2	91	15
91-09	0.5	0	4.5 5	335	2	88	20
Example 1(d)							
91-10	1.00	4.00	0 5	335	2	94	20
91-11	1.25	3.75	0 5	335	2	97	26

**TABLE 2 COMPARISON OF CALCULATED OCTANE NUMBERS FOR SAMPLES
FROM RUN # 90-05 (WITH ZSM-5) and RUN # 91-11 (WITH SILICALITE)**

	RUN # 90-05	RUN # 91-11	LSR GASOLINE	COMMERCIAL GASOLINE
<u>Weight%</u>				
Paraffins	47.62	40.02	N.A.	50(30-86)
Olefins	18.73	26.12	N.A.	9(0.1-26)
Naphthenes	6.19	6.84	N.A.	5.5(1.5-10)
Aromatics	12.10	16.62	N.A.	35(5-55)
Oxygenate	0.19	0.0	N.A.	N.A.
Unknowns	15.16	10.4	N.A.	<1
<u>Octane Numbers (a)</u>				
MON	60.8	69.9	61.6(b)	92+
RON	66.5	76.6	66.4(b)	92+
Antiknock Index	63.6	73.3	64.0	92+
(a) Calculated values based on PONA				
(b) Typical value for Light Straight Run (LSR) Gasoline				

EXAMPLE 2

This example demonstrates the applicability of the process of this invention with the trifunctional catalyst (Run 3.3) in comparison with bifunctional or singular catalyst systems at high pressure, low temperature conditions.

EXPERIMENTAL DETAILS

The flow diagram of the experimental circuit 48 used in this example is shown in Figure 2. The feed gas streams of CO, H₂ and N₂ were fed through pressure filters 50, gas flow controllers 52, and check valves 54 into line 56. The gas flow controllers were connected to a gas blender console 58. The pressure in line 56 was monitored by test guage 60, pressure transducer 62 and meter 64. The gas mixture was passed vertically downwardly through the catalyst in a reactor 66. The reactor was housed in a clam-shell furnace 68. The temperature in the reactor was monitored by a K type thermocouple 70 and heat controller 72. Liquid product exiting the reactor 66 through line 74 was condensed and collected in vessel 76. Uncondensed gases exiting the reactor passed through the vessel 76 to gas line 78. The reactor pressure was controlled by a back pressure regulator 80, pressure transducer 82 and meter 84 in line 78. The uncondensed gases in line 78 were passed through a molecular sieve trap 86, filter 88, volumetric flowmeter 90 and bubble meter 92. The gases were then passed by a gas exit reduction furnace 94 to a gas chromatograph 96 for analysis. Hydrocarbon liquids trapped in vessel 76 were subjected to PIANO analysis for normal paraffins, iso-paraffins, aromatics, napthenics, and olefins.

As indicated, tests of the trifunctional catalyst admixtures were conducted at lower temperatures and higher pressure than described in Example 1. Operating parameters were fixed as follows: Temperature between 230°C and 270°C GHSV 900, pressure 500 psig, H₂/CO ratio 2.0 with a nitrogen tracer. The catalyst mixtures were prepared as set out in Table 3. The catalysts were milled to a narrow mesh size and packed into a vertical reactor of diameter 1-centimetre to a length 10 centimetres and a volume of 7.15 cc. A standard catalyst reduction sequence was followed: temperature was increased at

1 5°C/min up to 100°C and 200°C and 450°C with a hold time of 1 hour at 100°C
2 and 200° and hold time of 36 hours at 450°C. The reduction gas was H₂.

3 As shown in Table 4, operating with a high hydrogen ratio relative
4 to CO of 2.0 the trifunctional catalyst ABC provides much higher CO conversion
5 compared with the three bifunctional catalyst combinations, even though those
6 were tested at higher temperatures (250°C - 267°C versus 231°C for ABC). Total
7 CO conversion to hydrocarbons was superior with ABC as was the product slate.
8 ABC liquid product was 90% gasoline range with a high proportion of isoparaffins
9 and naphthenes, which provide good octane values, and a low proportion of
10 mono-aromatics, which are toxic materials. Standard Fischer-Tropsch cannot
11 achieve grater than 40-50% selectivity for a given premium product in one step.
12 (New Trends In Coactivation, Ed. L. Gucci, ELSEVIER, 1991, P. 206).

13 Under the reaction conditions employed, the zeolite catalyst B was
14 not effective alone or in combination with the methanol synthesis catalyst C,
15 providing CO conversion of only 25.6% (Run 4.0), and no hydrocarbons.
16 However, when a small amount of FT catalyst A was included (catalyst type
17 ABC, Run 3.3), CO conversion increased to 91% and hydrocarbon yield was
18 48.6%. Using the FT catalyst A in a combination with the zeolite catalyst B also
19 give inferior hydrocarbon yield and a low efficiency to gasoline-range products.

20 The benefit of Run 3.3, over Run 3.8, the comparative two-part
21 catalyst is shown dramatically in Figure 3. A hydrocarbon product having a very
22 narrow molecular weight range is produced by the process of this invention at
23 the high pressure, low temperature conditions.

24 This example demonstrates a very strong and unexpected synergy
25 when the trifunctional catalyst ABC is used under conditions of high hydrogen
26 feed gas ratios of approximately 2.0 or greater, which ratios have never been
27 tested before. Prior art would have predicted extremely high CO₂ yields whereas
28 the yields observed were only those typical of FT catalysts and benefits occurred
29 in total hydrocarbon yield, hydrocarbon C₅₊ (liquids) yields, gasoline range
30 hydrocarbon selectively and a superior liquid product slate with high energy value
31 and low toxicity.

TABLE 3 TRIFUNCTIONAL CATALYST ADMIXTURES¹ USED IN LOW-TEMPERATURE TESTS**EXAMPLE 2**

Run Number	3.3 ²	3.8	3.9	4.0	3.4	3.7	3.5
Catalyst Type	ABC	ABD	ADC	DBC	DDC	DBD	ADD
A2, wt ratio	1.00	1.00	1.00	0	0	0	1.00
B4, wt ratio	1.60	1.60	0	1.60	0	1.60	0
C2, wt ratio	4.55	0	4.55	4.55	4.55	0	0
D, wt ratio	0	4.55	1.60	1.00	2.60	5.55	7.17

- Total bed volumes were 7.15 cc and length 10 cc. Volume ratios of catalysts were A-type: B-type: C-type, 1:4:5 with inert filler D replacing one of the others in same cases.
- Only Run 3.3 is in accordance with the process of this patent; all other runs in the table are for purpose of comparison.

TABLE 4 LOW-TEMPERATURE HIGH PRESSURE TEST OF TRIFUNCTIONAL CATALYST (EXAMPLE 2)

Run Number (see Table 2)	3.3 ¹	3.8	3.9	4.0	3.4	3.7	3.5
Catalyst type	ABC	ABD	ADC	DBC	DDC	DBD	ADD
Temperature, °C(furnace)	231	250	267	258	252	250	250
CO Conversion, %	91.4 ²	37.7	13.4	25.6 ³	6.8	.	..
Hydrocarbon Yield, %	48.6	27.2	0.5	0	6.7	.	..
Efficiency: g C ₅ /hr	0.23	0.17	0.006	0	0	.	..
g (C ₅ -C ₁₁)/hr	0.21	0.08	0.002	0	0	.	..
Hydrocarbon Selectivity							
C ₃ -C ₄ (LPG range)	4	1	1	0	***	.	..
C ₅ -C ₁₁ (gasoline range)	90	49	40	0	***	.	..
C ₁₂ -C ₁₉ (diesel range)	6	32	48	0	***	.	..
C ₂₀ + (wax range)	0.1	18	11	0	***	.	..
(C₅ - C₁₁) Composition, %							
n-paraffins	18	26	69	0	***	.	..
iso-paraffins	41	15	19	0	***	.	..
aromatics	9	11	4	0	***	.	..
naphthenes	18	9	6	0	***	.	..
olefins	14	39	2	0	***	.	..
benzene	0.1	0.4	0.2	0	***	.	..
toluene	0.3	0.9	0.5	0	***	.	..
Mass balances, %							
total	104	102	101	100	101	.	..
carbon	100	104	100	93	100		
hydrogen	102	102	98	100	100		
oxygen	101	104	105	104	100		
Analysis period, hrs							
	74-	91-	0-	0-	0-	0-	0-
	144	163	136	142	49	24	66

- Only Run 3.3 is in accordance with the process of this patent: the other runs are for comparison purposes.
- CO conversion activity loss was 3.1 vol %/100 h.
- Product was mainly methanol and dimethyl ether.
- Product was 99% methanol.
- No Activity.
- Activity Negligible.
- No hydrocarbons produced in these ranges.

Table 5 shows the superiority of Run 3.3 to both the commercial SASOL FT- process and the Mobil Methanol-to-gasoline (MTG) process, since Run 3.3. provided a narrower product distribution centred on gasoline, the most valuable commodity. Furthermore Run 3.3. was a direct conversion of syngas to hydrocarbon, whereas the MTG process requires the manufacture of the intermediate compound methanol as feedstock.

TABLE 5 Distribution of C₃ - C₁₉₊ products

	SASOL ^{3,4} FIXED BED	RUN 3.3 ¹	MOBIL ^{2,3,4} (ZSM-5)
LPG C ₃ , C ₄	11	4	18
Gasoline C ₅ -C ₁₂	25	90	82
Diesel C ₁₃ -C ₁₈	17	6	0
Heavy Oil C ₁₉₊	47	0.1	0
Aromatics, % of gasoline	0	9	39

1. Only the data from Run 3.3 is in accordance with the present invention.
2. Product from methanol feed to ZSM-5 zeolite
3. Iron Fischer-Tropsch catalyst
4. Source - From Encyclopedia of Chemical Technology, Edited by Kirk-Othmer, Third Edition, Volume 5, p. 46. Interscience Publishers, New York, N.Y.

EXAMPLE 3

This example is included to compare the trifunctional catalyst processes of this invention with a bifunctional catalyst process such as taught by Dwyer.

The trifunctional catalyst admixture test was conducted with a high H_2/CO ratio of 2.0 obtained from a natural gas reforming (Run 06). For comparison purposes, the methanol synthesis catalyst mixtures was left out in a comparison test, run 05. The catalyst mixtures, as set out in Table 6, were reduced over 30-hour periods with hydrogen while controlling the reduction temperature below 300°C. Catalyst bed size was 4 cc and the tests were operated in a horizontal mode. An internal thermocouple was used to measure catalyst bed temperature. Pressure was 200 psig and the gas hourly space velocity was 900.

Reformer gas derived from natural gas feedstock already contains abundant hydrogens (i.e. H_2/CO molar ratio of 2.0 or greater). Promoting the further increase in hydrogen and reduction in CO would be highly counter-productive. Nevertheless, a test of these ideas was conducted, with surprising and counterintuitive results. The prior art teaches that the inclusion of a methanol synthesis catalyst, as in Run 06, would increase CO selectivity to CO_2 by the watergas shift reaction causing a reduction in hydrocarbon yield in comparison with the same catalyst system not containing the WGS catalyst (Run 05). However, the results were contrary to expectations. The trifunctional catalyst admixture (ABC) (Run 06) containing the WGS catalyst (C-type) gave superior CO conversion, hydrocarbon yield and lower CO_2 selectivity in

1 comparison with the bifunctional catalyst (ABD) of Run 05 (Table 7).

2 **Table 6** Catalysts used in Example 3

3	Run Number	06	05
4	Catalyst Type	ABC	ABD
5	A1, wt ratio	1.00	1.00
6	B2, wt ratio	1.89	1.89
7	C3, wt ratio	5.64	0
8	D, wt ratio	0	4.09

9 Total bed volume was 4cc. Volume ratios of catalysts were A-type: B-type: C-
10 type, 1:4:5 with inert filler D replacing the C-type catalyst in Run 06.

11 **Table 7¹** (Example 3)

12	Run number	06	05
13	Catalyst type	ABC	ABD
14	Temperature furnace °C	313	326
15	Temperature Catalyst °C	334	336
16	Temperature differential °C	19	10
17	CO Conversion %	90	61
18	Hydrocarbon yield %	58	37
19	C ₅₊ yield	39	23

20 **Selectivities**

21	CO ₂	36	41
22	C ₁ + C ₂ (gases)	9	11
23	C ₃ + C ₄ (LPG range)	11	12
24	C ₅₊	44	36

25 **(C₅ - C₁₁) Composition, %**

26	n-paraffins	44	11
27	iso-paraffins	24	22
28	Aromatics	9	14
29	Naphthenes	7	9
30	Olefins	16	44
31	Mono-aromatics	1.6	2.7

32 ¹ Operating Conditions: GHSV = 900, inlet pressure 200 psi, H₂/CO ratio 2.0.
33 See Table 5 for the catalyst compositions.

34 ² Run 05 is similar to the process of Dwyer et al for comparison purposes.
35 The entire disclosures of all applications, patents and publications,

1 cited above and below, are hereby incorporated by reference. Also incorporated
2 by reference is applicants' Parent Application 07/606,755, filed October 31, 1990,
3 and the Continuation application thereof, being Serial No. 07/795,153, filed
4 November 20, 1991, of which this application is a continuation-in-part.

1 Claims:

2 1. A catalytic process for the production of a hydrocarbon mixture
3 having a higher percentage of paraffinic and olefinic hydrocarbons than aromatic
4 hydrocarbons, comprising:

5 providing a gas mixture of hydrogen and carbon monoxide having
6 a molar ratio of hydrogen to carbon monoxide which is greater than about 1.9;

7 reacting the gas mixture at elevated pressure and temperature in
8 contact with a trifunctional catalyst mixture consisting essentially of a first
9 Fischer-Tropsch catalyst having catalytic activity for converting hydrogen and
10 carbon monoxide reactants into hydrocarbons, a second catalyst having catalytic
11 activity for the conversion of methanol into hydrocarbons, and a third catalyst
12 having catalytic activity for the water-gas shift reaction and the methanol
13 synthesis reaction;

14 to produce a hydrocarbon mixture boiling in the gasoline and diesel
15 range, said trifunctional catalyst having a relative proportion of said first catalyst
16 to said second and third catalysts effective to provide said hydrocarbon mixture
17 having a higher percentage of paraffinic and olefinic hydrocarbons than aromatic
18 hydrocarbons.

19 2. The process as set forth in claim 13 in which the molar ratio
20 of hydrogen to carbon monoxide is at least 2.0 and less than 3.

21 3. The process as set forth in claim 13 in which the molar ratio
22 of hydrogen to carbon monoxide is at least 2.0 and less than 2.5.

23 4. The process as set forth in claim 13 in which the reaction is
24 conducted at a temperature in the range 200 to 400°C and at a pressure greater
25 than 200 psig.

26 5. The process as set forth in claim 13 in which the reaction is
27 conducted at a temperature in the range 220 to 360°C and at a pressure greater
28 than 200 psig.

1 6. The process as set forth in claim 13 in which the reaction is
2 conducted at a temperature in the range 200 to 240°C and at a pressure greater
3 than 500 psig.

4 7. The process as set forth in claim 6, wherein the pressure is
5 at least 500 psig.

6 8. The process as set forth in claim 1, in which the process is
7 conducted in a single reactor, and wherein the components of the trifunctional
8 catalyst are in intimate admixture.

9 9. The process are set forth in claim 1, wherein the Fischer-
10 Tropsch catalyst is an iron or cobalt catalyst.

11 10. The process as set forth in claim 9, wherein the Fischer-
12 Tropsch catalyst is a potassium-promoted fused iron oxide catalyst.

13 11. The process as set forth in claim 9, wherein the methanol
14 conversion catalyst is a crystalline aluminosilicate or a crystalline silicate.

15 12. The process as set forth in claim 11, wherein the methanol
16 conversion catalyst is a synthetic crystalline zeolite ZSM-5 or silicalite catalyst.

17 13. The process as set forth in claim 11, wherein the water gas
18 shift and methanol synthesis catalyst is an oxide of one or more (i) zinc and (ii)
19 copper.

20 14. The process as set forth in claim 13, wherein the water gas
21 shift and methanol synthesis catalyst is a Cu-Zn-O catalyst which is reduced to
22 remove a substantial portion of the oxides.

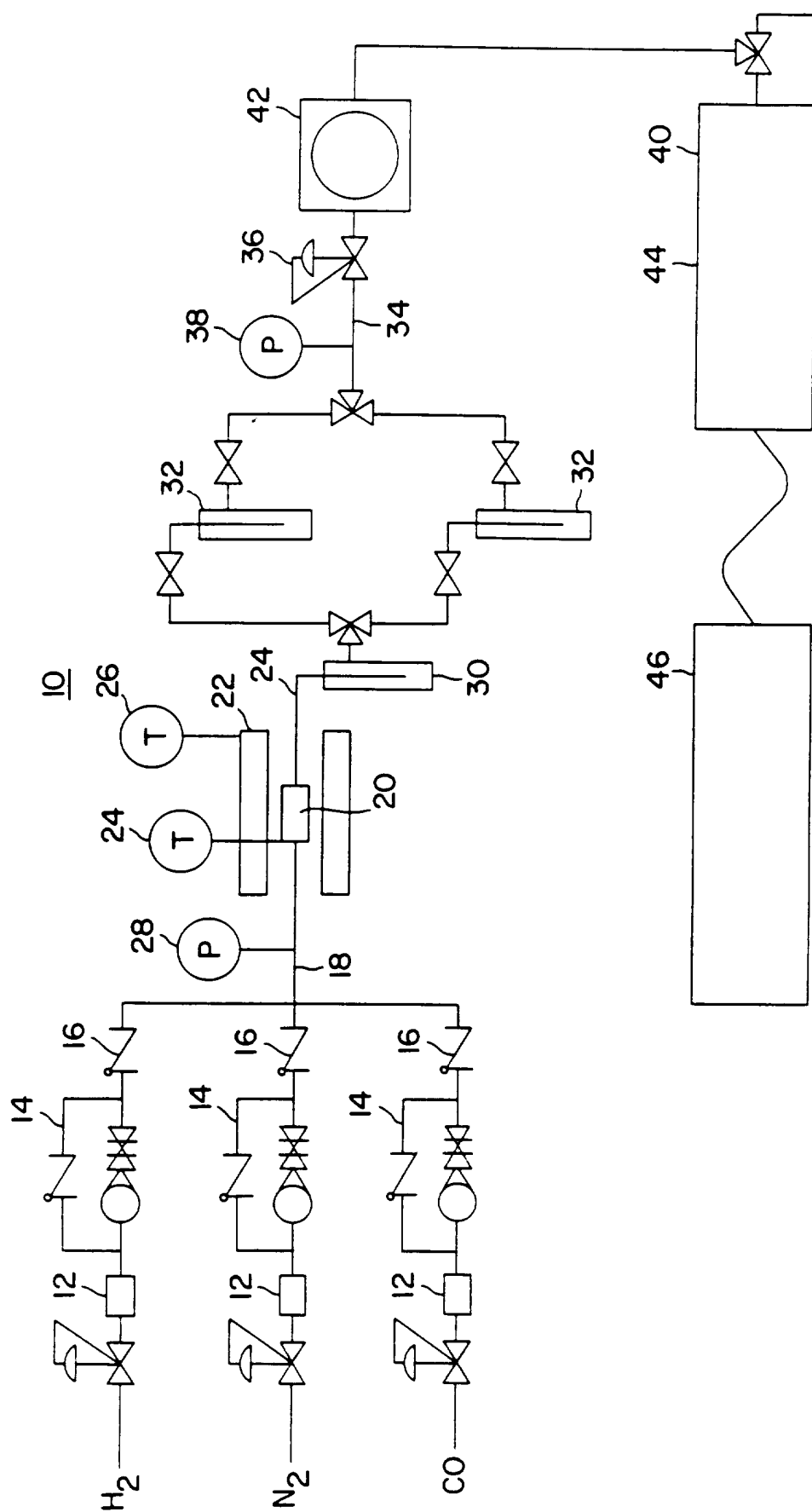


FIG. 1

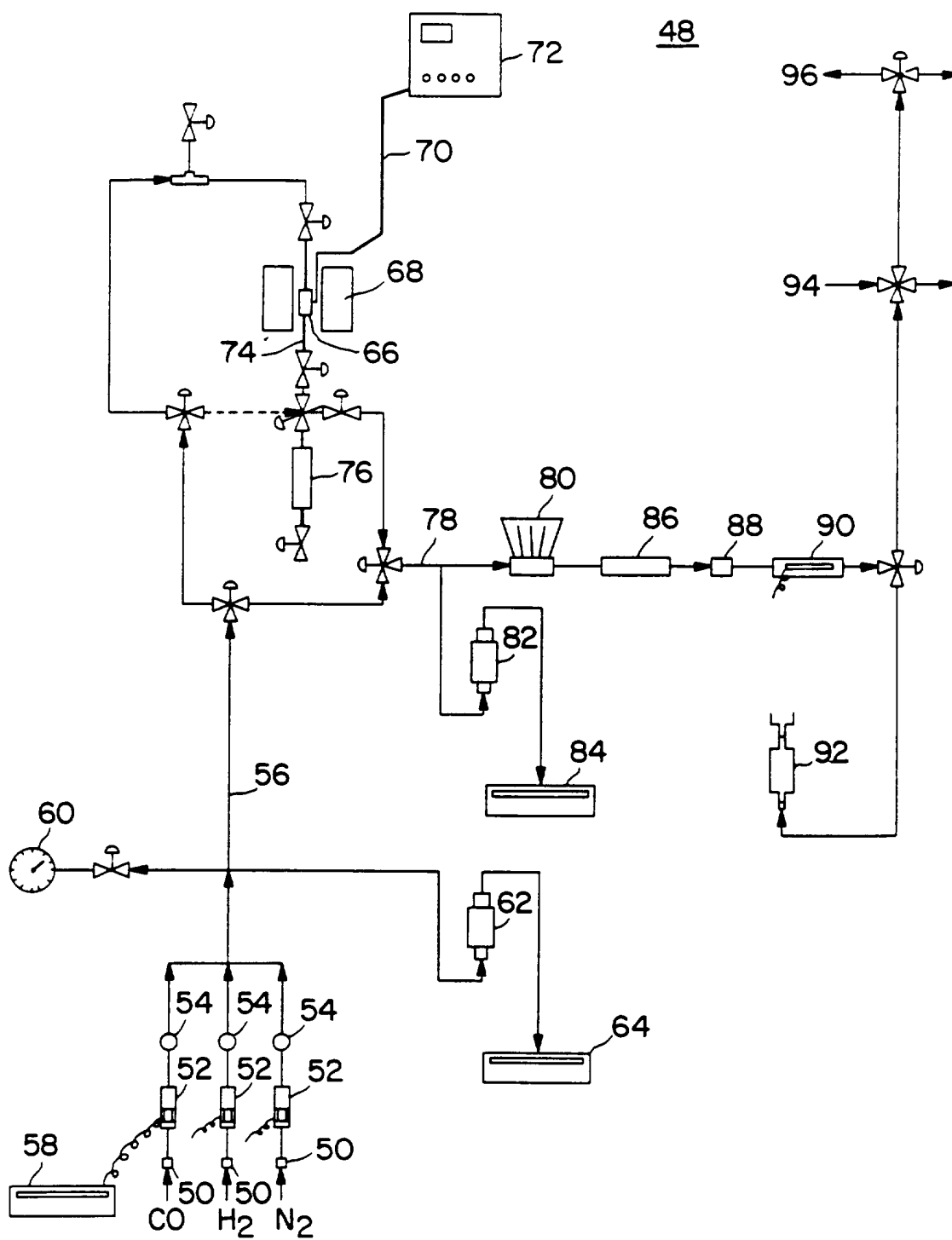


FIG. 2

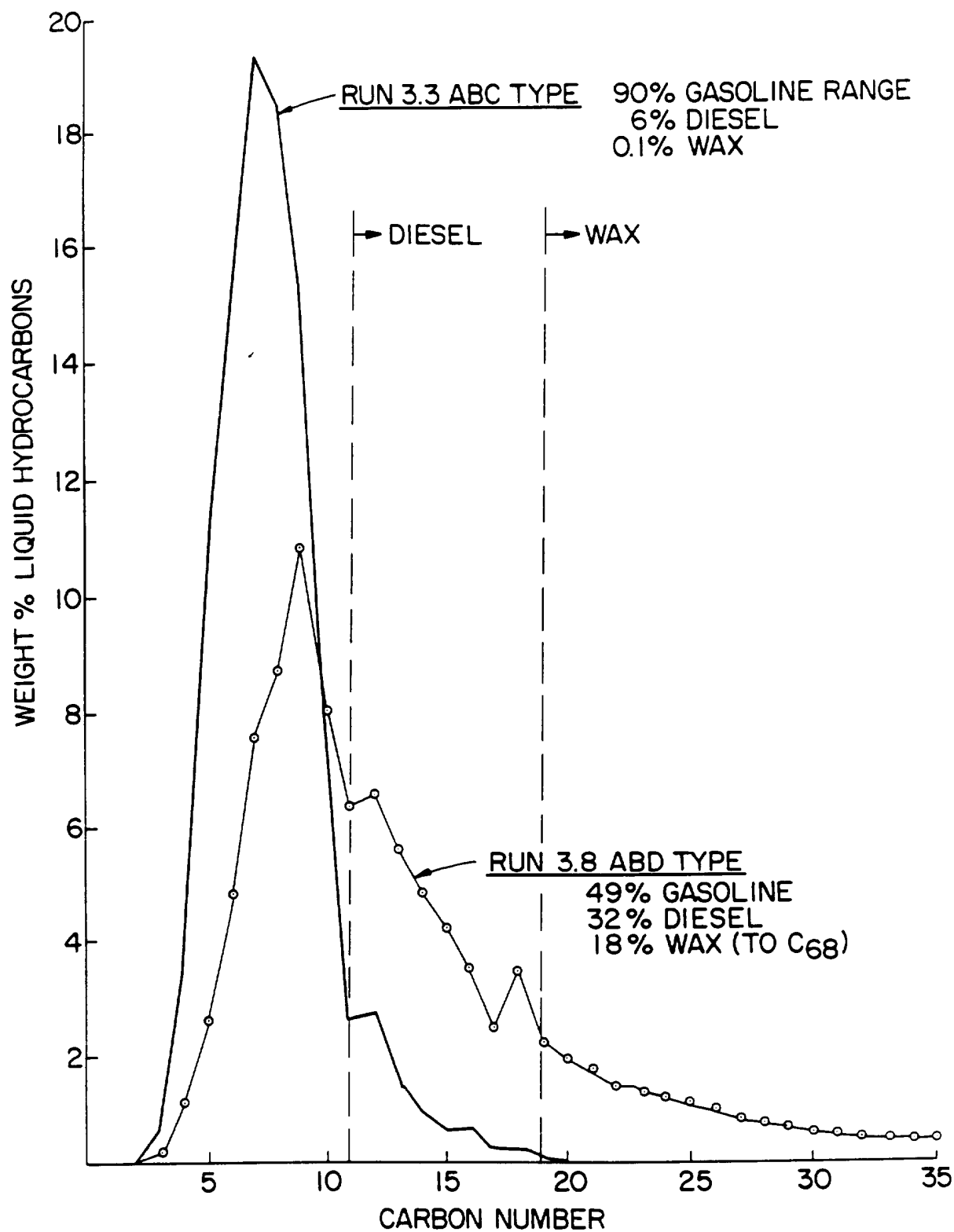


FIG. 3

INTERNATIONAL SEARCH REPORT

Intern al Application No
PCT/CA 94/00477

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C07C1/04

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	FR,A,2 320 923 (AIR PRODUCTS AND CHEMICALS) 11 March 1977 see claims ---	1-14
A	FR,A,2 443 447 (SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ) 4 July 1980 ---	
E	US,A,5 344 849 (AYASSE) 6 September 1994 see claims -----	1-14

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

- *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 when the document is taken alone
- *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

Date of the actual completion of the international search

5 April 1995

Date of mailing of the international search report

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INTERNATIONAL SEARCH REPORT

Intern al Application No
PCT/CA 94/00477

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		GB-A-	1547247	06-06-79

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		GB-A, B	2037316	09-07-80
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US-A-5344849	06-09-94	NONE		