

⑫ **EUROPEAN PATENT APPLICATION**

⑳ Application number: **84102932.5**

⑥① Int. Cl.<sup>3</sup>: **C 07 C 29/15, C 07 C 31/02**  
**// B01J23/16**

㉑ Date of filing: **16.03.84**

③⑩ Priority: **18.03.83 US 476674**

⑦① Applicant: **THE DOW CHEMICAL COMPANY, Dow Center 2030 Abbott Road Post Office Box 1967, Midland Michigan 48640 (US)**

④③ Date of publication of application: **26.09.84**  
**Bulletin 84/39**

⑦② Inventor: **Quarderer, George J., 4309 Moorland Drive, Midland St. Michigan 48640 (US)**  
Inventor: **Cochran, Gene A., 1403 Dilloway Drive, Midland Michigan 48640 (US)**

⑧④ Designated Contracting States: **BE DE FR GB IT NL**

⑦④ Representative: **Casalonga, Axel et al, BUREAU D.A. CASALONGA OFFICE JOSSE & PETIT Baaderstrasse 12-14, D-8000 München 5 (DE)**

⑤④ **Catalytic process for producing mixed alcohols from hydrogen and carbon monoxide.**

⑤⑦ A Fischer-Tropsch reaction to form alcohols from hydrogen and carbon monoxide, using a catalyst containing:

(1) at least one element selected from the group consisting of molybdenum, tungsten, rhenium and mixtures thereof in free or combined form;

(2) a promoter comprising an alkali or alkaline earth element in free or combined form; and optionally

(3) a support;

forms an alcohol fraction boiling in the range of motor gasoline in at least about 20 percent CO<sub>2</sub> free carbon selectivity. The so-formed alcohol fraction is useful as an additive for motor gasoline.

**EP 0 119 609 A1**

①⑫ **EUROPEAN PATENT APPLICATION**

②① Application number: **84102932.5**

⑤① Int. Cl.<sup>3</sup>: **C 07 C 29/15, C 07 C 31/02**  
**// B01J23/16**

②② Date of filing: **16.03.84**

③⑩ Priority: **18.03.83 US 476674**

⑦① Applicant: **THE DOW CHEMICAL COMPANY, Dow Center 2030 Abbott Road Post Office Box 1967, Midland Michigan 48640 (US)**

④③ Date of publication of application: **26.09.84**  
**Bulletin 84/39**

⑦② Inventor: **Quarderer, George J., 4309 Moorland Drive, Midland St. Michigan 48640 (US)**  
Inventor: **Cochran, Gene A., 1403 Dilloway Drive, Midland Michigan 48640 (US)**

⑧④ Designated Contracting States: **BE DE FR GB IT NL**

⑦④ Representative: **Casalonga, Axel et al, BUREAU D.A. CASALONGA OFFICE JOSSE & PETIT Baaderstrasse 12-14, D-8000 München 5 (DE)**

⑤④ **Catalytic process for producing mixed alcohols from hydrogen and carbon monoxide.**

⑤⑦ A Fischer-Tropsch reaction to form alcohols from hydrogen and carbon monoxide, using a catalyst containing:

(1) at least one element selected from the group consisting of molybdenum, tungsten, rhenium and mixtures thereof in free or combined form;

(2) a promoter comprising an alkali or alkaline earth element in free or combined form; and optionally

(3) a support;

forms an alcohol fraction boiling in the range of motor gasoline in at least about 20 percent CO<sub>2</sub> free carbon selectivity. The so-formed alcohol fraction is useful as an additive for motor gasoline.

**EP 0 119 609 A1**

4,151,190 and 4,199,522. The references describe some of the herein used catalysts but do not teach that the catalyst is useful for making commercially significant quantities of alcohols.

5 U.S. Patent 2,490,488 discloses that molybdenum sulfide methanation catalysts acquire Fischer-Tropsch activity when promoted with an alkaline compound of an alkali metal. The example of the invention shows a 30% selectivity to C<sub>3</sub>+ hydrocarbons and oxygenates.  
10 Of this 30%, no more than 44% boils near or above 65°C the boiling point of methanol. Accordingly the maximum possible alcohol selectivity is no more than 13.2% (44% of 30%).

U.S. Patent 2,539,414 describe a Fischer-Tropsch  
15 process with molybdenum carbide catalysts. It teaches that the catalyst may be used to form oxygenates and at column 3, lines 66-71 teaches that one might get alcohols or hydrocarbons by varying the conditions.

G. T. Morgan et al., J. Soc. Chem. Ind.,  
20 Vol. 51, 1932 January 8, pp. 1T-7T, describe a process for making alcohols with chromium/manganese oxide catalysts promoted with alkali.

A number of references teach production of alcohols using rhodium catalysts. Some of these contain  
25 molybdenum as an optional ingredient. U.S. Patent 4,014,913 discloses a catalyst containing rhodium and thorium or uranium and iron or molybdenum or tungsten for the production of ethanol. U.S. Patent 4,096,164 discloses the use of rhodium in combination with molybdenum or tungsten and Example A discloses that use of  
30

a molybdenum-on-silica catalyst yielded 4.4 percent oxygenates.

EPO application 81-33,212 (Chemical Abstracts 96:51,800a) discloses a similar process using rhodium in combination with one or more of a long list of metals which includes molybdenum.

EPO application 79-5,492 (Chemical Abstracts 92:166,257b), Hardman et al., discloses the production of alcohols using a 4-component catalyst. The first component is copper, the second is thorium, the third an alkali metal promoter and the fourth a long list of metals one of which is molybdenum. Chemical Abstracts 96:106,913x, Diffenbach et al., disclose a nitrated iron catalyst which is promoted with molybdenum for making alcohols from synthesis gas.

To make a commercially significant alcohol process, one must use a catalyst and conditions which are highly efficient. To be efficient the catalyst must yield a high ratio of mass of product per mass of catalyst in a given period of time. The catalyst must be stable and active for long periods of time between regenerations. This may be particularly difficult to accomplish when the  $H_2/CO$  ratio of the feed gas is low, such as less than 2 to 1. Ideally the catalyst will have a high selectivity to a commercial product to avoid purification or removal and disposal of by-products and to avoid separation into two or more product streams.

It is an object of this invention to prepare alcohols in a Fischer-Tropsch type reaction from  $H_2/CO$

synthesis gas. It is a preferred object of this invention to make a high yield of alcohols with a catalyst which is selective to alcohols boiling in the range of motor gasoline and that is stable, particularly at low  
5 H<sub>2</sub>/CO ratios, and active over long periods of time.

One or more of these objects of the invention are effected by a process for making alcohols comprising contacting a mixture of hydrogen and carbon monoxide with a catalyst comprising:

- 10 (1) at least one element selected from the group consisting of molybdenum tungsten, rhenium and mixtures thereof in free or combined form;
- (2) a promoter comprising an alkali or alkaline earth element in free or combined form; and  
15 optionally
- (3) a support;

to form an alcohol fraction boiling in the range of motor gasoline in at least 20 percent CO<sub>2</sub> free carbon selectivity.

It is a feature of this invention, that high  
20 yields and selectivity may be obtained without the use of rhodium, copper, ruthenium, cobalt, zinc or iron. An advantage of the invention is that high production rates may be obtained at high selectivities. Under preferred conditions, these catalysts may yield high C<sub>1</sub>-C<sub>4</sub> alcohol  
25 productivity. Up to about 0.3 weight parts C<sub>1</sub>-C<sub>4</sub> alcohol/hr/weight part of catalyst may be achieved. Because of the high selectivity, complex purification steps may be avoided and the alcohol product may have a low acid content and have a high octane blending value.

The hydrogen and carbon monoxide required for this process can be obtained by methods known in the art. Examples are gasification of hydrocarbonaceous materials such as coal, high specific gravity oils, or natural gas; as a by-product of partial combustion cracking of hydrocarbons; by steam reforming of liquid or gaseous hydrocarbons; through the water-gas shift reaction; or some combination of these. The two components may also be generated separately and combined for the subject reaction.

10 The molar ratio of hydrogen to carbon monoxide in the feed gas which contacts the catalyst ranges generally from 0.25 to 100, preferably from 0.5 to 5 and most preferably from 0.7 to 3.

Impurities in the feed gas may or may not have an effect on the reaction, depending on their nature and concentration. Carbon dioxide is preferably present at a partial pressure of less than one atmosphere (0.1 MPa) and at that pressure has little deleterious effect. If reactor effluent gas is recycled to the feed, oxygenates, water, and carbon dioxide are preferably removed.

20 Hydrocarbons are most preferably also removed from the recycle stream prior to reintroduction into the reactor.

Generally, the selectivity to alcohols is dependent on the pressure. In the normal operating ranges, the higher the pressure at a given temperature, the more selective the process will be to alcohols. The minimum contemplated gauge pressure is 500 psig (3.55 MPa). The preferred minimum is 750 psig (5.27 MPa) with 1,000 psig (7.00 MPa) being a more preferred minimum.

30 While 1,500 psig (10.45 MPa) to 4,000 psig (27.7 MPa) is the most desirable range, higher pressures may be used and are limited primarily by cost of the high pressure vessels and compressors needed to carry out

the higher pressure reactions. A typical maximum is 10,000 psig (69.1 MPa) with 5,000 psig (34.6 MPa) a more preferred maximum. A most preferred operating pressure is 3,000 psig (20.8 MPa) for unsupported MoS<sub>2</sub> catalysts.

The selectivity to alcohols is also a function of temperature and is interrelated with the pressure function. The minimum temperature used is governed by productivity considerations and the fact that at temperatures below about 200°C volatile catalytic metal carbonyls may form. Accordingly, the minimum temperature is generally 200°C.

At a constant pressure, as the temperature increases, the selectivity to alcohols decreases. In other words, at lower pressures one is limited to lower maximum temperatures in order to obtain a given selectivity. For example, at 500 psig (5.27 MPa), the maximum temperature to obtain a net selectivity to alcohols of greater than 20 percent is 325°C. At 1,000 psig (7.00 MPa), a net selectivity of 20 percent or more may be achieved at a temperature of 350°C or less. At a pressure of 1,500 psig (10.45 MPa), a net selectivity to alcohols of 20 percent or greater may be obtained at 375°C or less. At higher pressures, one may obtain 20 percent selectivity at up to 400°C. However, the preferred range of operation is from 240°C to 325°C.

The H<sub>2</sub>/CO gas hourly space velocity (GHSV) is a measure of the volume of hydrogen plus carbon monoxide gas at standard temperature and pressure passing a given volume of catalyst in an hour's time. This may range from 100 to 10,000 hour<sup>-1</sup> and preferably from 300 to 5,000 hour<sup>-1</sup>.

Selectivity to the alcohols generally increases as the space velocity increases. However, conversion of carbon monoxide decreases as space velocity increases.

5 Preferably at least a portion of the unconverted hydrogen and carbon monoxide in the effluent gas from the reaction, more preferably after removal of product alcohols, water and carbon dioxide formed and even more preferably any hydrocarbons formed, may be recycled to the reaction. The amount of recycle is expressed as  
10 the recycle ratio which is the ratio of moles of gases in the recycle stream to the moles of gases in the fresh feed stream. A recycle ratio of zero is within the scope of the invention with at least some recycle preferred. A recycle ratio of at least one is more preferred and at  
15 least three is most preferred.

In addition, the synthesis should be carried out at as little feed conversion per pass as is compatible with economic constraints related to the separation of the alcohol product from unreacted feed and  
20 hydrocarbon gases. Accordingly one would increase the space velocity and recycle ratios to preferably obtain about 15-25% conversion per pass.

With preferred catalysts and under preferred conditions of temperatures, pressures,  $H_2/CO$  ratio, GHSV  
25 and recycle ratio, 0.1 or more or weight parts of alcohols per hour may be formed per weight part of catalyst. Under the more preferred conditions of 300°C, 1500 psig (10.3 MPa), 5,000  $hour^{-1}$  and a  $H_2/CO$  ratio of 1.25:1, with a Mo/K on carbon catalyst, 0.3 weight parts  
30 of alcohol or more per hour per weight part of catalyst may be obtained. Under the most preferred conditions of



280°C, 3,000 psig (20.7 MPa), a GHSV of 5,000 and a H<sub>2</sub>/CO ratio of 1.2; with a bulk MoS<sub>2</sub> catalyst 0.6 weight parts of alcohols or more per hour per weight part of catalyst may be obtained.

5 Under the most preferred conditions, alcohols may be obtained in about an 85 percent CO<sub>2</sub> free carbon selectivity. The CO<sub>2</sub> free carbon selectivity is defined as 100 times the moles of carbon present in a product  
10 fraction divided by the total moles of carbon in all products which are not CO<sub>2</sub> or unconverted feed. For example, if one mole of ethanol is found in the alcohol fraction, this is counted as 2 moles of carbon. Carbon dioxide and water are not counted as products in this calculation.

15 The first component of the catalyst preferably consists essentially of at least one member selected from the group consisting of molybdenum tungsten, rhenium and mixtures thereof in free or combined form. Molybdenum and tungsten are preferred and molybdenum is most  
20 preferred.

The molybdenum, tungsten or rhenium may be present in the catalyst in "free or combined form" which means that it may be present as a metal, an alloy or a compound of the element. Representative compounds  
25 include the sulfides, carbides, oxides, halides, nitrides, borides, salicylides, oxyhalides, carboxylates such as acetates, acetyl acetates, oxalates, etc., carbonyls, and the like. Representative compounds also include the elements in anionic form such as molybdates, phos-  
30 phomolybdates, tungstates, phosphotungstates, and the like, and include the alkali, alkaline earth, rare earth and actinide series salts of these anions. The sulfides,

carbonyls, carbides and oxides are preferred with the sulfide being most preferred.

Narrower definitions of the invention may be obtained by not using sulfide-containing components to make the catalyst and by maintaining the feed gas at less than 100 ppm sulfur. Molybdenum catalysts are generally not adversely affected by up to 10 ppm sulfur in the H<sub>2</sub>/CO feed.

The molybdenum, tungsten or rhenium may be present in an amount based on the weight of the total catalyst of at least two percent, preferably at least 5 percent with an upper limit of 70 percent and preferably 30 percent of the total catalyst when the catalyst is supported.

When unsupported molybdenum, tungsten or rhenium is present, it is present in about stoichiometric quantities in relation to other elements with which it may be combined as a compound. Other materials would also have to be considered with respect to fraction of catalyst that is the active metal, such as, agglomerating agents, binders, pelleting lubricants, promoters and possible other catalytic materials.

The second component of the catalyst is the promoter.

The promoter may consist essentially of one or more alkali elements or alkaline earth elements in free or combined form. Alkali elements include lithium, sodium, potassium, rubidium and cesium. Alkaline earth elements include: beryllium, magnesium, calcium, strontium and barium. Alkali elements and in particular,

sodium and potassium, are preferred. Potassium is most preferred.

5 The promoter may be present in free or combined form as a metal, oxide, hydroxide, sulfide or as a salt or a combination of these. The alkaline promoter is preferably present at a level sufficient to render the support or the bulk catalyst neutral or basic. The promoter is generally present, based on the weight of the finished catalyst, in an amount of at least 0.05 weight percent  
10 as a free element in the finished catalyst. Preferably it is present in an amount of at least 0.1 percent and most preferably at least 0.5 percent. Large amounts up to 20 percent of the promoter may be present. Preferably the promoter is present at less than 10 percent.

15 The promoter may be added as an ingredient to the molybdenum, tungsten or rhenium component or to the support or may be part of one of the other components such as sodium or potassium molybdate or as an integral part of the support. For example, carbon supports prepared from coconut shells often contain small amounts  
20 of alkali metal oxides or hydroxides or the support may contain a substantial amount of the promoter such as when the support is magnesia.

25 An optional third component of the catalyst is a support which may assume any physical form such as pellets, granules, beads, extrudates, etc. The supports may be coprecipitated with the active metal species, or the support in powder form may be treated with the active metal species and then used as is or formed into the  
30 aforementioned shapes, or the support may be formed into the aforementioned shapes and then treated with the active catalytic species.

The catalytic species may be dispersed on the support by methods known in the art. Examples include: impregnation from solution, vapor deposition, intimate physical mixing and the like. One or more of these methods may be used. A preferred method of depositing the catalytic species on a support is a combination of an incipient wetness technique and physical mixing with decomposition of a carbonyl.

A first step in the preferred method of placing the catalyst and/or promoters on the support is known as the incipient wetness technique. Water- or solvent-soluble salts of the metals to be dispersed on the support are chosen. The soluble salts which may be a single salt or more than one salt are dissolved in a quantity of solvent which may be aqueous, nonaqueous or a mixed solvent. A sufficient quantity of the resulting solution is added to the support in an amount no more than will be completely absorbed by the support. The solvent is then evaporated to leave the salt dispersed on the support. Depending on the solubility of the salt chosen and on the quantity of the element desired to be dispersed on the support, this process may be performed once or several times. Impregnations with two or more species may be performed by codissolving them in the solvent or by adding them separately in different quantities or types of solvent. In addition to evaporating the solvent, the loaded support may be heated in air, hydrogen, nitrogen or other atmosphere to obtain the catalytic species in their final form. Reduction in hydrogen at mildly elevated pressures at from 250°C to 500°C is preferred. The wetting, evaporating and heating steps may be repeated several times in order to achieve the desired concentration of catalytic species or promoter on the support.

In the second step of the preferred method, a carbonyl of the metal to be dispersed is dry mixed with the resultant metal on a support from the incipient wetness impregnation step. This metal may be the same  
5 or different from the first metal. After intimate mixing, the mixture is calcined in flowing nitrogen to drive off CO and yield the catalyst ready for use.

Exemplary support materials include: the aluminas, basic oxides, the silicas, carbons, or suitable solid compounds of magnesium, calcium, strontium,  
10 barium, scandium, yttrium, lanthanum and the rare earths, titanium, zirconium, hafnium, vanadium, niobium, tantalum, thorium, uranium, and zinc. Oxides are exemplary compounds. Preferably the supports are neutral or basic or  
15 may be rendered neutral or basic by addition of the alkaline promoters. The aluminas include the alpha, gamma, and eta types. The silicas include for example, silica gel, diatomaceous earth, and crystalline silicates.

The carbons, which are preferred, include activated carbons such as those prepared from coals and coal-  
20 like materials, petroleum-derived carbons and animal- and vegetable-derived carbons. Preferably the carbon support will have a surface area of 1-1500 m<sup>2</sup>/g, more preferably 10-1000 m<sup>2</sup>/g and most preferably 100-500 m<sup>2</sup>/g as measured  
25 by the BET nitrogen test. Preferably, micropores (<20 Å (<2 nm)) are minimized and at least twenty percent of the volume of the pores is comprised of pores having a diameter of from about 20 Å (2 nm) to about 600 Å (60 nm).  
30 Examples include coconut shell charcoal, coals, petroleum cokes, carbons formed by pyrolyzing materials such as vinylidene chloride polymer beads, coal, petroleum coke, lignite, bones, wood, lignin, nut shells, petroleum residues, charcoals, etc.

Based upon the weight of the total catalyst, the support when present generally comprises at least 20 percent of the catalyst and generally not more than 98 percent of the catalyst. Preferably the support  
5 comprises at least 50 weight percent and most preferably at least 70 weight percent of the catalyst.

For several reasons the preferred form of the catalyst is the agglomerated sulfide. Certain forms of molybdenum sulfide are most preferred.

10 Molybdenum sulfide catalysts may be made by thermal decomposition of ammonium tetrathiomolybdate or other thiomolybdates as disclosed in U.S. Patent 4,243,553; from purchased active molybdenum sulfides or by calcining  $\text{MoS}_3$ . Preferred is the  
15 decomposition of ammonium tetrathiomolybdate that is formed by precipitation from a solution of ammonium heptamolybdate with ammonium sulfide followed by spray drying and calcining to form the molybdenum sulfide. The molybdenum sulfide may also be precipitated directly  
20 on to a support, but the unsupported molybdenum sulfide is preferred. Tungsten or rhenium sulfides may be similarly made. An unsupported catalyst preferably has a surface area of at least  $10 \text{ m}^2/\text{g}$  and more preferably more than  $20 \text{ m}^2/\text{g}$  as measured by the BET  
25 nitrogen surface area test.

The alkaline (earth) promoter may be added to the active catalytic element prior to, during or after the formation of the sulfide by physical mixing or solution impregnation. The active metal sulfide  
30 may then be combined with binders such as bentonite

clay, and/or pelleting lubricants such as Sterotex® and formed into shapes for use as a catalyst.

5 The finished catalyst may be used in a fixed bed, moving bed, fluid bed, ebullated bed or a graded bed wherein concentration and/or activity of the catalyst varies from inlet to outlet in similar manner to known catalysts. The catalyst may be used in powdered form or may be formed into shapes with or without a binder.

10 The catalysts of the invention may be employed individually or in combination with other inventive catalysts or with other previously proposed catalysts and activators for the claimed process. In general, the presently taught catalysts when used per se, embody numerous advantages including those mentioned above. On the other  
15 hand, in combination with conventional catalysts, they may tend, progressively, to modify the usual effects in accordance with their individual characteristics so that quantitatively intermediate results may be achieved. In short, the catalysts of the present invention may be com-  
20 bined, for example, with typical hydrogenation catalysts such as cobalt and nickel, and with dehydration catalysts such as aluminas and zeolites to effect desired additional results.

25 However, the catalysts of the invention preferably contain less than 25 weight percent, based on the total weight of carbon oxide hydrogenation active metals, of other carbon oxide hydrogenation active metals and more preferably less than 20 weight percent and most preferably less than 2 weight percent or even  
30 are essentially free of other carbon oxide hydrogenating components. By essentially free it is meant that

other carbon oxide hydrogenating components do not significantly alter the character or quantity of the alcohol fraction. For example, a significant change would be a five percent change in the amount of the alcohol fraction or a five percent change in the percentage of any alcohol in the alcohol fraction.

Carbon oxide hydrogenating components present in thus limited quantities or excluded are preferably those that contain chromium, manganese, iron, cobalt, copper, zinc, ruthenium and rhodium. More preferably, in addition to the above-mentioned components, those that contain: halogen, titanium, vanadium, cerium, thorium, uranium, iridium, palladium, platinum, silver and cadmium are excluded. Most preferably, components containing chromium, manganese group IIIB elements, including the lanthanides and actinides, groups IVB, VB, VIII, IB and IIB elements are excluded.

Under preferred conditions the catalyst is stable for long periods of time and under ideal conditions may be stable and active for as many as 3000 hours or more. Activity and selectivity are preferably substantially retained after 100 hours of operation, more preferably after 500 hours and most preferably after 1000 hours operation. In the case of reduced oxide catalysts, declines in activity and selectivity may generally be regenerated by reduction with hydrogen after which the catalyst may regain most of its original activity and be used for another long period of time before regenerating again.

At the conditions described above, the process yields substantial quantities of alcohols. Under



preferred conditions, the weight units per hour of alcohols boiling in the range of motor gasoline per weight unit of catalyst may exceed 0.2. Under ideal conditions, it may exceed 0.25 and even 0.3.

5                   Of the alcohols formed with supported  $\text{MoO}_3$   
catalysts, the largest single component is methanol  
which is typically above 20 weight percent of the  
alcohol fraction and generally above 40 weight percent  
but generally less than 70 weight percent and pre-  
10                   ferably less than 60 weight percent of the alcohols  
formed. The next most abundant component may be  
ethanol which is typically greater than 15 weight  
percent of the alcohol fraction and often approaches  
or exceeds 30 weight percent. The  $\text{C}_5+$  alcohols are  
15                   generally 10 weight percent or less of the alcohol  
fraction.

The alcohol fraction formed at greater than  
a 20 percent  $\text{CO}_2$  free carbon selectivity boils in the  
motor gasoline range. The minimum boiling pure alcohol  
20                   is methanol at  $64.7^\circ\text{C}$ . ASTM D-439 calls for a  $225^\circ\text{C}$  end-  
point for automotive gasoline. Accordingly the alcohol  
fraction formed at greater than a 20 percent  $\text{CO}_2$  free  
carbon selectivity may boil in the range of from about  
 $60^\circ\text{C}$  to about  $225^\circ\text{C}$  when distilled by ASTM D-86. Other  
25                   alcohols may boil outside this range but preferably do  
not. It is not necessary that the entire liquid product  
boil in this range, but it is preferred. It is not  
necessary that the alcohol fraction meet all the dis-  
tillation specifications for motor gasolines - only that  
30                   it boil within the broad range of motor gasolines. For  
example, it need not be within 50 percent evaporated  
limits as set by ASTM D-439. Only 20 carbon mole percent

of the total CO<sub>2</sub> free product must be alcohols that boil in this range. The alcohol fraction formed may be used as a motor fuel blending stock. Preferably, the alcohol fraction formed will have a research octane blending value in motor gasoline of greater than about 100, more preferably greater than about 110 and most preferably greater than about 120.

Preferably, a C<sub>1</sub>-C<sub>8</sub> alcohol fraction is formed in at least about 20 percent CO<sub>2</sub> free carbon selectivity and most preferably a C<sub>1</sub>-C<sub>4</sub> alcohol fraction is formed in at least about 20 percent CO<sub>2</sub> free carbon selectivity.

The C<sub>1</sub>-C<sub>4</sub> alcohol fraction may contain methanol, ethanol, 2-propanol, 1-propanol, 1-butanol, 2-butanol, and 2-methyl-1-propanol, but doesn't generally contain substantial 2-methyl-2-propanol. In addition to these named alcohols the C<sub>1</sub>-C<sub>8</sub> alcohol fraction may contain the C<sub>5</sub>-C<sub>8</sub> alcohols wherein the hydroxyl group may be attached to a carbon which is attached to one or two other carbon atoms.

Under preferred conditions, the amount of water formed is substantially less than the amount of alcohols formed. Typically there is less than 20 weight percent and preferably less than 10 weight percent water based on the quantity of alcohol. This water may be removed by known techniques if the alcohol fraction is to be used as a motor fuel additive.

The product mixture, as formed under preferred conditions, contains only small portions of other oxygenated compounds besides alcohols. These other compounds may not be deleterious to using the product, as is, in motor fuels.

In all cases, the alcohol fraction is formed in at least 20 percent CO<sub>2</sub> free carbon selectivity. Preferably the alcohol fraction is formed in at least 30 percent CO<sub>2</sub> free carbon selectivity, more preferably greater than 50 percent and ideally can be greater than 70 percent.

Preferably the co-products formed with the alcohol fraction are primarily gaseous products. That is C<sub>1</sub>-C<sub>4</sub> hydrocarbons. Preferably C<sub>5</sub>+ hydrocarbons are coproduced at less than 20 percent CO<sub>2</sub> free carbon selectivity, more preferably at less than 10 percent and most preferably at less than 5 percent. Lower amounts of normally liquid hydrocarbons make the normally liquid alcohols easier to separate from by-products.

Generally, alcohol selectivity may be increased by increasing pressure, space velocity, product gas recycle ratio and by decreasing H<sub>2</sub>/CO feed ratio and temperature.

EXAMPLES

20 Catalyst Supports

Examples 1, 2 and 5 incorporate supports of Calgon<sup>®</sup> Type BPL III Granular Carbon. This is made from selected grades of bituminous coal combined with suitable binders. The mean particle size by weight calculated from the sieve analysis is 113 $\mu$ . The bulk density is 0.55 g/cm<sup>3</sup>. The specific surface area evaluated from the three-parameter BET equation using nitrogen adsorption is 1159 m<sup>2</sup>/g. Total pore volume was measured by the nitrogen uptake at saturation. The mean pore diameter, calculated from the equation

$$D = 4 \times \frac{(\text{Total pore volume})}{(\text{specific surface area})} \times 10^4$$

is 28 Å (2.8 nm), assuming that the total pore volume is contained in a cylindrical pore having surface area  $S_{BET}$ .

5 Thirty-three (33) percent of the pores are mesopores as calculated from, percent mesoporosity equals

$$\frac{(\text{cumulative volume of pores in } 20\text{-}600 \text{ Å } (2.0\text{-}60 \text{ nm}) \text{ range})}{(\text{total volume of pores})} \times 100.$$

10 Example 4 incorporates a group of supports including Union Carbide® MBV, MBT, SBV, TS-1564 and TS-1567 carbons, which are now available from Witco Chemical Corporation. The MBV and MBT carbons are coal-based. The SBV carbon is coconut shell-based.

15 The averages of the supports' properties are: particle size - 3/16-inch (4.7 mm) extrudates; bulk density - 0.67 g/cm<sup>3</sup>; specific surface area - 1179 m<sup>2</sup>/g; mean pore diameter - 18 Å (1.8 nm); and 27 percent mesoporosity.

Catalyst Preparation

20 The catalyst for Examples 3, 6, 7 and 8 is SN-5613, purchased as is from American Cyanamid Company. It is described by the seller as having a surface area of 330 m<sup>2</sup>/g, 20 percent molybdenum and 1.5 percent potassium on a wide pore carbon. The catalyst comes as 1/16-

25 -inch (4.7 mm) extrudates having a bulk density of 0.63 g/cm<sup>3</sup>.

For Examples 1, 2 and 5, the following method which yields approximately 75 g of catalyst is used.

Using the incipient wetness technique, 50.0 g of carbon is impregnated with a solution consisting of 27.7 g of  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$  and 2.7 g of  $\text{K}_2\text{CO}_3$  dissolved in a mixture of 10 cm<sup>3</sup> of aqueous 30 percent  $\text{H}_2\text{O}_2$  and 30 cm<sup>3</sup> of water. The wet carbon is air-dried at room temperature and then calcined in a 2 percent  $\text{O}_2$ /98 percent  $\text{N}_2$  atmosphere at 300°C for 2 hours. The catalyst for Examples 1 and 2 is initially reduced in flowing  $\text{H}_2$  at 500°C, 30 psig (0.31 MPa) and 450 hr<sup>-1</sup> for 16 hours. The catalyst for Example 5 is initially reduced in flowing  $\text{H}_2$  at 500°C, 50 psig (0.45 MPa) and 200 hr<sup>-1</sup> for 4 hours. (Note: The preceding recipe is typical for a small batch of catalyst. Multiple catalyst batches are prepared and mixed for Example 5). In Examples 1, 2 and 5, the catalysts contain 21 percent molybdenum and 1.5 percent potassium.

The following method which yields approximately 135 g of catalyst is used for Example 4.

Using the incipient wetness technique, 100 g of carbon is impregnated with a solution consisting of 12.21 g  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$  and 4.68 g of  $\text{K}_2\text{CO}_3$  dissolved in a mixture of 4.55 cm<sup>3</sup> of aqueous 30 percent  $\text{H}_2\text{O}_2$  and 53.03 cm<sup>3</sup> of distilled water. The wet carbon is dried in slowly moving air at 35°C for 6-8 hours then calcined in flowing  $\text{N}_2$  at 350°C for 2-4 hours. The catalyst is loaded with 22.547 g of  $\text{Mo}(\text{CO})_6$  by dry mixing the solids at 80°C in air for 1-2 hours and then is calcined at 350°C in flowing  $\text{N}_2$  for 2-4 hours. The  $\text{Mo}(\text{CO})_6$  loading and calcination are repeated two additional times to give a total of 67.64 g of  $\text{Mo}(\text{CO})_6$  loaded. The catalyst is initially reduced in flowing  $\text{H}_2$  at 500°C, 50 psig (0.45 MPa) and 215 hr<sup>-1</sup> for 4 hours. (Note: The preceding recipe is typical for a small batch of

catalyst. Multiple catalyst batches are prepared and mixed for Example 4. In Example 4, catalysts average 22.5 percent molybdenum and 2.0 percent potassium.

5                   The catalyst for Example 9 is alkalized MoS<sub>2</sub> on carbon.

                  A solution, heated to 50°-60°C, consisting of 11.9 g of (NH<sub>4</sub>)<sub>6</sub> Mo<sub>7</sub>O<sub>24</sub>·4H<sub>2</sub>O, 2.5 g K<sub>2</sub>CO<sub>3</sub>, and 71.1 g of aqueous 22% (NH<sub>4</sub>)<sub>2</sub>S is added dropwise to  
10 20 g 12-20 mesh MBV activated carbon (available from Witco Chemical Company) until the carbon is saturated. This takes about half of the solution. After air-drying at room temperature until the carbon no longer appears wet, the carbon is heated in flowing nitrogen  
15 at a temperature increasing by 2°C per minute until 300°C is reached. The 300°C temperature is held for one hour. The next day the impregnated carbon is air dried at 150°C for fifteen minutes, then re-impregnated with the remainder of the above solution. A small  
20 amount of aqueous 22% (NH<sub>4</sub>)<sub>2</sub>S is added to the solution before reheating it. After air drying the heating step is repeated. The sample shown in Table I is taken after several hundred hours of exposure of this catalyst to the reactants and reaction conditions.

25                   The catalyst of Example 10 is unsupported or bulk alkalized molybdenum disulfide (MoS<sub>2</sub>). It is made by thermally decomposing ammonium tetrathiomolybdate by heating in nitrogen at a temperature increasing by 5°C/minute until 580°C is reached. This temperature  
30 is held for one hour. This mixture is ground together with sufficient potassium hydroxide to give 4 percent

potassium in the final mixture. This catalyst has a surface area of about 27 m<sup>2</sup>/g. The feed in this example includes 20 ppm hydrogen sulfide.

The catalyst of Example 11 is an alkalized  
5 molybdenum disulfide. Molybdenum trisulfide is prepared by treating a solution of 15 g (NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub>·4H<sub>2</sub>O dissolved in 106 cm<sup>3</sup> 22% aqueous (NH<sub>4</sub>)<sub>2</sub>S at 60°C with 100 cm<sup>3</sup> concentrated acetic acid in 300 cm<sup>3</sup> water. The precipitate is dried and calcined at 500°C for one  
10 hour in nitrogen to form molybdenum disulfide. This molybdenum disulfide is combined in a mortar in the following proportions: 66% MoS<sub>2</sub>; 20% bentonite clay; 10% K<sub>2</sub>CO<sub>3</sub>; and 4% Sterotex® lubricant. These ingredients are ground together and some is pelleted. Unpelleted  
15 material is used for the test. The feed for this example contains 50 ppm hydrogen sulfide.

The catalysts used in Examples 12-15 are prepared by obtaining experimental samples of molybdenum disulfide from Climax Molybdenum of Michigan,  
20 Ann Arbor, Michigan. The designations are: 1619-6-2, at 129 m<sup>2</sup>/g; 1619-8-2 at 95 m<sup>2</sup>/g; 1619-12-2 at 82 m<sup>2</sup>/g and 1619-13-2 at 85 m<sup>2</sup>/g for Examples 12-15 respectively. Each of the molybdenum sulfides is combined in a mortar with bentonite clay; potassium carbonate and  
25 Sterotex® pelleting lubricant to give catalysts containing 66% MoS<sub>2</sub>; 20% clay; 10% potassium carbonate and 4% lubricant. After mixing together with a pestle these mixtures are pelleted and used to make alcohols. The feed in Examples 12-15 contains 50 ppm  
30 hydrogen sulfide.

The catalyst for Examples 16-18 is alkalized molybdenum disulfide made by thermally decomposing  $(\text{NH}_4)_2\text{MoS}_4$ . A solution of  $(\text{NH}_4)_2\text{MoS}_4$  is prepared by mixing a solution of 180 g of  $(\text{NH}_4)_4\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$  in 400  $\text{cm}^3$  of water containing 100  $\text{cm}^3$  of concentrated ammonium hydroxide with 1300  $\text{cm}^3$  of 22%  $(\text{NH}_4)_2\text{S}$  solution. After stirring at 50°-60°C for two hours, the  $(\text{NH}_4)_2\text{MoS}_4$  solution is poured into a large shallow dish and evaporates to dryness overnight. The dry, dark-red  $(\text{NH}_4)_2\text{MoS}_4$  is calcined for one hour at 500°C in nitrogen. The resulting black molybdenum disulfide is combined 66%  $\text{MoS}_2$ ; 10% potassium carbonate; 20% bentonite clay and 4% Sterotex® pelleting lubricant. The catalyst is then pelleted to 3.2 mm diameter pellets. The feed in Example 16 contains 24 ppm hydrogen sulfide.

The catalyst for Example 19 is alkalized rhenium sulfide. Ten grams of  $\text{Re}_2\text{O}_7$  is dissolved in 300  $\text{cm}^3$  of water, and then is neutralized with concentrated ammonium hydroxide to pH 9. Twenty five grams of  $\text{Na}_2\text{S}_2\text{O}_3\cdot 5\text{H}_2\text{O}$  is then dissolved in the basic  $\text{Re}_2\text{O}_7$  solution. One hundred cubic centimeters of concentrated sulfuric acid is added to precipitate black  $(\text{Re}_2\text{S}_7)$  which is filtered, dried and calcined for one hour at 500°C in nitrogen to give  $\text{ReS}_2$ . The  $\text{Na}_2\text{S}_2\text{O}_3$  supplies the alkali to the catalyst. For the test, 5.4 g of  $\text{ReS}_2$  is mixed with 3  $\text{cm}^3$  of tabular alumina and loaded into the reactor and reduced in hydrogen containing 3%  $\text{H}_2\text{S}$  at 450°C for 17 hours.

The catalyst for Example 20 is alkalized tungsten disulfide. This is prepared by dissolving 29.5 g  $\text{Na}_2\text{WO}_4$  in 300  $\text{cm}^3$  water and adding 100  $\text{cm}^3$  of 22%  $(\text{NH}_4)_2\text{S}$  to give a green solution of  $(\text{NH}_4)_2\text{WS}_4$ .



Acidification of this solution causes precipitation of dark red  $WS_3$  which is filtered, dried and calcined at  $500^\circ C$  for one hour in nitrogen to yield  $WS_2$ . For the test, 8.5 g of  $WS_2$  and 0.5 g  $K_2CO_3$  are ground  
5 together with mortar and pestle. This is then mixed with  $8\text{ cm}^3$  of tabular alumina loaded into the reactor and reduced in hydrogen containing 3%  $H_2S$  at  $450^\circ C$  for 17 hours.

The catalyst for Example 21 is reduced,  
10 alkalized  $WO_3$  on carbon. Using a stock solution of 13.2 g  $(NH_4)_{10}W_{12}O_{41} \cdot 11H_2O$  in  $250\text{ cm}^3$  of water, 14.5 g of carbon beads made by pyrolyzing polyvinylidene chloride are impregnated four times by soaking for one hour in  $10\text{ cm}^3$  of hot solution. Between impreg-  
15 nations, the wet carbon is air dried at room temperature, then vacuum dried at  $100^\circ C$  overnight. After the four impregnations, the catalyst is heated in nitrogen, at  $0.4^\circ C/\text{minute}$  to  $450^\circ C$ . This temperature is held for six and a half hours. Alkali is added  
20 dropwise to the catalyst as a solution of 0.27 g potassium carbonate dissolved in  $4\text{ cm}^3$  water. This catalyst is air dried at room temperature overnight and then treated in flowing hydrogen at  $500^\circ C$  before being exposed to  $H_2/CO$  feed. The finished catalyst  
25 contains 8.6 wt % tungsten and 2.0 wt % potassium.

Preparation of Alcohols

Examples 1, 2, 9-15 and 19-21:

In the general method used in these Examples, the reactor consists of a  $\frac{1}{2}$ -inch (1.27 cm) stainless  
30 steel tube packed with catalyst. The total volume of catalyst is about 10 cubic centimeters. Premixed hydrogen, carbon monoxide, and nitrogen feed gases

from a cylinder are compressed and regulated at the pressures stated. The feed gas mixture contains hydrogen and carbon monoxide at the ratios stated and about 5 percent by volume of nitrogen serving as an internal standard. Hydrogen sulfide is present in the feed streams as stated in the catalyst discussion. The mixed feed gas passes through a bed of activated carbon at room temperature to remove iron and other carbonyls. The feed gas mixture then passes at the stated hourly space velocities through the fixed bed reactor which is maintained at the stated reaction temperatures by an electric furnace. The reactor products pass through a pressure letdown valve and flow past a gas chromatograph sampling point into a dry ice cooled condenser. Liquid products from the condenser are collected, sampled and analyzed.

Examples 3, 6-8 and 12-15:

In the method used in these Examples, the reactor is a ½-inch (1.27 cm) stainless steel tube packed with catalyst. The total volume of catalyst is about 40 cubic centimeters. Premixed carbon monoxide and nitrogen from a cylinder pass through a molecular sieve bed at ambient temperature to remove iron and other carbonyls. Hydrogen from a cylinder is then mixed with the carbon monoxide and nitrogen and the mixture is compressed to the pressures stated. The feed gas mixture contains hydrogen and carbon monoxide at the ratios stated and about 5 percent by volume of nitrogen serving as an internal standard. The feed to Examples 12-15 contains 50 ppm H<sub>2</sub>S. The feed gas mixture is preheated and then passes at the stated hourly space velocities through the fixed bed reactor which is maintained at the

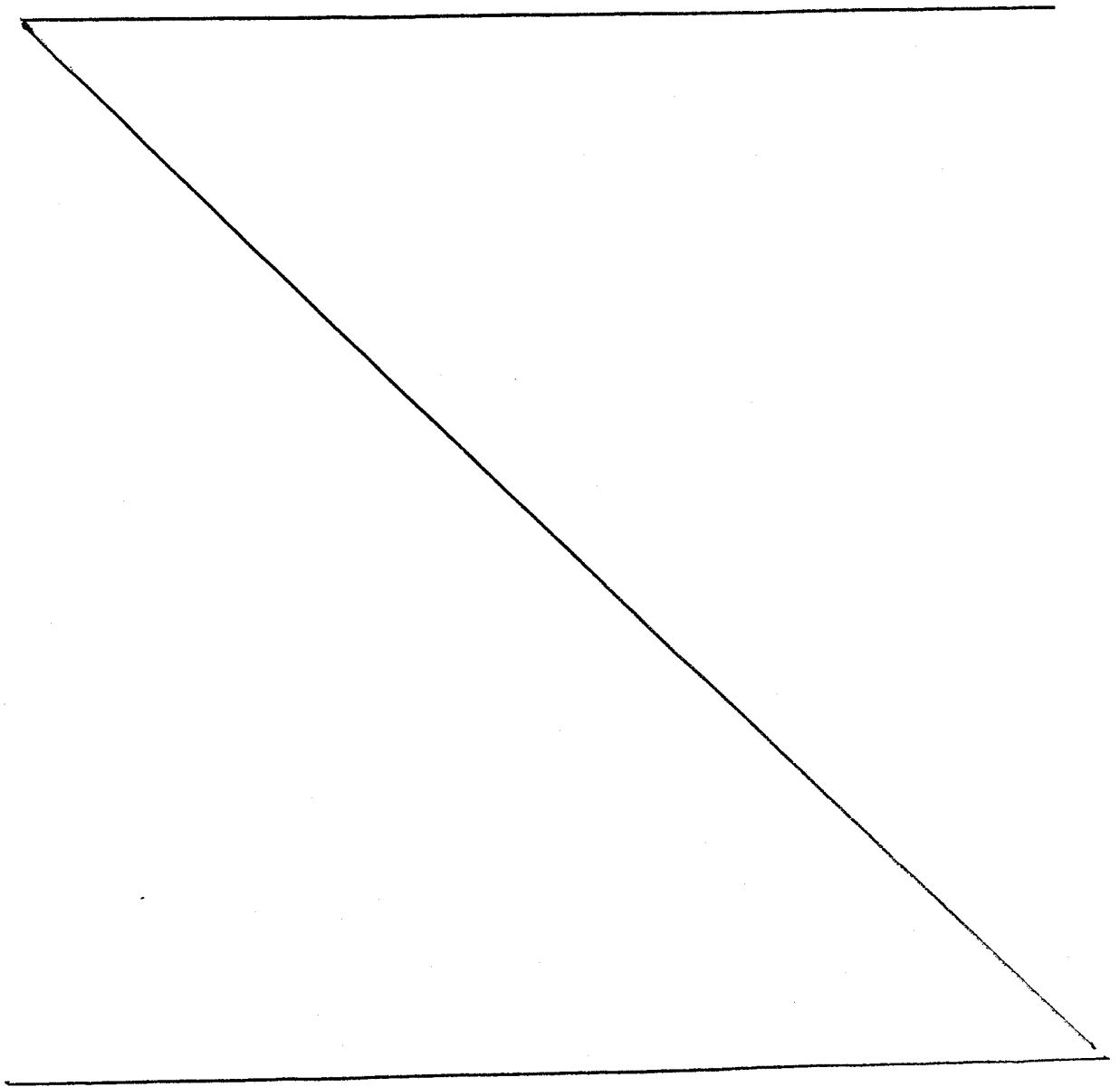
stated reaction temperatures by an electric furnace. The reactor products pass into a vapor/liquid separator at room temperature. The product gases leaving the separator flow past a gas chromatograph sampling point, through a pressure letdown valve into a dry ice cooled condenser. Liquid products are collected, sampled and analyzed.

Example 4:

In Example 4, the reactor consists of a jacketed stainless steel pipe packed with catalyst. The total volume of catalyst is about one cubic foot (0.028 m<sup>3</sup>). The reactor jacket carries a heat-transfer fluid to remove the heat of reaction. The carbon monoxide feed gas passes through a bed of activated carbon at room temperature to remove iron and other carbonyls. The hydrogen and carbon monoxide feed gases are then mixed at the ratio stated. Five percent by volume of nitrogen is added to the feed gas as an internal standard and the mixture is compressed to the pressure stated. The feed gas mixture is preheated to the stated reaction temperature and then passed through the fixed bed reactor at the stated hourly space velocity. The reactor products pass through a water-cooled condenser into a high pressure vapor/liquid separator. The product liquids from the high pressure separator pass through a pressure letdown valve into a low pressure vapor/liquid separator. The product gases leaving the high pressure separator pass through a pressure letdown valve, are combined with the gases from the low pressure separator, and flow past a gas chromatograph sampling point. Liquid products from the low pressure separator are collected in a receiver where they may be sampled and analyzed.

Example 5:

In Example 5, the reactor consists of a jacketed stainless steel pipe with internal tubes and a fluidized bed catalyst. The total volume of catalyst is about 0.65 cubic foot (0.018 m<sup>3</sup>). The reactor jacket and internal tubes carry a heat transfer fluid to remove the heat of reaction. The feed gas and product recovery systems described in Example 4 are used for the fluidized bed reactor. The reactants serve as the fluidizing medium.



TABLE

<u>Example</u>	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>
Temp. (°C)	262	235	300	318
5 Pressure (psig)	1063	1230	1500	1500
(MPa)	(7.43)	(8.58)	(10.45)	(10.45)
H <sub>2</sub> /CO (molar ratio)	0.84	0.82	1.21	1.50
GHSV (hr <sup>-1</sup> )	372	220	1950	1121
Recycle ratio	0	0	0	0
CO Conversion (%)	23.4	31.8	20.2	41.4
10 Wt. Units CO converted per wt. units of catalyst per hr	0.097	0.079	0.324	0.324
CO <sub>2</sub> produced <sup>1</sup> (%)	40.2	36.9	36.9	38.5
15 Selectivities <sup>2</sup> (%)				
Gas Phase				
CH <sub>4</sub>	26.0	19.2	17.5	29.8
C <sub>2-4</sub> hydrocarbons	<u>17.2</u>	<u>13.4</u>	<u>15.1</u>	<u>18.5</u>
Subtotal	43.2	32.6	32.6	48.3
20 Liquid Phase				
Methanol	25.0	22.9	25.6	28.3
Ethanol	12.4	14.1	17.3	12.5
Propanols	6.8	8.9	10.1	5.4
Butanols	2.0	2.9	2.7	1.1
Pentanols	0.3	1.6	0.6	-
25 Subtotal	<u>46.5</u>	<u>50.4</u>	<u>56.3</u>	<u>47.3</u>
Other oxygenates <sup>3</sup> and hydrocarbons	10.3	17.0	11.1	4.4
H <sub>2</sub> O <sup>4</sup> (wt. %)	2.9	1.9	3.8	5.8

30 <sup>1</sup>100 x moles of CO<sub>2</sub> formed for each mole of CO converted in the reactor.

<sup>2</sup>Selectivities, except for CO<sub>2</sub>, are based on carbon mole selectivity on a CO<sub>2</sub> free basis.

<sup>3</sup>Assumed a carbon number of 4 for other oxygenates.

35 <sup>4</sup>Water is calculated as weight percent of the liquid phase.

TABLE (cont'd)

Example	5	6	7	8
Temp. (°C)	297	301	300	300
Pressure (psig)	1010	2000	2500	2500
5 (MPa)	(7.07)	(13.89)	(17.34)	(17.34)
H <sub>2</sub> /CO (molar ratio)	0.82	1.21	1.21	1.21
GHSV (hr <sup>-1</sup> )	1747	1950	1950	1500
Recycle ratio	0	0	0	0
CO Conversion (%)	26.8	25.5	31.0	27.8
10 Wt. unit CO converted per wt. unit of cata- lyst per hr	0.523	0.410	0.498	0.343
CO <sub>2</sub> produced <sup>1</sup> (%)	45.0	37.6	37.3	37.3
15 Selectivities <sup>2</sup> (%)				
Gas Phase				
CH <sub>4</sub>	36.6	16.8	15.8	15.9
C <sub>2+</sub> hydrocarbons	34.0	14.2	13.5	14.6
Subtotal	70.6	31.0	29.3	30.5
20 Liquid Phase				
Methanol	12.2	23.4	26.0	21.3
Ethanol	8.3	15.5	17.4	16.2
Propanols	3.6	8.3	8.9	9.1
Butanols	-	3.0	3.1	3.4
Pentanols	-	0.6	1.1	1.3
25 Subtotal	24.1	50.8	56.5	51.3
Other oxygenates <sup>3</sup> and hydrocarbons	5.3	18.2	14.2	18.2
H <sub>2</sub> O <sup>4</sup> (wt. %)	5.9	3.4	3.7	3.6

30 <sup>1</sup>100 x moles of CO<sub>2</sub> formed for each mole of CO converted in the reactor.

<sup>2</sup>Selectivities, except for CO<sub>2</sub>, are based on carbon mole selectivity on a CO<sub>2</sub> free basis.

<sup>3</sup>Assumed a carbon number of 4 for other oxygenates.

35 <sup>4</sup>Water is calculated as weight percent of the liquid phase.

TABLE (cont'd)

<u>Example</u>	<u>9</u>	<u>10</u>	<u>11</u>
Temp. (°C)	260	262	255
5 Pressure (psig) (MPa)	1200 (8.38)	1175 (8.21)	1500 (10.45)
H <sub>2</sub> /CO (molar ratio)	1.02	0.76	1.02
GHSV (hr <sup>-1</sup> )	1283	676	3171
Recycle ratio	0	0	0
CO Conversion (%)	14.7	16.5	16.3
10 Wt. units CO converted per wt units of cata- lyst per hr	0.177	0.121	0.26
CO <sub>2</sub> produced <sup>1</sup> (%)	22.1	28.0	24.5
15 Selectivities <sup>2</sup> (%)			
Gas Phase			
CH <sub>4</sub>	10.9	10.6	12.6
C <sub>2</sub> + hydrocarbons	3.5	2.7	2.2
Subtotal	14.4	13.3	14.8
20 Liquid Phase			
Methanol	56.3	42.5	33.8
Ethanol	22.8	32.7	24.9
Propanols	5.3	7.5	5.6
Butanols	1.1	1.4	1.6
Pentanols	0.03	0.1	0.1
25 Subtotal	85.53	84.2	65.8
Other oxygenates <sup>3</sup> and hydrocarbons	0.07	2.5	19.4
H <sub>2</sub> O <sup>4</sup> (wt. %)	1.2	0.8	1.9

30 <sup>1</sup>100 x moles of CO<sub>2</sub> formed for each mole of CO converted in the reactor.

<sup>2</sup>Selectivities, except for CO<sub>2</sub>, are based on carbon mole selectivity on a CO<sub>2</sub> free basis.

<sup>3</sup>Assumed a carbon number of 4 for other oxygenates.

35 <sup>4</sup>Water is calculated as weight percent of the liquid phase.

TABLE (cont'd)

Example	12	13	14	15
Temp. (°C)	255	258	250	250
Pressure (psig)	1350	1350	1350	1350
5 (MPa)	(9.41)	(9.41)	(9.41)	(9.41)
H <sub>2</sub> /CO (molar ratio)	1.0	1.0	1.0	1.0
GHSV (hr <sup>-1</sup> )	2254	3140	2300	1934
Recycle ratio	0	0	0	0
CO Conversion (%)	13.3	14.6	15.5	14.0
10 Wt. units CO converted per wt. units of cata- lyst per hr	0.15	0.24	0.18	0.14
CO <sub>2</sub> produced <sup>1</sup> (%)	25.6	26.2	26.0	27.8
Selectivities <sup>2</sup> (%)				
15 Gas Phase				
CH <sub>4</sub>	10.8	15.2	14.1	15.0
C <sub>2-4</sub> hydrocarbons	1.6	2.5	2.8	3.3
Subtotal	12.4	17.7	16.9	18.3
Liquid Phase				
20 Methanol	35.2	33.0	30.5	30.6
Ethanol	26.6	25.7	24.6	27.0
Propanols	7.0	5.8	5.8	5.8
Butanols	2.0	1.9	2.0	1.6
Pentanols	0.3	0.5	0.5	0.3
25 Subtotal	71.1	66.9	63.4	65.3
Other oxygenates <sup>3</sup> and hydrocarbons	16.5	15.4	19.7	16.4
H <sub>2</sub> O <sup>4</sup> (wt. %)	1.4	1.5	1.6	1.7

30 <sup>1</sup>100 x moles of CO<sub>2</sub> formed for each mole of CO converted in the reactor.

<sup>2</sup>Selectivities, except for CO<sub>2</sub>, are based on carbon mole selectivity on a CO<sub>2</sub> free basis.

<sup>3</sup>Assumed a carbon number of 4 for other oxygenates.

35 <sup>4</sup>Water is calculated as weight percent of the liquid phase.



TABLE (cont'd)

<u>Example</u>	<u>16</u>	<u>17</u>	<u>18</u>
Temp. (°C)	260	265	284
5 Pressure (psig)	2000	3050	3050
(MPa)	(13.89)	(21.13)	(21.13)
H <sub>2</sub> /CO (molar ratio)	1.1	1.2	1.2
GHSV (hr <sup>-1</sup> )	3150	3900	5220
Recycle ratio	0	0	0
CO Conversion (%)	10.2	14.5	26.1
10 Wt. Units CO converted per wt. units of cata- lyst per hr	0.158	0.271	0.659
CO <sub>2</sub> produced <sup>1</sup> (%)	27.0	24.7	28.3
15 Selectivities <sup>2</sup> (%)			
Gas Phase			
CH <sub>4</sub>	14.4	11.2	17.8
C <sub>2-4</sub> hydrocarbons	0.0	0.5	2.6
Subtotal	14.4	11.7	20.4
Liquid Phase			
20 Methanol	49.0	48.1	43.3
Ethanol	25.2	25.8	23.2
Propanols	6.9	7.8	7.1
Butanols	1.6	2.7	2.4
Pentanols	-	-	-
25 Subtotal	82.7	84.4	76.0
Other oxygenates <sup>3</sup> and hydrocarbons	2.9	3.9	3.6
H <sub>2</sub> O <sup>4</sup> (wt. %)	0.78	1.55	1.55

30 <sup>1</sup>100 x moles of CO<sub>2</sub> formed for each mole of CO converted in the reactor.

<sup>2</sup>Selectivities, except for CO<sub>2</sub>, are based on carbon mole selectivity on a CO<sub>2</sub> free basis.

<sup>3</sup>Assumed a carbon number of 4 for other oxygenates.

35 <sup>4</sup>Water is calculated as weight percent of the liquid phase.

TABLE (cont'd)

Example	19	20	21
Temp. (°C)	284	300	309
Pressure (psig)	1350	1450	1440
5 (MPa)	(9.41)	(10.10)	(10.03)
H <sub>2</sub> /CO (molar ratio)	0.9	1.0	1.12
GHSV (hr <sup>-1</sup> )	-	-	242
Recycle ratio	0	0	0
CO Conversion (%)	6.8	10.0	7.8
10 Wt. Units CO converted per wt. units of catalyst per hr	.09	-	0.017
CO <sub>2</sub> produced <sup>1</sup> (%)	36.8	-	32.5
Selectivities <sup>2</sup> (%)			
15 Gas Phase			
CH <sub>4</sub>	48.8	-	19.5
C <sub>2-4</sub> hydrocarbons	5.7	-	2.3
Subtotal	54.5	70	21.8
20 Liquid Phase			
Methanol	33.1	} 30 <sup>5</sup> }	} 78.2 <sup>5</sup>
Ethanol	10.3		
Propanols	1.2		
Butanols	0.2		
Pentanols	0		
25 Subtotal	44.8		
Other oxygenates <sup>3</sup> and hydrocarbons	0.7		
H <sub>2</sub> O <sup>4</sup> (wt. %)	10.0	-	-

30 <sup>1</sup>100 x moles of CO<sub>2</sub> formed for each mole of CO converted in the reactor.

<sup>2</sup>Selectivities, except for CO<sub>2</sub>, are based on carbon mole selectivity on a CO<sub>2</sub> free basis.

<sup>3</sup>Assumed a carbon number of 4 for other oxygenates.

35 <sup>4</sup>Water is calculated as weight percent of the liquid phase.

<sup>5</sup>The liquid samples are not analyzed for alcohols but based on experience are expected to contain substantial alcohols.

It must be noted that in the description the following abbreviations have the following meanings :

C1-C4 Alcohol means alcohols containing 1,2,3 or 4 C atoms,  
C1-C8 alcohol fraction means alcohol fractions containing 1,2,3,4,5,6,7 or 8 C atoms ,  
C5-C8 alcohols means alcohols containing 5,6,7 or 8 C atoms.

WE CLAIM:

1. A process for producing alcohols comprising contacting hydrogen and carbon monoxide in the presence of a catalyst comprising:

- (1) at least one element selected from the group consisting of molybdenum, tungsten, and rhenium, in free or combined form;
- (2) a promoter comprising an alkali or alkaline earth element, in free or combined form; and optionally
- (3) a support;

to form an alcohol fraction boiling in the range of motor gasoline in at least about 20 percent CO<sub>2</sub> free carbon selectivity.

2. The process of Claim 1 wherein the mole ratio of hydrogen to carbon monoxide is from about 0.7 to about 3.

3. The process of Claim 2 conducted at a pressure of from about 1,500 psig (10.3 MPa) to about 4,000 psig (27.6 MPa).

4. The process of Claim 3 conducted at a temperature of from about 240°C to about 325°C.

5. The process of Claim 2 wherein the H<sub>2</sub>/CO gas hourly space velocity is from about 300 to about 5,000 hr<sup>-1</sup>.

6. The process of Claim 5 wherein at least a portion of unconverted hydrogen and/or carbon monoxide feed is recycled to the reaction.

7. The process of Claim 6 wherein the alcohol fraction and any hydrocarbons formed are substantially removed from the recycled feed prior to recycling.

8. The process of Claim 7 wherein carbon dioxide is substantially removed from the recycled feed prior to recycling.

9. The process of Claim 1 wherein the alcohol fraction contains from about 20 to about 70 weight percent of methanol.

10. The process of Claim 1 wherein the alcohol fraction contains at least about 15 weight percent ethanol.

11. The process of Claim 10 wherein the alcohol fraction contains less than about five weight percent C<sub>5</sub>+ alcohols.

12. The process of Claim 1 wherein the distillation endpoint of the alcohol fraction is equal to or less than 225°C.

13. The process of Claim 1 to form an alcohol fraction containing C<sub>1</sub>-C<sub>8</sub> alcohols in at least 20 percent CO<sub>2</sub> free carbon selectivity.

14. The process of Claim 1 to form an alcohol fraction containing C<sub>1</sub>-C<sub>4</sub> alcohols in at least about 20 percent CO<sub>2</sub> free carbon selectivity.

15. The process of Claim 1 wherein the alcohol fraction is produced at a rate of about 0.1 weight parts or more of alcohol fraction per weight part of catalyst per hour.

16. The process of Claim 1 wherein the support is present and is neutral or basic or is rendered neutral or basic by the addition of alkaline promoter.

17. The process of Claim 1 wherein the promoter consists essentially of sodium or potassium in free or combined form.

18. The process of Claim 1 wherein the promoter is present at a level of at least about 0.5 percent by weight as free element in the total catalyst.

19. The process of Claim 1 wherein the catalyst contains molybdenum.

20. The process of Claim 19 wherein the molybdenum is present as a carbonyl, sulfide, carbide or oxide of the element, as the free element or as a mixture of these.

21. The process of Claim 20 wherein the molybdenum is present as a sulfide.

22. The process of Claim 19 wherein the molybdenum is present at a level of at least about 5 percent by weight of the total catalyst.

23. The process of Claim 19 wherein the catalyst contains less than 25 weight percent of carbon monoxide hydrogenation active metals other than the molybdenum.

24. The process of Claim 19 wherein the catalyst is essentially free of iron, cobalt, copper, zinc, ruthenium or rhodium.

25. The process of Claim 24 wherein the catalyst is essentially free of halogen, titanium, vanadium, cerium, thorium, uranium, iridium, palladium, platinum, silver or cadmium.



DOCUMENTS CONSIDERED TO BE RELEVANT			EP 84102932.5
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 3)
A	US - A - 4 362 821 (JIANG-JEN LIN) * Claims 1-4,16,17 * --	1-4	C 07 C 29/15 C 07 C 31/02// B 01 J 23/16
D,A	US - A - 4 243 553 (ALFRED W. NAU- MANN et al.) * Claim 1 * --	1	
X	US - A - 4 219 445 (JACK N. FINCH) * Claims 1-4,7 * --	1,23- 25	
X	US - A - 4 210 597 (YUN-YANG HUANG) * Columns 4-6 * --	1-5,9- 18	
D,X	US - A - 4 199 522 (CRAIG B. MUR- CHISON et al.) * Claims; column 5, lines 2-10 * --	1,2,4, 5,16- 25	TECHNICAL FIELDS SEARCHED (Int. Cl. 3)  C 07 C 1/00 C 07 C 27/00 C 07 C 29/00 C 07 C 31/00 B 01 J 23/00 B 01 J 27/00 B 01 J 31/00
D,X	US - A - 4 151 190 (CRAIG B. MUR- CHISON et al.) * Abstract; claims; example 3 * --	1,2,5, 16-25	
D,X	US - A - 4 096 164 (PAUL CLIFFORD ELLGEN et al.) * Claims; examples A,B,M-AB * --	1-5,19, 20,22- 25	
D,A	US - A - 2 539 414 (WALTER G. FRANKENBURG) * Claim; column 3, lines 66-71 * --	1,19, 20,22- 25	
The present search report has been drawn up for all claims			
Place of search VIENNA		Date of completion of the search 21-05-1984	Examiner REIF
<p><b>CATEGORY OF CITED DOCUMENTS</b></p> <p>X : particularly relevant if taken alone  Y : particularly relevant if combined with another document of the same category  A : technological background  O : non-written disclosure  P : intermediate document</p> <p>T : theory or principle underlying the invention  E : earlier patent document, but published on, or after the filing date  D : document cited in the application  L : document cited for other reasons</p> <p>&amp; : member of the same patent family, corresponding document</p>			



DOCUMENTS CONSIDERED TO BE RELEVANT			CLASSIFICATION OF THE APPLICATION (Int. Cl. <sup>3</sup> )
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	
D,X	<p><u>US - A - 2 490 488</u> (S. GRANT STEWART)</p> <p>* Claims; column 2, lines 20-52 *</p> <p>--</p>	1-4, 16-25	
X	<p><u>EP - A1 - 0 030 110</u> (THE BRITISH PETROLEUM COMPANY LIMITED)</p> <p>* Claims; page 3, line 10 - page 6, line 14; table *</p> <p>--</p>	1-7,9-11,16-20	
A	<p><u>DE - A - 2 004 490</u> (THE BRITISH PETROLEUM COMPANY LTD.)</p> <p>* Claim 1 *</p> <p>--</p>	1	TECHNICAL FIELDS SEARCHED (Int. Cl. <sup>3</sup> )
D,X	<p><u>EP - B1 - 0 005 492</u> (THE STANDARD OIL COMPANY)</p> <p>* Claims 1,5,11; column 2, lines 45-51; column 3, lines 9-45; column 5, lines 47-55 *</p> <p>--</p>	1-4,9-11,16-18	
D,A	<p>INDUSTRIAL AND ENGINEERING CHEMISTRY, vol. 44, no. 10, October 1952</p> <p>R.B. ANDERSON et al. "Synthesis of Alcohols by Hydrogenation of Carbon Monoxide" pages 2418-2424</p> <p>* Page 2419, table I; page 2420, tables III, V *</p> <p>----</p>	1	