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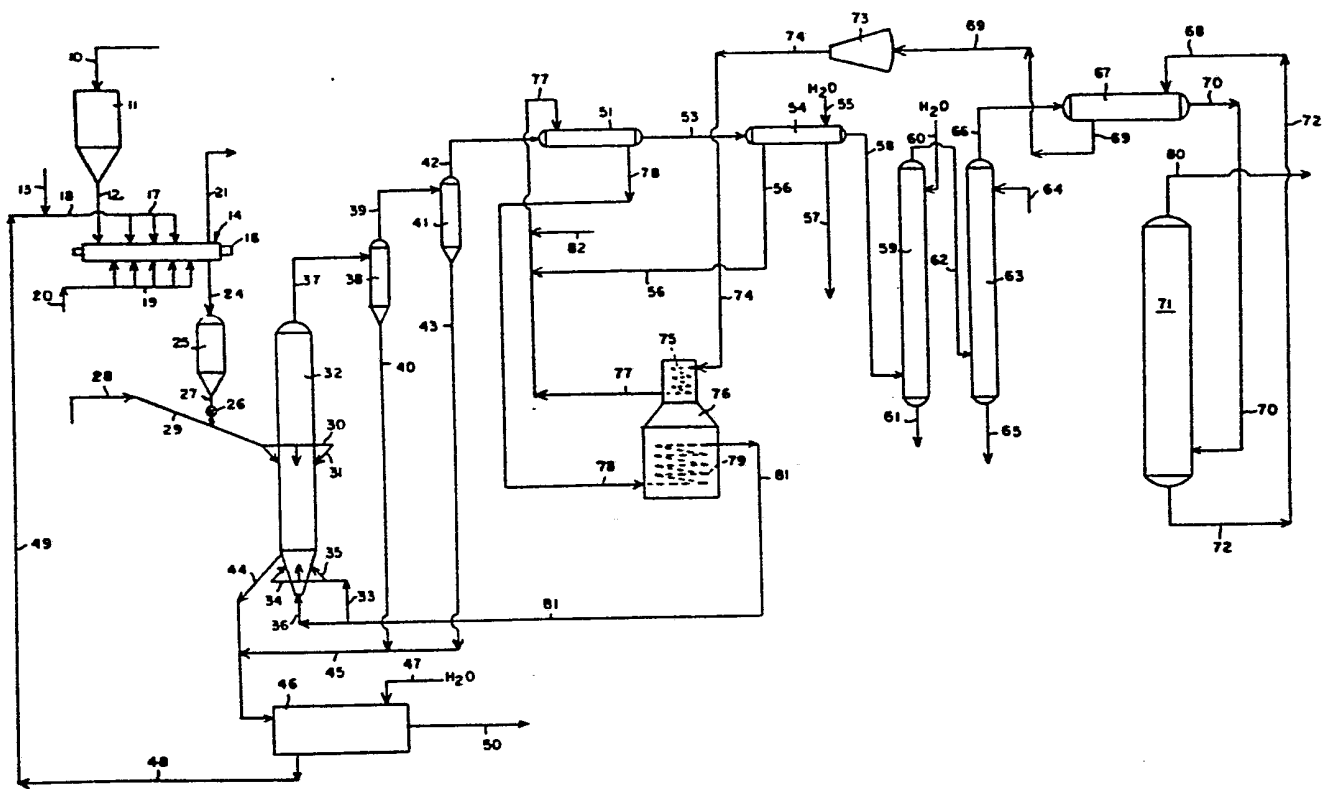
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(54) **Production of a chemical synthesis product gas from a carbonaceous feed material and steam.**

(57) A high purity chemical synthesis gas is produced by reacting steam in a gasifier (32) with a carbonaceous feed material in the presence of a carbon-alkali metal catalyst and substantially equilibrium quantities of added hydrogen and carbon monoxide, fed in via nozzles (35), at reaction conditions to produce a raw product gas. The raw product gas is treated in vessels (38), (41) to remove solid particles, and in vessels (51, 54, 59 and 63) for the removal of steam and acid gases. The thus purified gas contains, primarily, carbon monoxide, hydrogen and methane. Methane is removed in a heat transfer unit (67) and a cryogenic unit (71), thereby recovering carbon monoxide and hydrogen from the treated gas as a chemical synthesis product gas. The remaining mixture of steam and methane is passed with further steam into a steam reforming furnace (76) where the methane reacts with the steam to produce carbon monoxide and hydrogen. The effluent from the reforming furnace (76) is passed into the gasifier (32).

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1 BACKGROUND OF THE INVENTION

2 1. Field of the Invention: This invention
3 relates to the gasification of coal and similar carbonaceous
4 materials and is particularly concerned with a catalytic
5 gasification process carried out in the presence of a
6 carbon-alkali metal catalyst to produce a chemical synthesis
7 gas.

8 2. Description of the Prior Art: Existing and
9 proposed processes for the manufacture of synthetic gaseous
10 fuels from coal or similar carbonaceous materials normally
11 require the reaction of carbon with steam, alone or in
12 combination with oxygen, at temperatures between about
13 1200°F. and about 2500°F. to produce a gas which may contain
14 some methane but consists primarily of hydrogen and carbon
15 monoxide. This gas can be used directly as a synthesis gas
16 or a fuel gas with little added processing or can be
17 reacted with additional steam to increase the hydrogen-to-
18 carbon monoxide ratio and then fed to a catalytic
19 methanation unit for reaction with carbon monoxide and
20 hydrogen to produce methane. It has been shown that
21 processes of this type can be improved by carrying out the
22 initial gasification step in the presence of a catalyst
23 containing an alkali metal constituent. The alkali metal
24 constituent accelerates the steam-carbon gasification
25 reaction and thus permits the generation of synthesis gas
26 at somewhat lower temperatures than would otherwise be
27 required. Processes of this type are costly because of the
28 large quantities of heat that must be supplied to sustain

1 the highly endothermic steam-carbon reaction. One method
2 of supplying this heat is to inject oxygen directly into
3 the gasifier and burn a portion of the carbon in the feed
4 material being gasified. This method is highly expensive
5 in that it requires the existence of a plant to manufacture
6 the oxygen. Other methods for supplying the heat have been
7 suggested, but these, like that of injecting oxygen, are
8 expensive.

9 It has been recently found that difficulties
10 associated with processes of the type described above, can
11 largely be avoided by carrying out the reaction of steam
12 with carbon in the presence of a carbon-alkali metal
13 catalyst and substantially equilibrium quantities of added
14 hydrogen and carbon monoxide. Laboratory work and pilot
15 plant tests have shown that catalysts produced by the
16 reaction of carbon and alkali metal compounds such as
17 potassium carbonate to form carbon-alkali metal compounds or
18 complexes will, under the proper reaction conditions,
19 equilibrate the gas phase reactions occurring during gasifi-
20 cation to produce methane and at the same time supply
21 substantial amounts of exothermic heat within the gasifier.
22 This additional exothermic heat of reaction essentially
23 balances the overall endothermicity of the reactions
24 involving solid carbon and thus results in a substantially
25 thermoneutral process in which the injection of large
26 amounts of oxygen or the use of other expensive methods of
27 supplying heat are eliminated.

28 The catalytic effect of carbon-alkali metal cata-
29 lysts on the gas phase reactions, as distinguished from the
30 solid-gas reactions or the reactions of carbon with steam,
31 hydrogen or carbon dioxide, allows the following exothermic
32 reactions to contribute substantially to the presence of
33 methane in the effluent gas and drastically reduces the
34 endothermicity of the overall reaction:



4 Under the proper operating conditions, these reactions can
5 be made to take place within the gasification zone and
6 supply large amounts of methane and additional exothermic
7 heat which would otherwise have to be supplied by the
8 injection of oxygen or other means. Laboratory and pilot
9 plant tests have shown that constituents of the raw product
10 gas thus produced are present in equilibrium concentrations
11 at reaction conditions and consist primarily of hydrogen,
12 carbon monoxide, carbon dioxide, methane and steam. It has
13 been proposed (see U.S. Patent No. 4,094,650) to utilize
14 steam gasification in the presence of a carbon-alkali metal
15 catalyst to produce a high Btu product gas by treating the
16 raw produce gas for removal of steam and acid gases,
17 principally carbon dioxide and hydrogen sulfide; cryogeni-
18 cally separating carbon monoxide and hydrogen in amounts
19 equivalent to their equilibrium concentration in the raw
20 product gas from the methane in the treated gas; withdrawing
21 methane as a high Btu product gas; and recycling the carbon
22 monoxide and hydrogen to the gasifier. The presence in
23 the gasifier of the carbon-alkali metal catalyst and
24 equilibrium quantities of recycle carbon monoxide and
25 hydrogen, which tend to suppress reactions that would other-
26 wise produce additional hydrogen and carbon monoxide,
27 results in a substantially thermoneutral reaction to
28 produce essentially methane and carbon dioxide. Since the
29 overall reaction is substantially thermoneutral, only a
30 small heat input is required to preheat the carbonaceous
31 feed material and to maintain the reactants at reaction
32 temperatures by compensating for heat losses from the
33 gasifier. This small amount of heat may be supplied by
34 preheating the gaseous reactants in a conventional preheat
35 furnace.

1 It has also been proposed (see U.S. Patent No.
2 4,118,204) to utilize steam gasification of a carbonaceous
3 feed material in the presence of a carbon-alkali metal
4 catalyst to produce an intermediate Btu product gas by
5 treating the raw product gas withdrawn from the gasifier
6 for the removal of steam and acid gases, principally carbon
7 dioxide and hydrogen sulfide; recovering a portion of the
8 treated gas as the intermediate Btu product gas; contacting
9 the remainder of the treated gas with steam in a steam
10 reformer under conditions such that the methane in the
11 treated gas reacts with the steam to produce additional
12 hydrogen and carbon monoxide; and passing the effluent from
13 the reformer into the gasifier. The amounts of hydrogen
14 and carbon monoxide produced in the reformer compensate
15 for the amounts of those gases removed in the treated gas
16 that is withdrawn as intermediate Btu product gas. Thus
17 the reformer effluent will normally contain carbon monoxide
18 and hydrogen in amounts equivalent to the equilibrium
19 quantities of those gases present in the raw product gas
20 and will therefore supply the substantially equilibrium
21 quantities of hydrogen and carbon monoxide required in
22 the gasifier along with the carbon-alkali metal catalyst
23 and steam to produce the thermoneutral reaction that
24 results in the formation of essentially methane and carbon
25 dioxide.

26 SUMMARY OF THE INVENTION

27 This invention provides a process for the
28 generation of a high purity chemical synthesis gas by the
29 substantially thermoneutral reaction of steam with coal,
30 petroleum coke, heavy oil, residuum and other carbonaceous
31 feed materials in the presence of carbon-alkali metal
32 catalyst and added hydrogen and carbon monoxide. In
33 accordance with the invention, it has now been found that
34 a chemical synthesis gas can be generated by reacting
35 steam with a carbonaceous feed material in a reaction zone
36 at a temperature between about 1000°F. and about 1500°F.

1 and a pressure in excess of about 100 psia, preferably
2 between about 200 and about 800 psia, in the presence of a
3 carbon-alkali metal catalyst and sufficient added hydrogen
4 and carbon monoxide to provide substantially equilibrium
5 quantities of hydrogen and carbon monoxide in the reaction
6 zone at reaction temperature and pressure thereby producing
7 an effluent gas consisting essentially of equilibrium
8 quantities, at reaction temperature and pressure, of meth-
9 ane, carbon monoxide, carbon dioxide, steam and hydrogen;
10 withdrawing the effluent gas from the reaction zone and
11 treating it for the removal of steam and acid gases to pro-
12 duce a treated gas containing primarily carbon monoxide,
13 hydrogen and methane; recovering carbon monoxide and
14 hydrogen from the treated gas as a chemical synthesis
15 product gas; contacting at least a portion of the remainder
16 of the treated gas consisting primarily of methane with
17 steam in a steam reforming zone under conditions such that
18 at least a portion of the methane reacts with the steam
19 to produce carbon monoxide and hydrogen; and passing the
20 effluent from the reforming zone into the reaction zone.

21 It is normally desirable that the reforming zone
22 effluent contain carbon monoxide and hydrogen in amounts
23 equivalent to the equilibrium quantities of those gases
24 present in the effluent gas withdrawn from the reaction
25 zone so that the effluent from the steam reforming zone
26 will supply the substantially equilibrium quantities of
27 hydrogen and carbon monoxide required in the reaction zone
28 along with the carbon-alkali metal catalyst and steam to
29 produce the thermoneutral reaction that results in the
30 formation of essentially methane and carbon dioxide. If
31 the reforming zone effluent contains less than the desired
32 amount of carbon monoxide and hydrogen, additional amounts
33 of these gases may be added to the gasifier. Preferably,
34 a slip stream of the chemical synthesis product gas is
35 used for this purpose. If the reforming zone effluent
36 contains more than the desired amount of carbon monoxide

1 and hydrogen, the excess can be mixed with the reaction zone
2 effluent, passed through the downstream processing scheme,
3 and withdrawn as a portion of the chemical synthesis gas
4 product.

5 A sufficient amount of steam is normally fed to
6 the reforming zone so that enough unreacted steam is
7 present in the steam reforming zone effluent to provide
8 substantially all the steam necessary to supply the reac-
9 tions taking place in the reaction zone. The reforming
10 zone is normally operated at conditions such that its
11 effluent may also be used to supply the heat needed to
12 preheat the carbonaceous feed material to reaction tempera-
13 ture and compensate for heat losses from the reaction zone.
14 This is normally achieved if the temperature of the
15 reforming zone effluent is between about 100°F. and about
16 300°F. higher than the temperature in the reaction zone
17 and the effluent is passed without substantial cooling into
18 the reaction zone.

19 The process of the invention, unlike similar
20 processes proposed in the past, utilizes the thermoneutral
21 reaction of steam with a carbonaceous feed material to
22 produce a high purity chemical synthesis gas that has
23 wide spread industrial applications.

24 BRIEF DESCRIPTION OF THE DRAWING

25 The drawing is a schematic flow diagram of a
26 process carried out in accordance with the invention for
27 the manufacture of a chemical synthesis gas by the gasifica-
28 tion of coal or similar carbonaceous solids with steam in
29 the presence of a carbon-alkali metal catalyst and added
30 equilibrium quantities of hydrogen and carbon monoxide.

31 DESCRIPTION OF THE PREFERRED EMBODIMENTS

32 The process depicted in the drawing is one for
33 the production of a chemical synthesis gas by the gasifica-
34 tion of bituminous coal, subbituminous coal, lignite, coal
35 char, coke or similar carbonaceous solids with steam at
36 a high temperature in the presence of a carbon-alkali

1 metal catalyst prepared by impregnating the feed solids
2 with a solution of an alkali metal compound or mixture
3 of such compounds and thereafter heating the impregnated
4 material to a temperature sufficient to produce an inter-
5 action between the alkali metal and the carbon present.
6 The solid feed material that has been crushed to a particle
7 size of about 8 mesh or smaller on the U.S. Sieve Series
8 Scale is passed into line 10 from a feed preparation
9 plant or storage facility that is not shown in the
10 drawing. The solids introduced into line 10 are fed
11 into a hopper or similar vessel 11 from which they are
12 passed through line 12 into feed preparation zone 14.
13 This zone contains a screw conveyor or similar device,
14 not shown in the drawing, that is powered by a motor 16,
15 a series of spray nozzles or similar devices 17 for the
16 spraying of an alkali metal-containing solution supplied
17 through line 18 onto the solids as they are moved through
18 the preparation zone by the conveyor, and a similar set
19 of nozzles or the like 19 for the introduction of a hot
20 dry gas, such as flue gas, into the preparation zone. The
21 hot gas, supplied through line 20, serves to heat the
22 impregnated solids and drive off the moisture. A mixture
23 of water vapor and gas is withdrawn from zone 14 through
24 line 21 and passed to a condenser, not shown, from which
25 water may be recovered for use as makeup or the like.
26 The majority of the alkali metal-containing solution is
27 recycled through line 49 from the alkali metal recovery
28 portion of the process, which is described hereafter.
29 Any makeup alkali metal solution required may be introduced
30 into line 18 via line 13.

31 It is preferred that sufficient alkali metal-
32 containing solution be introduced into preparation zone 14
33 to provide from about 1 to about 50 weight percent of an
34 alkali metal compound or mixture of such compounds on the
35 coal or other carbonaceous solids. From about 5 to about
36 30 percent is generally adequate. The dried impregnated
37 solid particles prepared in zone 14 are withdrawn through

1 line 24 and passed to a closed hopper or similar vessel 25
2 from which they are discharged through a star wheel feeder
3 or equivalent device 26 in line 27 at an elevated pressure
4 sufficient to permit their entrainment into a stream of
5 high pressure steam, recycle product gas, inert gas or
6 other carrier gas introduced into line 29 via line 28.
7 The carrier gas and entrained solids are passed through
8 line 29 into manifold 30 and fed from the manifold through
9 feed lines 31 and nozzles, not shown in the drawing, into
10 gasifier 32. In lieu of or in addition to hopper 25 and
11 star wheel feeder 26, the feed system may employ parallel
12 lock hoppers, pressurized hoppers, aerated standpipes
13 operated in series, or other apparatus to raise the input
14 feed solids stream to the required pressure level.

15 It is generally preferred to operate the gasifier
16 32 at a pressure between about 100 and 1500 psia, the most
17 preferred range of operation being between about 200 and
18 800 psia. The carrier gas and entrained solids will
19 normally be introduced at a pressure somewhat in excess of
20 the gasifier operating pressure. The carrier gas may be
21 preheated to a temperature in excess of about 300°F.,
22 but below the initial softening point of the coal or other
23 feed material employed. Feed particles may be suspended
24 in the carrier gas in a concentration between about 0.2
25 and about 5.0 pounds of solid feed material per pound of
26 carrier gas. The optimum ratio for a particular system
27 will depend in part upon the particle size and density,
28 the molecular weight of the gas employed, the temperature
29 of the solid feed material and the input gas stream, the
30 amount of alkali metal compound employed and other factors.
31 In general, ratios between about 0.5 and about 4.0 pounds
32 of solid feed material per pound of carrier gas are
33 preferred.

34 Gasifier 32 contains a fluidized bed of carbon-
35 aceous solids extending upward within the vessel above an
36 internal grid or similar distribution device not shown in

1 the drawing. The bed is maintained in the fluidized state
2 by means of steam, hydrogen and carbon monoxide introduced
3 through line 33, manifold 34 and peripherally spaced injec-
4 tion lines and nozzles 35 and through bottom inlet line 36.
5 The particular injection system shown in the drawing is not
6 critical and hence other methods for injecting the steam,
7 hydrogen and carbon monoxide may be employed. In some
8 instances, for example, it may be preferred to introduce the
9 gases through multiple nozzles to obtain more uniform
10 distribution of the injected fluid and reduce the possibil-
11 ity of channeling and related problems. The space velocity
12 of the rising gases within the fluidized bed will normally
13 be between about 2 and about 300 actual volumes of steam,
14 hydrogen and carbon monoxide per hour per volume of
15 fluidized solids.

16 Within the fluidized bed in gasifier 32, the
17 carbonaceous solids impregnated with the alkali metal com-
18 pound or mixture of such compounds are subjected to a temper-
19 ature within the range between about 1000°F. and about
20 1500°F., preferably between about 1200°F. and 1400°F. At
21 such a temperature the alkali metal constituents interact
22 with the carbon in the carbonaceous solids to form a carbon-
23 alkali metal catalyst, which will under proper reaction
24 conditions equilibrate the gas phase reactions occurring
25 during gasification to produce additional methane and at
26 the same time supply substantial amounts of additional
27 exothermic heat in situ. Due to the gas phase equilibrium
28 conditions existing as a result of the carbon-alkali metal
29 catalyst and due to the presence of equilibrium quantities
30 of hydrogen and carbon monoxide injected with the steam
31 near the lower end of the bed, the net reaction products
32 will normally consist essentially of methane and carbon
33 dioxide. Competing reactions that in the absence of the
34 catalyst and the hydrogen and carbon monoxide would ordinar-
35 ily tend to produce additional hydrogen and carbon monoxide
36 are suppressed. At the same time, substantial quantities

1 of exothermic heat are released as a result of the
2 reaction of hydrogen with carbon oxides and the
3 reaction of carbon monoxide with steam. This exo-
4 thermic heat tends to balance the endothermic heat
5 consumed by the reaction of the steam with carbon,
6 thereby producing an overall thermoneutral reaction.
7 So far as the heat of reaction is concerned, the gas-
8 ifier is therefore largely in heat balance. The heat
9 employed to preheat the feed coal to the reaction temp-
10 erature and compensate for heat losses from the gasi-
11 fier is supplied for the most part by excess heat in
12 the gases introduced into the gasifier through lines
13 35 and 36. In the absence of the exothermic heat pro-
14 vided by the catalyzed gas phase reactions, these
15 gases would have to be heated to substantially higher
16 temperatures than those employed here.

17 The carbon-alkali metal catalyst utilized in
18 the process of the invention is prepared by heating an
19 intimate mixture of carbon and an alkali metal constitu-
20 tent to an elevated temperature, preferably above 800°F.
21 In the process shown in the drawing and described above,
22 the intimate mixture is prepared by impregnating the
23 carbonaceous feed material with an alkali metal-contain-
24 ing solution and then subjecting the impregnated solids
25 to a temperature above 800°F in the gasifier itself. It
26 will be understood that the alkali metal catalyst uti-
27 lized in the process of this invention can be prepared
28 without impregnation onto the carbonaceous solids to
29 be gasified, and without heating in the gasifier.
30 The heating step, for example, may be carried out in a
31 solid feed preparation zone or in an external heater.
32 The carbonaceous solids used will in most instances be
33 the ones which are to be gasified but in some variations
34 of the process carbonaceous materials other than the
35 feed solids may be used. In some cases inert carriers
36 having carbon deposited on their outer surface may be

1 used. Suitable inert carriers include silica, alumina,
2 silica-alumina, zeolites, and the like. The catalyst
3 particles, whether composed substantially of carbon
4 and an alkali metal constituent or made up of carbon
5 and an alkali metal constituent deposited on an inert
6 carrier, may range from fine powders to coarse lumps,
7 particles between about 4 and about 100 mesh on the
8 U.S. Sieve Series Scale generally being preferred.
9 The size selected for use in a particular operation will
10 normally depend in part on the gas velocities and other
11 conditions within the system in which the catalyst is to
12 be used. In fluidized bed systems, the particle size
13 is in part dependent upon the conditions under which
14 the bed is to be operated. In fixed or moving bed
15 systems, the catalyst particle size is generally of less
16 importance.

17 Any of a variety of alkali metal constituents
18 can be used in preparing the carbon-alkali metal catalyst.
19 Suitable constituents include alkali metals themselves
20 and alkali metal compounds such as alkali metal carbon-
21 ates, bicarbonates, formates, biphosphates, oxalates,
22 amides, hydroxides, acetates, sulfates, hydrosulfates,
23 sulfides, and mixtures of these and other similar com-
24 pounds. All of these are not equally effective and
25 hence a catalyst prepared from certain alkali metal con-
26 stituents can be expected to give somewhat better re-
27 sults under certain conditions than do others. In
28 general, cesium, potassium, sodium and lithium salts
29 derived from organic or inorganic acids having ioni-
30 zation constants less than about 1×10^{-3} and alkali
31 metal hydroxides are preferred. The cesium compounds
32 are the most effective, followed by the potassium,
33 sodium and lithium compounds in that order. Because
34 of their high activity, relatively low cost compared
35 to cesium compounds, and ready availability, potassium
36 compounds or sodium compounds are generally employed.

1 Potassium carbonate and potassium hydroxide are es-
2 pecially effective.

3 In the embodiment of the invention shown in
4 the drawing, the alkali metal constituent and the car-
5 bonaceous solids are combined to form an intimate mix-
6 ture by dissolving a water soluble alkali metal compound
7 in an aqueous carrier, impregnating the carbonaceous
8 solid with the resulting aqueous solution by soaking or
9 spraying the solution onto the particles, and thereafter
10 drying the solids. It will be understood that other me-
11 thods of forming such an intimate mixture may be used.
12 For example, in some cases the carbonaceous material can
13 be impregnated by suspending a finely divided alkali
14 metal or alkali metal compound in a hydrocarbon solvent
15 or other inert liquid carrier of suitably low vis-
16 cosity and high volatility and thereafter treating the
17 solids with the liquid containing the alkali metal con-
18 stituent. In other cases, it may be advantageous to
19 pelletize a very finely divided alkali metal or alkali
20 metal compound with carbon in an oil or similar binder
21 and then heat the pellets to an elevated temperature.
22 Other catalyst preparation methods, including simply
23 mixing finely divided carbonaceous material with a
24 powdered alkali metal salt and thereafter heating the
25 mixture to the desired temperature, can in some cases
26 also be used.

27 The mechanisms which take place as the result
28 of combining the carbonaceous solids and alkali metal con-
29 stituents and then heating them to elevated temperatures
30 are not fully understood. Apparently, the alkali metal
31 reacts with the carbon to form carbon-alkali metal com-
32 pounds and complexes. Studies have shown that neither
33 carbonaceous solids nor the alkali metal constituents
34 alone are fully effective for establishing equilibrium
35 conditions for gas phase reactions involving steam,
36 hydrogen, carbon monoxide, carbon dioxide and methane

1 and that catalytic activity is obtained only when a com-
2 pound or complex of the carbon and alkali metal is pre-
3 sent in the system. Both constituents of the catalyst are
4 therefore necessary. Experience has shown that these
5 catalysts are resistant to degradation in the presence
6 of sulfur compounds, that they resist sintering at high
7 temperatures, and that they bring gas phase reactions
8 involving the gases normally produced during coal gasi-
9 fication into equilibrium. As a result of these and
10 other beneficial properties, these catalysts have pro-
11 nounced advantages over other catalysts employed in the
12 past.

13 Referring again to the drawing, the gas leav-
14 ing the fluidized bed in gasifier 32 passes through
15 upper section of the gasifier, which serves as a dis-
16 engagement zone where the particles too heavy to be
17 entrained by the gas leaving the vessel are returned to
18 the bed. If desired, this disengagement zone may include
19 one or more cyclone separators or the like for removing
20 relatively large particles from the gas. The gas with-
21 drawn from the upper part of the gasifier through line
22 37 will normally contain an equilibrium mixture at
23 reaction temperature and pressure of methane, carbon
24 dioxide, hydrogen, carbon monoxide, and unreacted steam.
25 Also present in this gas are hydrogen sulfide, ammonia
26 and other contaminants formed from the sulfur and nitro-
27 gen contained in the feed material, and entrained fines.
28 This raw product gas is introduced into cyclone sep-
29 arator or similar device 38 for removal of the larger
30 fines. The overhead gas then passes through line 39
31 into a second separator 41 where small particles are
32 removed. The gas from which the solids have been sep-
33 arated is taken overhead from separator 41 through line
34 42 and the fines are discharged downward through dip
35 legs 40 and 43. These fines may be returned to the
36 gasifier or passed to the alkali metal recovery por-

1 tion of the process.

2 In the system shown in the drawing, a stream
3 of high ash content char particles is withdrawn through
4 line 44 from gasifier 32 in order to control the ash
5 content of the system and permit the recovery and recycle
6 of alkali metal constituents of the catalyst. The
7 solids in line 44, which may be combined with fines re-
8 covered from the gasifier overhead gas through dip legs
9 40 and 43 and line 45, are passed to alkali metal recovery
10 unit 46. The recovery unit will normally comprise a
11 multistage countercurrent leaching system in which the
12 high ash content particles are countercurrently contacted
13 with water introduced through line 47. An aqueous solu-
14 tion of alkali metal compounds is withdrawn from the unit
15 through line 48 and recycled through lines 49 and 18
16 to feed preparation zone 14. Ash residues from which sol-
17 uble alkali metal compounds have been leached are with-
18 drawn from the recovery unit through line 50 and may
19 be disposed of as land fill or further treated to re-
20 cover added alkali metal constituents.

21 The gas leaving separator 41 is passed through
22 line 42 to gas-gas heat exchanger 51 where it is cooled
23 by indirect heat exchange with a gaseous mixture of met-
24 hane and steam introduced through line 77. The cooled
25 gas is then passed through line 53 into waste heat
26 boiler 54 where it is further cooled by indirect heat
27 exchange with water introduced through line 55. Suf-
28 ficient heat is transferred from the gas to the water to
29 convert it into steam, which is withdrawn through line 56.
30 During this cooling step, unreacted steam in the gas
31 from exchanger 51 is condensed out and withdrawn as
32 condensate through line 57. The cool gas exiting waste
33 heat boiler 54 through line 58 is passed to water
34 scrubber 59. Here the gas stream passes upward through
35 the scrubber where it comes in contact with water in-
36 jected into the top of the scrubber through line 60.
37 The water absorbs ammonia and a portion of the hydrogen

1 sulfide in the gas stream and is withdrawn from the
2 bottom of the scrubber through line 61 and passed to
3 downstream units for further processing. The water
4 scrubbed gas stream is withdrawn from the scrubber
5 through line 62 and is now ready for treatment to remove
6 bulk amounts of hydrogen sulfide and other acid gases.

7 The gas stream is passed from water scrubber
8 59 through line 62 into the bottom of solvent scrubber
9 63. Here the gas passes upward through the contacting
10 zone in the scrubber where it comes in contact with a
11 down-flowing stream of solvent such as monoethanolamine,
12 diethanolamine, a solution of sodium salts of amino acids,
13 methanol, hot potassium carbonate or the like introduced
14 into the upper part of the solvent scrubber through line
15 64. If desired, the solvent scrubber may be provided
16 with spray nozzles, perforated plates, bubble cap plates,
17 packing or other means for promoting intimate contact
18 between the gas and the solvent. As the gas rises
19 through the contacting zone, hydrogen sulfide, carbon
20 dioxide and other acid gases are absorbed by the sol-
21 vent, which exits the scrubber through line 65. The
22 spent solvent containing carbon dioxide, hydrogen sul-
23 fide and other contaminants is passed through line 65
24 to a stripper, not shown in the drawing, where it is
25 contacted with steam or other stripping gas to remove
26 the absorbed contaminants and thereby regenerate the
27 solvent. The regenerated solvent may then be reused
28 by injecting it back into the top of the scrubber via
29 line 64.

30 A clean gas containing essentially methane,
31 hydrogen, and carbon monoxide in amounts substantially
32 equivalent to the equilibrium quantities of those
33 gases in the raw product gas withdrawn from gasifier 32
34 through line 37 is withdrawn overhead from the solvent
35 scrubber via line 66. The methane content of the gas
36 will normally range between about 20 and about 60 mole

1 percent and the gas will be of an intermediate Btu heat-
2 ing value, normally containing between about 400 and about
3 750 Btu's per standard cubic foot.

4 The intermediate Btu gas withdrawn overhead from
5 solvent scrubber 63 through line 66 is introduced into
6 heat transfer unit 67 where it passes in indirect heat ex-
7 change with liquid methane introduced through line 68. The
8 methane vaporizes within the heat transfer unit and is dis-
9 charged as methane gas through line 69. The vaporizing
10 methane chills the intermediate Btu gas, which is primarily
11 composed of methane hydrogen and carbon monoxide, to a low
12 temperature approaching that required for liquefaction of
13 the methane contained in the gas, after which the chil-
14 led gas is passed through line 70 into cryogenic unit 71.
15 Here the gas is further cooled by conventional means until
16 the temperature reaches a value sufficiently low to liquefy
17 the methane under the pressure conditions existing in the
18 unit. Compressors and other auxiliaries associated with
19 the cryogenic unit are now shown. The amount of pressure re-
20 quired for the liquifaction step will depend in part upon
21 the pressure at which the gasifier is operated and the pres-
22 sure losses which are incurred in the various portions of
23 the system. A substantially pure stream of liquefied meth-
24 ane is taken off through line 72 and passed through line 68
25 into heat transfer unit 67 as described earlier. Hydrogen
26 and carbon monoxide are withdrawn overhead from cryogenic
27 unit 71 through line 80 and recovered as a chemical synthe-
28 sis product gas. Normally, the cryogenic unit is operated
29 and designed in such a manner that less than about 10 mole
30 percent of methane, preferably less than about 5 mole per-
31 cent, remains in the product gas removed through line 80.
32 Thus, the chemical synthesis gas produced in the process is
33 one of extremely high purity and therefore has many indus-
34 trial applications.

1 The recycle methane gas removed from heat trans-
2 fer unit 67 through line 69 is passed to compressor 73
3 where its pressure is increased to a value from about 25
4 psi to about 150 psi above the operating pressure in
5 gasifier 32. The pressurized gas is withdrawn from com-
6 pressor 73 through line 74 and passed through tubes 75
7 located in the convection section of steam reforming
8 furnace 76. Here, the high pressure gas picks up heat via
9 indirect heat exchange with the hot flue gases generated
10 in the furnace. The methane gas is removed from the
11 tubes 75 through line 77 and mixed with steam, which is
12 generated in waste heat boiler 54 and injected into line
13 77 via line 56. The mixture of methane gas and steam is
14 then passed through line 77 into gas-gas heat exchanger 51
15 where it is heated by indirect heat exchange with the raw
16 product gas removed from separator 41. The heated mixture
17 is removed from exchanger 51 and passed through line 78
18 to steam reforming furnace 76.

19 The preheated mixture of steam and methane gas
20 in line 78 is introduced into the internal tubes 79 of
21 the steam reforming furnace where the methane and steam
22 react with one another in the presence of a conventional
23 steam reforming catalyst. The catalyst will normally
24 consist of metallic constituents supported on an inert
25 carrier. The metallic constituent will normally be
26 selected from Group VI-B and the iron group of the Periodic
27 Table and may be chromium, molybdenum, tungsten, nickel,
28 iron, and cobalt, and may include small amounts of potassi-
29 um carbonate or a similar compound as a promoter. Suitable
30 inert carriers include silica, alumina, silica-alumina,
31 zeolites, and the like.

32 The reforming furnace is operated under condi-
33 tions such that the methane in the feed gas will react
34 with steam in the tubes 79 to produce hydrogen and carbon
35 monoxide according to the following equation:

1
$$\text{H}_2\text{O} + \text{CH}_4 \rightarrow 3\text{H}_2 + \text{CO}$$

2 The temperature in the reforming furnace will normally be
3 maintained between about 1200°F and about 1800°F, pre-
4 ferably between about 100°F and about 300°F above the
5 temperature in gasifier 32. The pressure will range be-
6 tween about 10 and about 30 psi above the pressure in the
7 gasifier. The mole ratio of steam to methane introduced
8 into the reactor will range between about 2:1 and about
9 15:1, preferably between about 3:1 and about 7:1. The
10 reforming furnace may be fired by a portion of the methane
11 gas removed from heat transfer unit 67 via line 69, a
12 portion of the intermediate Btu gas removed from solvent
13 scrubber 63 through line 66, or a similar fuel gas.

14 The gaseous effluent stream from the steam
15 reforming furnace, which will normally be a mixture
16 consisting primarily of hydrogen, carbon monoxide, and
17 unreacted steam, is passed, preferably without substan-
18 tial cooling, through lines 81, 36, and 33 into gasifier
19 32. This stream is the primary source of the hydrogen,
20 carbon monoxide, and steam required in the gasifier in
21 addition to the carbon-alkali metal catalyst to produce
22 the thermoneutral reaction that results in the formation
23 of essentially carbon dioxide and methane. It is there-
24 fore desirable that the reforming furnace effluent
25 contain sufficient carbon monoxide and hydrogen to supply
26 the substantially equilibrium quantities of those gases
27 required in the gasifier and sufficient unreacted steam
28 to provide substantially all of the steam required by the
29 reactions taking place in the gasifier.

30 As pointed out previously, substantial quantities
31 of exothermic heat are released in the gasifier as a result
32 of the reaction of hydrogen with carbon oxides and the
33 reaction of carbon monoxide with steam. Thus, the carbon
34 monoxide and hydrogen in the reformer effluent stream
35 comprises a substantial portion of the heat input into the
36 gasifier. To supply the desired amounts of hydrogen and

1 carbon monoxide in the effluent, sufficient methane should
2 normally be present in the feed to the reforming furnace
3 so that enough carbon monoxide and hydrogen is produced by
4 steam reforming the methane to compensate for the amount
5 of hydrogen and carbon monoxide removed in the chemical
6 synthesis product gas withdrawn from the process overhead
7 of cryogenic unit 71 through line 80. If there is insuffi-
8 cient methane in the feed to the reforming furnace, the
9 conditions in the gasifier may be altered so that addition-
10 al methane is produced in the raw product gas. Alterna-
11 tively, a slip stream of the chemical synthesis product
12 gas may be used to make up any deficiency in the amounts
13 of carbon monoxide and hydrogen required. If, on the
14 other hand, there is more than the desired amount of
15 methane in the feed to the reforming furnace, the condi-
16 tions in the gasifier may be altered to decrease the amount
17 of methane produced in the raw product gas, the excess
18 methane may be withdrawn as a byproduct stream from line
19 74 prior to subjecting it to steam reforming, or the
20 excess methane may be reformed to produce additional
21 carbon monoxide and hydrogen that can be passed from line
22 81 into line 42 and recycled through the downstream
23 portion of the process. If the amount of steam added via
24 line 56 to the reforming furnace feed stream in line 78
25 is not sufficiently in excess of the amount consumed in
26 the furnace so as to provide the desired quantity of
27 unreacted steam in the reformer effluent, additional steam
28 may be injected into line 78 through line 82.

29 For the purposes of thermal efficiency, it is
30 preferable that the steam reforming step of the process be
31 utilized in such a manner as to obviate the need for a
32 separate preheat step. This may be achieved by operating
33 the reforming furnace so that the heat content of the
34 effluent is sufficient to preheat the carbonaceous feed
35 material to reaction temperature and maintain all of the
36 reactants at such temperature by compensating for heat

1 losses during gasification. Normally, this may be
2 accomplished if the temperature of the effluent is between
3 about 100°F and about 300°F higher than the operating
4 temperature in the gasifier. For optimum thermal effi-
5 ciency it is important that the effluent from the steam
6 reforming furnace be passed to the gasifier in such a
7 manner as to avoid substantial cooling. As used herein
8 "heat content" refers to the sum of the heats of formation
9 plus the sum of the sensible heats for each component in
10 the reforming furnace effluent.

11 It will be apparent from the above discussion
12 that the effluent from the reforming furnace 76 will
13 supply substantially all of the heat required in gasifier
14 32. The effluent will not only contain sufficient sensible
15 heat to preheat the carbonaceous feed material to reaction
16 temperature and maintain all the reactants at such temp-
17 erature by compensating for heat losses during gasifica-
18 tion, but it will also contain sufficient amounts of
19 carbon monoxide and hydrogen which react in the gasifier
20 to produce enough exothermic heat to substantially
21 balance the endothermic heat consumed by the reaction of
22 the steam with carbon.

23 It will be apparent from the foregoing that the
24 invention provides a process for producing a high purity
25 chemical synthesis gas from the steam gasification of a
26 carbonaceous material such as coal in the presence of a
27 carbon-alkali metal catalyst and substantially equili-
28 brium quantities of added hydrogen and carbon monoxide.
29 The process of the invention has advantages over existing
30 coal gasification processes that may be used to generate a
31 chemical synthesis gas in that its gasifier operates at
32 lower temperature, it is more energy efficient, and it
33 does not require the injection of oxygen to supply heat,
34 thereby obviating the need for an expensive oxygen plant.

1 The following Table shows the conversion of the
2 units employed in the specification and claims into S.I.
3 units.

4 TABLE

5	<u>Pound</u>	<u>kg</u>
6	0.2	0.09
7	5.0	2.27
8		
9	<u>°F</u>	<u>°C</u>
10	100	38
11	300	149
12	800	427
13	1000	538
14	1200	649
15	1400	760
16	1500	816
17	1800	983
18	2500	1370
19	<u>p.s.i.</u>	<u>kPa</u>
20	100	6.90×10^2
21	200	1.38×10^3
22	800	5.52×10^3
23	1500	1.04×10^4

WHAT WE CLAIM IS:

1. A process for the production of a chemical synthesis product gas from a carbonaceous feed material and steam characterized by comprising the steps of:

(a) reacting said steam with said carbonaceous feed material in a reaction zone at a reaction temperature between about 1000^oF and about 1500^oF and at a reaction pressure in excess of about 100 psia, in the presence of a carbon-alkali metal catalyst and sufficient added hydrogen and carbon monoxide to provide substantially equilibrium quantities of hydrogen and carbon monoxide in said reaction zone at said reaction temperature and pressure;

(b) withdrawing from said reaction zone an effluent gas containing substantially equilibrium quantities, at said reaction temperature and pressure, of methane, carbon dioxide, steam, hydrogen and carbon monoxide;

(c) treating said effluent gas for the removal of steam and acid gases to produce a treated gas containing primarily carbon monoxide, hydrogen and methane;

(d) recovering substantially all of the carbon monoxide and hydrogen from said treated gas as a chemical synthesis product gas;

(e) contacting at least a portion of the remainder of said treated gas comprised substantially of methane with steam in a steam reforming zone under conditions such that at least a portion of the methane present reacts with said steam to produce hydrogen and carbon monoxide; and

(f) passing the effluent from said steam reforming zone into said reaction zone without substantial cooling, thereby supplying said added hydrogen and carbon monoxide required in said reaction zone, and wherein said reforming zone is operated at conditions such that the heat content of said effluent from said steam reforming zone is sufficient to supply substantially all of the heat needed to preheat said carbonaceous feed material to said reaction temperature.

2. A process according to claim 1 further characterized in that the said carbon-alkali metal catalyst is prepared by treating said carbonaceous feed material with an alkali metal compound and thereafter heating the treated coal to said reaction temperature in said reaction zone.

3. A process according to claim 1 or claim 2 further characterized in that the said carbonaceous feed material comprises coal.

4. A process according to any one of claims 1-3 further characterized in that the said reaction pressure is between about 200 psia and about 800 psia.

5. A process according to any one of claims 1-4 further characterized in that the said reaction temperature is between about 1200°F and about 1400°F.

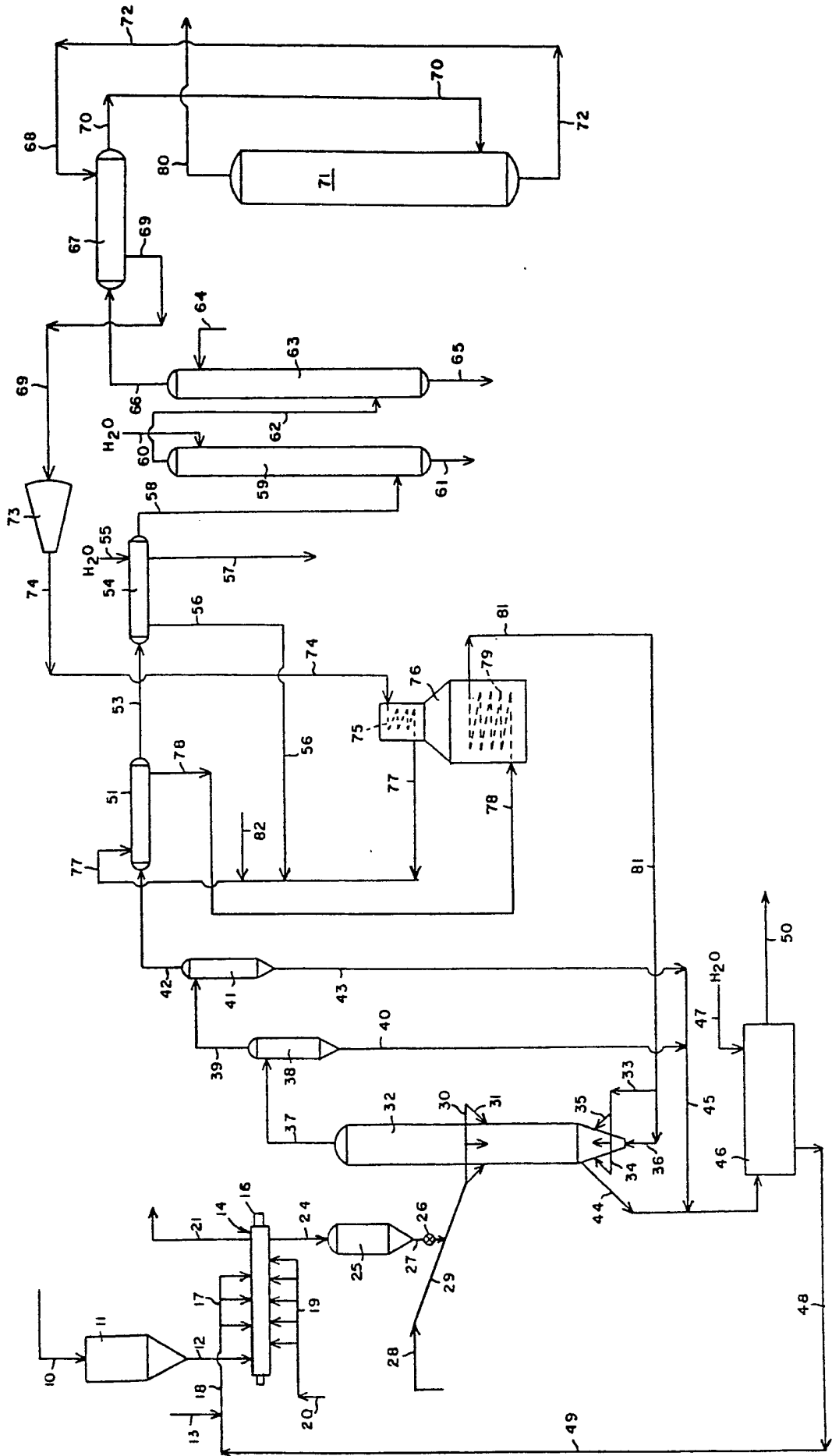
6. A process according to any one of claims 1-5 further characterized in that the said chemical synthesis product gas contains less than about 10 mole percent methane.

7. A process according to any one of claims 1-6 further characterized in that sufficient steam is contacted with said methane in said steam reforming zone so that the effluent from said zone will contain enough unreacted steam to supply substantially all the steam required in said reaction zone.

8. A process according to any one of claims 1-7 further characterized in that the temperature of said effluent from said steam reforming zone is between about 100°F and about 300°F higher than said reaction temperature in said catalytic gasification zone.

9. A process according to any one of claims 3-8 further characterized in that the said coal is impregnated with an aqueous solution of a potassium compound and dried prior to the introduction of said coal into said catalytic gasification zone.

10. A process according to claim 9 further characterized in that the said aqueous solution comprises alkali metal compounds recovered from char withdrawn from said catalytic gasification zone.





DOCUMENTS CONSIDERED TO BE RELEVANT			CLASSIFICATION OF THE APPLICATION (Int. Cl. 3)
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	
D	FR - A - 2 381 820 (EXXON) * Pages 19-21, claims * & US - A - 4 118 204 --	1-5, 7-10	C 10 J 3/54 3/00
	US - A - 3 929 431 (KOH) * Column 4, lines 5-69; column 5 - column 11; column 12, lines 1-6 * --	1-5	
	FR - A - 2 393 052 (G.H.T.) * Page 5, lines 4-40 * --	1,3	TECHNICAL FIELDS SEARCHED (Int.Cl. 3)
A	FR - A - 2 416 255 (G.H.T.)		C 10 J 3/54 3/00
A	US - A - 2 652 319 (SWEETSER)		
A	US - A - 3 775 072 (WHITE)		
DA	US - A - 4 094 650 (KOH) ----		
			CATEGORY OF CITED DOCUMENTS
			X: particularly relevant A: technological background O: non-written disclosure P: intermediate document T: theory or principle underlying the invention E: conflicting application D: document cited in the application L: citation for other reasons
<input checked="" type="checkbox"/> The present search report has been drawn up for all claims			&: member of the same patent family, corresponding document
Place of search	Date of completion of the search	Examiner	
The Hague	05-09-1980	WENDLING	