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(54) Title: CONVERTIBLE METHANOL/FISCHER-TROPSCH PLANT AND METHOD

(57) Abstract

Lower molecular weight organic materials are converted to more valuable products in a variable flow, selectively operated multiproduct plant. The plant includes a reformer (12, 25) to produce syngas from the hydrocarbon feed, multi output valving (13) to direct the syngas product stream to one or both of a methanol reactor (18) and a Fischer-Tropsch (FT) products plant (19), depending on the ambient value of these chemicals. Prior to introducing the syngas into the FT plant 19, the CO_2 and H_2 are removed by scrubbers (12, 13) and recycled appropriately.

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CONVERTIBLE METHANOL/FISCHER-TROPSCH PLANT AND METHOD

CROSS-REFERENCE TO RELATED APPLICATION

This application is a non-provisional application claiming the benefits of provisional application No. 60/133,147 filed May 7, 2000.

FIELD OF THE INVENTION

This invention relates to improved plants and processes for the manufacture of organic chemicals from natural gas and other low molecular weight feedstocks.

BACKGROUND OF THE INVENTION

All industries go through cycles of excess capacity and not enough capacity. The chemical industry is no exception. Changing industry economics due to changes in public tastes, governmental regulation and environmental considerations all affect the industry. For example, the finding of methyl t-butyl ether (MTBE) in California ground waters is leading to legislation forbidding its use as a gasoline additive. Methanol is a raw material for the manufacture of MTBE and this legislation combined with over capacity may render some methanol plants uneconomic.

Basically, the plant of this invention is designed to ameliorate such problems for methanol plants. The plants combine a syngas-producing reformer of a methanol reactor with a Fischer-Tropsch (FT) reactor. These problems are discussed at some length by Frank C. Brown in Petroleum Technology Quarterly, Spring 2000, pp. 84-90 with regard to both the industry and the invention herein. The plant is piped to eliminate or modulate the production of one of the hydrocarbons, alcohols and hydrogen products of the combined plant so as to produce the most profitable product or mix of products at any given time. The plants can be easily separated for upgrade or the scrapping of either the methanol or FT plant

Each of the reactors of the new plants and their operations is well known. Thus, the T.E. O'Hare et al, paper given to the 1986 International Gas Research Conference, Sept. 8-11, 1986 in Toronto Canada describes the "Liquefaction of Natural Gas to Methanol for Shipping and Storage". The specific technology was developed by the Department of Applied Science, Brookhaven National Laboratory, Associated Universities, Inc. The process described utilizes a four-part operation. Natural gas and steam are subjected to catalytic secondary reforming to obtain syngas. The syngas is sparged through a liquid catalyst solution and then cooled to recover a methanol stream at 120°C at about 194 psi absolute.

U.S. Patents 5,621,155; 5,620,670 and 5,543,437 issued to C. B. Benham, M. S. Bohn and D. L. Yakobson of Rentech, Inc. of Denver, Colorado. These patents teach a process utilizing a natural gas feedstock which is reformed to form a syngas which, after carbon dioxide removal, is fed to a Fischer-Tropsch (FT) reactor to form water, a variety of alcohols and C_5 and C_{20} hydrocarbon products, e.g., liquids and waxes. These references are exemplary of an extensive body of literature.

SUMMARY OF THE INVENTION

A multipurpose plant package includes a methanol plant and a FT plant utilizing a shared syngas reformer. The reformer is plumbed to feed all its product to the methanol plant or to the FT plant or to both plants simultaneously.

To manufacture methanol, the reformer syngas product is compressed and fed to a methanol reactor to provide a methanol stream. To provide both methanol and FT products, the CO_2 and H_2 are removed from a portion of the syngas stream and the purified syngas is fed to the FT reactor while the remaining portion of syngas stream is fed to the methanol reactor. To obtain only FT products, the entire syngas stream is fed to the FT reactor.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a functional diagram of one form of a three-reactor plant of this invention.

Figure 2 is a diagram of a preferred FT process.

DETAILED DESCRIPTION OF THE DRAWINGS

Figure **1** depicts a combined methanol and FT reactor adaptable for the primary production of methanol and FT products. Block A identifies the existing methanol plant less the reformer.

Steam 10 and natural gas 11 are piped to the reformer 12. When the market justifies the production of only methanol, valve 13 directs all the reformer 12 output to a syngas compressor 14. The compressed syngas is fed to the methanol reactor 15. Reactor 15 products are distilled in tower 16 from whence methanol is recovered and the high ends are flared or recycled as fuel.

To operate totally as a FT products plant, valve 13 is used to direct all of the syngas to a CO_2 absorption unit 17. The recovered CO_2 is then recycled to the reformer 12 while the remaining gases are treated in an H_2 removal unit 18. The H_2 is preferably used as fuel for the reformer or marketed. The remaining syngas is fed to the FT reactor 19. The H_2:CO ratio of the FT reactor feed is preferably about 2:1 or less. The remaining FT reactor 19 products are passed into the FT product separation unit 21. Tail gas from column 21 can be flared, used as reformer 12 fuel or used as a feedstock.

Figure **2** depicts a more preferred flowsheet based on the use of the entire output of reformer 12 to produce methanol FT producers. In the diagram of Figure 2, the methanol plant has been taken off line through the use of the valving 13 of Fig. 1. The synthesis gas and steam feedstocks utilized to produce methanol are now introduced into the FT plant of Fig. 2. The natural gas and steam are fed to the reformer 25 through the piping of line 26. Fuel for heating reformer 25 is supplied through piping 27. The hot gases from reformer 25 are cooled, then passed through compressor 28 and introduced into CO_2 absorption unit 29. CO_2 from absorber 29 is recycled through compressor 31 to reformer 25. The remaining synthesis gas is passed through H_2 recovery unit 30 where the H2:CO ratio is reduced to below 2:1. Then the steam produced in the FT reactor 32 can be used for power generation. The remaining products exiting reactor 32 are then separated in product separator 33. Water and hydrocarbons can be recovered while the hydrocarbon gases are recycled for use as a fuel, as a feed to reformer 25 or as feed to the FT reactor 32 via line 33 and compressor 34.

The percentage of the CO_2 removed from the syngas leaving the reformer should reduce the CO_2 content of the H_2 scrubber 30 feeds to about 5% or less and preferably as low as 0.5%. The operation of the H_2 scrubber 30 should provide the FT reactor 32 with a feed having a H_2:CO ratio of less than 2:1 and greater than 1:1. The tail gas recycle to the reformer 25 should be between 0% and 20% of the total tail gas from product separator 33. The tail gas recycled to the FT reactor 32 via CO_2 scrubber 29 should be 80 to 100%. Any remaining tail gas is available for use as reformer fuel.

GENERAL TEACHING OF THE INVENTION

The Figures depict the skeletal backbone of the multiple product chemical plants. Computerized controls and equipment are necessary to maintain fluid and gas volume throughputs, the desired temperatures and pressures. The sensors needed to provide data for actuating the controls and the conditions of practical and optimum unit operations of each of the reformer and methanol and FT reactors are well known.

The preferred reformer process for operation with the preferred FT unit operation utilizes a nickel-based, alkali-promoted catalyst which permits a substantial CO_2 input, e.g., about 20 to about 40% and preferably about 30 to about 35% and a reduced steam input of about 2.2:1 steam to carbon. The pressure drop across the reformer will range from about 30 to 80 psi and preferably about 35-65 psi.

The FT reactor is operated at temperatures of 220 to 280°C and preferably 230 to 270°C and more preferably at 250 to 265°C. The FT reactor operating pressures are generally 100 to 600 psia; preferably from 150 to 550 psia and more preferably 300 to 500 psia. The term “scrubber” is defined here as any equipment utilized to remove the identified syngas component. The methanol reactor operating temperature is from 150 to 300°C, preferably from 175 to 250°C and more preferably 200 to 235°C. The methanol reactor operating pressures are 700 – 1400 psi, preferably 750 to 1300 psi and more preferably 800 – 1200 psi absolute. The FT reactor is preferably operated utilizing the preferred and most preferred conditions and catalysts of the Rentech, Inc. references cited previously. The methanol reactor catalyst can be any of copper, zinc and aluminum.

The reformer operation is often the plant bottleneck. One or more of pressure drop, burner firing rate, tube heat reflux emissions, or a combination of these three will limit the total plant capacity. For FT plants, the design objectives include maximizing the production of C_5+ hydrocarbons, minimizing consumption of natural gas, and minimizing the size of the major unit operations and hence capital cost.

Iron-based FT catalysts promote the water-gas shift reaction:

$$CO + H_2O = H_2 + CO_2$$

Carbon dioxide is therefore a byproduct of the FT reaction. As such, it is important to recycle the carbon dioxide back to the reformer to improve carbon efficiency. The carbon dioxide scrubber unit shown in Figs. 1 and 2 delivers carbon dioxide to the reformer where it is partially converted back to carbon monoxide by the water-gas shift reaction in the reformer. The carbon dioxide absorbers preferably remove carbon dioxide to low levels, preferably to approximately 0.5% on a volume basis in the exiting syngas stream, so that the maximum carbon production efficiency can be achieved.

The hydrogen removal unit is used to ensure that the FT reactor is fed with a reasonable ratio of hydrogen to carbon monoxide. For the example calculations, the ratio was set to 1:4:1.

As noted previously, the tail gas from the FT reactor, after separation of the liquid products and carbon dioxide, is split three ways. Approximately 5% is purge gas and can be used as fuel. Approximately 90% is recycled to the CO_2 removal unit in order that unreacted CO can be further converted in the FT reactor. The remaining tail gas is sent to the reformer where light hydrocarbons produced by the FT reactor can be reformed into carbon monoxide and hydrogen. This small recycle stream reduces the build up of light hydrocarbons in the main recycle loop.

The flowsheet in Fig. 2 was modeled to determine yield, natural gas consumption/reformer heat duty and pressure drop, and liquid hydrocarbon yield based on a plant which originally produced 75,000 gallons/day of methanol. The table below gives the important results.

Reformer heat duty (net)	137 MMBTU/hr
Reformer pressure drop	60 psid
Total natural gas consumption	9.94 MMSCFD
C_5-yield	932 bbl/day
Plant efficiency	10.1 MMBTU/bbl

All fuel MMBTU are lower heating values.

Feed gas flow of the major unit operations are given below:

Reformer	46
CO_2 absorber 1	82
H_2 removal	67
FT	60
Product separation	44

All flows are given in MMSCFD (standard temperature and pressure are 60°F and 14.69 psia). The preferred catalyst and reactor for the FT plant is precipitated iron catalyst with potassium and copper promoters in a slurry reactor. The catalyst mass concentration ratios in the slurry generally range from about 10 to about 20%, more preferably from about 10 to about 20% and most preferably about 15% (oxide basis) with a preferred catalyst size of about 30 μm. The space velocity is about 1.5 to about 6, preferably about 2 to about 5 and most preferably 2.5 normal liters syngas per hour per gram of catalyst.

The superficial velocity ranges from about 3 to about 30 and preferably from about 7.5 to about 12 cm/sec.

For methanol plants, syngas is generally compressed to about 1100 psig. The compressor of the methanol plant can be used to advantage for the FT retrofit, especially if the methanol plant is off-line or mothballed. The compressor after the reformer in Fig. 2 is one stage of the methanol plant compressor. It boosts the syngas from the reformer outlet from about 225 psig to about 500 psig. The benefit is three-fold. First, the back end of the plant operates more efficiently at higher pressure. Second, smaller vessels are required. Third, recycle loops are facilitated. For example, minimal compression of the tail gas is needed to recycle it to the reformer or to the first carbon dioxide absorber. The second compressor shown in Fig. 2 boosts the carbon dioxide pressure from the scrubber to the reformer inlet and can be another stage of the original methanol compressor. The FT product compressor 34, shown in Fig. 2, boots the tail gas pressure for the separator 33 to that of the CO_2 scrubber 29. The FT product compressor 34 can be another stage of methanol compressor 28.

CLAIMS

What is claimed is:

Claim 1. A reactor package for the production of methanol and/or FT products and hydrogen comprising

a syngas reformer having steam, lower molecular weight hydrocarbon and recycle CO_2 input piping; and output piping means for piping syngas product to a multi output valve;

a methanol plant having a syngas compressor piped to receive syngas from the multi output valve and to feed the compressed syngas into a methanol reactor, the methanol reactor having piping connected to deliver methanol to a distillation tower and the distillation tower having one or both of an exhaust flare and/or recycle piping to return at least one component of the exhaust to the syngas reformer; and

a FT reactor plant having at least one CO_2 scrubber and at least one H_2 scrubber for purifying the syngas received from the syngas reformer and piping directing the syngas stream from the multiproduct valve through the CO_2 at least one scrubber and the H_2 scrubber into the FT reactor, piping exhausting the FT reactor products into a product separator means to recover the FT products and further piping to conduct the FT reactor light gases to at least one of a flare to the reformer and to the FT reactor.

Claim 2.

The reactor package of Claim 1 wherein the reformer contains an alkali promoted nickel catalyst.

Claim 3.

The reactor package of Claim 2 wherein the catalyst usage permits a CO_2 feedstock having a molar of about 20% to about 40%.

Claim 4.

The reactor package of Claim 2 wherein the catalyst permits a CO_2 feedstock of about 30 to about 35%.

Claim 5.

The reactor package of Claim 2 wherein the reformer feedstock has a steam- to-carbon ratio of about 2.2:1.

Claim 6.

The reactor package of Claim 2 preconfigured to operate within a pressure drop range of about 50 to about 80 psi.

Claim 7.

The reactor package of Claim 6 preconfigured to operate within a pressure drop range of about 55 to about 65 psi.

Claim 8.

The reactor package of Claim 1 wherein the FT reactor contains a potassium and copper promoted precipitated iron catalyst of particle sizes of 0.5 to 1.00 microns.

Claim 9.

The reactor package of Claim 1 wherein the FT reactor contains a potassium and copper promoted precipitated iron catalyst of particle sizes of 2 to 6 microns.

Claim 10.

The plant of Claim 8 wherein the FT reactor contains an amount of catalyst during operation which ranges from about 10 to about 30% of the slurry by mass.

Claim 11.

The reactor of Claim 6 wherein the reactor is preconfigured to operate within a space velocity range of about 2.3 normal liters of syngas per hour per gram of catalyst.

Claim 12

The reactor of Claim 6 wherein the reactor is preconfigured to operate within a space velocity range of about 2.5 normal liters of syngas per hour per gram of catalyst.

Claim 13.

The reactor of Claim 6 including controllers to maintain a superficial throughput velocity ranging from about 5 to about 30 cm/sec.

Claim 14.

The reactor of Claim 6 including controllers to maintain a superficial throughput velocity ranging from about 5 to about 7.5 cm/sec.

Claim 15.

A multi-purpose plant package which includes a methanol plant and a FT plant utilizing a shared reformer comprising:

feedstock plumbing means for introducing at least steam and substantially hydrocarbon feedstocks into the syngas reformer;

reformer means for producing syngas;

multi-purpose valve means; plumbed to the reformer, to a syngas compressor, and to a CO_2 scrubber; for controlling the flow of syngas from the reformer to the methanol plant and to the FT plant;

a syngas compressor, plumbed to the methanol reactor means, for conveying compressed syngas to the methanol reactor means, to a CO2 scrubber and to receive gaseous FT product from the FT product separator;

methanol reactor means, plumbed to a distillation tower, for separating methanol and by-products;

CO_2 means for removing CO_2 from the syngas plumbed to a hydrogen separator means;

hydrogen separator means, plumbed to FT reactor means, for removing hydrogen from the syngas;

FT reactor means, plumbed to an FT reactor product separator means, for converting syngas to FT products; and

FT product separator means for separating FT gas, liquid and solid products.

Claim 16.

The multi-purpose plant package of Claim 15 further including plumbing means for transferring gaseous FT products from the FT reactor product separator means to a FT reactor product compressor for transferring the FT product to the CO_2 scrubber.

Claim 17.

The multi-purpose plant package of Claim 15 further including plumbing means for transferring compressed CO_2 from the CO_2 scrubber to the CO_2

recycle compressor and further including plumbing and a CO_2 compressor means for returning compressed CO_2 to the reformer means.

Claim 18.

A process for operating a multiple process, multiple product chemical plant for the production of methanol and/or FT products and hydrogen comprising:

introducing into a syngas reformer a sweet lower molecular hydrocarbon feedstock and water, reacting the feedstock and water utilizing a commercial nickel catalyst to produce a syngas stream containing CO_2 and H_2 and introducing air and the compressed syngas into a methanol reactor to form a methanol stream, and removing CO_2 and hydrogen to produce higher purity syngas, CO_2 and H_2 streams;

segregating the CO_2 for recycle to the gaseous FT product compressor means and/or for other usage;

segregating the H_2 for recycle to the syngas reformer and/or other usage;

introducing the syngas stream into a FT reactor and producing FT solids, liquids and gases and segregating the FT products.

Claim 19. All inventions taught herein.

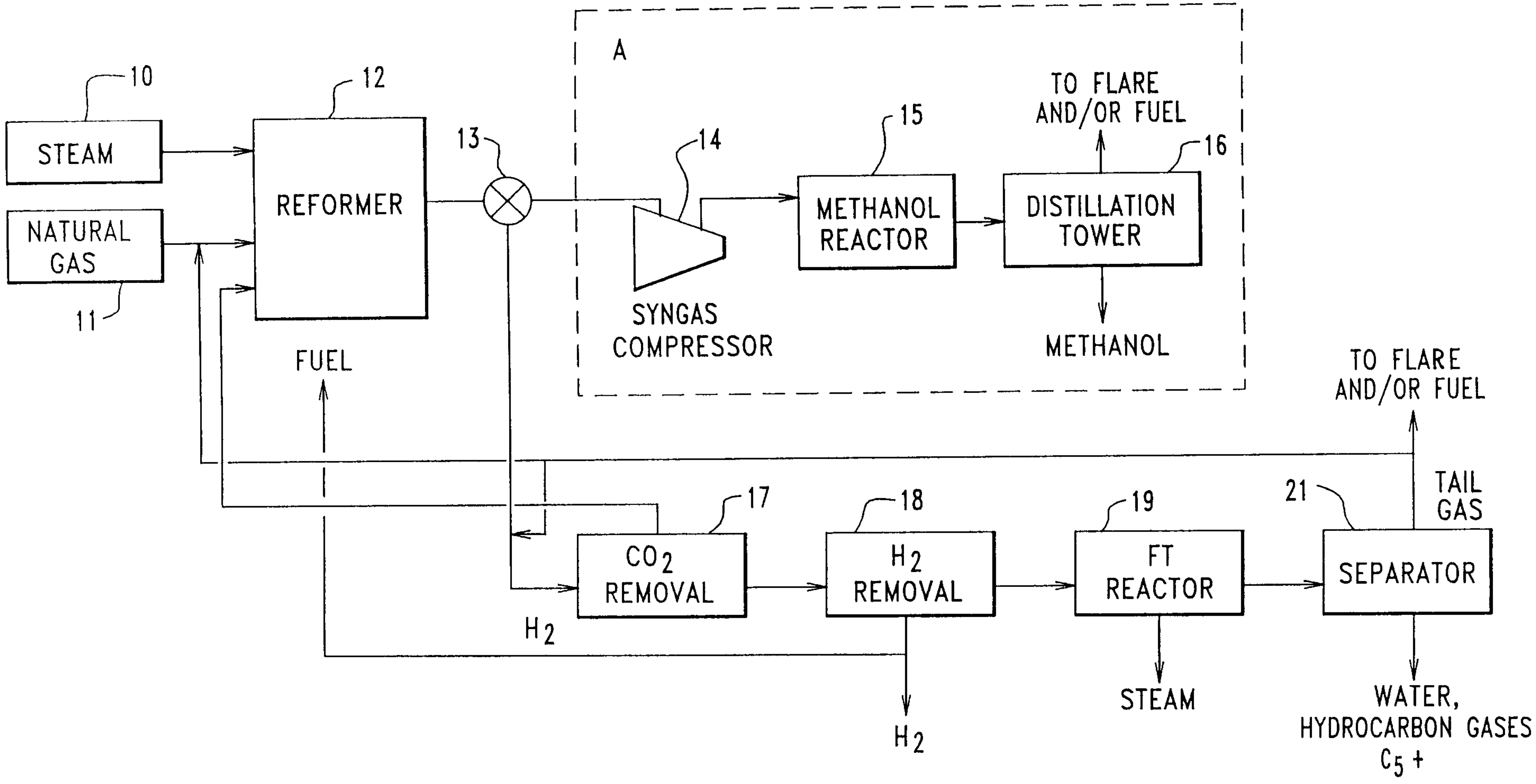
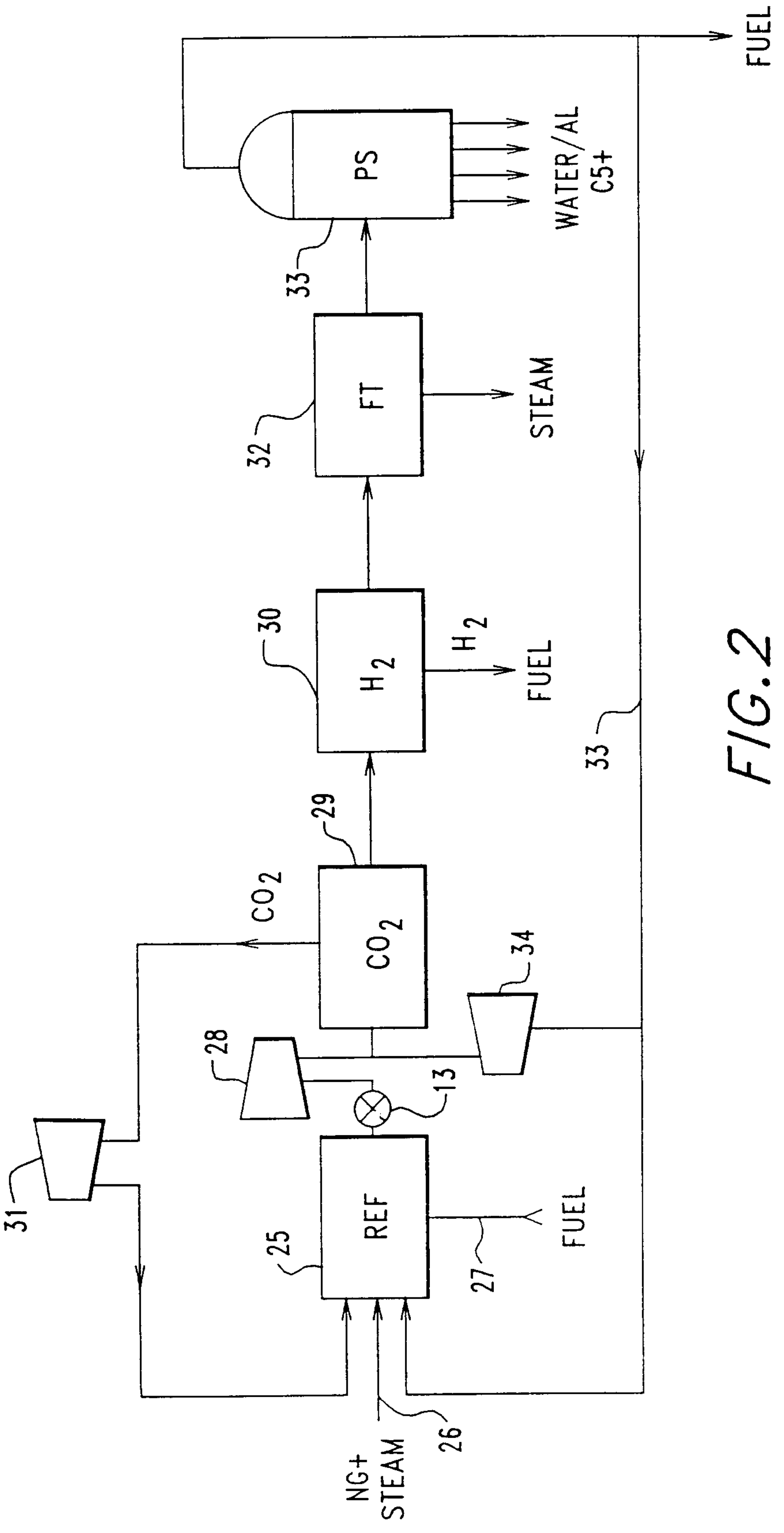

10
STEAM
NATURAL GAS
11
12
REFORMER
FUEL
13
A
14
SYNGAS COMPRESSOR
15
METHANOL REACTOR
16
DISTILLATION TOWER
TO FLARE AND/OR FUEL
METHANOL
17
CO_2 REMOVAL
H_2
18
H_2 REMOVAL
H_2
19
FT REACTOR
STEAM
21
SEPARATOR
TAIL GAS
TO FLARE AND/OR FUEL
WATER, HYDROCARBON GASES C_5 +

FIG. 1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H$_2$
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FUEL
FT
32
STEAM
PS
33
WATER/AL
C5+
FUEL
33

FIG. 2

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 00/12808

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C10G2/00 C07C31/04 C07C1/04

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C07C C10G

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

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

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 178 007 A (SHELL INT RESEARCH) 16 April 1986 (1986-04-16) claims 1,5,12 page 5, line 23 - line 28 -----	1,15,18, 19

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

☒ Patent family members are listed in annex.

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INTERNATIONAL SEARCH REPORT

Information on patent family members

Int ..ional Application No
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