

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
26 February 2009 (26.02.2009)

PCT

(10) International Publication Number
WO 2009/026090 A1

(51) International Patent Classification:

C10L 3/10 (2006.01) **C10K 1/34** (2006.01)
C10K 1/14 (2006.01)

(21) International Application Number:

PCT/US2008/073128

(22) International Filing Date: 14 August 2008 (14.08.2008)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:

60/956,505 17 August 2007 (17.08.2007) US

(71) Applicant (for SM only): **SHELL OIL COMPANY**
[US/US]; One Shell Plaza, P.O. Box 2463, Houston, Texas
77252-2463 (US).

(71) Applicant (for all designated States except US): **SHELL
INTERNATIONALE RESEARCH MAATSCHAPPIJ
B.V.** [NL/NL]; Carel van Bylandtlaan 30, NL-2596 HR The
Hague (NL).

(72) Inventors; and

(75) Inventors/Applicants (for US only): **RIPPERGER,
Gary Lee** [US/US]; 16439 Willingham Way, Houston,

Texas 77095 (US). **TREYBIG, Michael Norris** [US/US];
4200 Scotland, Apt. 73, Houston, Texas 77001 (US).

(74) Agent: **STEWART, Charles W.**; Shell Oil Company, One
Shell Plaza, P.O. Box 2463, Houston, Texas 77252-2463
(US).

(81) Designated States (unless otherwise indicated, for every
kind of national protection available): AE, AG, AL, AM,
AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA,
CH, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE,
EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID,
IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK,
LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW,
MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL, PT,
RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TJ,
TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM,
ZW.

(84) Designated States (unless otherwise indicated, for every
kind of regional protection available): ARIPO (BW, GH,
GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM,
ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM),
European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI,
FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MT, NL,
NO, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG,
CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

— with international search report

(54) Title: A PROCESS FOR REMOVING SULFUR FROM A FUEL GAS STREAM ADDITIONALLY CONTAINING DI-
OLEFINS AND OXYGEN

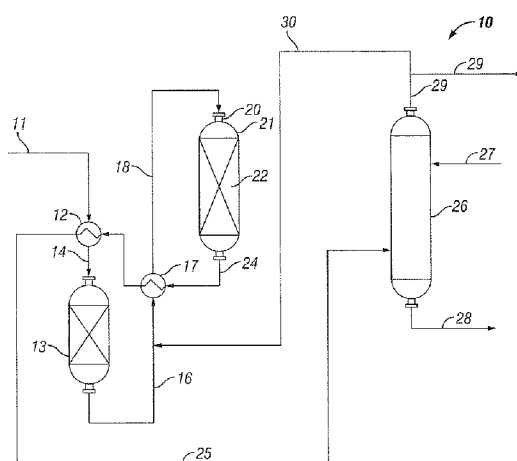


FIG. 1

(57) Abstract: Disclosed is a process for the removal of sulfur from a fuel gas stream that additionally contains diolefins and oxygen as well as organic sulfur compounds by pretreating the fuel gas stream in a pretreatment reactor in order to significantly reduce the amounts of any diolefins and oxygen contained therein prior to the hydrosulfurization in a hydrotreater reactor wherein organic sulfur compounds are converted to hydrogen sulfide. The hydrogen sulfide formed is removed from the hydrotreated gas stream by use of an absorption treatment method, such as amine treatment, to yield a treated fuel gas stream having a reduced concentration of hydrogen sulfide and an overall sulfur content that is low enough to meet stringent sulfur regulation requirements.

WO 2009/026090 A1

**A PROCESS FOR REMOVING SULFUR FROM A FUEL GAS STREAM
ADDITIONALLY CONTAINING DIOLEFINS AND OXYGEN**

5 This invention relates to a process for removing sulfur from a fuel gas stream additionally containing diolefins and oxygen.

 There are presently federal regulations that impose certain maximum total sulfur concentration limits on refinery
10 fuel gas streams and there is a trend in certain states and municipalities toward the imposition of even more stringent sulfur requirements for these streams. Among the various approaches that are useful in removing sulfur from refinery fuel gas streams to meet the sulfur regulations, caustic
15 scrubbing and absorption methods are typically used. However, with the significantly lower limits that are being placed on the amount of total sulfur that may be contained within a refinery fuel gas stream, these methods tend to be unsuitable for providing treated refinery fuel gas streams that meet the
20 lower sulfur concentration requirements. Certain of the refinery fuel gas streams such as a coker unit dry gas or a fluid catalytic cracking unit gas can contain concentrations of certain sulfur compounds that are difficult to acceptably be removed there from by traditional caustic or absorption
25 scrubbing and other methods to the lower sulfur concentration levels required by the newer regulations.

 One inventive process proposed for use in the removal of sulfur from fuel gas streams that contain organic sulfur and significant concentrations of light olefins is that as
30 described and claimed in U. S. provisional application no. 60/911,422, filed 12 April 2007, entitled "A Process for Removing Sulfur From a Fuel Gas Stream," which application is incorporated herein by reference. In this process, highly reactive fuel gas streams that contain significant amounts of

light olefin compounds are processed by a catalytic hydrotreating method. The disclosure recognizes the highly exothermic nature of the olefin hydrogenation reaction and notes that it is this attribute of the olefin saturation
5 reaction that causes problems with the hydrotreating of olefin-containing fuel gas streams such as those found in crude oil refinery processes.

The aforementioned provisional application also discloses an inventive process for the hydrotreating of the
10 refinery fuel gas streams that are yielded from the numerous process units of a crude oil refinery. While these refinery fuel gas streams typically contain organic sulfur and olefins, a number of them also contain small concentrations of diolefins and oxygen. The presence of diolefins and oxygen
15 is problematic since diolefins and oxygen can react to form peroxides, which can polymerize, resulting in fouling in the hydrotreater reactor. Diolefins can also react to form polymers that can also cause fouling in the hydrotreater reactor. Additionally, oxygen can also react with hydrogen
20 sulfide to produce water vapor and elemental sulfur. The sulfur that is produced from this reaction can also foul equipment and catalyst in the hydrotreater reactor.

To address the problem associated with the hydrotreating of an organic sulfur compound-containing fuel gas stream that
25 additionally contains diolefins and oxygen, it would be desirable to have a process that effectively removes organic sulfur from such a fuel gas stream with a reduced risk of reactor fouling due to polymer formation or the formation of elemental sulfur. The present invention provides such a
30 process.

Accordingly, provided is a process for removing sulfur from a fuel gas stream that additionally contains diolefins and oxygen as well as organic sulfur compounds, wherein said

process comprises: introducing said fuel gas stream into a pretreatment reactor wherein it is contacted with hydrogen in the presence of a catalyst under conditions that the diolefins contained in said fuel gas stream are substantially converted to olefins and the oxygen contained in said fuel gas stream is substantially converted to water vapor; introducing said fuel gas stream reduced in diolefins and oxygen from the pretreatment reactor into a hydrotreater reactor containing a hydrotreating catalyst, wherein said fuel gas stream is contacted under hydrodesulfurization process conditions with hydrogen in the presence of said hydrotreating catalyst, wherein organic sulfur compounds are substantially converted to hydrogen sulfide; and treating said hydrotreated fuel gas to remove hydrogen sulfide therefrom thereby yielding a treated fuel gas stream having a reduced concentration of hydrogen sulfide and organic sulfur compounds. By "substantial conversion" of diolefins to olefins in the pretreatment reactor is meant a conversion of at least 50 %, preferably a conversion of at least 70 %, and most preferably a conversion of at least 99 %. . By "substantial conversion" of oxygen to water vapor in the pretreatment reactor is meant a conversion of at least 50 %, preferably a conversion of at least 60 %, and most preferably a conversion of at least 99 %.

FIG. 1 is a process flow schematic that presents one or more embodiments of the inventive process for removing organic sulfur from a fuel gas stream that contains diolefins and oxygen in addition to organic sulfur compound compounds.

The invention relates to the processing of a fuel gas stream that contains concentrations of organic sulfur, diolefins and oxygen, by pretreating the fuel gas stream in a pretreatment reactor in order to significantly reduce the amounts of any diolefins and oxygen that are contained

therein prior to the primary hydrotreating reaction which converts organic sulfur to hydrogen sulfide. In the context of a crude oil refinery, hydrotreating is proposed as a means for removing organic sulfur from one or more refinery fuel
5 gas streams followed by the use of an absorption treatment method, such as amine treatment, to thereby remove the hydrogen sulfide from the hydrotreated fuel gas stream to yield a treated fuel gas stream having a reduced concentration of hydrogen sulfide and an overall sulfur
10 content that is low enough to meet many of the more stringent sulfur regulation requirements.

The fuel gas stream of the inventive process, in addition to organic sulfur compounds, will contain a concentration of at least one diolefin and may also contain a
15 concentration of oxygen. As noted earlier herein, the presence of diolefins and oxygen in a fuel gas stream that contains organic sulfur compounds can cause the undesirable formation of polymers which can foul heat exchange equipment and the hydrotreating reactor when the fuel gas stream is
20 hydrotreated by contacting it under hydrodesulfurization process conditions with a hydrotreating catalyst.

The amounts of organic sulfur compounds, diolefins and oxygen present in the fuel gas stream can vary widely depending upon the particular source of the fuel gas. But,
25 typically, the diolefin concentration of the fuel gas stream of the inventive process will be in the range of from 2 ppmv to 2.0 vol %, more typically, in the range of from 5 ppmv to 1.5 vol %, and most typically in the range of from 10 ppmv to 1.0 vol%. Typically, if oxygen is present in the fuel gas
30 stream, it will be present in the range of from 10 ppmv to 5.0 vol %, more typically from 100 ppmv to 3.0 vol %, and most typically from 150 ppmv to 1.5 vol %

The organic sulfur compounds that can be present in the fuel gas stream can include organic sulfur compounds that include thiol compounds, thiophene compounds, disulfide compounds and carbonyl sulfide. The thiol compounds can
5 include one or more of the various aliphatic mercaptans, such as, for example, methyl mercaptan, ethyl mercaptan, propyl mercaptan, butyl mercaptan, and amyl mercaptan, and aromatic mercaptans, such as, for example, phenyl mercaptan. The thiopheneic compounds can include thiophene and any of the
10 benzothiophenes and substituted thiophenes.

The concentration of the mercaptans in the fuel gas stream is generally in the range upwardly to 5000 ppmv (0.5 volume percent of the fuel gas stream). But, for the inventive process, the mercaptan concentration in the fuel
15 gas stream to be treated will, typically, be more than 20 ppmv and in the range of from 20 ppmv to 3000 ppmv. More typically, the mercaptan concentration is in the range of from 40 ppmv to 2000 ppmv, and, most typically, from 45 ppmv to 1500 ppmv.

20 The organic sulfur compounds that include thiophenes, organic disulfides and carbonyl sulfide are the more difficult compounds to remove from a fuel gas stream by use of conventional sulfur removal methods. The concentration of the these organic sulfur compounds in the fuel gas stream of
25 the inventive process can, collectively, be in the range of from 1 ppmv to 500 ppmv, but, typically, the collective concentration of these organic sulfur compounds will be in the range of from 2 to 300 ppmv, and, more typically, from 3 to 200 ppmv. The specific concentration of the carbonyl
30 sulfide in the fuel gas stream can be upwardly to 500 ppmv, and, more typically, from 1 to 300 ppmv.

The total concentration of all the organic sulfur compounds, including thiol compounds, thiophene compounds,

disulfide compounds and carbonyl sulfide, contained in the fuel gas stream of the inventive process is, typically, in the range of from 40 ppmv to 5000 ppmv. More typically, the total concentration of all the organic sulfur compounds
5 contained in the fuel gas stream to be treated is in the range of from 45 ppmv to 3000 ppmv, and, most typically, from 50 ppmv to 2000 ppmv.

The fuel gas stream treated by the inventive process will typically also contain light olefins, the amount of
10 which will vary depending upon the particular source or sources of the fuel gas stream. The concentration of light olefins can range from as low as 0.1 vol %, upwardly to 50 volume percent (%) of the fuel gas stream. For instance, an FCC dry gas will contain significantly higher quantities of
15 light olefins as compared to fuel gas streams from other sources, but, typically, the light olefin concentration of the fuel gas stream of the inventive process will be in the range of from 0.1 vol % to 45 vol %, more typically, from 0.5 vol % to 40 vol %, and, most typically, from 1 vol % to 30
20 vol %.

The inventive process is particularly useful in the processing of refinery fuel gas streams that are produced from any one or more of the numerous process units of a crude oil refinery. These refinery streams may separately be
25 introduced into the pretreatment reactor and hydrotreater reactor of the inventive process, or they may be combined in any manner and by any means and introduced as one or more combined feeds into the pretreatment reactor and hydrotreater reactor. Typical refinery gas streams that can be feed
30 streams to the pretreatment reactor and hydrotreater reactor of the inventive process are those generated by a delayed coker unit, such as the coker dry gas and coker propylene vapor, a fluid catalytic cracking unit, such as the FCC dry

gas, a flare gas recovery system, tank vents, and vapor overheads from crude unit atmospheric and vacuum towers. The gas streams yielded from these process units can have significant concentrations of organic sulfur compounds. The types and concentrations of the organic sulfur compounds are as previously described in detail herein. Many of these refinery gas streams will also have concentrations of diolefins and may have a concentration of oxygen. Among the refinery gas streams believed to have concentrations of diolefins and oxygen include those from such refinery units as a fluid catalytic cracking unit, a delayed coker unit, and vapor and flare gas recovery systems. Typical diolefin compounds found in these streams include propadiene, butadiene and pentadienes.

15 An additional characteristic of the refinery fuel gas streams is that they can include significant concentration levels of light or lower olefin compounds, such as ethylene, propylene, butenes and pentenes. More typically, the lower olefin compounds contained in the refinery fuel gas streams of the inventive process include those selected from the group consisting of ethylene, propylene, butylenes and any combination thereof. Typical concentration ranges for these light olefins in the refinery gas streams are as previously described herein.

25 In addition to organic sulfur compounds, diolefins, oxygen and light olefins, the fuel gas streams that can be treated in accordance with the invention may also contain carbon dioxide and carbon monoxide. The presence of carbon dioxide in the fuel gas stream can result in the undesirable formation of carbonyl sulfide (COS) in addition to the hydrogenation conversion of the organic sulfur that is contained in the fuel gas to hydrogen sulfide. This occurs as a result of the equilibrium reaction that takes place within

the hydrotreater reactor between hydrogen sulfide and carbon dioxide to yield carbonyl sulfide and water, which reaction is represented as follows: $\text{H}_2\text{S} + \text{CO}_2 = \text{COS} + \text{H}_2\text{O}$. The formation of the carbonyl sulfide is undesirable because it is more difficult to remove from gas streams by the use of standard amine treatment methods than is hydrogen sulfide.

Therefore, in one embodiment of the inventive process involving a fuel gas stream additionally containing carbon dioxide and/or carbon monoxide, the fuel gas stream is first subjected to a pretreatment reaction to convert diolefins to olefins and oxygen to water vapor, and is then subjected to hydrodesulfurization in a hydrotreater reactor producing hydrogen sulfide and COS, and the hydrotreated fuel gas stream is subsequently subjected to a hydrolysis or catalytic reduction step in order to reduce the COS concentration in the hydrotreated fuel stream prior to the removal of hydrogen sulfide by amine treatment or other means. A suitable process for the catalytic reduction of COS, including suitable catalysts and process conditions, is described in U.S. Application No.60/940,211, filed 25 May, 2007, entitled "A Process for Removing Sulfur from a Fuel Gas Stream Additionally Containing Carbon Dioxide and Light Olefins", which application is incorporated herein by reference.

In accordance with the process of the present invention, the fuel gas stream containing diolefins and oxygen as well as organic sulfur compounds is contacted with hydrogen in the presence of a catalyst in a pretreatment reactor under relatively mild conditions, resulting in the conversion of diolefins to olefins and the conversion of oxygen to water vapor.

Any suitable catalyst, including conventional hydrotreating catalysts, capable of converting diolefins to olefins and oxygen to water vapor, can be used in the

pretreatment reactor. Typically such catalysts will include one or more active metal components on a support material. The metal component can include a Group VIB metal component or a Group VIII metal component, or both metal components. It is preferred for the catalyst to comprise both a Group VIB metal component and a Group VIII metal component. The catalyst in the pretreatment reactor can also include a promoter such as a phosphorous component.

The Group VIII metal component of the catalyst in the pretreatment reactor is selected from those Group VIII metal or metal compounds that, in combination with the other components of the catalyst composition, suitably provide a catalyst. The Group VIII metal can be selected from the group consisting of nickel, cobalt, palladium and platinum. Preferably, the Group VIII metal is either nickel or cobalt and, most preferably, the Group VIII metal is cobalt.

The Group VIII metal component contained in the catalyst composition can be in the elemental form or in the form of a metal compound, such as, for example, oxides, sulfides and the like. The amount of Group VIII metal in the catalyst composition can be in the range of from about 0.1 to about 6 weight percent elemental metal based on the total weight of the catalyst composition. Preferably, the concentration of Group VIII metal in the catalyst composition is in the range of from 0.3 weight % to 5 weight %, and, most preferably, the concentration is in the range of from 0.4 weight % to 4.5 weight %.

The Group VIB metal component of the catalyst composition is selected from those Group VIB metal or metal compounds that, in combination with the other elements of the catalyst composition, suitably provide a catalyst. The Group VIB metal can be selected from the group consisting of chromium, molybdenum and tungsten. The preferred Group VIB

metal is either molybdenum or chromium and, most preferred is molybdenum.

The Group VIB metal component contained in the catalyst composition can be in the elemental form or in the form of a metal compound, such as, for example, oxides, sulfides and the like. The amount of Group VIB metal in the catalyst composition can be in the range of from about 2 to about 25 weight percent elemental metal based on the total weight of the catalyst composition. Preferably, the concentration of Group VIB metal in the catalyst composition is in the range of from 4 weight % to 18 weight %, and, most preferably, the concentration is in the range of from 5 weight % to 16 weight %.

The support material of the hydrotreating catalyst can be any material that suitably provides a support for the metal hydrogenation components of the hydrotreating catalyst including porous refractory oxides. Examples of possible suitable porous refractory oxides include silica, magnesia, silica-titania, zirconia, silica-zirconia, titania, titania-alumina, zirconia-alumina, silica-titania, alumina, silica-alumina, and alumino-silicate. The alumina can be of various forms, such as, alpha alumina, beta alumina, gamma alumina, delta alumina, eta alumina, theta alumina, boehmite, or mixtures thereof. The preferred porous refractory oxide is amorphous alumina. Among the available amorphous aluminas, gamma alumina is most preferred. The porous refractory oxide generally has an average pore diameter in the range of from about 30 Angstroms to about 500 Angstroms, preferably, from 50 Angstroms to 400 Angstroms, and, most preferably, from 60 Angstroms to 300 Angstroms. The total pore volume of the porous refractory oxide, as measured by standard mercury porosimetry methods, is in the range of from about 0.2 cc/gram to about 2 cc/gram. Preferably, the pore volume is in

the range of from 0.3 cc/gram to 1.5 cc/gram, and, most preferably, from 0.4 cc/gram to 1 cc/gram. The surface area of the porous refractory oxide, as measured by the B.E.T. method, generally exceeds about 50 m²/gram, and it is
5 typically in the range of from about 100 to about 500 m²/gram.

A preferred catalyst for use in the pretreatment reactor is a catalyst comprising cobalt/molybdenum on an alumina support. A particularly preferred catalyst comprises from 3
10 to 4 weight % cobalt, 13 to 14 weight % molybdenum on an alumina support having a surface area of approx. 240 m²/gram and a pore volume of approx. 0.53 cc/gram.

The temperature and pressure conditions within the pretreatment reactor are controlled so as to provide suitable
15 conditions for the hydrogenation of diolefins and oxygen contained in the fuel gas stream introduced into the pretreatment reactor. The contacting temperature in the pretreatment reactor should be "relatively mild". By "relatively mild" is meant a temperature in the general range
20 of from 150 °F (65.6 °C) to 400 °F (204.4 °C), preferably, from 250 °F (121.1 °C) to 350 °F (176.7 °C), and, most preferably, from 300 °F (148.9 °C) to 350 °F (176.7 °C). As for the contacting pressure in the pretreatment reactor, it should generally in the range of from 30 psig to 1000 psig,
25 preferably, from 50 psig to 400 psig, and, most preferably, from 70 psig to 300 psig. The flow rates at which the fuel gas stream is charged to the pretreatment reactor of the inventive process are generally such as to provide a gaseous hourly space velocity (GHSV) in the range of from 0.01 hr⁻¹
30 to 6000 hr⁻¹. The term "gaseous hourly space velocity," as used herein, means the numerical ratio of the rate at which the fuel gas stream, including added hydrogen, if any, that is charged to the pretreatment reactor in volume (at standard

temperature and pressure conditions) per hour divided by the volume of hydrotreating catalyst contained in the pretreatment reactor to which the fuel gas stream is charged. The preferred GHSV in the pretreatment reactor is the range
5 of from 0.05 hr^{-1} to 4000 hr^{-1} , more preferably, from 100 hr^{-1} to 3500 hr^{-1} , and, most preferably, from 500 hr^{-1} to 3200 hr^{-1} .

After substantial removal of olefins and oxygen in the pretreatment reactor, the fuel gas stream depleted in
10 diolefins and oxygen is passed to a hydrotreater reactor, which includes a reactor vessel that defines a volume and in which is contained one or more beds of hydrotreating catalyst. The fuel gas stream is introduced into the hydrotreater reactor wherein it is contacted with hydrogen in
15 the presence of a hydrotreating catalyst as hereafter described. The reaction conditions within the reactor vessel are maintained at hydrodesulfurization conditions in order to promote the catalytic conversion of the organic sulfur compounds to hydrogen sulfide. A hydrotreater reactor
20 effluent, or hydrotreated fuel gas, leaving the hydrotreater reactor will have a hydrogen sulfide concentration and may also have a carbonyl sulfide concentration, depending on whether carbon dioxide was present in the feed gas stream to the hydrotreater reactor as discussed above.

25 Any suitable hydrogenation catalyst, including conventional hydrotreating catalysts that comprise a metal component on a support material, can be used in one or more beds in the hydrotreater reactor. The metal component can include a Group VIB metal component or a Group VIII metal
30 component, or both metal components. It is preferred for the hydrotreating catalyst to comprise both a Group VIB metal component and a Group VIII metal component. The hydrotreating

catalyst can also include a promoter such as a phosphorous component.

The Group VIII metal component of the hydrotreating catalyst composition is selected from those Group VIII metal or metal compounds that, in combination with the other components of the catalyst composition, suitably provide a hydrotreating catalyst. The Group VIII metal can be selected from the group consisting of nickel, cobalt, palladium and platinum. Preferably, the Group VIII metal is either nickel or cobalt and, most preferably, the Group VIII metal is cobalt.

The Group VIII metal component contained in the hydrotreating catalyst composition can be in the elemental form or in the form of a metal compound, such as, for example, oxides, sulfides and the like. The amount of Group VIII metal in the hydrotreating catalyst composition can be in the range of from about 0.1 to about 6 weight percent elemental metal based on the total weight of the hydrotreating catalyst composition. Preferably, the concentration of Group VIII metal in the hydrotreating catalyst composition is in the range of from 0.3 weight % to 5 weight %, and, most preferably, the concentration is in the range of from 0.4 weight % to 4.5 weight %.

The Group VIB metal component of the hydrotreating catalyst composition is selected from those Group VIB metal or metal compounds that, in combination with the other elements of the hydrotreating catalyst composition, suitably provide a hydrotreating catalyst. The Group VIB metal can be selected from the group consisting of chromium, molybdenum and tungsten. The preferred Group VIB metal is either molybdenum or chromium and, most preferred, is molybdenum.

The Group VIB metal component contained in the hydrotreating catalyst composition can be in the elemental

form or in the form of a metal compound, such as, for example, oxides, sulfides and the like. The amount of Group VIB metal in the hydrotreating catalyst composition can be in the range of from about 2 to about 25 weight percent
5 elemental metal based on the total weight of the hydrotreating catalyst composition. Preferably, the concentration of Group VIB metal in the hydrotreating catalyst composition is in the range of from 6 weight % to 18 weight %, and, most preferably, the concentration is in the
10 range of from 7 weight % to 16 weight %.

The support material of the hydrotreating catalyst can be any material that suitably provides a support for the metal hydrogenation components of the hydrotreating catalyst including porous refractory oxides. Examples of possible
15 suitable porous refractory oxides include silica, magnesia, silica-titania, zirconia, silica-zirconia, titania, titania-alumina, zirconia-alumina, silica-titania, alumina, silica-alumina, and alumino-silicate. The alumina can be of various forms, such as, alpha alumina, beta alumina, gamma alumina,
20 delta alumina, eta alumina, theta alumina, boehmite, or mixtures thereof. The preferred porous refractory oxide is amorphous alumina. Among the available amorphous aluminas, gamma alumina is most preferred.

The porous refractory oxide generally has an average
25 pore diameter in the range of from about 30 Angstroms to about 500 Angstroms, preferably, from 50 Angstroms to 400 Angstroms, and, most preferably, from 60 Angstroms to 300 Angstroms. The total pore volume of the porous refractory oxide, as measured by standard mercury porosimetry methods,
30 is in the range of from about 0.2 cc/gram to about 2 cc/gram. Preferably, the pore volume is in the range of from 0.3 cc/gram to 1.5 cc/gram, and, most preferably, from 0.4 cc/gram to 1 cc/gram. The surface area of the porous

refractory oxide, as measured by the B.E.T. method, generally exceeds about 50 m²/gram, and it is typically in the range of from about 100 to about 500 m²/gram.

The temperature and pressure conditions within the
5 hydrotreater reactor vessel are controlled so as to provide suitable hydrodesulfurization reaction conditions for the hydrogenation of the organic sulfur compounds contained in the fuel gas stream introduced into the hydrotreater reactor vessel. The contacting temperature should generally be in the
10 range of from 230 °C (446 °F) to 480 °C (896 °F), preferably, from 255 °C (491 °F) to 450 °C (842 °F), and, most preferably, from 238 °C (460 °F) to 430 °C (806 °F). As for the contacting pressure, it should generally in the range of from 30 psig to 1000 psig, preferably, from 50 psig to 500 psig, and, most
15 preferably, from 70 psig to 400 psig.

The flow rates at which the fuel gas stream is charged to the hydrotreater reactor vessel of the inventive process are generally such as to provide a gaseous hourly space velocity (GHSV) in the range of from 0.01 hr⁻¹ to 6000 hr⁻¹.
20 The term "gaseous hourly space velocity," as used herein, means the numerical ratio of the rate at which the fuel gas stream, including added hydrogen, if any, that is charged to the hydrotreater reactor vessel in volume (at standard temperature and pressure conditions) per hour divided by the
25 volume of hydrotreating catalyst contained in the hydrotreating reactor vessel to which the fuel gas stream is charged. The preferred GHSV is in the range of from 0.05 hr⁻¹ to 4000 hr⁻¹, more preferably, from 0.1 hr⁻¹ to 3500 hr⁻¹, and, most preferably, from 0.2 hr⁻¹ to 3200 hr⁻¹.

30 As a result of the hydrodesulfurization reactions of the hydrotreating step, the hydrotreated fuel gas that exits the hydrotreater reactor will have a significantly reduced organic sulfur concentration that is below the organic sulfur

concentration of the fuel gas stream that is introduced as a feed to the hydrotreater reactor for hydrodesulfurization. But, the hydrotreated fuel gas will also contain an amount of hydrogen sulfide that needs to be removed therefrom in order
5 to ultimately provide a treated fuel gas stream that has a reduced concentration of hydrogen sulfide that is low enough to comply with regulations regarding sulfur concentration limits for fuel gas streams that are to be combusted. One method for removing the hydrogen sulfide from the
10 hydrotreated fuel gas stream is by use of any suitable method or means of absorption treating that utilizes an amine absorbent.

As discussed above, one problem with the use of amine absorption techniques in the removal of the hydrogen sulfide
15 from the hydrotreated fuel gas of the inventive process is that the hydrotreated fuel gas also can have a concentration of carbonyl sulfide which is difficult to remove by the use of standard amine absorption techniques.

In the embodiment of the present invention involving a
20 hydrolysis or catalytic reduction step, the hydrotreated fuel gas is introduced into a hydrolysis reactor that contains a hydrolysis or reduction catalyst. Within the hydrolysis reactor, the hydrotreated fuel gas is contacted with a reducing compound, under suitable hydrolysis reaction
25 conditions, in the presence of a hydrolysis catalyst. The hydrolysis reaction includes the reaction of carbonyl sulfide with a reducing compound, such as, water, carbon monoxide, and hydrogen, to yield at least hydrogen sulfide. The hydrolysis reactor effluent, thus, contains a reduced
30 concentration of carbonyl sulfide and is yielded from the hydrolysis reactor. Suitable hydrolysis reaction conditions and hydrolysis catalysts are described in U.S. Application

No. 60/940,211, mentioned above, and incorporated herein by reference.

Because of the heat released from the hydrogenation reactions within the hydrotreater reactor, the hydrotreated
5 fuel gas stream will have a temperature that is significantly higher than the temperature of the fuel gas stream that is introduced into the hydrotreater reactor at the hydrotreater reactor inlet. As already noted, in those embodiments of the invention having a hydrolysis reactor, it is desirable for
10 the hydrotreated fuel gas stream to be cooled prior to its introduction into the hydrolysis reactor. This cooling can be done by any suitable method or means known to those skilled in the art, but it is preferred to recover a portion of the heat that is released by the hydrogenation reactions in the
15 hydrotreater reactor and contained in the hydrotreated fuel gas stream by exchanging heat energy contained therein with at least a portion of the fuel gas stream that is introduced into the pretreatment reactor and/or hydrotreater reactor. This may be accomplished by the use of a feed/effluent heat
20 exchanger that provides heat exchange means for exchanging heat energy between at least a portion of the fuel gas stream feed into the pretreatment reactor and/or hydrotreater reactor and at least a portion of the hydrotreated fuel gas stream, to thereby provide the hydrotreated fuel gas stream
25 having a desired hydrolysis reactor inlet temperature and a fuel gas stream having a desired pretreatment reactor inlet temperature and/or a desired hydrotreater reactor inlet temperature.

The hydrolysis reactor effluent can further be treated
30 to remove the hydrogen sulfide therefrom by the use of any suitable means or method for reducing the hydrogen sulfide content of the hydrolysis reactor effluent, or portions thereof, so as to provide a treated fuel gas stream having a

reduced concentration of hydrogen sulfide that, generally, is less than 100 ppmv. It is, however, desirable to provide a treated fuel gas stream that has a hydrogen sulfide concentration of less than 80 ppmv, and, more desirably, the hydrogen sulfide concentration of the treated fuel gas stream is less than 60 ppmv. It is especially desirable for the treated fuel gas stream to have a hydrogen sulfide concentration of less than 40 ppmv, and, more especially, less than 10 ppmv. This reduced concentration of hydrogen sulfide provides a treated fuel gas that will meet most of the more stringent sulfur regulations and that has a suitably low hydrogen sulfide concentration such that it may be combusted or burned in typical combustion devices or means for combusting or burning treated fuel gas. Examples of such combustion means include the burners that are used in refinery heaters, furnaces, flares, and other equipment.

A preferred method of treating the hydrotreater reactor effluent (or hydrolysis reactor effluent in those embodiments of the invention having a hydrolysis reactor), is to remove the hydrogen sulfide by the use of traditional absorption scrubbing of the gas stream to remove the hydrogen sulfide contained therein. This is done by contacting the hydrotreater reactor effluent or hydrolysis reactor effluent, or a portion thereof, with a suitable absorbent and yielding a treated fuel gas having the reduced concentration of hydrogen sulfide and the absorbent that is rich in hydrogen sulfide. Among the absorption processes that may suitably be used to treat the hydrolysis reactor effluent, amine treating is preferred. Amine treating includes the use of any known amine absorbent, such as, for example, monoethanolamine (MEA), diethanolamine (DEA), methyldiethanolamine (MDEA), diisopropylamine (DIPA), and diglycolamine (DGA).

In one embodiment of the invention, a feature is provided to address certain of the problems associated with the hydrotreating of refinery gas streams that contain high concentrations of light olefins and the high heat release
5 resulting therefrom. It has been determined that either a portion of the treated fuel gas stream (or the hydrolysis reactor effluent in embodiments of the invention having a hydrolysis reactor), can be combined with the refinery gas stream that is charged to the hydrotreater reactor to serve
10 as a diluent to help in the control of the temperature across the hydrotreater reactor. The use of the treated fuel gas stream for recycle or as a diluent is preferable, since this stream will have very little, if any, hydrogen sulfide and carbon dioxide because of their removal by the amine
15 treatment. Use of a stream with little or no hydrogen sulfide or carbon dioxide is preferable, in view of the tendency of these compounds to push the equilibrium reaction toward making carbonyl sulfide.

Reference is now made to the process flow schematic of
20 FIG. 1, which includes for illustrative purposes various embodiments of the inventive process. Depicted in FIG.1 is a fuel gas treating process 10 for the removal of sulfur from a fuel gas stream that additionally contains diolefins and oxygen as well as organic sulfur compounds. The fuel gas
25 stream containing added hydrogen is passed by way of conduit 11 into a heat exchanger 12. The heat exchanger 12 provides for a heated fuel gas stream that passes from heat exchanger 12 to pretreatment reactor 13 by way of conduit 14. The feed gas stream depleted in diolefins and oxygen leaves the
30 pretreatment reactor via conduit 16 and passes through heat exchanger 17 and conduit 18 and is introduced into hydrotreater reactor 21 through reactor inlet 20. The hydrotreater reactor 21 defines a hydrotreater reactor volume

in which is contained a bed of hydrotreating catalyst 22 over which the fuel gas stream is passed and whereby it is contacted with hydrogen under hydrodesulfurization process conditions. A hydrotreated fuel gas that contains hydrogen sulfide is yielded from the hydrotreater reactor 21 as a hydrotreater reactor effluent stream by way of conduit 24.

As a result of the hydrogenation reactions that take place in the hydrotreater reactor 21, the hydrotreated fuel gas has a hydrotreater reactor effluent temperature that is greater than the hydrotreater reactor inlet temperature. One way of recovering this heat of reaction from the hydrotreater effluent is to use the heat exchangers 12 and 17 as feed/effluent exchangers. In this embodiment effluent from the hydrotreater reactor 21 containing hydrogen sulfide and a reduced concentration of organic sulfur compounds passes through heat exchangers 12 and 17 into absorption unit 26 by way of conduits 24 and 25. The absorption unit 26 provides for the removal of hydrogen sulfide that is contained in the hydrotreater reactor effluent by contacting it with a suitable absorbent fluid. A lean absorbent fluid is introduced to the absorption unit 26 through conduit 27 and a rich absorbent fluid containing hydrogen sulfide that is removed from the hydrotreater reactor effluent passes from absorption unit 26 by way of conduit 28. A treated fuel gas having a significantly reduced concentration of hydrogen sulfide passes from the absorption unit 26 by way of conduit 29 to any suitable combustion device or means (not shown) for burning or combusting the treated fuel gas, such as, for example, burners that are used in refinery heaters, furnaces, flares and other equipment.

In cases of fuel gas streams additionally containing carbon dioxide and/or carbon monoxide, the effluent from the hydrotreater reactor may in addition to hydrogen sulfide also

contain carbonyl sulfide. In this embodiment, the effluent from the hydrotreater reactor would be passed into a hydrolysis reactor (not shown) to catalytically reduce the carbon disulfide, prior to being introduced into absorption unit 26.

Various recycle streams may be used to control and improve upon the hydrodesulfurization conditions within the hydrotreater reactor 21. For example, a portion of the treated fuel gas stream may be recycled and used as either a diluent to be combined with the fuel gas stream that is charged to the hydrotreater reactor 21 or as a quench stream that is introduced directly into the hydrotreater reactor 21. FIG. 1 shows a portion of the treated fuel gas stream exiting absorption unit through conduit 29 passing by way of conduit 30 to be combined with the fuel gas stream entering hydrotreater reactor 21 via conduits 16 and 18.

In embodiments having a hydrolysis reactor, the effluent from the hydrolysis reactor can also be used for recycle or as a diluent. However, because the treated fuel gas stream has had a significant portion of the hydrogen sulfide and carbon dioxide removed therefrom by the absorption unit 26, it is preferred to use the treated fuel gas stream as a recycle stream or as a diluent.

25

C L A I M S

1. A process for removing sulfur from a fuel gas stream that additionally contains diolefins and oxygen as well as organic
5 sulfur compounds, wherein said process comprises:

introducing said fuel gas stream into a pretreatment reactor wherein it is contacted with hydrogen in the presence of a catalyst under conditions that the diolefins contained in said fuel gas stream are substantially converted to
10 olefins and the oxygen contained in said fuel gas stream is substantially converted to water vapor;

introducing said fuel gas stream depleted in diolefins and oxygen into a hydrotreater reactor wherein said fuel gas stream is contacted with hydrogen in the presence of a
15 hydrotreating catalyst under hydrodesulfurization process conditions, yielding from said hydrotreater reactor a hydrotreated fuel gas containing hydrogen sulfide; and

treating said hydrotreated fuel gas to remove hydrogen sulfide therefrom, thereby yielding a treated fuel gas stream
20 having a reduced concentration of hydrogen sulfide and organic sulfur compounds.

2. The process of claim 1, wherein the fuel gas stream comprises from 2 ppmv to 2.0 vol % diolefins and from 10 ppmv
25 to 5.0 vol % oxygen, and wherein the pretreatment reactor inlet temperature is less than the hydrotreater reactor inlet temperature.

3. The process of claim 1 or 2, wherein the catalyst used in
30 the pretreatment reactor comprises from 0.3 to 5 weight % of a Group VIII metal and from 4 to 18 weight % of a Group VIB metal.

4. The process of claim 1, 2 or 3, wherein the temperature in pretreatment reactor is in the range of from 150°F to 400°F and the pressure in the pretreatment reactor is in the range 30 psig to 1000 psig.
- 5
5. The process of claim 1, 2, 3 or 4 wherein the hydrogen sulfide is removed from the hydrotreated fuel gas by utilizing an amine absorbent.
- 10 6. The process of claim 1, 2, 3, 4 or 5, wherein the hydrogen sulfide concentration in said treated fuel gas stream is less than 100 ppmv.
7. The process of claim 3, 4, 5 or 6, wherein the Group VIII
15 metal is cobalt and the Group VIB metal is molybdenum.
8. The process of any one of claims 1-7, wherein the hydrogen sulfide concentration in said treated fuel gas is less than 60 ppmv.
- 20
9. The process of any one of claims 1-8, wherein a portion of said treated fuel gas is recycled and combined with the fuel gas stream entering said hydrotreater reactor.
- 25 10. The process of any one of claims 1-9, wherein the hydrogen sulfide concentration in said treated fuel gas is less than 40 ppmv.
11. The process of any one of claims 1-10, wherein said fuel
30 gas stream additionally contains carbon dioxide and carbon monoxide, and wherein said hydrotreated fuel gas containing hydrogen sulfide and carbon disulfide is introduced into a hydrolysis reactor containing a hydrolysis catalyst to reduce

the carbonyl sulfide concentration in the hydrotreated fuel gas prior to treatment with an amine absorbent to remove hydrogen sulfide.

- 5 12. The process of any one of claims 1-11, wherein the temperature in pretreatment reactor is in the range of from 300°F to 350°F and the pressure in the pretreatment reactor is in the range 70 psig to 300 psig.
- 10 13. The process of any one of claims 1-12, wherein the hydrogen sulfide concentration in said treated fuel gas is less than 10 ppmv.
14. The process of any one of claims 3-13, wherein the
- 15 catalyst in the pretreatment reactor comprises 0.4 to 4.5 weight % cobalt and 5 to 16 weight % molybdenum on an alumina support.
15. The process of any one of claims 1-14, wherein a portion
- 20 of the heat that is released by the hydrogenation reactions in the hydrotreater reactor is recovered by exchanging the heat energy contained the hydrotreater reactor effluent with at least a portion of the fuel gas stream that is introduced into the pretreatment reactor or the hydrotreater reactor.
- 25 16. The process of any one of claims 1-15, wherein at least 70 % of the diolefins in said fuel gas stream are converted to olefins and at least 60 % of the oxygen in said fuel gas stream is converted to water vapor.
- 30 17. The process of any one of claims 1-16, wherein the fuel gas stream comprises from 5 ppmv to 1.5 vol % diolefins and from 100 ppmv to 3.0 vol % oxygen.

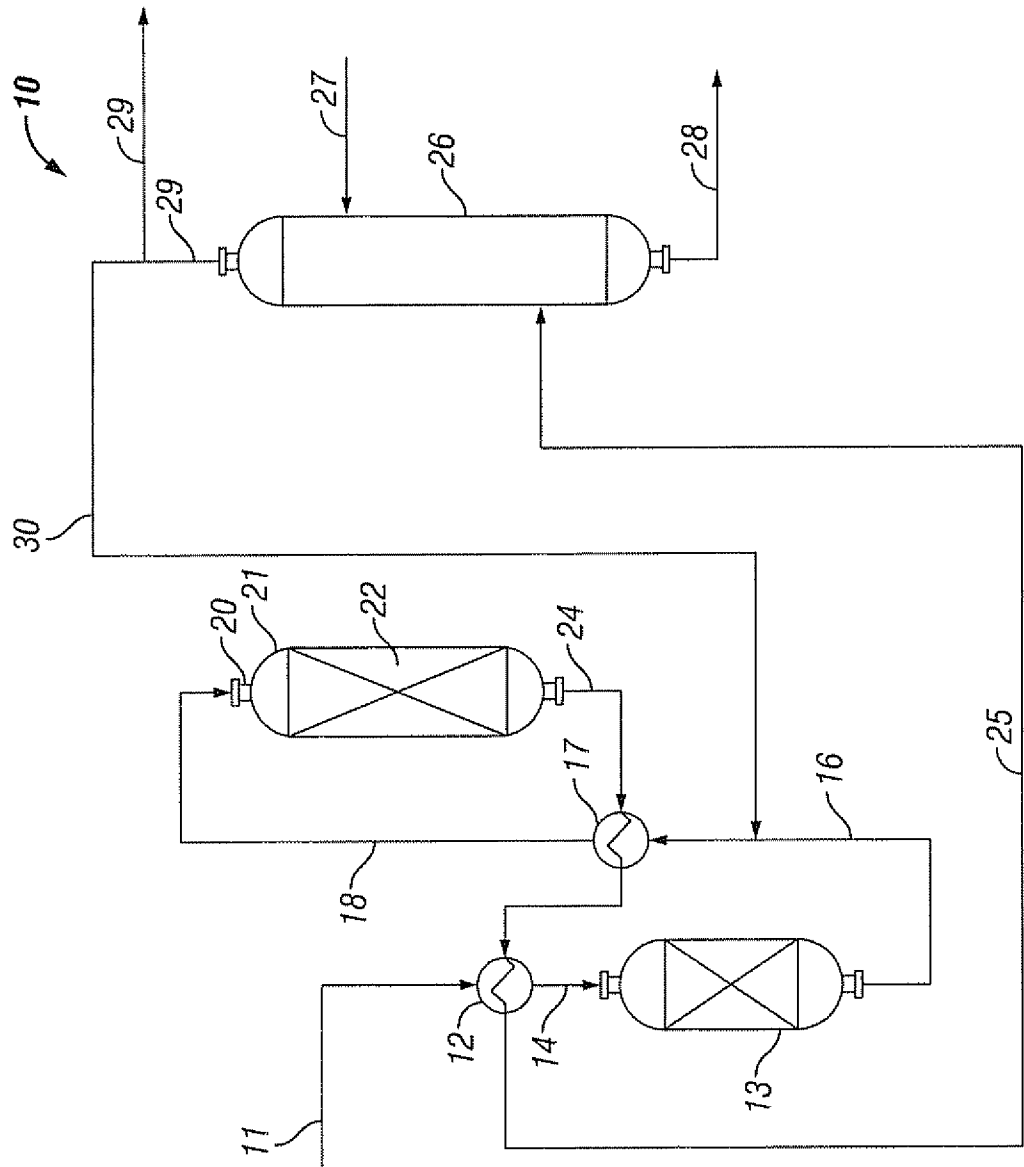


FIG. 1

INTERNATIONAL SEARCH REPORT

International application No

PCT/US2008/073128

A. CLASSIFICATION OF SUBJECT MATTER

INV. C10L3/10 C10K1/14 C10K1/34

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)

C10L C10K

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.
X	DATABASE WPI Week 198640 Thomson Scientific, London, GB; AN 1986-261044 XP002497645 & JP 61 188492 A (HITACHI LTD) 22 August 1986 (1986-08-22)	1-4, 6-8, 10, 12-14, 16, 17
Y	page 519, column 2; figure 2; example s	5, 9, 11, 15
Y	----- WO 98/07502 A (SHELL INT RESEARCH [NL]) 26 February 1998 (1998-02-26) page 5, line 6 - line 31 page 6, line 1 - page 8, line 32 page 9, line 27 - page 10, line 1 page 13, line 10 - line 26 page 14, line 33 - page 16, line 10; claim 1 ----- -/--	5, 9, 11, 15

☒ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents:

A document defining the general state of the art which is not considered to be of particular relevance

E earlier document but published on or after the international filing date

L document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

O document referring to an oral disclosure, use, exhibition or other means

P document published prior to the international filing date but later than the priority date claimed

T later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

X document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

Y document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

G document member of the same patent family

Date of the actual completion of the international search

29 September 2008

Date of mailing of the international search report

14/10/2008

Name and mailing address of the ISA/

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040,
Fax: (+31-70) 340-3016

Authorized officer

Pöllmann, Klaus

INTERNATIONAL SEARCH REPORT

International application No

PCT/US2008/073128

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	EP 0 140 191 A (FORD BACON & DAVIS INC [US]; UNION CARBIDE CORP [US]) 8 May 1985 (1985-05-08) page 17, line 10 - line 19; figure 1; example 1 -----	5, 9, 11, 15
Y	DATABASE WPI Week 199204 Thomson Scientific, London, GB; AN 1992-029845 XP002497646 & JP 03 277695 A (KAWASAKI STEEL CORP) 9 December 1991 (1991-12-09) abstract & JP 03 277695 A (KAWASAKI STEEL CORP) 9 December 1991 (1991-12-09) -----	9, 15
Y	MOELLER F W ET AL: "Methanation of coal gas for SNG" HYDROCARBON PROCESSING, GULF PUBLISHING CO. HOUSTON, US, vol. 53, 1 January 1974 (1974-01-01), pages 69-74, XP008096221 ISSN: 0018-8190 page 71, column 2, line 33 - page 72, column 1, line 20; figure 4 -----	9, 15

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2008/073128

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
JP 61188492	A	22-08-1986	JP 1754223 C	23-04-1993
			JP 4041197 B	07-07-1992
WO 9807502	A	26-02-1998	AT 208227 T	15-11-2001
			AU 710859 B2	30-09-1999
			AU 4457197 A	06-03-1998
			BR 9711322 A	17-08-1999
			CA 2263579 A1	26-02-1998
			CN 1230134 A	29-09-1999
			CZ 9900553 A3	12-01-2000
			DE 69708119 D1	13-12-2001
			DE 69708119 T2	06-06-2002
			DK 920351 T3	25-02-2002
			ES 2169428 T3	01-07-2002
			HU 9903150 A2	28-02-2000
			JP 2000516530 T	12-12-2000
			NO 990795 A	19-02-1999
			NZ 334727 A	29-09-2000
			PL 331847 A1	16-08-1999
			PT 920351 T	28-03-2002
			RU 2177361 C2	27-12-2001
			TR 9900356 T2	21-05-1999
			TW 438620 B	07-06-2001
			ZA 9707495 A	03-03-1998
EP 0140191	A	08-05-1985	CA 1221223 A1	05-05-1987
			JP 60097028 A	30-05-1985
JP 3277695	A	09-12-1991	NONE	