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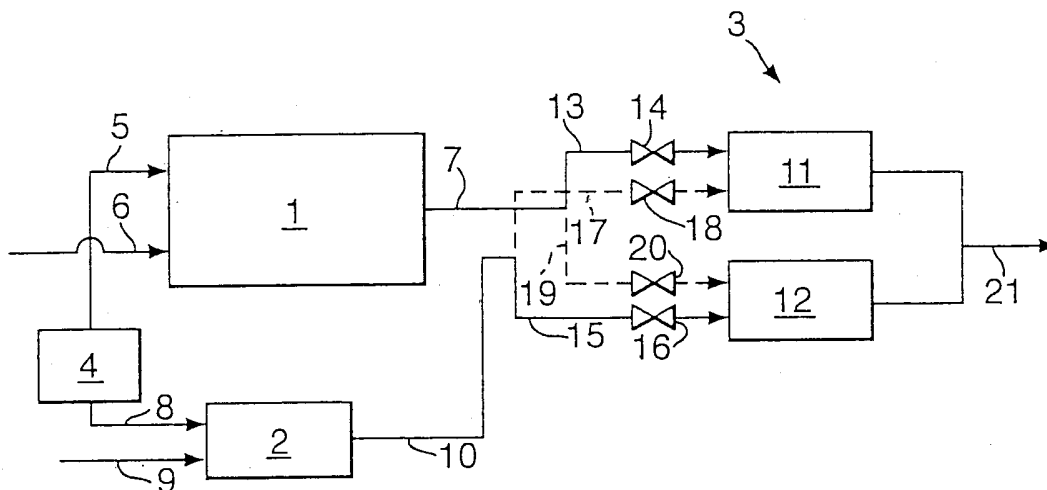
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(54) Title: REFORMING OF GTL FOR MARINE APPLICATIONS



(57) Abstract: A process for operating a marine engine (1) in combination with a catalytic partial oxidation reformer (2) and, optionally, an exhaust gas aftertreater (3), wherein: (a) a mixture of a first fuel and air, is introduced in the combustion chamber of the engine (1); (b) exhaust gas is discharged from the engine and optionally partly recirculated to the combustion chamber of the engine (1); (c) a second fuel and oxygen and/or steam are supplied to the catalytic partial oxidation reformer (2) to produce synthesis gas, wherein the second fuel comprises Fischer-Tropsch derived fuel; (d) at least part of the synthesis gas is supplied to: (i) the exhaust gas aftertreater (3); (ii) the combustion chamber of the engine (1); or to both.

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## REFORMING OF GTL FOR MARINE APPLICATIONS

Field of the Invention

The present invention relates to a process for operating a marine vessel in conjunction with a catalytic partial oxidation reformer and/or a NO<sub>x</sub> abatement system

5 Background of the Invention

It is now recognised emissions from marine vessels or ships in inland waterways and coastal areas can be a significant contribution to air quality. Marine engines can be electric engines, spark ignition engines,  
10 compression ignition engines or turbines. Ships in the context of the present invention are to include all floating objects.

In order to reduce NO<sub>x</sub> emissions of marine engines, NO<sub>x</sub> reducing exhaust gas treatment systems have been  
15 developed. These NO<sub>x</sub> reducing systems typically comprise a NO<sub>x</sub> reducing catalyst.

In US 5,412,946 for example, a NO<sub>x</sub> reducing catalyst comprising Pt on zeolite have been described. Such a catalyst promote the reduction of NO<sub>x</sub> to nitrogen in the  
20 presence of a reducing compound. It has been described in the art to use hydrocarbons, hydrogen or synthesis gas as reducing compound for this type NO<sub>x</sub> reducing catalyst.

NO<sub>x</sub> reducing systems that comprise both a deNO<sub>x</sub> catalyst and a NO<sub>x</sub> sorbent are also known in the art. For  
25 example from US 5,874,057, US 5,473,887 and WO 01/34950. During lean operation, NO<sub>x</sub> is absorbed from the exhaust gas; during richer operation, the sorbent is regenerated and the catalyst promotes reduction of NO<sub>x</sub> to nitrogen.

It is disclosed that the exhaust gas can periodically be made richer (less oxygen) by adding fuel, hydrogen or synthesis gas to the lean exhaust gas.

5 An alternative method to reduce emissions of compression ignition internal combustion engines is by means of a process known in the art as fumigation. In a fumigation process, a gaseous fuel is mixed with the intake air of the engine prior to introducing the air/gaseous fuel mixture into the engine cylinder. Both 10 diesel fuel and the air/gaseous fuel mixture are introduced into the engine. Known gaseous fuels for fumigation are for example natural gas, liquefied petroleum gas (LPG), and hydrogen gas.

15 Another method for reducing emissions, especially  $\text{NO}_x$ , in an internal combustion engine is by exhaust gas recirculation (EGR).  $\text{NO}_x$  emissions are reduced with the increase of exhaust gas recirculation. A high level of recirculation, however, can result in poor combustion. Various ways have been reported in the art by which 20 recirculated exhaust gas may be enriched. In L.K.S Teo et al. "Hydrogen and Biodiesel Mixtures as Fuels for the Compression Ignition Engine" Proceedings of the THIESEL 2002 Conference on Thermo- and Fluid-Dynamic Processes in Diesel Engines, Birmingham, for example, the addition of 25 hydrogen to recirculated exhaust gas has been described.

In order to ensure compliance with future limits on marine emissions there is a need to further reduce emissions, in particular the emission of nitrogen oxides.

Summary of the Invention

30 It has now been found that, for marine engines, emissions can be further reduced by using a fuel comprising a Fischer-Tropsch derived hydrocarbon stream as engine fuel in combination with the use of synthesis

gas derived from a fuel comprising Fischer-Tropsch fuel for advanced aftertreatment of the exhaust gas and/or advanced operation of the marine engine.

Accordingly, the present invention relates to a  
5 process for operating a marine engine in combination with a catalytic partial oxidation reformer and, optionally, an exhaust gas aftertreater, wherein:

(a) a mixture of a first fuel and air, is introduced in the combustion chamber of the engine;

10 (b) exhaust gas is discharged from the engine and optionally partly recirculated to the combustion chamber of the engine;

(c) a second fuel and oxygen and/or steam are supplied to the catalytic partial oxidation reformer to produce  
15 synthesis gas, wherein the second fuel comprises Fischer-Tropsch derived fuel;

(d) at least part of the synthesis gas is supplied to:

(i) the exhaust gas aftertreater;

(ii) the combustion chamber of the engine; or to both.

20 Brief Description of the Drawings

Different embodiments of the invention are described in detail and by way of example with reference to schematic Figures 1 to 4.

Figure 1 shows a process according to the invention  
25 wherein synthesis gas is supplied to a NO<sub>x</sub> abatement system.

Figure 2 shows a process according to the invention wherein synthesis gas is supplied to the combustion chamber of the engine.

30 Figure 3 shows a process according to the invention wherein synthesis gas is supplied to the combustion chamber of the engine together with recirculated exhaust gas.

Figure 4 shows a process according to the invention wherein synthesis gas is supplied to both a NO<sub>x</sub> abatement system and a solid oxide fuel cell.

Detailed Description of the Invention

5 In the process according to the present invention, a marine engine is operated in combination with a catalytic partial oxidation reformer. Reference herein to a catalytic partial oxidation reformer is to a catalytic reaction zone for steam reforming, autothermal reforming  
10 or partial oxidation of a hydrocarbon fuel to form synthesis gas, i.e. a gas mixture containing hydrogen and carbon oxides. These reactions are described in more detail in the art, for example in Fuel Chemistry Division Reprints 2002, 47(2), 542.

15 The reformer produces synthesis gas that is used for operating the compression ignition internal combustion engine in such way that emissions are reduced.

The second fuel, i.e. the fuel for the reformer, comprise Fischer-Tropsch derived fuel. By "Fischer-Tropsch derived" is meant that the fuel is, or derives  
20 from, a synthesis product of a Fischer-Tropsch condensation process. The Fischer-Tropsch reaction converts carbon monoxide and hydrogen into longer chain, usually paraffinic, hydrocarbons :

25 
$$n(\text{CO} + 2\text{H}_2) = (-\text{CH}_2-)_n + n\text{H}_2\text{O} + \text{heat},$$

in the presence of an appropriate catalyst and typically at elevated temperatures and/or pressures.

The fuel may be obtained directly from the Fischer-Tropsch reaction, or indirectly for instance by  
30 fractionation of a Fischer-Tropsch synthesis product or from a hydrotreated Fischer-Tropsch synthesis product. Hydrotreatment can involve hydrocracking to adjust the boiling range (see, e.g. GB-B-2077289 and EP-A-0147873)

and/or hydroisomerisation which can improve cold flow properties by increasing the proportion of branched paraffins. EP-A-0583836 describes a two-step hydrotreatment process in which a Fischer-Tropsch  
5 synthesis product is firstly subjected to hydroconversion under conditions such that it undergoes substantially no isomerisation or hydrocracking (this hydrogenates the olefinic and oxygen-containing components), and then at least part of the resultant product is hydroconverted  
10 under conditions such that hydrocracking and isomerisation occur to yield a substantially paraffinic hydrocarbon fuel. The desired fuel fraction(s) may subsequently be isolated for instance by distillation.

Other post-synthesis treatments, such as  
15 polymerisation, alkylation, distillation, cracking-decarboxylation, isomerisation and hydroreforming, may be employed to modify the properties of Fischer-Tropsch condensation products, as described for instance in US-A-4125566 and US-A-4478955.

20 Preferably, the same fuel is used for the engine and for the reformer, i.e. the first fuel and the second fuel are the same. This has the advantage that only one fuel storage tank is needed to provide fuel to both the engine and the reformer. However it is also envisaged that the  
25 marine engine is operated using a conventional marine diesel fuel as the first fuel and the reformer is run on the preferred Fischer-Tropsch derived fuel as the second fuel.

30 The use of Fischer-Tropsch derived fuel in a marine engine has several advantages. These fuels are highly paraffinic and thus have a high cetane number when the engine is a compression ignition engine. Also, there fuels have a low sulphur content, thereby reducing the

risk of sulphur poisoning of any catalytic system. Moreover, these fuels are inherently clean and thus result in lower emissions of particles (soot), NO<sub>x</sub>, hydrocarbons and carbon monoxide. Reference is made in this respect to R.H. Clark et al. "The Environmental Benefits of Shell GTL Diesel", Proceedings of the 4<sup>th</sup> Int. Fuels Colloquium, 15-16 January 2003, Tech. Akad. Esslingen, Germany. Furthermore Fischer-Tropsch derived fuel is biodegradable and non-toxic and hence a relatively benign actor in the aquatic environment. This makes the use of said fuel in environmental sensitive areas very attractive. Examples of such areas are nature reserves, harbours and fishing grounds.

It is known, for example from WO 99/19249, that Fischer-Tropsch derived fuels are very suitable fuels for catalytic reformers. We have demonstrated that Fischer-Tropsch derived diesel and other Fischer-Tropsch derived streams are particularly suitable for reforming because they are paraffinic and sulphur-free. See for example SAE paper 2004-01-1926. An advantage of Fischer-Tropsch derived fuels over conventional internal combustion fuels in reformers is its cleanliness (no sulphur and reduced soot formation).

In order to benefit from these properties, both the first fuel and the second fuel comprise preferably at least 10% (v/v) of Fischer-Tropsch derived fuel, more preferably at least 50% (v/v), even more preferably at least 80% (v/v), still more preferably consist of substantially only Fischer-Tropsch derived fuel.

The marine engine may be a spark ignition engines, compression ignition engines or turbines. Preferably the marine engine is a marine compression ignition engine. It will be appreciated that the first fuel as such has to be



suitable for compression ignition internal combustion engines. Thus, the first fuel has to meet the requirements for fuels for such engines, such as cetane number, flash point, total aromatics content, total sulphur content, as well as the specifications relating to the distillation curve and to the cold flow properties of the fuel. Therefore, the part of the first fuel or the entire first fuel that is not a Fischer-Tropsch derived fuel is preferably a diesel base fuel, such as petroleum derived gasoil, optionally in combination with oxygenates such as alcohols or fatty acid methyl esters and conventional diesel fuel additives. It has been found that less additives are needed in a fuel for a compression ignition internal combustion engine, if part of the fuel is a Fischer-Tropsch derived fuel. This implies that if the first and the second fuel are the same, the reformer is also fed with a fuel that has less additives as compared to a conventional diesel fuel. This is advantageous since some diesel additives could negatively affect the catalyst stability.

The Fischer-Tropsch derived fuel is preferably a gasoil, i.e. the fraction that is boiling in the gasoil boiling range suitably boiling substantially between 170 and 380 °C. By boiling substantially in said boiling range is here meant that more than 95 vol% of the fuel boils between 170 and 380 °C.

In the process according to the invention, the engine exhaust emissions are further reduced by using synthesis gas for advanced aftertreatment and/or advanced engine operation. Such further reductions may be achieved by supplying synthesis gas to an exhaust gas aftertreater, for example a NO<sub>x</sub> abatement system, and/or to the combustion chamber of the engine.

The synthesis gas is produced in a catalytic partial oxidation reformer. The reaction that takes place in the reformer may be steam reforming, partial oxidation, autothermal reforming or a combination thereof. Suitable catalysts and reaction conditions for such reformers are known in the art. The fuel is reacted with water (steam reforming), oxygen (partial oxidation) or both (autothermal reforming or partial oxidation). Preferably, the reaction is partial oxidation or autothermal reforming, since no external heat source is needed to maintain these reactions.

Air will typically be used as oxygen source for the reformer. Alternatively, exhaust gas from the engine may be used as source for oxygen and/or steam. If exhaust gas is used as steam source for the reformer, the exhaust gas may be introduced as such in the reformer or water may be condensed out of the exhaust gas before being introduced in the reformer.

In one aspect of the invention, exhaust gas of the engine (i.e. the part of the exhaust gas that is not recirculated to the combustion chamber of the engine and not fed to the reformer) is supplied to a NO<sub>x</sub> abatement system. At least part of the synthesis gas produced is also supplied to the NO<sub>x</sub> abatement system.

The NO<sub>x</sub> abatement system preferably comprises a NO<sub>x</sub> trap, which trap comprises a NO<sub>x</sub> reducing catalyst and a NO<sub>x</sub> sorbent. Such NO<sub>x</sub> traps are known in the art, for example from WO 01/34950 and US 5,473,887. A typical example of a suitable NO<sub>x</sub> trap is the combination of platinum on an alumina support as catalyst and barium oxide as sorbent. In one embodiment of the invention, the NO<sub>x</sub> abatement system comprises a single NO<sub>x</sub> trap. The NO<sub>x</sub>

trap is continuously supplied with exhaust gas and intermittently supplied with synthesis gas. During the period that only exhaust gas is supplied to the NO<sub>x</sub> trap, NO<sub>x</sub> is absorbed on the sorbent, for example as Ba(NO<sub>3</sub>)<sub>2</sub> if the trap comprises a BaO sorbent. During the period that exhaust gas and synthesis gas are supplied to the NO<sub>x</sub> trap, the trap is regenerated and the catalyst promotes reduction of NO<sub>x</sub> to nitrogen.

In another embodiment of the invention, the NO<sub>x</sub> abatement systems comprises two NO<sub>x</sub> traps as described hereinbefore. The two traps are operated in a so-called swing mode. One trap is supplied with exhaust gas and absorbs NO<sub>x</sub> (absorption mode) and the other trap is supplied with synthesis gas and desorps NO<sub>x</sub> that is reduced to nitrogen (regeneration mode) and vice versa. Each trap is thus alternately supplied with exhaust gas and synthesis gas. An advantage of this swing mode operation as compared to the above-described operation of a single trap is that the regeneration is performed in the absence of oxygen, resulting in a more efficient regeneration.

A specific advantage of the use of Fischer-Tropsch derived fuel in both the engine and the reformer is that the fuel contains no sulphur and thus, the exhaust gas and the synthesis gas will contain less sulphur oxides. Sulphur oxides can strongly adsorb on a NO<sub>x</sub> trap and thus have a negative effect on the performance of such trap.

In still another embodiment, the NO<sub>x</sub> abatement system, comprises a NO<sub>x</sub> reducing catalyst without a NO<sub>x</sub> sorbent. Such NO<sub>x</sub> abatement systems are known in the art. Typically, such systems comprises a platinum supported on a zeolite. Exhaust gas and synthesis gas are

simultaneously supplied to the catalyst. The catalyst promotes the reduction of NO<sub>x</sub> to nitrogen; the synthesis gas acts as reducing agent.

5 In a second aspect of the invention, at least part of the synthesis gas is supplied to the combustion chamber of the engine. In one embodiment (fumigation), synthesis gas is supplied to the combustion chamber by mixing it with the intake air prior to introducing the air to the combustion chamber. In an alternative embodiment  
10 (enriched EGR), synthesis gas is added to recirculated exhaust gas and together they are supplied to the combustion chamber.

In the fumigation embodiment, it may be necessary to ensure that the synthesis gas concentration in the intake  
15 air stream is below the flammability limit. Further, it will be appreciated that one should take care that the overall fuel-to-air ratio is optimised - wherein fuel is defined as first fuel plus synthesis gas supplied to the combustion chamber. Preferably, the amount of synthesis  
20 gas supplied to the combustion chamber of the engine is such that the volumetric ratio of synthesis gas-to-first fuel that is supplied to the combustion chamber is at most 25%, more preferably at most 20%.

If synthesis gas and recirculated exhaust gas are  
25 together supplied to the combustion chamber (enriched EGR), the volumetric ratio of 'combined synthesis gas plus exhaust gas' to 'first fuel' supplied to the combustion chamber is preferably at most 25%. The combined synthesis gas plus exhaust gas is usually  
30 admitted to the combustion chamber through a special valve.

The introduction of part of the synthesis gas into the combustion chamber (fumigation or enriched EGR) may

be combined with synthesis gas assisted aftertreatment, such as the above-described synthesis gas assisted NO<sub>x</sub> abatement.

5 The invention is also directed to a method of regeneration of the marine NO<sub>x</sub> abatement system by directly by contacting the Fischer-Tropsch derived fuel with the NO<sub>x</sub> abatement system catalyst. This to either regenerate a system for NO<sub>x</sub> storage or to perform direct selective catalytic reduction. Applicants found that this  
10 method of regenerating may also find use in NO<sub>x</sub> abatement systems other than marine NO<sub>x</sub> abatement systems. Examples of such other systems are for example the systems used in automotive applications.

15 In the process according to the invention, at least part of the synthesis gas produced is used for advanced aftertreatment or advanced engine operation. Additionally, part of the synthesis gas may be supplied to a fuel cell for electricity generation. In this way, it is possible to provide a marine vessel with on-board  
20 electricity generation. The thus-obtained electricity may for example be applied for auxiliary power, e.g. for air conditioning, or for advanced valve control. The fuel cell can be a solid oxide fuel cell or a molten carbonate fuel cell Alternatively the syngas can be processed  
25 further to make a hydrogen rich stream suitable for a low temperature fuel cell, for example a Proton Exchange Membrane system.

30 In a final embodiment of the invention the electricity could be used directly to power the vessel via an electric propulsion system. The electric propulsion system is suitable present on-board the ship as auxiliary propulsion power means, for example in addition to a spark ignition engine, a compression

ignition engine or a turbine engine. The quiet operation of the vessel and the benign nature of the fuel make this an ideal combination in environmentally sensitive areas.

The invention is also directed to sailing vessels  
5 provided with means to generate electricity using a fuel cell. Preferably the fuel cell is a solid oxide fuel cell or a molten carbonate fuel cell. Said fuel cell operates using synthesis gas as prepared according the above methods. Such a vessel is advantageous because, in this  
10 way, it is possible to provide a sailing vessel with on-board electricity generation, while not having to use the main propulsion engine, for example the compression ignition internal combustion marine engine. This is advantageous because the latter engine makes noises and  
15 causes vibrations on board the sailing vessel, which are not desired during sailing. The thus-obtained electricity may for example be applied for auxiliary power, e.g. for navigation equipment, refrigerators, audio equipment, hair dryers and other equipment which run on electricity and which may be found on board of, luxury, sailing  
20 yachts.

In some regatta situations sailing vessels are not allowed to use their main compression ignition internal combustion for obvious reasons. However electricity  
25 generation is then often a problem. By providing on-board a catalytic partial oxidation reformer, a fuel cell and a Fischer-Tropsch derived fuel as described above these problems are overcome. This so-called "liquid electricity" is easily stored, has a low toxicity, has a  
30 high oxidative and thermal stability and is biodegradable. The invention is thus also directed to the use of a Fischer-Tropsch derived fuel to store

electricity for a prolonged time on board a marine vessel.

#### Detailed Description of the Drawings

5 The invention is now illustrated by means of schematic drawings 1 to 4. Means for flow control, heat exchangers and other means for process control are not shown.

10 In Figure 1 is shown a process for operating a compression ignition internal combustion engine 1 in combination with a catalytic partial oxidation reformer 2 and a NO<sub>x</sub> abatement system 3, wherein synthesis gas is supplied to NO<sub>x</sub> abatement system 3. Fuel (Fischer-Tropsch derived gasoil) from fuel storage tank 4 and air are supplied to engine 1 via lines 5 and 6, respectively. The fuel is vaporised and vaporised fuel and air are mixed before being combusted in the combustion chamber (not shown) of engine 1. Exhaust gas is discharged from the engine via line 7. Catalytic partial oxidation reformer 2 comprises a catalyst bed for partial oxidation. Fuel from storage tank 4 and air are supplied to reformer 2 via lines 8 and 9, respectively. Synthesis gas is produced and discharged from reformer 2 via line 10. NO<sub>x</sub> abatement system 3 comprises two NO<sub>x</sub> traps 11, 12. NO<sub>x</sub> trap 11 is supplied with the exhaust gas from line 7 via line 13 and valve 14. NO<sub>x</sub> trap 12 is supplied with the synthesis gas from line 10 via line 15 and valve 16. When the amount of NO<sub>x</sub> absorbed on NO<sub>x</sub> trap 11 has exceeded a certain limit, trap 11 is regenerated by supplying synthesis gas to it via line 17 and valve 18. During regeneration of NO<sub>x</sub> trap 11, NO<sub>x</sub> trap 12 is supplied with exhaust gas via line 19 and valve 20 for NO<sub>x</sub> absorption. Treated exhaust

gas is discharged from NO<sub>x</sub> abatement system 3 via line 21.

In Figure 2 is shown a process for operating a compression ignition internal combustion engine 1 in combination with a catalytic partial oxidation reformer 2, wherein synthesis gas is supplied to the combustion chamber of engine 1. The synthesis gas that is discharged from reformer 2 via line 10 is added to the intake air of engine 1.

In Figure 3 is shown a process for operating a compression ignition internal combustion engine 1 in combination with a catalytic partial oxidation reformer 2, wherein synthesis gas and recirculated exhaust gas are together supplied to the combustion chamber of engine 1. A part of the exhaust gas discharged from engine 1 via line 7 is recirculated to the combustion chamber of engine 1 via line 22. The synthesis gas that is discharged from reformer 2 via line 10 is added to the recirculated exhaust gas in line 22.

In Figure 4 is shown a process for operating a compression ignition internal combustion engine 1 in combination with a catalytic partial oxidation reformer 2 and a NO<sub>x</sub> abatement system 3, wherein part of the synthesis gas is supplied to NO<sub>x</sub> abatement system 3 and part of the synthesis gas is supplied to solid oxide fuel cell 23. In this embodiment, only part of the synthesis gas discharged from reformer 2 via line 10 is supplied to NO<sub>x</sub> abatement system 3 via line 24. The remainder of the synthesis gas is led to the anode 25 of fuel cell 23 via line 26. Air is led to the cathode 27 of fuel cell 23 via line 28. The anode and cathode reactions of the fuel cell are allowed to take place and electricity is generated



and fuel cell off-gas is discharged from the fuel cell  
via line 29.

C L A I M S

1. A process for operating a marine engine in combination with a catalytic partial oxidation reformer and, optionally, an exhaust gas aftertreater, wherein:
- 5 (a) a mixture of a first fuel and air, is introduced in the combustion chamber of the engine;
- (b) exhaust gas is discharged from the engine and optionally partly recirculated to the combustion chamber of the engine;
- 10 (c) a second fuel and oxygen and/or steam are supplied to the catalytic partial oxidation reformer to produce synthesis gas, wherein the second fuel comprises Fischer-Tropsch derived fuel;
- (d) at least part of the synthesis gas is supplied to:
- 15 (i) the exhaust gas aftertreater;
- (ii) the combustion chamber of the engine; or to both.
2. A process according to claim 1, wherein the marine engine is a compression ignition engine.
3. A process according to any one of claims 1-2, wherein the first fuel and the second fuel are the same fuel.
- 20 4. A process according to claim 1 or 3, wherein the first fuel and the second fuel comprise at least 10% (v/v) Fischer-Tropsch derived fuel, preferably at least 50% (v/v), more preferably at least 80% (v/v), even more preferably consist of Fischer-Tropsch derived fuel.
- 25 5. A process according to any one of claims 2-4, wherein the Fischer-Tropsch derived fuel is a gasoil.
6. A process according to any one of claims 2-5, which is a process for operating a compression ignition internal combustion engine in combination with a

catalytic partial oxidation reformer and a NO<sub>x</sub> abatement system as exhaust gas aftertreater, wherein the non-recirculated part of the exhaust gas and at least part of the synthesis gas are supplied to the NO<sub>x</sub> abatement system.

5

7. A process according to claim 6, wherein the NO<sub>x</sub> abatement system comprises a NO<sub>x</sub> trap comprising a NO<sub>x</sub> reducing catalyst and a NO<sub>x</sub> sorbent.

10

8. A process according to claim 7, wherein the non-recirculated part of the exhaust gas is continuously supplied to the NO<sub>x</sub> trap and the synthesis gas is intermittently supplied to the NO<sub>x</sub> trap.

15

9. A process according to claim 7, wherein the NO<sub>x</sub> abatement system comprises two NO<sub>x</sub> traps and wherein each trap is alternately supplied with the non-recirculated part of the exhaust gas and the synthesis gas such that one trap is supplied with the exhaust gas and the other trap with the synthesis gas.

20

10. A process according to claim 6, wherein the NO<sub>x</sub> abatement system comprises a NO<sub>x</sub> reducing catalyst without a NO<sub>x</sub> sorbent and the non-recirculated part of the exhaust gas and the synthesis gas are simultaneously and continuously supplied to the NO<sub>x</sub> reducing catalyst.

25

11. A process according to any one of claims 2-10, wherein at least part of the synthesis gas is supplied to the combustion chamber of the engine.

30

12. A process according to any one of claims 2-11, wherein at least part of the exhaust gas is recirculated to the combustion chamber of the engine.

13. A process according to claim 11, wherein the amount of synthesis gas supplied to the combustion chamber of the engine is such that the volumetric ratio of

'synthesis gas'-to-'first fuel' supplied to the combustion chamber is at most 25%, preferably at most 20%.

5 14. A process according to claim 11 and 12, wherein the amount of synthesis gas supplied to the combustion chamber and the amount of exhaust gas recirculated to the combustion chamber is such that the volumetric ratio of 'combined synthesis gas plus exhaust gas' to 'first fuel' supplied to the combustion chamber is at most 25%.

10 15. A process according to any one of the preceding claims, wherein part of the synthesis gas is supplied to a fuel cell to generate electricity.

15 16. A marine vessel provided with a marine compression ignition internal combustion engine, a catalytic partial oxidation reformer, an exhaust gas aftertreater, and a fuel cell for auxiliary power generation.

17. A sailing vessel provided with a catalytic partial oxidation reformer, a fuel cell and a Fischer-Tropsch derived fuel.

20 18. Use of a Fischer-Tropsch derived fuel to store electricity for a prolonged time on board a marine vessel.

Fig.1.

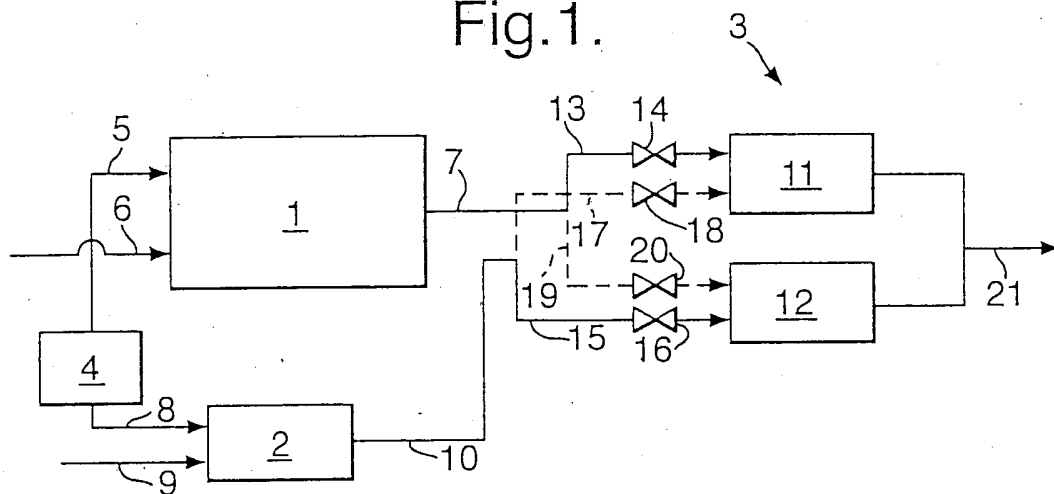


Fig.2.

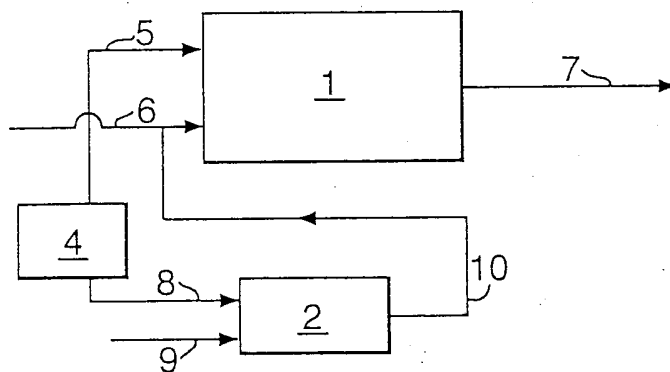


Fig.3.

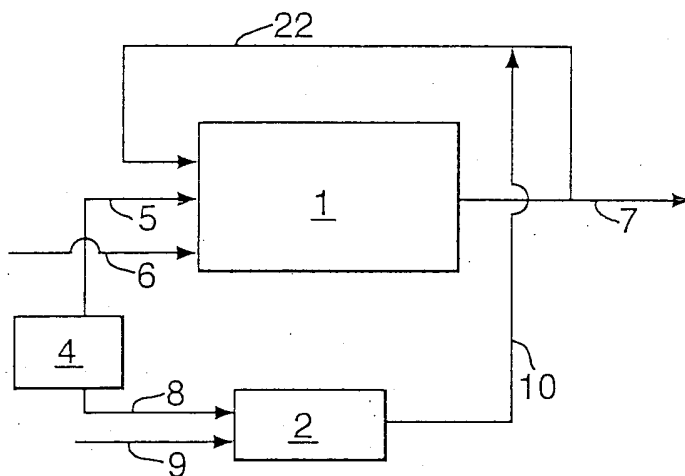
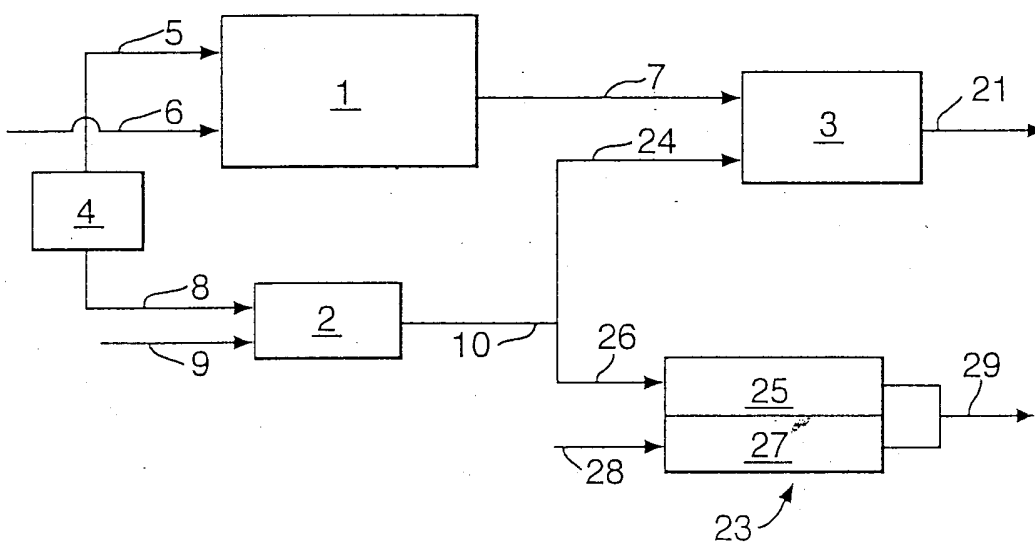


Fig.4.



# INTERNATIONAL SEARCH REPORT

International application No  
PCT/EP2006/060319

**A. CLASSIFICATION OF SUBJECT MATTER**  
 INV. F02M27/02 F02D19/08 F02B43/10 F01N7/00 F02M25/07  
 F02M25/10 F01N3/20

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)  
 F02D F02M F01N F02B H01M C10L C01B

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, PAJ

<b>C. DOCUMENTS CONSIDERED TO BE RELEVANT</b>		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2003/168263 A1 (BOTTI JEAN JOSEPH ET AL) 11 September 2003 (2003-09-11) abstract; figures	1-5, 11, 15-18
Y	paragraphs [0031], [0032], [0039], [0060]	6-10
A	paragraph [0055]	12-14
Y	----- US 2003/115857 A1 (PREIS MICHAEL ET AL) 26 June 2003 (2003-06-26) abstract; figures	6-10
A	page 1, paragraph 8 - paragraph 11 page 2, paragraph 22 - page 3, paragraph 26 ----- -/--	1-5, 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. *&' document member of the same patent family
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Date of the actual completion of the international search  <b>2 May 2006</b>	Date of mailing of the international search report  <b>15/05/2006</b>
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Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Authorized officer  <b>Jucker, C</b>
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## INTERNATIONAL SEARCH REPORT

International application No  
PCT/EP2006/060319

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 1 030 395 A (DELPHI TECHNOLOGIES INC) 23 August 2000 (2000-08-23) abstract; figures	1-5, 11-18
A	paragraphs [0012] - [0016], [0021], [0022], [0027] - paragraph [0016] -----	6-10
A	US 2002/194835 A1 (BROMBERG LESLIE ET AL) 26 December 2002 (2002-12-26) abstract; figures	1-15
A	paragraphs [0006], [0007], [0016], [0026] - paragraph [0007] -----	
A	GB 2 320 057 A (FORD MOTOR CO LTD) 10 June 1998 (1998-06-10) abstract; figure	1,11-14
A	page 2, line 30 - page 3, line 20 -----	
A	FR 2 801 603 A (INSTITUT FRANCAIS DU PETROL) 1 June 2001 (2001-06-01) abstract; figures	1
A	page 5, line 17 - page 8, line 7 page 9, line 23 - page 11, line 20 -----	
A	EP 0 147 873 A (SHELL INT RESEARCH MAATSCHAPPIJ BV) 10 July 1985 (1985-07-10) cited in the application abstract	1
A	page 1, line 20 - page 2, line 32 -----	
A	US 4 125 566 A (DINH CHAN TRIN ET AL) 14 November 1978 (1978-11-14) cited in the application abstract	1
A	column 1, line 33 - line 50 & WO 99/19249 A (SHELL INT RESEARCH MAATSCHAPPIJ BV (NL); DE JONG KRIJN P ET AL (NL)) 22 April 1999 (1999-04-22) cited in the application abstract	1
P,A	page 1, line 1 - line 11 page 3, line 10 - page 7, line 17 page 9, line 23 - line 33 -----	
P,A	WO 2005/054657 A (SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V.; CRACKNELL, ROGER FRANC) 16 June 2005 (2005-06-16) abstract; claims 1-14; figures 1-4 -----	1-15



## INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2006/060319

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
US 2003168263	A1	11-09-2003	EP 1047144 A1 US 6609582 B1	25-10-2000 26-08-2003
US 2003115857	A1	26-06-2003	DE 10161696 A1 EP 1319813 A2 JP 2003247413 A	26-06-2003 18-06-2003 05-09-2003
EP 1030395	A	23-08-2000	US 6655325 B1	02-12-2003
US 2002194835	A1	26-12-2002	CA 2383551 A1 EP 1212520 A1 JP 2003529012 T WO 0114698 A1	01-03-2001 12-06-2002 30-09-2003 01-03-2001
GB 2320057	A	10-06-1998	NONE	
FR 2801603	A	01-06-2001	NONE	
EP 0147873	A	10-07-1985	AU 566159 B2 AU 3286284 A BR 8404510 A CA 1231105 A1 DE 3469727 D1 ES 8601081 A1 GB 2146350 A IN 161735 A1 JP 1941772 C JP 6031321 B JP 60081288 A NZ 209491 A US 4594468 A ZA 8407084 A	08-10-1987 21-03-1985 06-08-1985 05-01-1988 14-04-1988 16-02-1986 17-04-1985 30-01-1988 23-06-1995 27-04-1994 09-05-1985 23-01-1987 10-06-1986 24-04-1985
US 4125566	A	14-11-1978	AU 507906 B2 AU 2794777 A CA 1094579 A1 DD 132440 A1 DE 2736566 A1 FR 2362208 A1 GB 1541204 A PL 200297 A1 ZA 7704985 A	28-02-1980 22-02-1979 27-01-1981 27-09-1978 23-02-1978 17-03-1978 21-02-1979 24-04-1978 26-07-1978
WO 9919249	A	22-04-1999	AT 231102 T AU 737880 B2 AU 1335199 A BR 9813035 A CA 2306938 A1 CN 1275961 A DE 69810805 D1 DE 69810805 T2 ID 24366 A JP 2001519311 T NO 20001927 A PL 339812 A1 TW 440541 B US 6673270 B1	15-02-2003 06-09-2001 03-05-1999 15-08-2000 22-04-1999 06-12-2000 20-02-2003 11-12-2003 13-07-2000 23-10-2001 13-04-2000 02-01-2001 16-06-2001 06-01-2004

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2006/060319

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2005054657	A	16-06-2005	NONE