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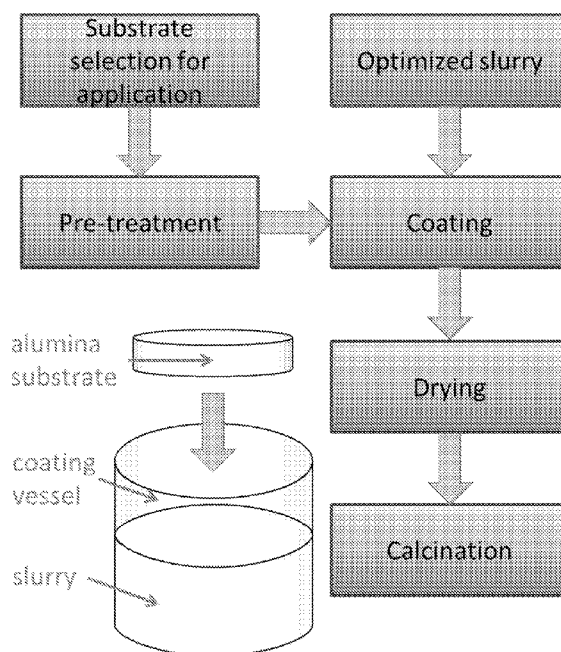


Figure 1

(57) Abstract: The present invention relates to a method for catalytic partial oxidation of hydrocarbons into syngas in a reactor, to the reactor, and to a method for producing a catalytic oxygen permeable membrane system for use in the reactor. The membrane system is prepared by providing a monolith membrane support, pretreating the membrane support, and coating it, drying and precalcining it, and repeating steps coating, drying and precalcining steps at least once, before providing final calcination to the coated membrane support, whereby the membrane system is obtained.



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A method and reactor for catalytic partial oxidation of hydrocarbons

Field of the invention

The present invention relates to a membrane system for use in catalytic oxidation of hydrocarbons, and to a reactor and method using the membrane system.
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Background

Partial oxidation (POX) is a chemical reaction which occurs when a substoichiometric fuel-air mixture is partially combusted in a reformer, creating a hydrogen-rich syngas. A distinction is made between thermal partial oxidation (TPOX) taking place at high temperatures of about 1200 °C, and catalytic partial oxidation (CPOX) characterised by the use of a catalyst reducing the need for high temperatures.
10

Catalytic partial oxidation (CPOX) enhances the reforming of hydrocarbons into syngas i.e. it is an attractive way to produce H₂ hydrogen and CO carbon monoxide from hydrocarbon fuels. The formed syngas may further be upgraded to a wide range of products such as liquid hydrocarbons fuels, alcohols, synthetic natural gas and fertilizers. The oxidation reaction requires an oxygen containing source which may be either air or pure oxygen. Addition of air into the reaction gas is an economically feasible alternative but it typically leads to increase of nitrogen content in the product gas which is not suitable for the downstream processes such as Fischer-Tropsch. On the other hand, production of pure oxygen is very expensive.
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Various types of catalysts or catalyst combinations can be used in the CPOX reactions. Typically nickel or other metal catalysts have been applied but recently also several metal oxide catalysts have been developed providing better behaviour in terms of lower temperature ranges, decreased deactivation and blockage properties, enhanced selectivity and lower by-product formation.
25

Oxygen permeable membranes enable the oxygen ions to be selectively transported through the membrane while blocking nitrogen and other gases which remain on the other side of the membrane. It may act as a supplier of oxygen for partial oxidation. The pure oxygen separated from the air by an ox-
30

oxygen permeable membrane is more economic and environmentally friendly, and avoids the formation of nitrogen oxides in the reactor. The goal in an oxygen permeable membrane reactor is to combine both the separation and the reaction steps into one process, making it possible to exclude distillation as an additional separation process. Therefore, oxygen permeable membranes may suitably be used in a reformer reactor based on catalytic partial oxidation.

For example, zirconium oxide, ZrO_2 , based membrane catalysts have been applied as CPOX reforming catalysts.

FI110691B discloses a method for the purification of gasification gas obtained from a carbonaceous material. The purification is carried out by adding oxygen or an oxygen-containing gas to the gasification gas and by contacting the gas mixture with a solid catalyst. The catalyst contains at least one zirconium compound, such as zirconium oxide, which is used in particulate form as such or combined with an inert, honeycomb-structured support.

FI118647B discloses a method of reforming a gas containing tarry impurities, such as the gasification gas obtained by gasifying a fuel. In the two-stage reforming method, oxygenous gas is added to a gas flow after which the gas is brought into contact with a solid zirconium-based catalyst, such as zirconium oxide, at a high temperature. In the next stage, a metal catalyst, such as metallic nickel, is applied. The zirconium compound may further be used in pre-reforming the tar-bearing gas to achieve the aimed goals.

EP2606106 discloses zirconium-based mixed oxide or zirconium-based mixed hydroxide, additionally comprising cerium and/or lanthanum. For example, a mixed oxide or mixed hydroxide comprising at least 60 wt% zirconia and/or zirconium hydroxide, 10-25 wt% ceria and/or cerium hydroxide, and 1-10 wt% lanthana and/or lanthanum hydroxide is applied. Further a method for purifying gas produced from the gasification of carbonaceous materials, comprising the step of bringing the gas into contact with such mixed oxides or mixed hydroxides is disclosed.

Oxygen permeable catalytic membrane, such as $CeLaZrO_2$, allows the use of inexpensive air as the oxygen source because it only permeates oxygen into the reaction gas. Because the membrane has also catalytic activity, it utilizes the oxygen for the partial oxidation of the hydrocarbons.

Oxygen permeable membranes are difficult to apply for industrial processes. The main problems are the stability of the membrane in reaction gases containing high concentrations of CO, CO₂ and H₂O, thermal stability of the membrane and the installation of the membrane into the reactor.

- 5 Zirconium oxide based materials conduct oxygen and can be used as membrane materials. However, the adhesion of zirconia and zirconia based materials, for example, to ceramic surfaces or metallic surfaces, is very poor. It is difficult to produce coatings that would be durable enough in industrial scale application, especially at high temperatures and in reducing gas atmosphere.
- 10 Therefore, there is a need to increase the stability and durability of the oxygen permeable membranes suitable for use in catalytic partial oxidation processes. Moreover, reactor configurations suitable for industrial scale operation applying such oxygen permeable membranes are required to solve the large scale manufacturing issues and economical demands, as well.

15

Summary of the invention

An object of the present invention is to provide a process for the coating of a membrane support with a durable oxygen permeable membrane.

- 20 Another object of the present invention is to provide a reactor and process for an industrially applicable partial oxidation of hydrocarbons.

Yet, one object of the present invention is to provide a reactor and process for partial oxidation of hydrocarbons producing syngas with good yield and simple construction.

- 25 In one aspect, the present invention provides a method for producing a catalytic oxygen permeable membrane system depicted by claim 1.

In a further aspect, a reactor for catalytic partial oxidation of hydrocarbons into syngas is provided as depicted by claim 14, and a method for using the reactor by claim 16.

- 30 The method of the present invention provides a simple way of manufacturing catalytic oxidation membrane system on ceramic and metallic support. The

5 catalytic oxygen permeable membrane system obtained by the method according to the present invention is mechanically and chemically stable and durable under the catalytic oxidation and oxygen permeation conditions. The surface of the membrane does not flake or deteriorate due to temperature fluctuations or the harsh gaseous environment. The catalytic membrane layer reduces clog-
ging, it has an increased pick up of the catalytic material in consecutive application steps, and an enhanced adhesion to the support structure. The oxygen flux through the membrane system is enhanced compared to other commercially available perovskite systems.

10 No nitrogen penetration is observed and syngas of high purity may be produced using reasonably low processing temperature.

The reactor according to the present invention is able to efficiently and inexpensively remove tar and heavy hydrocarbons in the process of syngas manufacture.

15 For example, the problems such as carbon formation, blockage or corrosion of downstream process equipment induced by tar which is the by-product of the biomass gasification process may be avoided by the use of the membrane system and reactor of the current invention. Separate oxygen plant or oxygen production is not needed as the membrane separates the oxygen from air.
20 This leads to lower energy consumption and lower CAPEX (Capital expenditure) as the production units are combined.

Brief description of drawings

25 Figure 1 depicts a schematic process chart for manufacturing the membrane system according to the present invention.

Figures 2 A and B and 2 C and D compare the flaking and non-flaking appearances of the washcoat surfaces.

Figure 3 illustrates the oxygen permeation process within the membrane.

30 Figure 4 depicts a schematic functional view of the flows and reactions taking place in a partial oxidation membrane reactor according to the present invention.

Figure 5 illustrates an industrial scale reactor design for a catalytic oxidation utilising the method of the present invention.

Figure 6 shows the measured values of the oxygen flux through a membrane.

5 Detailed description of the invention

By “syngas” is meant synthesis gas obtained by oxidation of hydrocarbons into fuel gas mixture consisting primarily of hydrogen and carbon monoxide, and optionally some carbon dioxide.

10 By “Ce-La-Zr mixed metal oxide” is meant a mixture of metal oxides of Ce, La and Zr metals which are able to form a fluorite structure when heated.

Dense ceramic oxygen permeable membranes, which exhibit both electronic and ionic conductivity are advantageously used for oxygen separation from air. The partial pressure differences of the oxygen ions between the two sides of the membrane enable oxygen ions to be selectively transported through the
15 membrane which is depicted in the figure 3. At the same time, current transport of electronic charge carriers is required to maintain charge neutrality. No external electrodes are required for transportation due to electronic ionic conductivity, but elevated membrane operation temperature is necessary, preferably from 700 to 1000 °C. Owing to the nature of the oxygen vacancies, oxygen pu-
20 rity with 100 % selectivity may be obtained at high temperatures, which means that nitrogen or any other gas is blocked from the membrane material.

Several different types of membranes have been experimented on starting from the fluorite-type of compounds and arriving at the perovskite-type compounds which have high electric conductivity, high ionic conductivity and high
25 oxygen permeability at elevated temperatures.

The fluorite type compounds have the formulae MO_2 in which M is a host metal with oxidation state 4+, such as Zr^{4+} , Hf^{4+} or Ce^{4+} . The structure is stabilized by the presence of dopant cations, such as La^{3+} , Ce^{3+} or Y^{3+} . The host and do-
30 pant cation sites may further be substituted by other elements to increase the physico-chemical properties and the oxygen permeability of the membrane material.

Traditionally, the membranes are manufactured by preparing powders, shape forming the membranes and sintering them. The synthesis methods for powders include e.g. solid state, co-precipitation, sol-gel, hydrothermal methods, spray and freeze drying, plasma spraying, electronic beam evaporation and arc vaporization. Typically, ceramic shape forming processes involve compaction i.e. densification of precursor powders to produce dense ceramic membranes, followed by a sintering process. The mechanical property including strength and morphology, such as grain size, grain boundary and size distribution, of the membrane depends on the form of raw materials, the nature of the process and preparation conditions such as pH, temperature, additives, duration, and atmosphere, leading to an effect on the oxygen permeability.

In the first aspect, the present invention provides a method for producing a catalytic oxygen permeable membrane system. This method comprises the following steps also depicted by figure 1:

- i. Providing a membrane support.
- ii. Pretreating the membrane support.
- iii. Coating the pretreated membrane support.
- iv. Drying and precalcining the pretreated and coated membrane support.
- v. Repeating steps iii and iv at least once.
- vi. Providing final calcination to the coated membrane support, whereby the membrane system is obtained.

Porous ceramic monoliths are widely used as supports and may comprise varying material properties such as multichannel, clay-bonded or sintered α -alumina monolith, cordierite honeycomb monoliths, metal oxide monolith supports, optionally containing titania alone or in combination with other metal oxides, especially with alumina.

The membrane support of the present invention is advantageously ceramic material or metallic material.

In one embodiment the support is porous monolithic ceramic material, preferably porous monolithic alumina as it is easy to washcoat and is thermally stable.

In another embodiment the support is metallic material, preferably steel, Ni and Cr alloy or Fe based alloy.

The ceramic or metallic support may comprise several known configurations. The support is preferably in a form of a plate, disc or tube; more preferably a tubular support which is most advantageous for reactor layout and construction of the present invention.

- 5 Typically, porous α -alumina support may be produced by sintering a monodisperse alumina at temperatures from 1600°C to 1800°C. The use of clay, or other metal oxides, or fine α -alumina reactive binders can reduce the sintering temperature needed.

It is not necessary to pretreat the ceramic support.

- 10 The metallic membrane support of the present invention is pretreated by washing the support with an organic solvent, such as isopropanol and/or acetone, and then treating it either at high temperature, such as 800 – 900 °C, or by acid washing, such as with 2 minutes at HCl bath and 30 minutes at HNO₃ bath. The oxygen permeable catalytic membrane is formed as a thin coating layer on
15 the membrane support after the pretreatment of the support.

In a preferred embodiment the coating is provided by a washcoating procedure.

- The main function of the washcoating is to provide high surface area needed for the dispersion of catalytic metals. Additionally, washcoating can physically
20 separate the components and prevent undesired reactions between components of a complex catalytic system. The exact role of washcoating is neither always understood nor can it be explained.

- Conventionally, the membrane material is washcoated onto a monolithic substrate using silica sol or alumina sol as a binder. The binders are applied to
25 better adhere a catalytic membrane layer onto the support material. Nevertheless, binders are support material selective and suffer from separation from the support material, weak adhesion, too fast dehydration when exposed to air, clogging, and they tend to decrease the amount of the desired catalytic material. Occasionally, when alumina sol is used as binder, the resulting washcoat
30 slurry is not stable enough and the binder tends to separate from the catalytic material.

In the finished membrane system insufficient adhesion which leads to flaking is the main problem conventionally encountered.

When coating a support with a catalyst layer using a traditional washcoating procedure, the oxygen permeable CeLaZrO₂ membrane layer tends to seriously
5 flake off from the membrane system, as depicted by figures 2 C and D. This takes place in the practical operation conditions, in which there are fast temperature changes of several hundred degrees C. When the method of the present invention is applied a durable washcoat is obtained, adhering well onto the support, as depicted by figures 2 A and B.

10 Figures 2 C and D are from test series wherein there is traditionally applied binder, such as aluminasol in C and wherein in D there is not. Figure 2 A and B are from another test series wherein in A the coating is applied in one coating sequence, and in B thin coating layers are applied.

Washcoat materials include inorganic base metal oxides such as Al₂O₃ (aluminum oxide or alumina), SiO₂, TiO₂, CeO₂, ZrO₂, V₂O₅, La₂O₃ and zeolites.
15 Some of them are used as catalyst carriers, others are added to the washcoat as promoters or stabilizers, and others exhibit catalytic activity of their own.

The desired washcoat materials are characterized by high specific surface area and good thermal stability. The specific surface area is typically determined
20 by nitrogen adsorption measurement technique in conjunction with mathematical modelling known as the BET (Brunauer, Emmet, and Teller) method. Thermal stability is evaluated by exposing the samples of given material to high temperatures in a controlled atmosphere, usually in the presence of oxygen and water vapour. The loss of BET surface area, which is re-measured at
25 different time intervals during the test, indicates the degree of thermal deterioration of the tested material.

Conventionally, a washcoat is applied to the catalyst support from a water based slurry. The wet washcoated parts are dried and calcined at high temperatures. Precious metal catalysts may be either present in the washcoat slurry,
30 or they are applied in a second step such as impregnation. The supported catalyst is then dried and calcined to its final form. During the calcination, the catalyst precursors decompose to form the final catalyst, usually a metal or a metal oxide.

In the method of the present invention a mixed metal oxide, preferably Ce-La-Zr mixed oxide, catalyst membrane is prepared. The formed mixed metal oxide, preferably CeLaZrO_2 , layer is used as an oxygen permeable membrane, and simultaneously, as a catalyst for catalytic partial oxidation of hydrocarbons. This enables the use of air instead of oxygen for tar or heavy hydrocarbon reforming without syngas dilution by nitrogen.

The method according to the present invention reduces the investment and operation costs of, for example, biomass based production of liquid biofuels and chemicals, as there is no need for an oxygen separation process.

10 In one embodiment the washcoating comprises treating the membrane support with Ce-La-Zr mixed oxide based slurry for forming a coating thereon.

In an exemplary embodiment of the present invention CeLaZrO_2 catalytic membranes are prepared by washcoating procedure on alumina supports. The washcoating procedure resulted in a solid layer of CeLaZrO_2 on one side i.e. the reaction side of the substrate. The CeLaZrO_2 layer according to the present invention permeates only oxygen from air, and utilises it in the catalytic partial oxidation of hydrocarbons for which reaction CeLaZrO_2 is known to be active, and the membrane system is stable at the steam reforming conditions. The membrane system has been tested for its functionality and stability as oxygen permeable membrane and as a catalyst in conditions relevant to catalytic partial oxidation of hydrocarbons.

In one embodiment the Ce-La-Zr mixed oxide based slurry is prepared by mixing together the following starting materials in the following ranges:

15-25 % by weight of Ce-La-Zr mixed oxide in the form of solid powder,
25 60-80 % by weight of ion exchanged water,
1-10 % by weight acid, and
1-10 % by weight of zirconium nitrate solution.

In an exemplary embodiment the slurry comprises 17-23 % by weight of Ce-La-Zr mixed oxide in the form of solid powder, 65-75 % by weight of ion exchanged water, 3-6 % by weight acid, and 5-7 % by weight of zirconium nitrate solution.

In another exemplary embodiment the slurry comprises 18-22 % by weight of Ce-La-Zr mixed oxide in the form of solid powder, 68-72 % by weight of ion exchanged water, 4-5 % by weight acid, and 5.5-6.5 % by weight of zirconium nitrate solution.

- 5 Preferably the acid is selected from the group comprising nitric acid, sulphuric acid, phosphoric acid or hydrochloric acid. More preferably, the acid is nitric acid, most preferably concentrated nitric acid.

The solid Ce, La and Zr oxide powders are commercially available by several vendors. The ratios of Ce:La:Zr are 10-25 : 1-10 : 60 which provide high thermal stability, porosity and catalytic activity.

In one embodiment the Ce-La-Zr mixed oxide based slurry is prepared by mixing the starting materials i.e. solid powders of ceria, lanthania and zirconia with the ion exchanged water, acid and the nitrate solution for 1 h at 3000 rpm with a propeller mixer, at room temperature to obtain a solution which does not have immediate phase separation. A slurry thus obtained is applied onto the membrane support.

In one embodiment the membrane substrate is dipped into the coating slurry.

In another embodiment the slurry is applied onto the membrane substrate surface by spreading, painting, rolling, brushing or pasting.

- 20 The application method provides a thin layer of the slurry onto the membrane surface which attaches to the surface. Subsequently, the support is dried and precalcined.

In one embodiment the drying is performed by subjecting the wet surface of the coated pretreated membrane support to warm air. The temperature of the air is preferably at least 20 °C, more preferably at least 30 °C, most preferably at least from 40 to 50 °C. The drying takes only a short while due to the thinness of the coating layer, preferably less than 15 min, more preferably less than 10 minutes, such as from 5 to 10 minutes. The thinner the layer, the faster is the drying. Thick layers dry slowly and unevenly which can lead to cracking in the drying phase.

In one embodiment the precalcination temperature in step iv is from 400 to 600 °C, preferably from 450 to 550 °C, more preferably from 480 to 520 °C. This

leads to improved adhesion and reduces cracking especially with thicker coatings.

5 In one embodiment the duration of the precalcination is at least 5 minutes, preferably at least 10 minutes. The precalcination takes place at normal pressure and atmosphere, where after the coated pretreated membrane support is let to cool into room temperature.

10 In one embodiment steps iii-iv are repeated at least two times, preferably at least three times, more preferably at least four times, until the desired thickness is obtained for the mixed oxide coating. When the washcoat is applied as thin layers it has better adhesion to the support. The drying and calcination of the thin layers is more homogeneous than thick layers which prevents cracking. The method is simple and lead to high performance of the catalyst.

15 After the first precalcination the washcoating procedure is repeated to form additional thin layers of washcoat until the optimum washcoat thickness is reached. By repeating the washcoating, drying and precalcining stages, a dense nonflaking stable catalyst membrane layer is obtained onto the membrane support.

20 After coating the support by multiple precoating layers the coating is finalized by a final calcination. In one embodiment the final calcination temperature in step vi is from 700 to 900 °C, preferably from 750 to 850 °C, more preferably from 780 to 820 °C. The temperature should be preferably as close to maximum operation temperature as possible.

25 In one embodiment the duration of the final calcination is at least 50 minutes, preferably at least 60 minutes. The final calcination is similarly to the precalcination performed at normal pressure and atmosphere.

30 The above procedure according to the present invention results in a solid layer of Ce and La doped zirconia based washcoat. This catalytic membrane system is permeable only oxygen from air and is able to utilise the permeated oxygen in subsequent catalytic partial oxidation of hydrocarbon residues into syngas for which reaction the Ce and La doped zirconia based catalysts are known to be active and stable.

In one embodiment the thickness of the mixed oxide coating is at least 50 μm , preferably from 50 to 200 μm , more preferably from 130 to 160 μm . The preferable composition of coating is at least 60 wt% zirconia and/or zirconium hydroxide, 10-25 wt% ceria and/or cerium hydroxide, and 1-10 wt% lanthana and/or lanthanum hydroxide is applied.

The present invention provides material and procedure for the production of supported oxygen permeable catalytic membrane. The applicability of the system has been tested for the partial oxidation of hydrocarbons. The membrane was found durable and well suited for use in reducing syngas atmosphere, which is very challenging for the present state-of-the art membrane technology. The membrane is itself catalytically active and capable of selective decomposition of hydrocarbon mixture comprising tar and heavy hydrocarbons.

The present invention provides a simple preparation method for a mixed oxide catalytic membrane, such as CeLaZrO_2 catalytic membrane, for ceramic and metallic substrates that is based on washcoating procedure. A further advantage is that the washcoat slurry does not require the use of an additional binder as in conventional washcoating procedures. Moreover, the resulting washcoat forms a durable catalytic oxygen permeable membrane coating for reducing and moist gas atmosphere which tolerates high temperatures and rapid temperature fluctuations. The formed washcoat is mechanically stable withstanding the harsh conditions without starting to flake or otherwise degrade or deteriorate.

In the second aspect, the present invention provides a method for catalytic partial oxidation of hydrocarbons into syngas in a reactor suitable thereto. The method according to the present invention is characterised by the following steps of i'-v'.

i'. Heating the reactor by external heating means.

For the heating any suitable commonly known heating means may be applied, such as by partial oxidation of hydrocarbon components to H_2 . The amount of heat to be applied needs to be such that it enables the oxidation reaction at the outer surface of the catalytic oxygen permeable membrane system.

ii'. Providing air and hydrocarbons containing tar into the reactor.

The air is introduced into the reactor in line with the tubular catalytic oxygen permeable membrane system where from oxygen is transported through the membrane system and is contacted with the hydrocarbons which are provided to the outer surface of the membrane system. The air is depleted with oxygen
5 and the depleted and heated air is guided through the tubular catalytic oxygen permeable membrane system exiting it from the other end of the tubular catalytic oxygen permeable membrane system.

iii'. Contacting the air with the inner surface of at least one tubular membrane system according to the present invention, and guiding it through the membrane system while it is being depleted from oxygen.
10

When the air is contacted with the inner surface of a tubular membrane system oxygen is permeating the membrane system wall from the inner side of the tube into the outer side while nitrogen is flowing in line with the tubular membrane system and through the tube into the exit.

iv'. Contacting the hydrocarbons containing tar with the outer surface of membrane system, while they are being reacted into syngas.
15

The oxygen permeating through the wall of the tubular membrane system from the inner surface to the outer surface is reacting with the hydrocarbons on the outer surface thus producing syngas.

v'. Recovering the syngas and oxygen depleted air from the reactor.
20

The formed syngas may be recovered from the reactor bypassing the outer wall of the tubular membrane system from the inlet to the exit perpendicular direction to the tubular axis. The oxygen depleted air may be recovered from the reactor bypassing the inner wall of the tubular membrane system from the inlet
25 to the exit axially to the tubular membrane system.

In an exemplary embodiment of the present invention, the flow rate of the hydrocarbon containing gas at the inlet of reactor is 7 m³/h.

In an exemplary embodiment of the present invention, the flow rate of air at the inlet of reactor is about 3 vol% of O₂ in the inlet feedgas.

There are two alternatives for feeding oxygen to the catalytic partial oxidation process: First, addition of air to the reaction gas, which dilutes the product
30

syngas with N₂. And secondly, addition of oxygen produced in a separate oxygen plant, which adds complexity to the whole process. Moreover, before the syngas can be fed to a catalytic reactor, it usually needs to be desulfurized in a scrubbing or adsorption process. The method and set up of the present invention enables avoiding these drawbacks. The air being depleted from oxygen and being enriched with nitrogen is not in contact with the hydrocarbon feed or with the syngas product. The membrane system of the present invention is used to separate these material flows from each other.

In the method of the present invention it is surprisingly found that the Ce and La doped zirconia membrane system permeates oxygen with adequate O₂ flux to enable efficient hydrocarbon decomposition. The efficiency of the oxygen penetration or flow through the membrane is around 2 ml/(min*cm²) which is high enough to ensure sufficient oxygen supply for the hydrocarbon oxidation into syngas.

The catalytic partial oxidation of hydrocarbons and possibly tar containing inlet is performed in a catalytic partial oxidation reactor that comprises at least one tubular membrane system. The number of the membrane systems is dependent on the amount of gas flow and the dimensions of equipment applied such as pipe cross section area and length.

In an exemplary embodiment the membrane system of the reactor comprises totally or partly by zirconia based catalyst, such as CeLaZrO₂. The reactor may further contain other catalysts or catalyst layers, such as Ni.

In the reactor the lighter hydrocarbons are not converted and the heavier hydrocarbons are converted to CO, CO₂ and H₂.

The method of the present invention combines two functionalities of a relatively inexpensive material in a way that a new type of reactor construction is possible for the catalytic partial oxidation. It further enables the treatment of H₂S containing gases without separate prior purification. A major advantage is that it enables the use of inexpensive air as oxygen source for catalytic partial oxidation without nitrogen dilution of the product gas. This reduces the investment and operation costs of syngas production plant, which is especially important for bio-based feedstocks. The high costs have been one of the main obstacles in the industrial scale production of biomass based syngas and its processed products. The method of the present invention is also suitable for all syngas

applications where heavy condensable hydrocarbons cause problems, like coke oven gases, coal gasification gas, etc. Catalytic partial oxidation of heavy hydrocarbons like tars and PAH may be performed. And syngas may be produced for chemical and/or energy production by turbines and engines.

- 5 In the third aspect, the present invention provides a reactor set up for catalytic partial oxidation of hydrocarbons into syngas, comprising the following parts:

i)". An outer jacket configured to include the membrane system.

ii)" At least one tubular membrane system obtained by the method of the present invention as depicted above installed into the reactor jacket.

- 10 iii)" Inlet means configured to guide air inside into the tubular membrane system, through it, and exit means configured to recover the exiting air from the inside of the tubular membrane system.

- iv)" Inlet means configured to guide hydrocarbons into contact with the outer surface of the tubular membrane system, passing the tubular membrane system, and exit means configured to recover the exiting reacted hydrocarbons from the outer surface of the tubular membrane system.
- 15

- v)." Heating means configured to increase the temperature of the air and the hydrocarbons to a level wherein the oxidation reactions take place such as heat exchanger (LUVO) or air preheater for air heating. CPOX reaction provides heat to the catalyst surface.
- 20

In an exemplary embodiment the tubular membrane system comprises CeLaZrO₂ as partial oxidation catalyst. This catalyst may be used for oxidation of tar and heavy polyaromatic hydrocarbons, and simultaneously as an oxygen permeable membrane for reducing syngas.

- 25 One of the advantages of the reactor of the present invention is that it operates at surprisingly low temperature range, such as about 700 - 900 °C. The membrane system material provided by the present invention is very stable in reducing and steam containing gas atmospheres, and insensitive for sulphur poisoning.

- 30 The application of the reactor and method is particularly attractive in processes such as biomass, waste and coal gasification, pyrolysis, coke manufacturing in

steel industry and oil refining. The method of the present invention enables manufacturing of intensified catalytic reactors, such as catalytic heat exchanger reactors for these applications.

The invention will be further illustrated by the following non-limiting examples.

5

Examples

Example 1

A stable, non-flaking CPOX membrane system was produced by mixing together in a mixing vessel

- 10 20.00 w-% CeLaZrO₂ powder (from MEL Chemicals)
 69.70 w-% of deionized water
 4.3 w-% nitric acid, 20 % by weight (from Merck)
 6.00 w-% zirconium nitrate solution.

- The mixture was agitated for 1 h, at room temperature using a propeller agitator. After mixing the slurry was ready for application.
- 15

The alumina membrane support was dipped into the slurry, and the wet surface was dried using warm air blower for 10 minutes. The dried support was precalcined in oven at 500 °C for 10 minutes.

- The application of the slurry, drying and precalcining was repeated for 2 times until a desired thickness of 150 µm was obtained.
- 20

The support was installed into the oven for final calcination at 800 °C for 1 h.

The preparation method lead to non-flaking, even washcoat on the support.

Example 2

- Oxygen flux through the CPOX membrane system prepared according to example 1 was measured and compared to commercially available perovskite membrane systems of BaCo_{0.4}Fe_{0.4}Zr_{0.2}O₃ (BCFZ), La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O₃ (LSCF), La₂NiO₄ (LN) and La_{0.8}Sr_{0.2}MnO₃ (LSM).
- 25

The membranes were tested at oven set-point temperatures between 700 and 950 °C and at atmospheric pressure. The synthetic air (O₂/N₂ 20/80 vol%) flow rate was 0.45 l/min to the air-side of the membrane disc. The reaction gas contained 52.7 vol% toluene in nitrogen and its flow rate was 0.4 l/min to the reaction side of the membrane disc. The outlet reaction gas composition was measured by a gas chromatograph.

Figure 6 shows that the value of oxygen flow of the CPOX membrane system prepared according to example 1 exceeded clearly that of the references.

Claims

1. A method for producing a catalytic oxygen permeable membrane system, comprising the steps of
 - i. providing a membrane support, and
 - 5 ii. pretreating the membrane support, and
 - iii. coating the pretreated membrane support, and
 - iv. drying and precalcining the pretreated and coated membrane support, and
 - v. repeating steps iii and iv at least once,
 - 10 vi. providing final calcination to the coated membrane support, whereby the membrane system is obtained.
2. The method according to claim 1, wherein coating is provided by wash-coating method.
- 15 3. The method according to claim 2, wherein the washcoating method comprises treating the membrane support with Ce-La-Zr mixed oxide based aqueous slurry.
4. The method according to claim 3, wherein the Ce-La-Zr mixed oxide based aqueous slurry is prepared by mixing together the starting materials
20 comprising:
 - 15-25 % by weight of Ce-La-Zr mixed oxide in a form of solid powder,
 - 60-80 % by weight of ion exchanged water, and
 - 1-10 % by weight acid, and
 - 1-10 % by weight of zirconium nitrate solution.
- 25 5. The method according to claim 4, wherein the Ce-La-Zr mixed oxide based aqueous slurry is prepared by mixing the starting materials for 1 h at 3000 rpm with a propeller mixer, at room temperature.
6. The method according to any one of claims 1-5, wherein the drying is performed by subjecting the wet surface of the coated pretreated membrane
30 support to warm air, preferably at least 20 °C, for at least 5 minutes, preferably for at least 10 minutes.

7. The method according to any one of claims 1-6, wherein the precalcination temperature in step iv is from 400 to 600 °C, preferably from 450 to 550 °C, more preferably from 480 to 520 °C.
8. The method according to any one of claims 1-7, wherein the duration of the precalcination is at least 5 minutes, preferably at least 10 minutes, at normal pressure and atmosphere, where after the coated pretreated membrane support is let to cool into room temperature.
9. The method according to any one of claims 1-8, wherein the final calcination temperature in step vi is from 700 to 900 °C, preferably from 750 to 850 °C, more preferably from 780 to 820 °C.
10. The method according to any one of claims 1-9, wherein the duration of the final calcination is at least 50 minutes, preferably at least 60 minutes, at normal pressure and atmosphere.
11. The method according to any one of claims 1-8, wherein steps iii-iv are repeated at least two times, preferably at least three times, more preferably at least four times, until the desired thickness is obtained for the mixed oxide coating.
12. The method according to claim 11, wherein the thickness of the mixed oxide coating is at least 50 µm, preferably from 50 to 200 µm, more preferably from 130 to 160 µm.
13. The method according to any one of claims 1-12, wherein the substrate is ceramic material or metallic material, preferably porous ceramic material or tubular metallic material, preferably porous alumina or tubular steel or tubular Ni and Cr or Fe based alloys.
14. A reactor for catalytic partial oxidation of hydrocarbons into syngas, comprising
i". at least one tubular membrane system, wherein the membrane system is obtained by any one of the claims 1-13.
15. A reactor according to claim 14, comprising
i". an outer jacket configured to include the membrane system, and

- ii''. at least one tubular membrane system obtained by any one of the claims 1-13, installed into the reactor jacket, and
- iii''. inlet means configured to guide air inside into the tubular membrane system, through it, and exit means configured to recover the exiting air from the inside of the tubular membrane system, and
- iv''. inlet means configured to guide hydrocarbons into contact with the outer surface of the tubular membrane system, passing the tubular membrane system, and exit means configured to recover the exiting reacted hydrocarbons from the outer surface of the tubular membrane system, and
- v.'' heating means configured to increase the temperature of the air and the hydrocarbons to a level wherein the oxidation reactions take place.

16. A method for catalytic partial oxidation of hydrocarbons into syngas in a reactor, characterised by the steps of

- i'. heating the reactor by external heating means or by heat from CPOX reaction, and
- ii'. providing air and hydrocarbons containing tar into the reactor, and
- iii'. contacting the air with the inner surface of at least one tubular membrane system according to claim 1-13, and guiding it through the membrane system while it is being depleted from oxygen, and
- iv'. contacting the hydrocarbons containing tar with the outer surface of the membrane system, and guiding them through the membrane system while they are being reacted into syngas, and
- v'. recovering the syngas and oxygen depleted air from the reactor.

17. A method according to claim 17, wherein the air flow into the reactor is from 1 to 10 vol-% of the inlet gas flow.

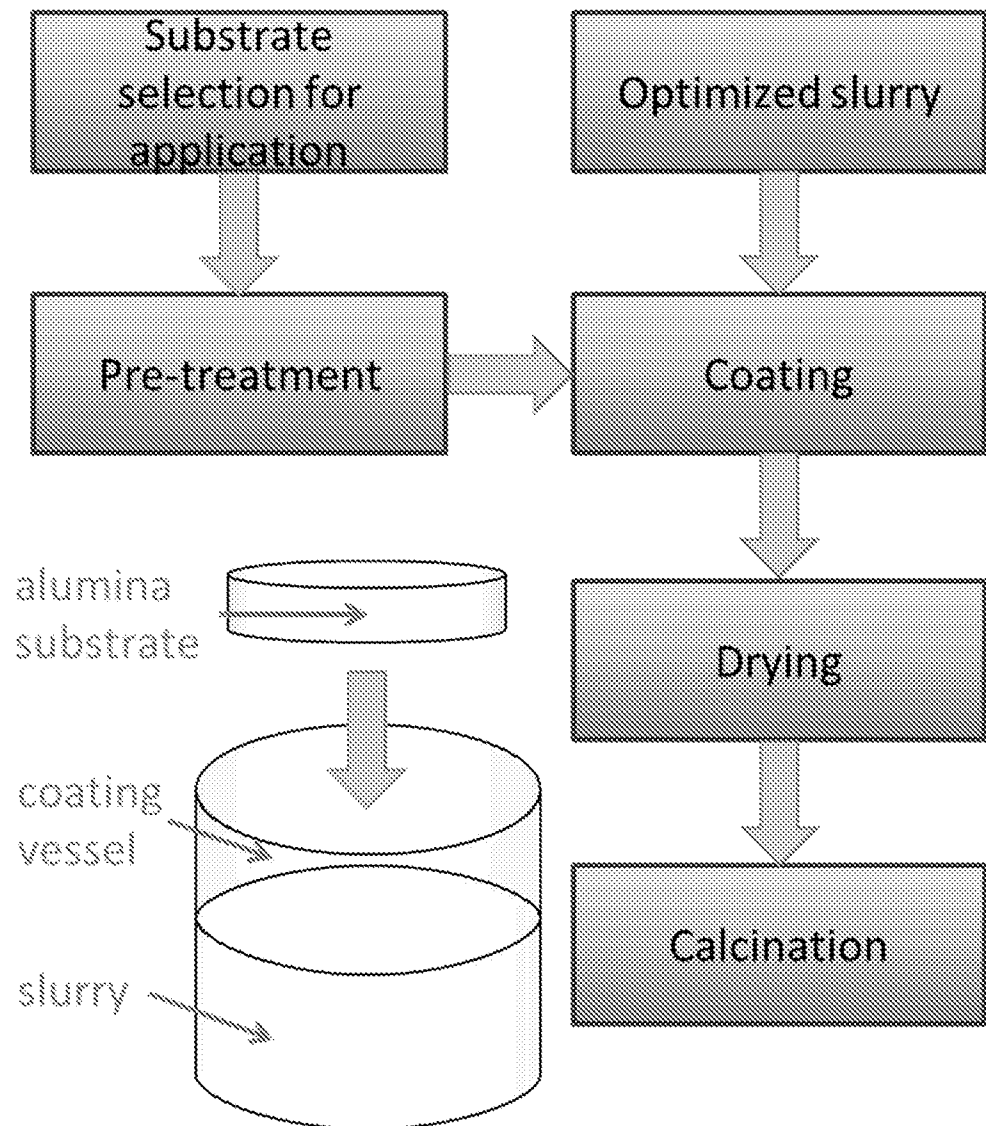


Figure 1



Figure 2 C and D



Figure 2 A and B

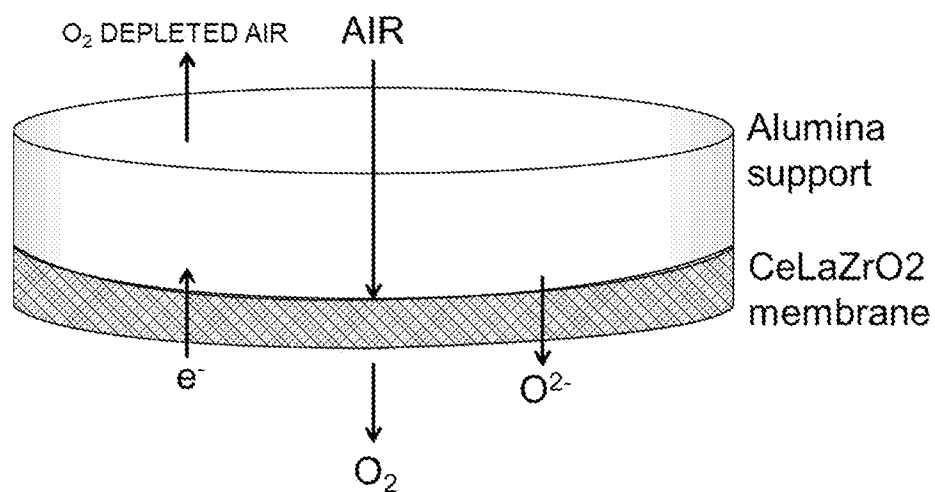


Figure 3

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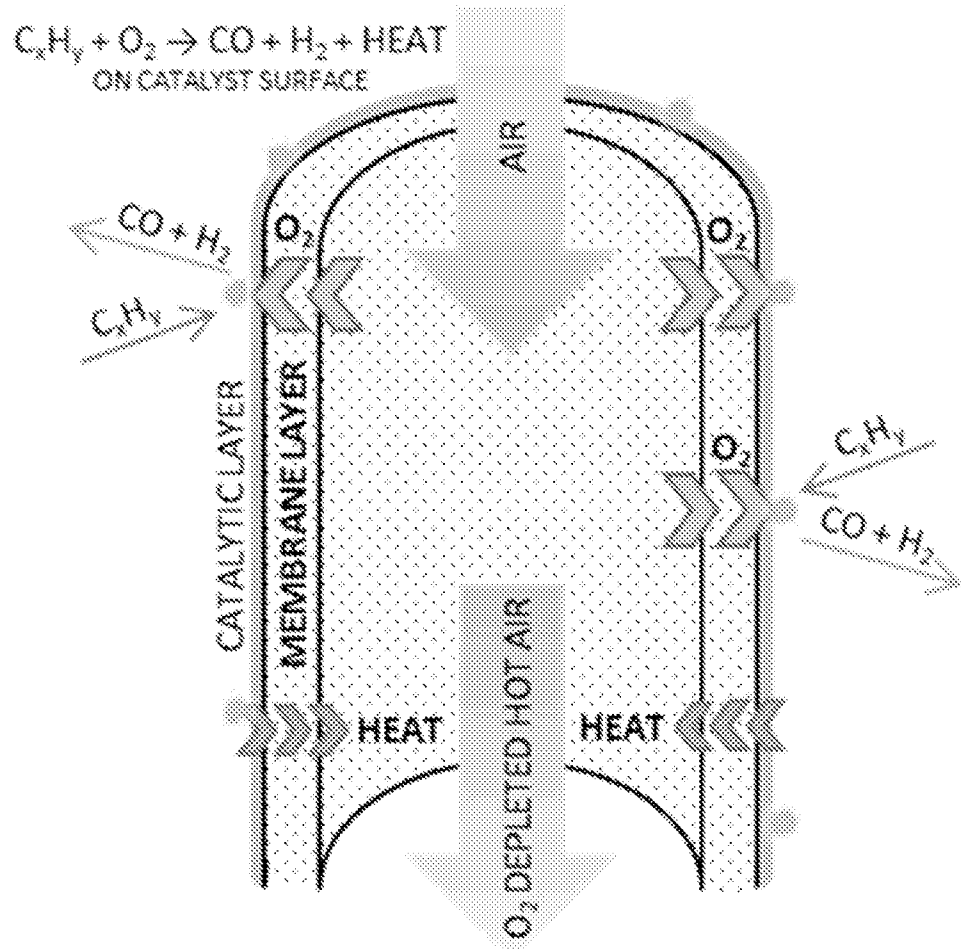


Figure 4

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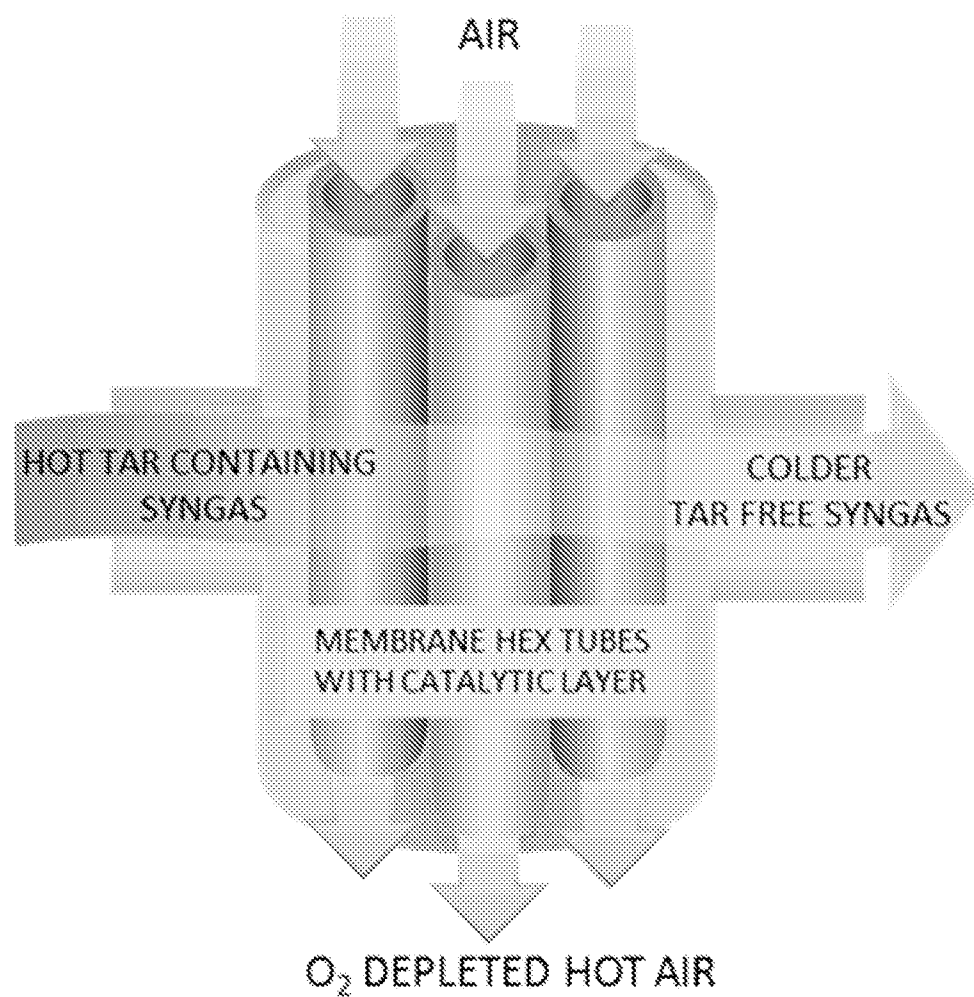


Figure 5

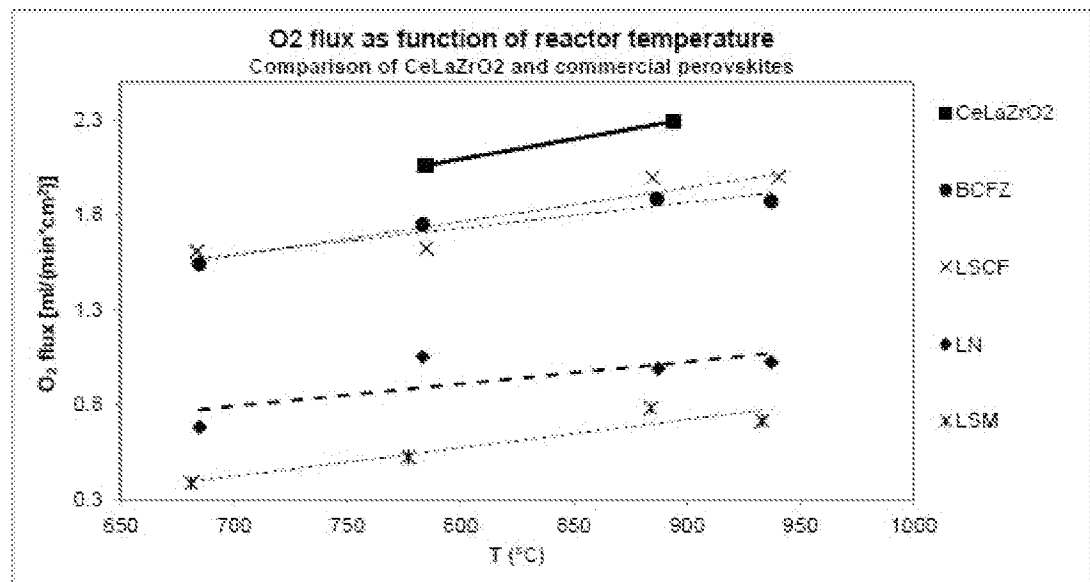


Figure 6

INTERNATIONAL SEARCH REPORT

International application No
PCT/FI2017/050436

A. CLASSIFICATION OF SUBJECT MATTER

INV. B01D67/00 B01D69/04 B01D69/10 B01D71/02 C01B3/38
C01B13/02

ADD.

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)

B01D B01J 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 practicable, 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	XIONG YIN ET AL: "Crafting La _{0.2} Sr _{0.8} MnO ₃ -[delta] membrane with dense surface from porous YSZ tube", JOURNAL OF SOLID STATE ELECTROCHEMISTRY ; CURRENT RESEARCH AND DEVELOPMENT IN SCIENCE AND TECHNOLOGY, SPRINGER, BERLIN, DE, vol. 10, no. 8, 6 May 2006 (2006-05-06), pages 643-650, XP019385458, ISSN: 1433-0768, DOI: 10.1007/S10008-006-0131-1 page 643 - page 645 -----	1,2,6-13
X	WO 2015/152494 A1 (KOREA ENERGY RESEARCH INST [KR]) 8 October 2015 (2015-10-08)	1,2,6-13
Y	abstract ----- -/-	3-5



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 application or patent 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

Date of the actual completion of the international search

5 September 2017

Date of mailing of the international search report

21/09/2017

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Marti, Pedro

INTERNATIONAL SEARCH REPORT

International application No
PCT/FI2017/050436

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2012/067210 A1 (SANE AJIT Y [US] ET AL) 22 March 2012 (2012-03-22) the whole document -----	14-17
X	EP 2 045 212 A1 (JAPAN SCIENCE & TECH AGENCY [JP]; TDK CORP [JP]) 8 April 2009 (2009-04-08) the whole document -----	14-17
X	US 6 355 093 B1 (SCHWARTZ MICHAEL [US] ET AL) 12 March 2002 (2002-03-12) the whole document -----	14-17
Y	WO 2012/022988 A1 (STEPHENSON HAZEL [GB]; BRADSHAW HEATHER [GB]; SIMELL PEKKA [FI]; SOLLA) 23 February 2012 (2012-02-23) cited in the application the whole document -----	3-5
A	WO 2014/059992 A1 (UNIV DANMARKS TEKNISKE [DK]) 24 April 2014 (2014-04-24) the whole document -----	1-17
A	LEI CAO ET AL: "Autothermal Reforming of Methane Over CeO ₂ -ZrO ₂ -La ₂ O ₃ Supported Rh Catalyst", CATALYSIS LETTERS, KLUWER ACADEMIC PUBLISHERS-PLENUM PUBLISHERS, NE, vol. 131, no. 3-4, 6 March 2009 (2009-03-06), pages 474-479, XP019728267, ISSN: 1572-879X, DOI: 10.1007/S10562-009-9888-Z the whole document -----	1-13

INTERNATIONAL SEARCH REPORT

International application No.
PCT/FI2017/050436

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

see additional sheet

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☒ As all searchable claims could be searched without effort justifying an additional fees, this Authority did not invite payment of additional fees.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- ☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- ☐ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. claims: 1-17

Method for producing a catalytic oxygen permeable membrane system, reactor for catalytic partial oxidation of hydrocarbons into syngas, and method for catalytic partial oxidation of hydrocarbons into syngas in a reactor.

1.1. claims: 1-13

Method for producing a catalytic oxygen permeable membrane system, comprising the steps of
i. providing a membrane support, and
ii. pretreating the membrane support, and
iii. coating the pretreated membrane support, and
iv. drying and precalcining the pretreated and coated membrane support, and
v. repeating steps iii and iv at least once,
vi. providing final calcination to the coated membrane support, whereby the membrane system is obtained.

1.2. claims: 14-17

Claims 14-15: Reactor for catalytic partial oxidation of hydrocarbons into syngas, comprising
i". at least one tubular membrane system, wherein the membrane system is obtained by any one of the claims 1 -13.
Claims 16_17: Method for catalytic partial oxidation of hydrocarbons into syngas in a reactor

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/FI2017/050436

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2015152494 A1	08-10-2015	KR 20150114711 A WO 2015152494 A1	13-10-2015 08-10-2015
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WO 2014059992 A1	24-04-2014	NONE	