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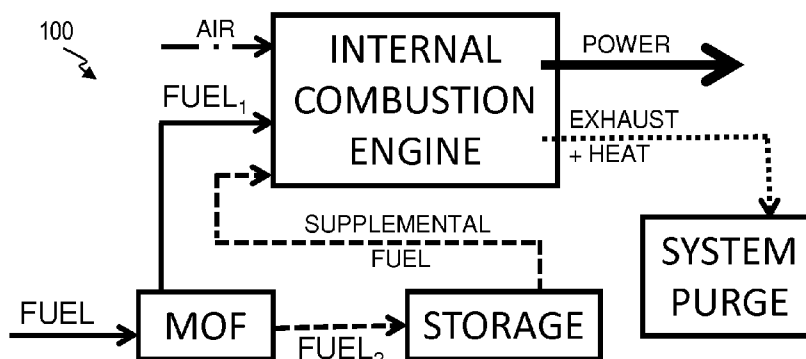


FIG 1

(57) Abstract: Systems and methods for separating hydrocarbons on an internal combustion powered vehicle via one or more metal organic frameworks are disclosed. Systems and methods can further include utilizing separated hydrocarbons and exhaust to generate hydrogen gas for use as fuel. In one aspect, a method for separating hydrocarbons can include contacting a first component containing a first metal organic framework with a flow of hydrocarbons and separating hydrocarbons by size. In certain embodiments, the hydrocarbons can include alkanes.

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## FUEL UPGRADING AND REFORMING WITH METAL ORGANIC FRAMEWORK

### BACKGROUND

5 Today, polluting emissions (NO<sub>x</sub>, SO<sub>x</sub>, CO, etc.) and particularly carbon dioxide (CO<sub>2</sub>) from fossil fuel transportation sector represents one third of the overall CO<sub>2</sub> emissions in the world; therefore reducing the CO<sub>2</sub> emission from vehicles is now an important global challenge. Efficiency of fossil based engines such as gasoline and diesel was always, and still is, the motivating element for many research and development programs worldwide and it is  
10 of prime importance in driving the worldwide economy. Engine efficiency and emissions are primarily related to the quality of combustion during both spark ignition of gasoline fuel and compression ignition of diesel fuel. In fact, high octane and cetane numbers, key quality parameters for gasoline and diesel, respectively, as well as (hydrogen) H<sub>2</sub> rich fuels, offer the promise of improvements in both emissions and efficiency.

15 Although the development of a fully H<sub>2</sub>-oriented automobile industry has been the focus of extensive research and development in academia and industry for many years, the questions of how to create, deliver and store H<sub>2</sub> economically and technically have still not been answered. Behind the apparent simplicity of direct H<sub>2</sub> fuel vehicles lay the problems of H<sub>2</sub> supply and on-board storage; these have no quick-fix solutions. On-board reforming  
20 technology, to produce high purity H<sub>2</sub> for fuel cells, does not offer clear advantages over gasoline/diesel internal combustion engines (ICE) vehicles.

Alternative approaches using metal organic frameworks (MOFs) for on-board reforming and upgrading of fossil fuels (gasoline, diesel, methanol or ethanol) to H<sub>2</sub> rich and high RON gasoline and high CN diesel for ICE systems can have many benefits in reducing  
25 the complications and capital investments needed to develop a fuel infrastructure that can support the emerging H<sub>2</sub> vehicle market.

### SUMMARY

In one aspect, a method for separating hydrocarbons can include contacting a first  
30 component containing a first metal organic framework with a flow of hydrocarbons and separating hydrocarbons by size. In certain embodiments, the hydrocarbons can include alkanes.

In certain embodiments, the method can include separating dibranched hydrocarbons from mono-branched hydrocarbons and linear hydrocarbons. The method can include

separating 2,3-dimethylbutane and 2,2-dimethylbutane. The method can include reforming gas using a metal organic framework, other catalysts or steam reforming. The method can include separating hydrocarbons in an automobile.

In certain embodiments, the method can include separating the hydrocarbons into  
5 hydrocarbons with low research octane number and hydrocarbons with high research octane number. The method can include moving the hydrocarbons with high research octane number to an internal combustion engine.

In certain embodiments, the internal combustion engine can produce an exhaust gas.  
In certain embodiments, the method can include reforming the exhaust gas.

10 In certain embodiments, the reformat can contain hydrogen.

In certain embodiments, the method can include feeding part of the reformat to the internal combustion engine. In certain embodiments, the exhaust gas can be reformed using a metal organic framework, a zeolite catalyst or steam reforming.

15 Other aspects, embodiments, and features will be apparent from the following description, the drawings, and the claims.

### BRIEF DESCRIPTION OF THE DRAWINGS

**Figure 1** illustrates a schematic view of a system and method for optimizing an internal combustion engine, according to one or more embodiments.

20 **Figure 2** illustrates a schematic view of a system and method for optimizing the performance of an ICE by generating H<sub>2</sub>, according to one or more embodiments.

**Figure 3** illustrates a schematic view of a device using one or more MOFs to separate hydrocarbons, according to one or more embodiments.

25 **Figure 4A** illustrates n-pentane and isopentane sorption isotherms at 393 K for the Y-fum-MOF, according to one or more embodiments.

**Figure 4B** illustrates n-butane and isobutene sorption isotherms at 393 K for the Y-fum-MOF, according to one or more embodiments.

30 **Figure 5A** illustrates a graphical view of single-component adsorption isotherms for pentane, isopentane, and 2,2,4-trimethylpentane on a zeolite-like metal-organic, according to one or more embodiments.

**Figure 5B** illustrates a graphical view of the adsorption of pentane and isopentane on a zeolite-like metal-organic framework, according to one or more embodiments.

## DETAILED DESCRIPTION

Methods and systems are described herein for separating fuel streams via one or more MOFs for use in optimizing ICE fuels, such as diesel and gasoline, and providing feed streams for fuel reformers. MOFs can separate fuel streams using various methods. The practicality of the adsorptive separation technology and its associated efficiency are strongly dependent and directly correlated to the intrinsic properties of the employed separation adsorbent. Adsorptive separation can be accomplished by one of three mechanisms: steric, kinetic, or equilibrium-based. The steric effect originates from molecular sieving properties of the adsorbent, wherein only relatively small and appropriately shaped molecules can diffuse into the adsorbent while the other molecules are totally excluded. In contrast, kinetic adsorption is based on the differences in diffusion rates of different adsorbate molecules.

Metal organic frameworks (MOFs) are a versatile and promising class of crystalline solid state materials which MOFs are architecturally robust and can have a porosity of greater than 50% of the MOF crystal volume. The surface area values of such MOFs can range from 200 to 7,000 m<sup>2</sup>/g, thus exceeding those of traditional porous materials such as zeolites and carbons. The ordered crystalline structures of MOFs allow porosity and functionality (e.g., permselectivity toward mono-branched and n-paraffins), to be tailored towards various applications while retaining isorecticular topologies. For example, MOFs with large pore apertures and low densities can be tailored for selective inclusion of large molecules and proteins, both as a storage means and/or as a reaction facilitation platform. MOFs can exhibit porosity through a configuration of one or more of channels and cages throughout the networked architecture.

Further, the thermal and chemical stability of many MOFs has made them amenable to post-synthetic covalent organic and metal-complex functionalization. These capabilities enable substantial enhancement of gas storage in MOFs and have led to their extensive study in the catalysis of organic reactions, activation of small molecules (hydrogen, methane, and water), hydrocarbon and gas separation, and fuel storage.

Generally, MOFs comprise a network of nodes and ligands, wherein a node has a connectivity capability at two or more functional sites, and a ligand has a connectivity capability at least at two functional sites, each of which connect to a node. Nodes are typically metal ions or metal containing clusters. Ligands are typically poly-functional, or polytopic, organic molecules, and comprise two or more functional sites capable of each connecting to a node. In some instances, ligands with node connectivity capability at two or more functional sites can also be characterized as nodes. Ligands can include two functional

sites capable of each connecting to a node, and optionally one or more additional functional sites which do not connect to nodes within a particular framework. In some embodiments, polytopic ligands can be heteropolytopic, wherein at least one of the two or more functional sites differs from another functional site.

5 A MOF can comprise a metal-based node and an organic ligand which extrapolate to form a coordination network. Such coordination networks have advantageous crystalline and porous characteristics affecting structural integrity and interaction with foreign species (e.g., hydrocarbons). The particular combination of nodes and ligands within a framework will dictate the framework topology and functionality. Through ligand modification or  
10 functionalization, the environment in the internal pores can be modified to suit specific applications.

MOF can be represented by the formula  $[(\text{node})_a(\text{ligand})_b(\text{solvent})_c]_n$ , wherein  $n$  represents the number of molecular building blocks. Solvent represents a guest molecule occupying pores within the MOF, for example as a result of MOF synthesis, and can be  
15 evacuated after synthesis to provide a MOF with unoccupied pores. Accordingly, the value of  $c$  can vary down to zero, without changing the definitional framework of the MOF. Therefore, in many instances, MOFs can be defined as  $[(\text{node})_a(\text{ligand})_b]_n$ , without reference to a solvent or guest molecule component.

Disclosed herein are systems and methods utilizing MOFs for upgrading ICE fuel,  
20 and optimizing ICE performance. MOFs suitable for the methods described herein can be chosen based on the pore aperture size of the MOF. The pore aperture size refers to the size of the aperture which gives access to a cage. In case of channels, the average pore diameter can be the same as the aperture size. MOFs suitable for the methods described herein can be chosen based on the average pore size of the MOF. An average pore size refers to the size of  
25 one or more of the channels and cages present within a MOF architecture. For example, a key parameter that drives the separation of aliphatic unbranched paraffins (i.e., n-paraffins) from branched paraffins (i.e., iso-paraffins) is the aperture size of an MOF.

### **Gasoline Upgrading**

30 Disclosed herein are systems and methods for optimizing the performance of an ICE by altering the Research Octane Number (RON) value of fuel. RON is a rating assigned to individual fuel constituents based on the performance of an engine fuelled by a particular fuel constituent. The weighted average of RON values for all individual fuel constituents indicate the RON value of a fuel. RON values is determined by running the fuel in a test engine with

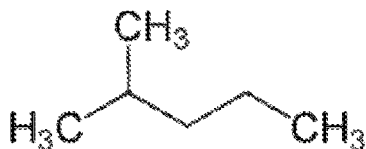
a variable compression ratio under controlled conditions, and comparing the results with those for mixtures of iso-octane and n-heptane. Generally, the magnitude of the RON value relates to the amount of compression a fuel constituent can withstand before igniting. Fuels with higher RON values increase the performance of non-compression ICEs (i.e., gasoline  
 5 ICEs), as fuel can be more highly compressed before being ignited. Gasoline with lower RON numbers can lead to engine knocking, which is detrimental to performance and engine longevity.

A higher degree of branching can increase the RON value of a paraffin isomer. As used herein, "paraffin" refers to alkanes, or saturated hydrocarbons molecules consisting of  
 10 hydrogen and carbon atoms connected by single bonds. Paraffins can include aliphatic (i.e., open chain) and cyclic alkanes. For example, an unbranched alkane such as n-hexane:

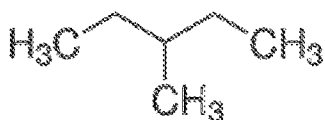


with a kinetic diameter of 3.8-4.3 Å, has a RON value of 30. Monobranched alkane 2-  
 methylpentane:

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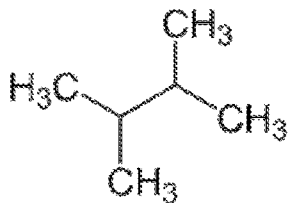


has a RON value of 75, and monobranched alkane 3-methylpentane:

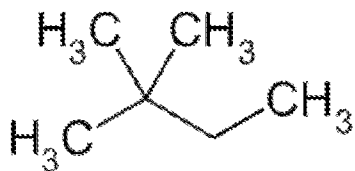


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with a kinetic diameter of 5 Å, has a RON value of 75. Similarly, dibranched alkane 2,3-  
 dimethylbutane:



with a kinetic diameter of 5.6 Å, has a RON value of 94, and dibranched alkane 2,2-  
 dimethylbutane:



with a kinetic diameter of 6.2 Å, has a RON value of 105. Accordingly, the dibranched paraffin isomers, such as hexanes, are more valuable gasoline constituents than monobranched paraffin isomers and unbranched paraffin isomers.

5           The systems and methods provided herein can optimize the performance of a gasoline ICE by isolating dibranched paraffins from mono-branched and n-paraffins to alter the RON value of fuel injected into the ICE. Figure 1 illustrates a system and method 100 for optimizing an ICE by separating a fuel into two or more streams. System and method 100 can be performed on-board a vehicle. System and method 100 comprises contacting a fuel  
10           with an MOF, and separating the fuel into a first fuel stream (Fuel<sub>1</sub>) and a second fuel stream (Fuel<sub>2</sub>). Fuel can be supplied by a fuel source, such as a fuel tank. Fuel can contact the MOF in a liquid state, a gaseous state, or combinations thereof.

          Suitable MOFs will be described below. In some embodiments, separating occurs by the MOF selectively sorbing one or more constituents of the fuel, and subsequently desorbing  
15           the selectively sorbed one or more constituents to form a first fuel stream or a second fuel stream. Sorption can include one or more of adsorption and desorption. In some embodiments, separating occurs by the MOF structure, in the form of a membrane or packed bed or column, selectively allowing one or more fuel constituents to permeate the MOF structure. An MOF has “permselectivity” for a constituent which is selectively permitted to  
20           permeate the MOF structure. Suitable MOFs generally have very rigid structures, which are capable of maintaining structural stability over a number of sorption/desorption cycles, and/or over a high volume of constituent permeation. In some embodiments, suitable MOFs will have aperture sizes between about 0.4 nm and about 0.6 nm, between about 0.45 and about 0.55 nm, or between about 0.4 and 0.5 nm. The MOF can separate the fuel based on the  
25           degree of branching of the fuel constituent isomers. Accordingly, the MOF can separate the fuel based on RON value. MOFs can separate fuel constituent isomers of butanes, pentanes, hexanes, heptanes, octanes, nonanes and decanes. In one embodiment, the first fuel stream has a higher RON value than the second fuel stream. In one embodiment, the second fuel stream has a higher RON value than the first fuel stream.

The first fuel stream can then be injected into an ICE in combination with air, wherein the first fuel stream is combusted, generating power, heat, and exhaust. The major components (i.e., those comprising greater than about 1%) of exhaust from a vehicle with an ICE typically include N<sub>2</sub>, CO<sub>2</sub>, CO, H<sub>2</sub>O, and O<sub>2</sub>. Minor components (i.e., those comprising less than about 1%) of ICE exhaust typically include SO<sub>x</sub> compounds (e.g., SO<sub>2</sub>, SO<sub>3</sub>), NO<sub>x</sub> compounds (e.g., NO, NO<sub>2</sub>), low molecular weight aldehydes (e.g., HCHO), low molecular weight organic acids (e.g., HCOOH), low molecular weight alcohols (e.g., CH<sub>3</sub>OH), and hydrocarbons (e.g., C<sub>n</sub>H<sub>m</sub>). For spark ignition (i.e., gasoline) ICEs, H<sub>2</sub> and CO typically comprise major components of exhaust. For compression ignition (i.e., diesel) ICEs, H<sub>2</sub> and CO typically comprise minor components of exhaust. In a vehicle utilizing oxy-combustion capture, the nitrogen is substantially removed from air to create an oxygen input stream. The exhaust from this type of vehicle typically contains significantly higher amounts of CO<sub>2</sub> and H<sub>2</sub>O by weight, and very small amounts of N<sub>2</sub>. Air can comprise ambient air, or a mixture of one or more of oxygen, nitrogen, and carbon dioxide. Heat and exhaust can be directed to a system purge. System purge can comprise an exhaust to atmosphere. System purge can comprise a storage vessel. For example, a storage vessel can collect one or more of H<sub>2</sub> or CO<sub>2</sub>. System purge can comprise a combination of exhaust to atmosphere and a storage vessel. The second fuel stream can be directed to storage. Fuel in storage can optionally be injected into the ICE as a supplemental fuel stream.

In one embodiment, the first fuel stream has a higher RON value than the second fuel stream, and is injected into the ICE to increase performance. The second fuel stream can be stored for subsequent discharge or removal. Alternatively or additionally, the second fuel stream can be injected into the ICE as supplemental fuel when high performance is not required or desired. For example, system and method 100 can selectively direct dibranched paraffin isomers into the first fuel stream to increase engine performance, and selectively direct monobranched and unbranched paraffin isomers into the second fuel stream. In a specific embodiment, system and method 100 can selectively direct 2,3-dimethylbutane and 2,2-dimethylbutane into the first fuel stream to increase engine performance, and selectively direct monobranched hexane isomers and n-hexane into the second fuel stream. In this specific embodiment, an MOF based membrane with high permselectivity toward monobranched and n-paraffins vs. di-branched paraffins, can be used.

In one embodiment, the first fuel stream has a lower RON value than the second fuel stream, and is injected into the ICE to provide a threshold level of performance. The second fuel stream can be stored for subsequent discharge or removal. Alternatively or additionally,



the second fuel stream can be injected into the ICE as supplemental fuel when higher performance is required or desired. For example, system and method 100 can selectively direct monobranched and unbranched paraffin isomers into the first fuel stream to provide a threshold level of performance, and selectively direct dibranched paraffin isomers into the second fuel stream. In a specific embodiment, system and method 100 can selectively direct monobranched hexane isomers and n-hexane into the first fuel stream to provide a threshold level of performance, and selectively direct 2,3-dimethylbutane and 2,2-dimethylbutane into the second fuel stream. In this specific embodiment, an MOF based membrane with high permselectivity toward mono-branched and n-paraffins vs. di-branched paraffins, can be used.

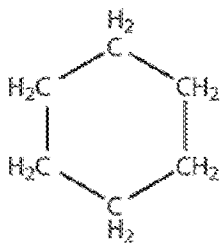
### Diesel Upgrading

Disclosed herein are systems and methods for optimizing the performance of a diesel ICE by altering the Cetane Number (CN) value of fuel. A CN value is similar to a RON value, but is applied to diesel fuels and is a measurement of the combustion during compression ignition. The CN value is used to measure the quality of this combustion according to the self-ignition delay. A higher CN value indicates a shorter self-ignition delay of a fuel more complete combustion of fuel. As fuel burns faster and more completely in a diesel ICE, the engine experiences greater performance and produces fewer harmful emissions. Conversely, fuels with low CN values are slower to ignite and do not burn completely.

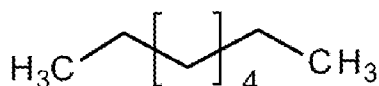
Generally, unbranched aliphatic paraffins have higher CN values than branched or cyclic isomers. For example, an unbranched alkane such as n-hexane:



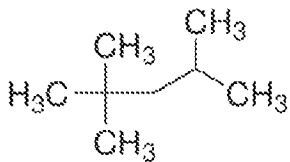
with a kinetic diameter of 3.8-4.3 Å, has a CN value of 45, while a cyclic cyclohexane isomer:



with a kinetic diameter of 6 Å, has a CN value of 15. Similarly, an unbranched alkane such as n-octane:



with a kinetic diameter of 4.3 Å, has a CN value of 64, while a branched 2,2,4-trimethylpentane isomer:



with a kinetic diameter of 6.2 Å, has a CN value of 14. Accordingly, the unbranched aliphatic paraffin isomers, such as n-hexane, are more valuable diesel fuel constituents than branched and cyclic paraffin isomers. Further,  $C_n$  paraffins have higher CN values than  $C_n$  olefins. As used herein, “oleffin” refers to alkenes, or unsaturated hydrocarbons molecules consisting of hydrogen and carbon atoms with at least one carbon-to-carbon double bond. Oleffins can include aliphatic (i.e., open chain) and cyclic alkenes.

The systems and methods provided herein can optimize the performance of a diesel ICE by isolating unbranched aliphatic paraffin isomers from branched and cyclic paraffin isomers to alter the CN value of fuel injected into the ICE. System and method 100, as illustrated in Figure 1, can also optimize a diesel ICE. System and method 100 comprises contacting a fuel with an MOF, and separating the fuel into a first fuel stream (Fuel<sub>1</sub>) and a second fuel stream (Fuel<sub>2</sub>). Fuel can be supplied by a fuel source, such as a fuel tank. Fuel can contact the MOF in a liquid state, a gaseous state, or combinations thereof.

Suitable MOFs will be described below. Suitable MOFs generally have very rigid structures, which are capable of maintaining structural stability over a number of sorption/desorption cycles. Separating occurs by the MOF selectively sorbing one or more constituents of the fuel, and subsequently desorbing the selectively sorbed one or more constituents to form a first fuel stream or a second fuel stream. Sorption can include one or more of adsorption and desorption. In some embodiments, separating occurs by the MOF structure, in the form of a membrane or packed bed or column, selectively allowing one or more fuel constituents to permeate the MOF structure. Suitable MOFs generally have very rigid structures, which are capable of maintaining structural stability over a number of sorption/desorption cycles, and/or over a high volume of constituent permeation. In some

embodiments, suitable MOFs will have aperture sizes between about 0.4 nm and about 0.6 nm, between about 0.45 and about 0.55 nm, or between about 0.4 and 0.5 nm. The MOF can separate the fuel based on the degree of branching and cyclic/aliphatic molecular construction of the fuel constituent isomers. Accordingly, the MOF can separate the fuel based on CN value. MOFs can separate fuel constituent isomers of butanes, pentanes, hexanes, heptanes, octanes, nonanes and decanes. In one embodiment, the first fuel stream has a higher CN value than the second fuel stream. In one embodiment, the second fuel stream has a higher CN value than the first fuel stream.

The first fuel stream can then be injected into an ICE in combination with air, wherein the first fuel stream is combusted, generating power, heat, and exhaust. Air can comprise ambient air, or a mixture of one or more of oxygen, nitrogen, and carbon dioxide. Heat and exhaust can be directed to a system purge. System purge can comprise an exhaust to atmosphere. System purge can comprise a storage vessel. For example, a storage vessel can collect one or more of H<sub>2</sub> or CO<sub>2</sub>. System purge can comprise a combination of exhaust to atmosphere and a storage vessel. The second fuel stream can be directed to storage. Fuel in storage can optionally be injected into the ICE as a supplemental fuel stream.

In one embodiment, the first fuel stream has a higher CN value than the second fuel stream, and is injected into the ICE to increase performance. The second fuel stream can be stored for subsequent discharge or removal. Alternatively or additionally, the second fuel stream can be injected into the ICE as supplemental fuel when high performance is not required or desired. For example, system and method 100 can selectively direct unbranched aliphatic paraffin isomers into the first fuel stream to increase engine performance, and selectively direct olefins and branched and cyclic paraffin isomers into the second fuel stream. Aromatic compounds and polynuclear aromatic compounds can optionally be directed into the second fuel stream. In a specific embodiment, system and method 100 can selectively direct aliphatic C<sub>7</sub>-C<sub>20</sub> n-paraffins into the first fuel stream to increase engine performance, and selectively direct cyclohexane and branched octane isomers into the second fuel stream. In this specific embodiment, an MOF based membrane with high permselectivity toward unbranched aliphatic paraffins vs. branched and cyclic paraffins, can be used.

In one embodiment, the first fuel stream has a lower CN value than the second fuel stream, and is injected into the ICE to provide a threshold level of performance. The second fuel stream can be stored for subsequent discharge or removal. Alternatively or additionally, the second fuel stream can be injected into the ICE as supplemental fuel when higher

performance is required or desired. For example, system and method 100 can selectively direct branched and cyclic paraffin isomers into the first fuel stream to provide a threshold level of performance, and selectively direct unbranched aliphatic paraffin isomers into the second fuel stream. In a specific embodiment, system and method 100 can selectively direct cyclohexane and branched octane isomers into the first fuel stream to provide a threshold level of performance, and selectively direct n-hexane and n-octane into the second fuel stream. In this specific embodiment, an MOF based membrane with high permselectivity toward unbranched aliphatic paraffins vs. branched and cyclic paraffins, can be used.

### 10 **On-board Fuel Reforming**

Disclosed herein are systems and methods for optimizing the performance of an ICE by altering the RON or CN value of fuel, and additionally generating H<sub>2</sub> and combining H<sub>2</sub> with the fuel. Combining a fraction of H<sub>2</sub> in combination with gasoline or diesel fuels before injection into an ICE can be beneficially increase engine performance and reduce harmful emissions. For gasoline-fuelled spark ignition engines, addition of H<sub>2</sub> can improve overall engine efficiency, lower hydrocarbon and NO<sub>x</sub> emissions, and smooth engine operation by reducing cycle-to-cycle variations of cylinder pressure. The benefits for direct-injection spark ignition include faster and more stable combustion, and reduction in the emission of particulate matter. As desired, H<sub>2</sub> can be added to non-diesel fuels such as gasoline and natural gas to promote fuel auto-ignition.

NO<sub>x</sub> emissions from diesel-powered engines are often relatively low compared to NO<sub>x</sub> emissions generated during spark ignition (e.g., from gasoline-powered engines). However, the presence of a large excess of oxygen in diesel exhaust means that the NO<sub>x</sub> + CO reaction, which is the key pathway for NO<sub>x</sub> reduction used on gasoline-fuelled vehicles, becomes much less favorable as the CO is consumed by direct reaction with O<sub>2</sub>. For diesel-fuelled compression ignition engines, the presence of H<sub>2</sub> can obviate the 'NO<sub>x</sub>-particulate tradeoff' and decrease both pollutants simultaneously.

The availability of H<sub>2</sub> on board a vehicle also enables a hybrid after treatment process to be operated, by creating a localized highly reducing atmosphere that allows NH<sub>3</sub> to be formed in situ during the fuel-rich regeneration of a NO<sub>x</sub> trap. The NH<sub>3</sub> can then act as a selective NO<sub>x</sub> reductant. For certain catalysts, such as silver for hydrocarbon-SCR, H<sub>2</sub> can play a major role to sustain its initial high activity by preventing the self-poisoning effect of surface nitration and inhibiting the dehydrogenation and cyclisation of adsorbed hydrocarbons.

Figure 2 illustrates a system and method 200 for optimizing the performance of an ICE by generating H<sub>2</sub> and injecting the H<sub>2</sub> into the ICE in combination with, or in series with, fuel. Additionally, system and method 200 further optimize performance of the ICE by separating a fuel into two or more streams. System and method 200 can be performed on-board a vehicle. System and method 200 comprises contacting a fuel with an MOF, and separating the fuel into a first fuel stream (Fuel<sub>1</sub>) and a second fuel stream (Fuel<sub>2</sub>). In some embodiments, fuel can comprise gasoline and/or diesel. Fuel can be supplied by a fuel source, such as a fuel tank. Fuel can contact the MOF in a liquid state, a gaseous state, or combinations thereof. Suitable MOFs will be described below. In some embodiments, separating occurs by the MOF selectively sorbing one or more constituents of the fuel, and subsequently desorbing the selectively sorbed one or more constituents to form a first fuel stream or a second fuel stream. Sorption can include one or more of adsorption and desorption. In some embodiments, separating occurs by the MOF structure, in the form of a membrane or packed bed or column, selectively allowing one or more fuel constituents to permeate the MOF structure. Suitable MOFs generally have very rigid structures, which are capable of maintaining structural stability over a number of sorption/desorption cycles, and/or over a high volume of constituent permeation. In some embodiments, suitable MOFs will have aperture sizes between about 0.4 nm and about 0.6 nm, between about 0.45 and about 0.55 nm, or between about 0.4 and 0.5 nm. In some embodiments, a suitable MOF aperture size can be determined based on the type of fuel being separated. For example, diesel fuel separation depends on the separation of aliphatic n-paraffins, and accordingly a suitable pore aperture can be up to about 0.49 nm, about 0.5 nm, or about 0.51 nm. Conversely, gasoline fuel separation depends on the separation of iso-paraffins from n-paraffins, and additionally or alternatively di-branched paraffins from mono-branched paraffins. Therefore Accordingly, a suitable pore aperture for MOFs used in gasoline separation, the range of desirable aperture can be broader, for example about 0.5 nm to about 0.6 nm.

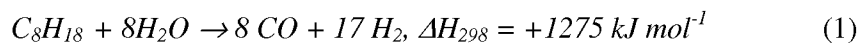
The MOF can separate the fuel based on the degree of branching of the fuel constituent isomers. Accordingly, the MOF can separate the fuel based on RON value. MOFs can separate fuel constituent isomers of butanes, pentanes, hexanes, heptanes, octanes, nonanes and decanes. In one embodiment, the first fuel stream has a higher RON value than the second fuel stream. In one embodiment, the second fuel stream has a higher RON value than the first fuel stream.

The first fuel stream can then be injected into an ICE in combination with air, wherein the first fuel stream is combusted, thereby generating power and heated exhaust. Air can

comprise ambient air, or a mixture of one or more of oxygen, nitrogen, and carbon dioxide. Heated exhaust can be directed to one or more of a system purge and a reformer. Exhaust can be treated before entering the reformer. For example, one or more of heat, CO, and CO<sub>2</sub> can be transferred from the exhaust sent to the system purge to the exhaust sent to the reformer. System purge can comprise an exhaust to atmosphere. System purge can comprise a storage vessel. For example, a storage vessel can collect one or more of H<sub>2</sub> or CO<sub>2</sub>. System purge can comprise a combination of exhaust to atmosphere and a storage vessel.

A portion of the second fuel stream can optionally be directed to storage. Fuel in storage can optionally be injected into the ICE as a supplemental fuel stream. At least a portion of the second fuel stream can be directed to the reformer in combination with at least a portion of the heated exhaust. Onboard reforming techniques can fall into one or more of the following general categories: a) Steam Reforming, b) Partial Oxidation, c) Thermal Dissociation, d) Exhaust-Gas Reforming.

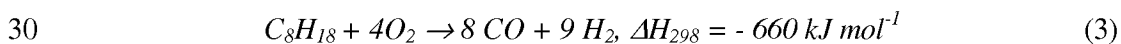
Through the recovery of waste heat, exhaust gas reforming can improve fuel economy and lower CO<sub>2</sub> and other polluting emissions of an ICE. Specifically, an exhaust gas reformer catalyzes endothermic reactions, such as wet and dry reforming, and provides a chemical mechanism for heat recovery. Steam reforming, or wet reforming, is useful in improving fuel heating value due to the endothermic nature of the process, as shown in Equation (1):



It is usually proposed that this energy requirement might be met by the reclamation of otherwise wasted energy by using heat-exchangers. In steam reforming, the required quantities of steam or/and thermal energy are supplied directly by hot engine exhaust gases. Dry reforming uses exhaust as a source of heat and co-reactants (i.e., CO<sub>2</sub>) in the conversion of some of the primary fuel into reformat over a supported metal catalyst, as shown in Equation (2):

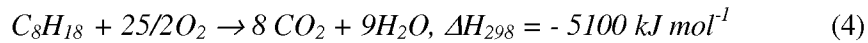


Conversely, partial oxidation is attractive as a means of producing H<sub>2</sub>-rich gaseous fuels without the need for any external supply of energy, as the reaction is itself exothermic as shown in Equation (3):



Unfortunately, the process consequently has a thermal efficiency of around 80%, implying a reduction in fuel heating value of around 20% across the reformer.

A representative (complete) combustion reaction is provided in Equation (4):



Incomplete combustion reactions will generate CO as an additional reaction product. In equations (1)-(4), the respective reactions are simplified by representing fuel as octane, and it should be understood that one or more various hydrocarbons, branched or unbranched, can additionally or alternatively comprise the fuel portion of each respective reaction.

In case of diesel reforming, a common catalyst is a bi-metallic Pt–Rh supported on ceria-zirconia, but its ability to catalyze wet reforming is inhibited by the presence of sulfur in the fuel.

By using a more sulfur-tolerant support material and by excluding Pt, which oxidizes exhaust SO<sub>2</sub> to SO<sub>3</sub> (the gas-phase species that accelerates sulfation of the support), a slightly less active but also less sulfur-sensitive catalyst can be designed.

After the second fuel stream and heated exhaust are directed to the reformer, reformat comprising H<sub>2</sub> is generated by one of the above discussed methods. The reformat comprising H<sub>2</sub> can be injected into the ICE in combination with the first fuel stream and or the second fuel stream. In some embodiments, reformat is processed before injection into the ICE in order to increase the concentration of H<sub>2</sub>. Such a system and method advantageously increases ICE performance by providing a first fuel stream having a higher RON value or CN value, and utilizing the second fuel stream to generate H<sub>2</sub> which can subsequently be injected into the ICE to increase efficiency and reduce polluting emissions such as one of more of NO<sub>x</sub> compounds, CO, and CO<sub>2</sub>.

System and method 200 can optionally comprise a reformat purge. Reformat can have the same composition as reformat purge. In some embodiments, reformat purge comprises treated reformat. For example, reformat purge can comprise reformat which has been treated to remove H<sub>2</sub>, CO, or CO<sub>2</sub>.

In a specific embodiment, system and method 200 can selectively direct 2,3-dimethylbutane and 2,2-dimethylbutane into the first fuel stream to increase engine performance, and selectively direct monobranched hexane isomers and n-hexane into the second fuel stream. In this specific embodiment, an MOF based membrane with high permselectivity toward mono-branched and n-paraffins vs. di-branched paraffins, can be used. In this specific embodiment, an MOF based membrane with high permselectivity toward mono-branched and n-paraffins vs. di-branched paraffins, can be used. The n-paraffins together with exhaust gas resulting from combustion of the di-branched paraffins will be directed toward the reformer.

Figure 3 illustrates a schematic view of a device using one or more MOFs to separate hydrocarbons (i.e., fuel) into different sizes. In Figure 3, 1 is a gas flow inlet, 2 is a housing including MOF (not shown), 3 is a gas outlet and 4 is a gas outlet. Hydrocarbons of different sizes can enter the housing through inlet 1, and MOF can separate the hydrocarbons based on their sizes and/or molecular structures. After separation, gas of one size and/or structure can exit through outlet 3 and gas of a second size and/or structure can exit through outlet 4.

### Examples of Suitable MOFs

An example of an MOF suitable for the systems and methods described herein is an Fcu-MOF. Examples of rare earth fcu-MOF compositions and methods of synthesis can be found in co-owned U.S. Patent Application No. 14/019,511, entitled "Tunable Rare-Earth FCU-Metal-Organic Frameworks", filed September 5, 2013, the disclosure of which is herein incorporated by reference in its entirety.

The metal organic framework composition can comprise  $M_6(OH)_{8-x}O_x(R_1COO)_8$ - $y(R_2CN_4)_y \cdot (H_2O)_z$ , wherein x can be an integer that ranges from 0 to 8, wherein y can be an integer that ranges from 0 to 8, wherein z can be an integer that ranges from 0 to 6, wherein  $R_1$  can include an aryl, a heteroaryl, a carbocyclyl, or a heterocyclyl, and wherein  $R_2$  can include an aryl, a heteroaryl, a carbocyclyl, or a heterocyclyl. M can be selected from the group consisting of Yttrium, Lanthanum, Cerium, Praseodymium, Neodymium, Samarium, Europium, Gadolinium, Terbium, Dysprosium, Holmium, Erbium, Thulium, Ytterbium and Lutetium,

The metal organic framework composition can comprise  $M_9(OH)_{11-x}O_xL$ , wherein x can be an integer that ranges from 0 to 11, wherein M can be a metal ion selected from the group consisting of Yttrium, Lanthanum, Cerium, Praseodymium, Neodymium, Samarium, Europium, Gadolinium, Terbium, Dysprosium, Holmium, Erbium, Thulium, Ytterbium and Lutetium; and wherein L can be a component that can associate with the metal ion. L can include a carboxylate group. L can include a tetrazole group. L can further associate with a compound. The compound can include include  $H_2O$ , Dimethylformamide (DMF), dimethylamine (DMA), Dimethyl Ammonium or formate.

L can include  $(RCOO)_{18-y-z}(CN_4)_y \cdot R'_z$ , wherein y can be an integer that ranges from 0 to 18, wherein z can be an integer that ranges from 0 to 6, wherein R can include an aryl, a heteroaryl, a carbocyclyl, or a heterocyclyl, and wherein  $R'_z$  can include a coordinating ligand. The coordinating ligand can include  $H_2O$ , Dimethylformamide (DMF), dimethylamine (DMA), dimethylammonium, or formate.



A metal organic framework can include a molecular building block. A molecular building block composition can include a metal ion component, and a ligand component including a core including at least one anionic group associated with the metal ion component and the core, wherein the metal ion component and the ligand can associate to form a 4, 6, 8, 10, 12, 14, or 18 connected cluster. The ligand component can include at least two anionic groups associated with the metal ion component. The anionic binding groups can be oriented 180 degrees from each other. The anionic binding groups can be oriented 120 degrees from each other.

The core can include an aryl, a heteroaryl, a carbocyclyl, or a heterocyclyl. The core can include three anionic groups. The core can include four anionic groups. The molecular building block composition can include an oxo component. The oxo component can include a hydroxide group. The oxo component can include an oxide group. The oxo component can include a hydroxide group and an oxide group. The ligand component can include a carboxylate group. The ligand component can include a tetrazole group. The ligand component can include a carboxylate group and a tetrazole group.

The molecular building block can include a hexanuclear cluster. The metal organic framework can comprise a nonanuclear cluster. The metal organic framework can include a 12-connected net; a 4, 12-connected net; a 4, 8-connected net; a 6-connected net; a 3, 8-connected net; an 8-connected net; a 3, 18-connected net, or a 6, 12-connected net.

A molecular building block composition can include  $L_9M_6(OH)_8$ , wherein M can be selected from the group consisting of Yttrium, Ytterbium and Terbium. A molecular building block composition can include  $L_{10}M_6(OH)_8$ , wherein M can be selected from the group consisting of Yttrium and Terbium.

A metal organic framework composition can include oxybis(benzoic) acid and a rare earth metal; benzenetrisbenzoic acid and a rare earth metal; 5-((4-carboxybenzyl)oxy)isophthalic acid and a rare earth metal; [1,1'-biphenyl]-3,4',5-tricarboxylic acid and a rare earth metal; 5-(4-carboxy-3-nitrophenoxy)isophthalic acid and a rare earth metal; thiophen dicarboxylic acid and a rare earth metal; Pyridine carboxylic acid and a rare earth metal; or thiophene-2,5-dicarboxylic acid and a rare earth metal.

An example of MOFs suitable for the systems and methods described herein are Zeolite-like MOFs (ZMOFs). ZMOFs represent a unique subset of MOFs that are topologically related to the pure inorganic zeolites and exhibit similar properties: (i) tunable apertures and cavities, (ii) chemical stability, (iii) ion exchange capability that make it possible to control and tune extraframework cations for the enhancement of interaction

toward specific guest molecules, (iv) tunable inorganic and organic components that permit facile alteration of pore size and/or organic functionality.

A ZMOF can be anionic, and can have a sodalite topology. The z ZMOF can include a linker and a metal. The metal can include Indium, Yttrium, or Cadmium, or a combination thereof. The linker can include an imidazole or pyrimidine moiety. A method for preparing a zeolite-like metal-organic framework membrane can include contacting a substrate with a solution mixture of carboxylic acid, an imidazole, a metal salt, and a nitric acid to form a zeolite-like metal-organic framework membrane.

A defect-free ZMOF thin-film membrane, with a pure phase sodalite topology (sod-zMOF(Im)) can be fabricated and used for fuel upgrading and reforming. This membrane showed a unique CO<sub>2</sub> separation properties for purification of H<sub>2</sub> and CH<sub>4</sub> due mainly to the combination of adsorption effect (charged framework) and the small window aperture of the sod-zMOF (4.1 Å). Because of the small windows aperture (4.1 Å) of sod-zMOF(Im) that allows the permeation/adsorption of n-paraffins (for example n-hexane (3.8-4.3 Å)), this membrane is an ideal starting materials to target molecular sieving of di-branched paraffins (such as 2,3 dimethylbutane (5.6 Å) and 2,2 dimethylbutane (6.2 Å)) from mono-branched and n-paraffins targeting gasoline upgrading to high RON numbers.

An example of an MOF suitable for the methods described herein is an ana-ZMOF. ana-ZMOFs have an ana topology are characterized by the formula  $[M^{III}(4, 5\text{-imidazole dicarboxylic acid})_2X(\text{solvent})_a]_n$  wherein M<sup>III</sup> comprises a trivalent cation of a rare earth element, X comprises an alkali metal element or alkaline earth metal element, and n represents the number of molecular building blocks. In some embodiments, M<sup>III</sup> comprises one or more of a trivalent cation of a rare earth element, including cerium (Ce<sup>3+</sup>), dysprosium (Dy<sup>3+</sup>), erbium (Er<sup>3+</sup>), europium (Eu<sup>3+</sup>), gadolinium (Gd<sup>3+</sup>), holmium (Ho<sup>3+</sup>), lanthanum (La<sup>3+</sup>), lutetium (Lu<sup>3+</sup>), neodymium (Nd<sup>3+</sup>), praseodymium (Pr<sup>3+</sup>), promethium (Pm<sup>3+</sup>), samarium (Sm<sup>3+</sup>), scandium (Sc<sup>3+</sup>), terbium (Tb<sup>3+</sup>), thulium (Tm<sup>3+</sup>), ytterbium (Yb<sup>3+</sup>), or yttrium (Y<sup>3+</sup>).

In some embodiments, the ligand is a heterofunctional ditopic ligand, such as 4,5-imidazole dicarboxylic acid (ImDC). ImDC possesses two *N*- and *O*-hetero-chelating moieties with a potential angle of 144°, as directed by the metal-nitrogen coordination. In some embodiments the ligand is one or more of 1H-Imidazole-2-carboxylic acid, 2,7-diaza-anthracene-1,8-dicarboxylic acid, pyrimidine-4,6-dicarboxylic acid, pyridine-2,5-dicarboxylic acid, or 2,7-diaza-anthracene-3,6-dicarboxylic acid; and/or benzene-1,2,4,5,tetracarboxylic acid, naphthalene-2,3,6,7-tetracarboxylic acid, anthracene-2,3,6,7-tetracarboxylic acid.

In some embodiments, X comprises one or more of an alkali metal element, including lithium, sodium, potassium, rubidium, caesium, or francium. In other embodiments, X comprises one or more of an alkaline earth metal element, including beryllium, magnesium, calcium, strontium, barium, or radium.

5 In some embodiments, the solvent can be H<sub>2</sub>O, N,N-dimethyl formamide (DMF), ethanol, 4,4'-trimethylene-dipiperidine, or 1,2-diaminocyclohexane. In other embodiments, the solvent guest molecules are evacuated. Consequently, a can vary down to zero, without any change in the definitional framework of the ana-ZMOF.

In particular, ana-ZMOFs can be used to kinetically separate linear paraffins from  
10 branched paraffins. Single component adsorption isotherms of linear paraffins and branched paraffins illustrate that the adsorption of linear paraffins is nearly double the adsorption of branched paraffins. In addition, an analysis of the kinetics of sorption on ana-ZMOF shows that linear paraffins are adsorbed at a much faster rate than branched paraffins. Consequently, ana-ZMOF is the ideal candidate material for kinetically separating linear paraffins from  
15 branched paraffins.

In some embodiments, the separation of linear paraffins from branched paraffins is kinetic-based, as opposed to equilibrium-based. In some embodiments, the separation is based on a difference in kinetic diameter and pore aperture size, wherein paraffins with a kinetic diameter that is less than the pore aperture diameter diffuse and/or adsorb on the ana-  
20 ZMOF and paraffins with a kinetic diameter that is greater than the pore aperture diameter remain in the bulk phase. In some embodiments, ana-ZMOF is used to separate paraffins with a kinetics diameter greater than about 4.2Å to 5Å. In some embodiments, the separation is based on a difference in time that it takes a paraffin to reach equilibrium for sorption on an ana-ZMOF, wherein the time it takes a branched paraffin to reach equilibrium is much  
25 greater than the time it takes a linear paraffin to do the same. In some embodiments, the separation is based on both a difference in kinetic diameter and/or pore size, and a difference in equilibrium times.

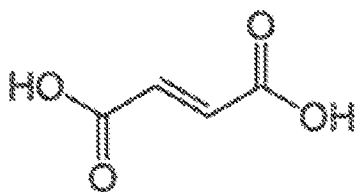
An example of an MOF suitable for the methods described herein is a fumarate-lanthanide fcu-MOF, or fcu-fumaric MOFs. fcu-fumaric MOFs can be characterized by  
30 RE<sub>6</sub>O<sub>4</sub>(OH)<sub>4</sub>(fumarate)<sub>6</sub>(solvent)<sub>x</sub>, and can be designed and synthesized to have pore apertures of about 4.3-3.5Å. Single component adsorption isotherms of linear and branched paraffins were investigated and showed significant and extremely fast adsorption of linear paraffins (such as butane, pentane, etc.) with type I adsorption isotherm. No adsorption of branched paraffins (isobutane, isopentane) was observed Fumarate-lanthanide fcu-MOFs are

ideal for sieving aliphatic paraffins from branched and cyclic paraffins, including the use of both adsorption and membrane technologies. Any linear ditopic ligand with one or more carboxylates, and with a similar size or shorter than a fumarate, can also be utilized. One example, is a squarate. The particular high chemical and thermal stability of this class of materials combined with the easy pore (and aperture) size tunability provides avenues for challenging paraffin/branched paraffin separation.

MOF compositions of the present embodiments include MOFs based on a series of isorecticular structures. These unique materials are built up from an original lanthanide based hexanuclear cluster connected by homo/heterofunctional ditopic ligand, which exhibit outstanding properties in term of separation of traces CO<sub>2</sub> from, CH<sub>4</sub>, O<sub>2</sub>, N<sub>2</sub> containing gas streams.

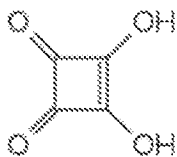
The use of reticular chemistry approach has been successfully implemented to purposefully fine tune the pore size of a rare earth (RE) fcu-platform. The purposeful selection of organic building block, such as fumaric acid or squaric acid, allows for a RE (Tb<sup>3+</sup> and Y<sup>3+</sup>) fcu MOF analogue that displays unprecedented substantially complete to complete sieving of branched paraffins from linear paraffins. This newly isolated MOF molecular sieve has a crystallographically determined window aperture of about 3.8 Å, which was found to represent, in this case, the crystallographic cut-off window size allowing a substantially complete to complete sieving of branched paraffins from linear paraffins. A combination of single and mixed gas/vapor adsorption and calorimetric studies confirm that n-pentane and n-butane were adsorbed into the pores of the fum-fcu-MOF with fast adsorption kinetics, while no adsorption was observed for mono-branched isopentane and isobutane.

As used herein, "fumaric acid" refers to a chemical compound of formula  
HO<sub>2</sub>CCH=CHCO<sub>2</sub>H:



The salts and esters of which are referred to as "fumarates".

As used herein, "squaric acid" or "quadratic acid" refers to a chemical compound of formula: C<sub>4</sub>H<sub>2</sub>O<sub>4</sub>



The salts and esters of which are referred to as “squarates”.

An example of an MOF suitable for the methods described herein is a SIFSIX MOF. SIFSIX MOFs can be identified generally as SIFSIX-n-M, wherein n is at least two, and M can comprise Cu, Zn, Co, Mn, Mo, Cr, Fe, Ca, Ba, Cs, Pb, Pt, Pd, Ru, Rh, and Cd. The SIFSIX-n-M MOF class is isorecticular across its metal analogues (i.e., each M analogue has the same framework topology) and is characterized by periodically arrayed hexafluorosilicate (SIFSIX) octahedral pillars. SIFSIX-n-M MOFs have many desirable characteristics, including tunable pore sizes, which lend the various analogues well to a number of industrial applications.

Ligands for SIFSIX MOFs can comprise a polydentate, or poly-functional ligand, such as a bi-functional ligand, a tri-functional ligand, or ligands with four or more functional sites. In some embodiments, a ligand can comprise an N-donor linker. Ligands can comprise a poly-functional ligand. In some embodiments, a ligand can comprise a plurality of N-donor functional groups. In some embodiments, a ligand can comprise a monocyclic or polycyclic group structure, wherein the cyclic groups can be aromatic or non-aromatic. In some embodiments, a ligand can comprise a nitrogen-containing monocyclic or polycyclic group structure. In some embodiments, a ligand can comprise a nitrogen-containing heterocyclic ligand, including pyridine, pyrazine, pyrimidine, pyridazine, triazine, thiazole, oxazole, pyrrole, imidazole, pyrazole, triazole, oxadiazole, thiadiazole, quinoline, benzoxazole, benzimidazole, and tautomers thereof.

#### **EXAMPLE 1: Steric Separation of Aliphatic n-Paraffins From Aliphatic iso-Paraffins Using Rare-Earth fcu-MOF**

An isorecticular rare earth (RE) fcu-MOF comprising a short fumarate (fum) ligand was used to separate aliphatic n-paraffins from aliphatic iso-paraffins. The RE-**fcu**-MOF platform was synthesized in the presence of fumaric acid to yield 12-connected RE (Y<sup>3+</sup> and Tb<sup>3+</sup>) fumarate based **fcu**-MOF with contracted aperture sizes. Both the Y and Tb analogues were characterized by classical octahedral and tetrahedral cages with the diameter of the largest spheres that can fit into these cages (taking into account the Van der Waals surface) are about 7.6 and 5.2 Å, respectively. In particular, the Y analogue crystallized in a cubic crystal system with Pn-3 space group with unit cell parameter  $a = 18.5353(9)$  Å. Each

yittrium cation ( $Y^{3+}$ ) was surrounded by four oxygen atoms from four  $\mu_3$ -OH groups, four oxygen atoms from carboxylate groups belonging to three crystallographically independent fumarate ligands, and one terminal water molecule. The adjacent Y ions are bridged via  $\mu_3$ -OH and deprotonated carboxylate groups in a bis-monodentate fashion giving rise to the 12-coordinated hexanuclear molecular building block (MBB),  $[Y_6(\mu_3\text{-OH})_8(\text{O}_2\text{C-})_{12}]$ . Each hexanuclear MBB is connected to 12 fumarate ligands to generate a 3-periodic MOF. The resultant crystal structure confirmed that the topology of the Y analogue corresponds to the expected fcu net, the only 12-connected edge transitive net. The hexanuclear cluster  $[Y_6(\mu_3\text{-OH})_8(\text{O}_2\text{C-})_{12}]$  MBBs, where the carbons atoms of the carboxylate moieties act as points of extension, coincide with the cuboctahedron vertex figure of the fcu net.

The choice of fumaric acid as ligand permits the precise control of the access to the cages through triangular windows apertures of ca. 4.7 Å. Such window apertures are advantageously slightly larger than most of linear paraffins (n-butane  $\approx$  4.3 Å) and shorter than most of mono and dibranched paraffins (iso-butane  $\approx$  5 Å). Accordingly, the Y and Tb analogues exhibited a perfect cut-off aperture size for the total separation of *n*-pentane-iso-pentane, n-butane-isobutane and paraffins-branched paraffins in general. Figure 4A illustrates pentane and isopentane sorption isotherms at 393 K for the Y-fum-MOF. Figure 4A illustrates n-pentane and isopentane sorption isotherms at 393 K for the Y-fum-MOF. Figure 4B illustrates n-butane and isobutene sorption isotherms at 393 K for the Y-fum-MOF.

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### **EXAMPLE 2: Kinetic Separation of Aliphatic n-Paraffins From Aliphatic iso-Paraffins Using ana-ZMOF**

Figure 5A illustrates a graphical view of single-component adsorption isotherms for pentane, isopentane, and 2,2,4-trimethylpentane on a zeolite-like metal-organic framework with ana topology, indicating the amount of pentane, isopentane, and 2,2,4-trimethylpentane adsorbed with changes in pressure at 20°C. With respect to the separation of n-pentane from isopentane, Figure 2 illustrates that the adsorption of pentane on an ana-ZMOF is almost double the adsorption of isopentane. With respect to 2,2,4-trimethylpentane, Figure 2 illustrates that 2,2,4-trimethylpentane was experimentally not observed adsorbing onto or diffusing into the pores of ana-ZMOF. In some embodiments, ana-ZMOF can be used as a molecular sieve to separate high octane rating gasoline components from low octane rating gasoline components comprising mono-branched paraffins and linear paraffins, with infinite selectivity.

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Figure 5B illustrates a graphical view of the adsorption of pentane and isopentane on a zeolite-like metal-organic framework with a topology, indicating the normalized pressure of pentane and isopentane as a function of time at 20°C. More specifically, Figure 5B illustrates that an analysis of the kinetics of sorption clearly show that pentane is adsorbed much faster than isopentane, with a time of greater than 5000 seconds for the sorption of isopentane to reach equilibrium.

**WHAT IS CLAIMED IS:**

1. A method for optimizing fuel for an internal combustion engine, the method comprising:  
    contacting a fuel with a metal organic framework;  
    selectively separating one or more constituents of the fuel to define a first fuel stream and a second fuel stream via the metal organic framework; and  
    injecting the first fuel stream into the internal combustion engine.
2. The method of claim 1 wherein the first fuel stream has a higher research octane value than the second fuel stream.
3. The method of claim 1, wherein the first fuel stream has a higher cetane number value than the second fuel stream.
4. The method of claim 1, wherein the second fuel stream is stored after separating.
5. The method of claim 4, wherein the second fuel stream is injected into the internal combustion engine after storing.
6. The method of claim 1, wherein the metal organic framework has a pore aperture of about 0.4 nm to about 0.6 nm.
7. The method of claim 1, wherein the metal organic framework is one or more of a SIFSIX MOF, an fcu-MOF, an ana-ZMOF, and cation exchanged ZMOFs.
8. The method of claim 1, wherein separating comprises separating dibranched paraffins from mono-branched and n-paraffins.
9. The method of claim 1, wherein separating comprises aliphatic C<sub>7</sub>-C<sub>20</sub> n-paraffins from one or more of cyclo-paraffins, branched paraffins, and oleffins.
10. A method for optimizing fuel for an internal combustion engine, the method comprising:  
    contacting a fuel with a metal organic framework;



selectively separating one or more constituents of the fuel to define a first fuel stream and a second fuel stream via the metal organic framework;

combusting the first fuel stream in the internal combustion engine to generate power and heated exhaust;

directing the heated exhaust and at least a portion of the second fuel stream to a reformer;

generating hydrogen gas in the reformer;

injecting the hydrogen gas into the internal combustion engine.

11. The method of claim 10 wherein the first fuel stream has a higher research octane value than the second fuel stream.

12. The method of claim 10, wherein the first fuel stream has a higher cetane number value than the second fuel stream.

13. The method of claim 10, wherein the metal organic framework has a pore aperture of about 0.4 nm to about 0.6 nm.

14. The method of claim 10, wherein the metal organic framework is one or more of a SIFSIX MOF, an fcu-MOF, an ana-ZMOF, and cation exchanged ZMOFs.

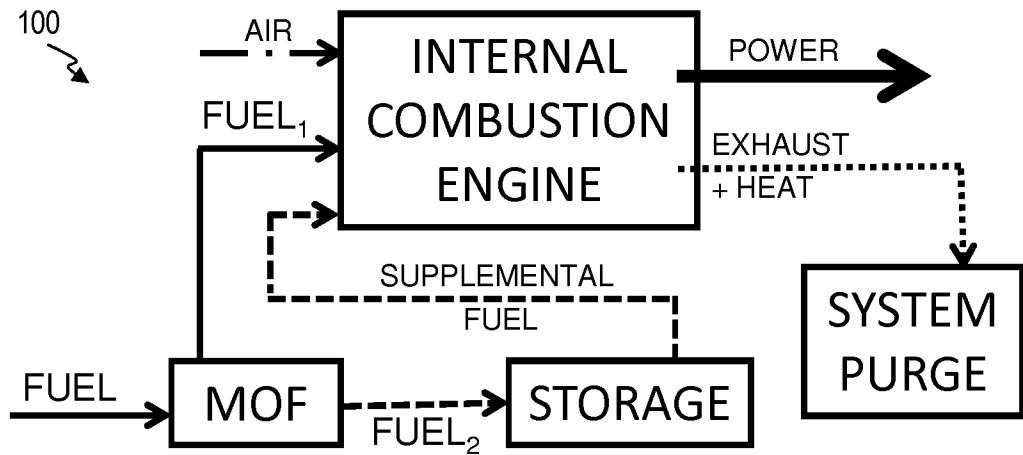
15. The method of claim 10, wherein optimizing includes one or more of increasing efficiency and decreasing pollutants.

16. The method of claim 15 wherein pollutants include one or more of NO<sub>x</sub> compounds, CO, and CO<sub>2</sub>.

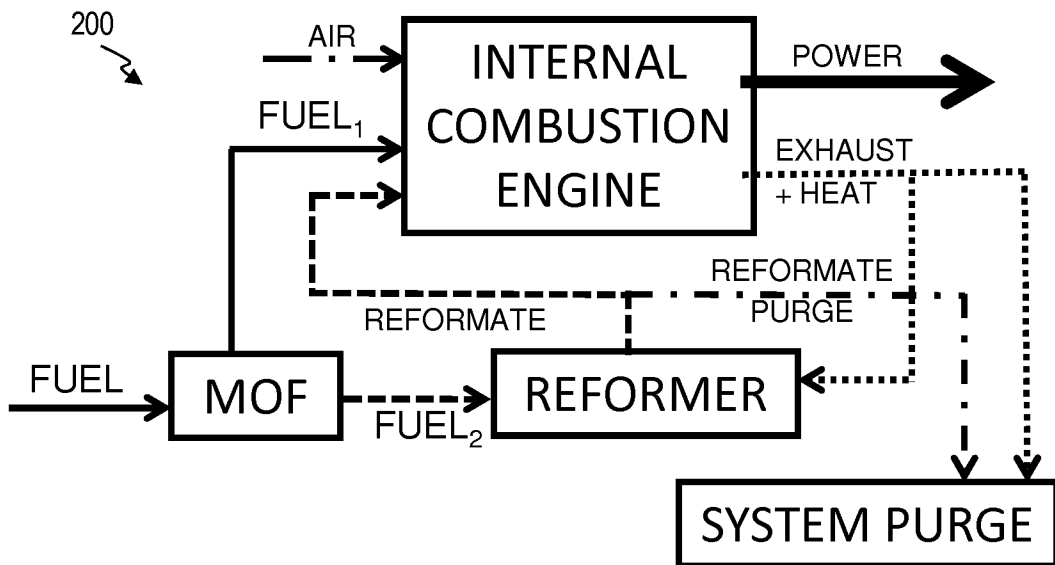
17. The method of claim 10, wherein the internal combustion engine is a compression ignition engine.

18. The method of claim 10, wherein the internal combustion engine is a spark ignition engine.

19. The method of claim 10, wherein separating comprises separating dibranched paraffins from mono-branched and n-paraffins.
  
20. The method of claim 10, wherein separating comprises aliphatic C<sub>7</sub>-C<sub>20</sub> n-paraffins from one or more of cyclo-paraffins, branched paraffins, and oleffins.



**FIG 1**



**FIG 2**

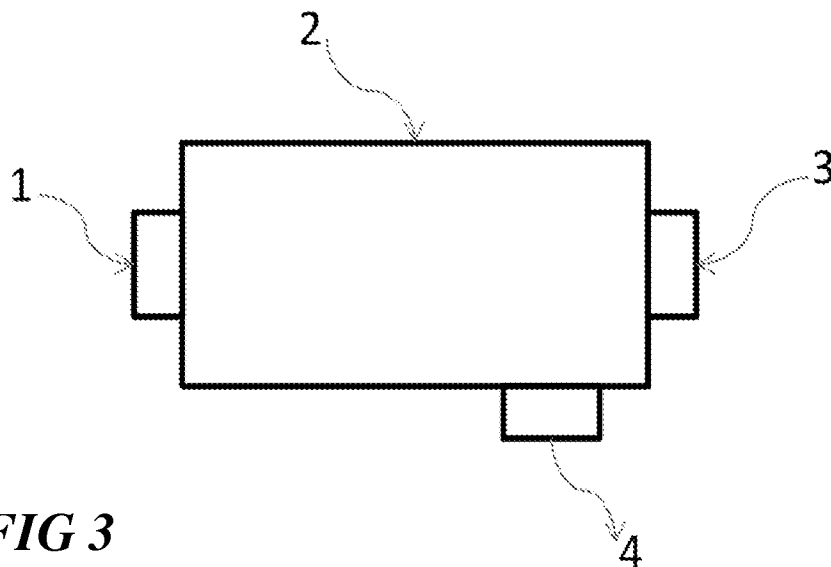


FIG 3

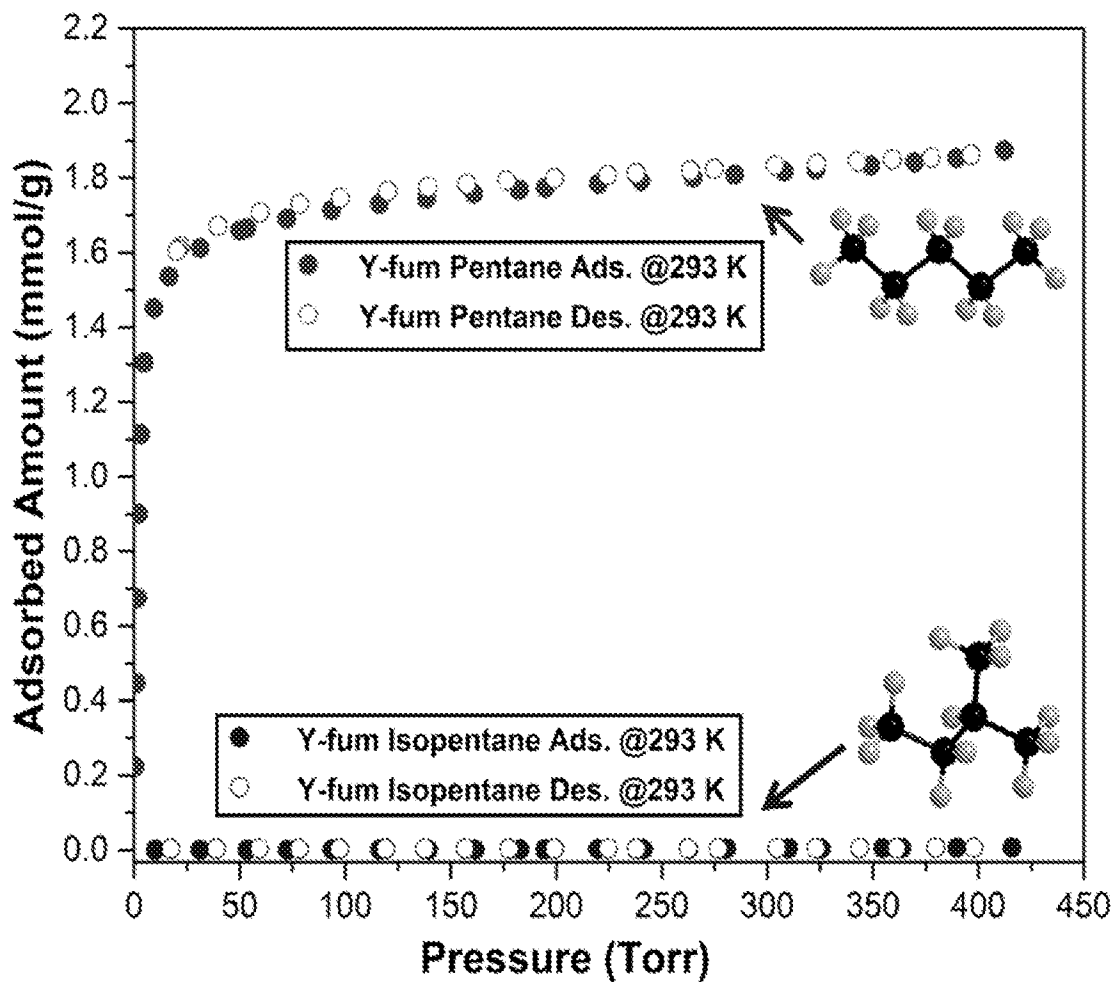


FIG 4A

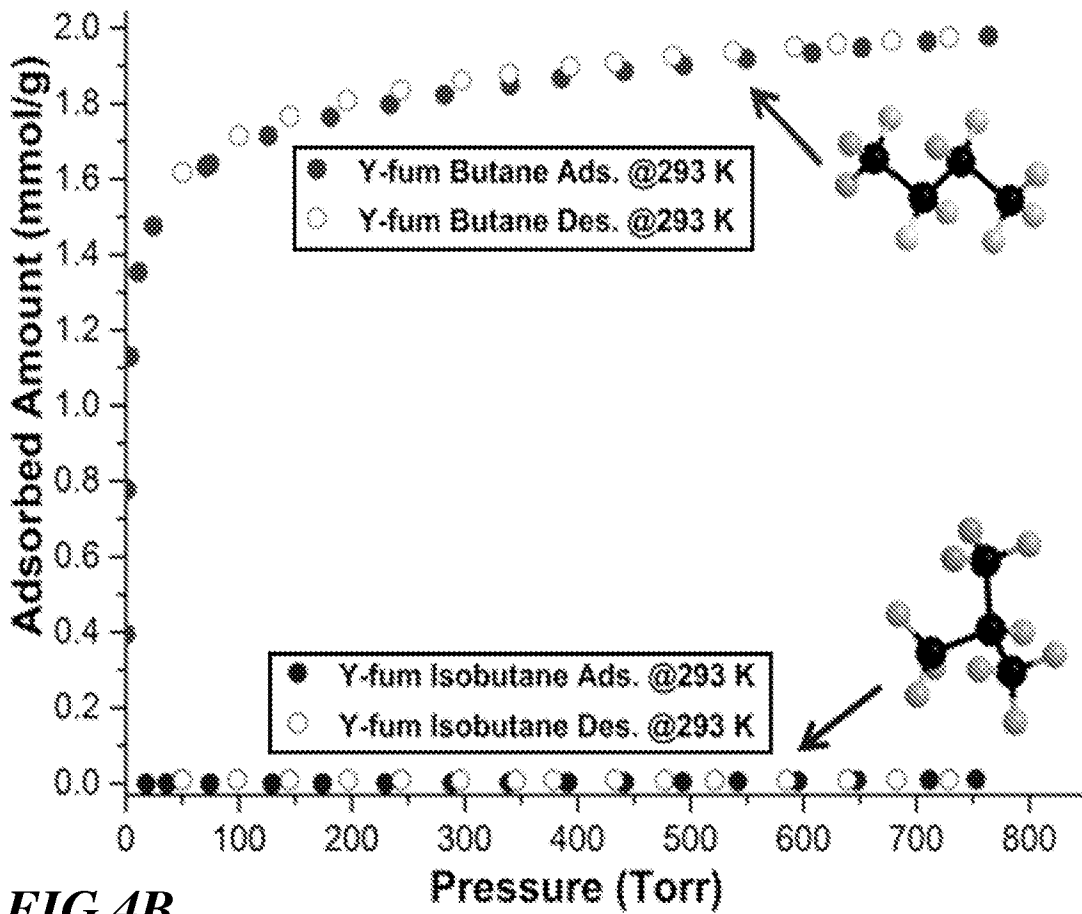


FIG 4B

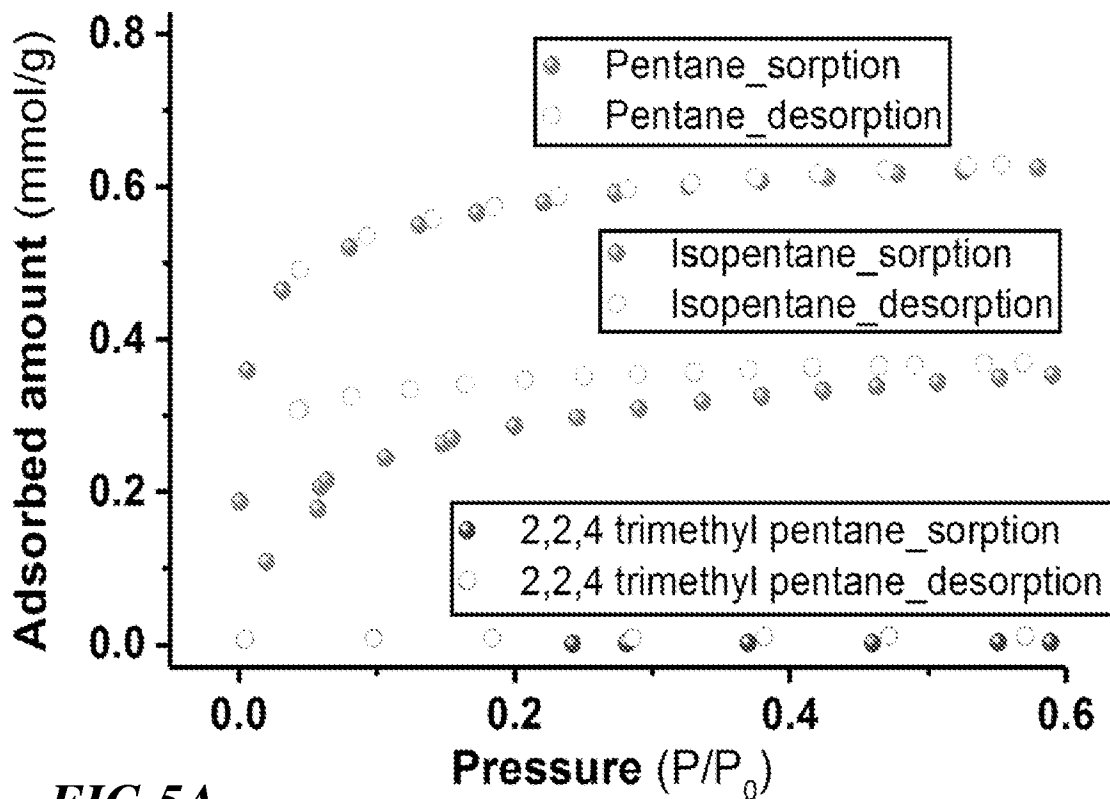
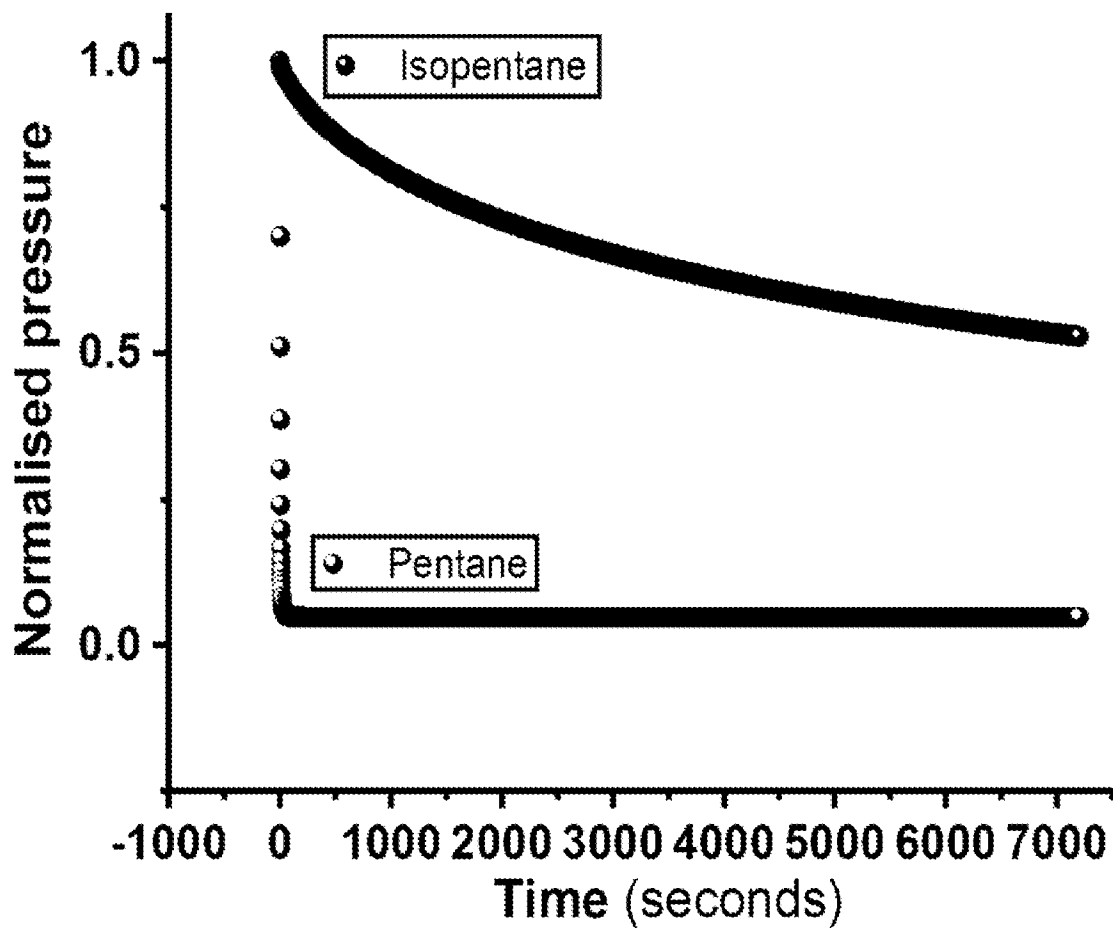


FIG 5A



**FIG 5B**

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/US2015/049774

<b>A. CLASSIFICATION OF SUBJECT MATTER</b> IPC(8) - B01J 20/28 (2015.01) CPC - B01J 20/226 (2015.11) According to International Patent Classification (IPC) or to both national classification and IPC		
<b>B. FIELDS SEARCHED</b> Minimum documentation searched (classification system followed by classification symbols) IPC(8) - B01D 53/14, 53/54; B01J 20/02, 20/22, 20/28; C01B 3/00; C07B 63/00 (2015.01) CPC - B01D 53/1475, 53/56; B01J 20/226, 20/2808; C01B 3/00; C07B 63/00 (2015.11)		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched USPC - 210/660; IPC(8) - B01D 53/14, 53/54; B01J 20/02, 20/22, 20/28; C01B 3/00; C07B 63/00; CPC - B01D 53/1475, 53/56; B01J 20/226, 20/2808; C01B 3/00; C07B 63/00 (keyword delimited)		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) Orbit, Google Patents, Google Scholar, Proquest. Search terms used: MOFs, ZMOFs, metal organic frameworks, metal organic materials, diesel, gasoline, petroleum, petrol, cetane, octane, paraffin, hexane isomers		
<b>C. DOCUMENTS CONSIDERED TO BE RELEVANT</b>		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 2009/0242038 A1 (SENGUPTA et al) 01 October 2009 (01.10.2009) entire document	1-6, 8-13, 15-20
Y	WO 2014/071351 A1 (THE REGENTS OF THE UNIVERSITY OF CALIFORNIA) 08 May 2014 (08.05.2014) entire document	1-6, 8-13, 15-20
Y	US 2012/0110984 A1 (SHIMADA et al) 10 May 2012 (10.05.2012) entire document	10-13, 15-20
A	WO 2012/175823 A1 (IFP ENERGIES NOUVELLES et al) 27 December 2012 (27.12.2012) see machine translation	1-20
A	US 2005/0056264 A1 (WEISSMAN et al) 17 March 2005 (17.03.2005) entire document	1-20
A	✓ HERM et al. Separation of Hexane Isomers in a Metal-Organic Framework with Triangular Channels. Science 340: 960-964, 24 May 2013 [retrieved on 29 October 2015]. Retrieved from the Internet: <URL: <a href="http://alchemy.cchem.berkeley.edu/static/pdf/papers/paper175.pdf">http://alchemy.cchem.berkeley.edu/static/pdf/papers/paper175.pdf</a> >.	1-20
A	NUGENT et al. Porous materials with optimal adsorption thermodynamics and kinetics for CO2 separation. Nature 495: 80-84, 07 March 2013 [retrieved on 26 October 2015]. Retrieved from the Internet: <URL: <a href="http://sqma.myweb.usf.edu/pages/pictures/publications/P_65.pdf">http://sqma.myweb.usf.edu/pages/pictures/publications/P_65.pdf</a> >.	1-20
A	✓ BRANT. Toward the Synthesis of Designed Metal-Organic Materials. Thesis. University of South Florida 1-86, 2008 [retrieved on 03 November 2015]. Retrieved from the Internet: <URL: <a href="http://scholarcommons.usf.edu/cgi/viewcontent.cgi?article=1147&amp;context=etd">http://scholarcommons.usf.edu/cgi/viewcontent.cgi?article=1147&amp;context=etd</a> >. see pages 53-56	1-20
<input type="checkbox"/> Further documents are listed in the continuation of Box C. <input type="checkbox"/> See patent family annex.		
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"E"	earlier application or patent but published on or after the international filing date	"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
"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)	"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
"O"	document referring to an oral disclosure, use, exhibition or other means	"&" document member of the same patent family
"P"	document published prior to the international filing date but later than the priority date claimed	
Date of the actual completion of the international search	Date of mailing of the international search report	
03 November 2015	10 DEC 2015	
Name and mailing address of the ISA/ Mail Stop PCT, Attn: ISA/US, Commissioner for Patents P.O. Box 1450, Alexandria, Virginia 22313-1450 Facsimile No. 571-273-8300	Authorized officer Blaine Copenheaver PCT Helpdesk: 571-272-4300 PCT OSP: 571-272-7774	