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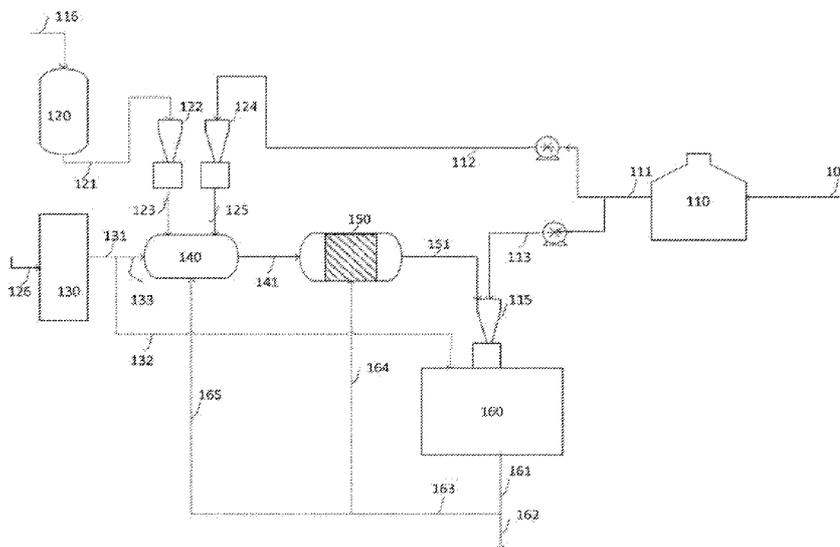


FIG. 1

(57) Abstract: The present invention is directed to an on-demand, on-board vehicle system and process the for conversion of a starting fuel comprising saturated hydrocarbons to a final fuel comprising one or more unsaturated hydrocarbons using an on-board reactor. The final fuel may have a higher Research Octane Number (RON) and/or lower cetane number than the starting fuel and may be supplied to an on-board engine only when the engine load requires a fuel with a higher RON and/or lower cetane number than the starting fuel, which also minimizes or eliminates the operating inefficiencies of octane "give away" and maximizes the economic operation of the vehicle.



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ON-BOARD CONVERSION OF SATURATED
HYDROCARBONS TO UNSATURATED HYDROCARBONS

RELATED APPLICATION DATA

[0001] This application claims the benefit of U.S. Provisional Patent Application Serial No. 62/372,608, filed August 9, 2016.

TECHNICAL FIELD

[0002] The present invention relates generally to an on-demand conversion of saturated hydrocarbons to unsaturated hydrocarbons on-board a vehicle or mobile unit.

BACKGROUND OF THE INVENTION

[0003] The background of this invention will address general topics involving hydrocarbons, octane and catalysts.

Hydrocarbons

[0004] Hydrocarbons are a type of organic compound composed of hydrogen and carbon. Petroleum-based fuels and products are largely made up of hydrocarbons of varying sizes. The smallest hydrocarbon is methane, which is composed of a single carbon atom and four hydrogen atoms. Hydrocarbons can vary upward in size from methane to consist of hundreds or thousands of individual atoms that are linked together in different ways, such as chains, rings, or other shapes.

[0005] The structure and properties of different hydrocarbons can vary widely, and hydrocarbons can be categorized into several types based on their properties, such as hydrocarbon compounds classed aliphatic (forming open chain structures) or aromatic (forming closed ring structures). Aliphatic and aromatic classifications of hydrocarbons are delineated based on the association of their structural features with their properties.

[0006] Aliphatic hydrocarbons are classified based on the type of bonds contained in the hydrocarbon molecule, which are: alkanes, alkenes, or alkynes. Alkanes have only single bonds between the carbons, alkenes contain at least one carbon-carbon double bond, and alkynes contain at least one carbon-carbon triple bond.

[0007] Aromatic hydrocarbons, also known as arenes, have a closed ring of alternating single and double bonds. These aromatic hydrocarbons have a structure with greater stability than non-aromatic hydrocarbons due to in part to the strength of bonds that exist between the atoms in the ring.

[0008] Hydrocarbons can also be classified as saturated or unsaturated based on whether the hydrocarbon molecule has single or multiple bonds between the carbon atoms. A saturated hydrocarbon has no double or triple bonds between its carbon atoms, which means this molecule is "saturated" with hydrogen because hydrogen atoms are located on every available bonding location in the molecule. Unsaturated molecules have at least one double or triple bond between carbons, and these bonds prevent hydrogen "saturation" of the molecule.

[0009] Alkanes are saturated hydrocarbons that contain only single bonds between the carbon atoms, and these alkane molecules typically follow the chemical formula C_nH_{2n+2} . A common example of an alkane is ethane (C_2H_6).

[0010] Alkenes are unsaturated hydrocarbon molecules that contain at least one carbon-to-carbon double bond, and alkenes typically have a chemical formula C_nH_{2n} . An example of an alkene is ethylene (C_2H_4). Alkenes are very common hydrocarbons used and processed in the petrochemical industry.

[0011] Alkynes are unsaturated hydrocarbons that contain at least one carbon-to-carbon triple bond, and alkynes typically have a chemical formula C_nH_n . A common example of an alkyne is ethyne (C_2H_2), also known as acetylene.

[0012] Cycloalkanes are saturated hydrocarbons having only carbon-to-carbon and carbon-to-hydrogen single bonds. These alkane molecules have a prefix of "cyclo" due to their configuration of carbon atoms in a ring structure.

[0013] Aromatic hydrocarbons are unsaturated hydrocarbons having alternating carbon-to-carbon single or double bonds in the molecule. The aromatic description was initially applied to these types of hydrocarbons because these compounds had a pleasant aroma.

[0014] Hydrocarbons having between four and twelve carbon atoms are prevalent in most petroleum-based fuels, regardless of whether they are alkanes, alkenes, alkynes, or cyclic molecules. In general, these hydrocarbons are used to produce energy, primarily through the combustion of these molecules. For example, gasoline is included in this group of hydrocarbons, and it includes a mixture of paraffins (alkanes), cycloalkanes (naphthenes),

and olefins (alkenes), where the usage of the terms paraffin and olefin is particular to the oil industry.

Octane Rating and Auto-Ignition

[0015] An important hydrocarbon found in most petroleum-based fuels is octane, which is an eight carbon molecule with the basic chemical formula of C_8H_{18} . Octane hydrocarbons have many possible structural configurations (isomers), but the condensed structural formula for octane is $CH_3(CH_2)_6CH_3$.

[0016] Octane is a component of fuels, such as gasoline, which contains a mixture of hydrocarbons refined from petroleum. Octane is volatile and very flammable, and an "octane rating" for fuel is a characteristic of octane's branched-chain isomers, especially iso-octane.

[0017] High fuel compressibility is of a primary concern to gasoline engines. By way of background, gasoline engines rely on the ignition of air and fuel compressed together as a mixture, and a gasoline mixture is preferably ignited in the compressed state using spark plugs. In spark-ignition engines, the compressed air-fuel mixture becomes heated due to the compression, and the spark plug triggers ignition of the compressed fuel mixture.

[0018] If the air-fuel mixture is heated or compressed too much, self-ignition of the fuel may occur before the initiation of a spark by the ignition system. Self-ignition or auto-ignition can cause higher pressures than engine components are designed to withstand, and self-ignition often results in a "knocking" or "pinging" engine sound that usually accompanies instances damage to the engine.

[0019] An octane number is the standard measure of the performance of an engine fuel, and an octane number is used to denote an engine fuel's resistance against auto-ignition. A tendency toward avoiding auto-ignition of gasoline fuel (often denoted by a high octane rating) is usually a preferred and desirable fuel characteristic for most engines. Put another way, because the higher the octane number indicates a greater amount of compression the fuel can withstand before igniting, gasoline engines used in high performance situations usually require higher compression ratios with higher octane ratings.

[0020] If a fuel with a low octane rating (auto-ignition tendency is higher) is contained in a gasoline fuel mixture, that fuel may ignite before the ignition system sparks - which is usually an undesirable occurrence in high performance engines. Fuels with lower octane numbers, however, may be well-suited for engines that do not compress fuel, such as diesel engines.

[0021] The most common type of octane number measure is a Research Octane Number (RON). Typically, RON 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 having iso-octane and n-heptane. Generally, the higher the RON octane rating, the more compression the fuel can withstand before auto-igniting.

[0022] There are different conventions for expressing octane ratings, so the same physical fuel may have several different octane ratings based on the measurement used. Octane rating is measured relative to a mixture of 2,2,4-trimethylpentane (an isomer of octane) and n-heptane, and one of the octane isomers, 2,2,4-trimethylpentane (isooctane) is used as the standard value in the octane rating scale associated with fuels.

[0023] Another rating used for fuel ignition is the cetane number, which is a measure of the ignition properties of fuel relative to cetane (C₁₆H₃₄) as a standard. Both octane numbers and cetane numbers measure the tendency of a fuel to spontaneously ignite. Cetane numbers indicate how readily a fuel will ignite, and octane numbers indicate the resistance of the fuel to auto-ignition. High octane number fuels usually have low cetane numbers, and *vice versa*, and lower cetane number fuels are better for high load operation of an engine.

[0024] Modern engines have moved toward turbocharging, intercooling, and exhaust gas recirculation, which result in lower in-cylinder temperatures and higher in-cylinder pressures. As a result of this modern shift in engine technology, the fuel recommended for use in modern engines usually has a high octane index.

[0025] The process for producing high octane fuels in a refinery is expensive in terms of capital and operational costs. These high costs are passed onto the purchaser in the form of higher fuel prices for high octane index fuel as compared to lower octane index fuel.

[0026] Although modern engines may require fuels with a high octane index at certain points of their operation, modern engines often do not require such high octane fuels at all times during the operating cycle. Using a high octane fuel as the only type of fuel in the engine can result in costly octane waste, referred to as octane "give away." Prior attempts to solve the problem of octane "give away" include using two separate tanks for carrying two fuels of different octane qualities with fuels being used from the different tanks based on different needs of the engine. This solution, however, has proven to be cumbersome and unacceptable because it does not resolve all the needs of the engine in an efficient or effective manner.

Catalysts

[0027] A known method of converting saturated to unsaturated hydrocarbons is through partial oxidation in the presence of a catalyst, but all known techniques using catalysts have proven to be less efficient and effective than desired for various reasons. Catalysts are substances that increase the rate of a chemical reaction without undergoing permanent chemical change in the process. A threshold amount of activation energy is usually required to start a chemical reaction. Catalyst examples capable of hydrocarbon conversion are disclosed in U.S. Patent No. 7,262,334, although known techniques of using a catalyst to convert saturated to unsaturated hydrocarbons continue to be plagued with problems.

[0028] A catalyst works by providing an alternative route for a reaction to proceed by requiring a lower amount of activation energy than the non-catalyzed reaction route. The threshold energy barrier that must be overcome for the reaction to proceed is lower in the catalyzed reaction than in the non-catalyzed reaction, allowing the reaction to proceed more rapidly.

[0029] Catalysts are classified in two general types - homogenous and heterogeneous. A homogenous catalyst is one where the catalyst is of the same phase as at least one of the reactants. Homogenous catalysts typically participate in one or more steps of the reaction mechanism, but are not part of the final product. The catalyst remains chemically unchanged after completion of the reaction. An example of a homogeneous catalyst involves an aqueous homogeneous catalyst added to an aqueous solution of reactants. In this type of reaction, the catalyst interacts with the reactants forming intermediates, which are substances that react more rapidly than the original reactants. The intermediates increase the interaction that can take place between reactants by providing a reaction route that requires less activation energy than if the catalyst was not present.

[0030] A heterogeneous catalyst is in a phase that is different from any of the reactants, and a heterogeneous catalyst typically involves a solid catalyst with liquid or gaseous reactants. These catalysts work by bringing the reactants close enough to one another to increase the interaction rate. Usually this happens when one or more of the reactants becomes adsorbed onto the surface of the catalyst, allowing the reactants to get close enough to facilitate interaction.

[0031] An example of a heterogeneous catalyst is a catalytic converter in an automobile. Carbon monoxide is a toxic by-product of the combustion reaction taking place in a gasoline engine, and carbon monoxide can react spontaneously with oxygen to produce carbon dioxide; however, even though the reaction is spontaneous, the process is slow.

[0032] A catalytic converter speeds up the conversion of CO to CO₂ process by providing a material (usually a metal, such as platinum) that attracts the gases to its surface. Once the carbon monoxide and oxygen are in close proximity on the surface of the catalytic material, the reaction to produce carbon dioxide can proceed more quickly, thereby reducing the amount of carbon monoxide exiting the exhaust system of the automobile.

[0033] A heterogeneous catalyst generally employs a support material that is selected based on the end use of the catalyst. The catalyst material is disposed on the support by various means, such as liquid deposition, heat deposition, chemical vapor deposition, or other means for depositing the catalyst on the support.

[0034] Supports for heterogeneous catalysts may include ceramics, ceramic foams, oxide compounds, metal and metal oxides, or other support materials. Examples of catalyst supports also include honeycombed ceramic foams with a surface having a ceramic sintered coating closing off the cells, as disclosed in U.S. Pat. No. 4,568,595, and foamed ceramic containing platinum/rhodium catalysts as an exhaust gas catalyst, as disclosed in U.S. Pat. No. 4,253,302.

[0035] In order to provide the optimal fuel mix, the conversion reaction rate needs to be optimized. As mentioned above, these known techniques of using a catalyst to convert saturated to unsaturated hydrocarbons continue to be plagued with unresolved problems, and these techniques have proven to be less efficient and effective than desired for various reasons.

SUMMARY OF THE INVENTION

[0036] The present invention is directed to processes and systems for converting saturated hydrocarbons to unsaturated hydrocarbons in a mobile, on-board reactor, which solves the octane "give away" problem by providing the necessary type and amount of octane fuel to the engine at the appropriate time, which is all accomplished through the real-time conversion of saturated hydrocarbons to unsaturated hydrocarbons on a vehicle reactor.

[0037] The present invention converts saturated hydrocarbons to one or more unsaturated hydrocarbons in an on-board reactor comprising the steps: (1) providing saturated hydrocarbons having 2 to 25 carbons comprising at least one of paraffins, cycloparaffins, and iso-paraffins, said saturated hydrocarbons being a starting gasoline fuel having a first Research Octane Number (RON) or a starting diesel fuel having a first Cetane Number (CN), (2) providing an on-board reactor having a catalyst capable of catalyzing saturated hydrocarbons to one or more unsaturated hydrocarbons, (3) directing at least some of the saturated hydrocarbons to the on-board reactor; converting the saturated hydrocarbons in the on-board reactor over the catalyst to form a final fuel having one or more unsaturated hydrocarbons, where the final fuel has a second RON that is higher than the starting gasoline fuel or a second CN that is lower than the starting diesel fuel; and (4) delivering the final fuel to an on-board engine.

[0038] The on-board engine in the present invention may be a spark ignition engine or a compression ignition engine. The on-board reactor for hydrocarbon conversion may be an on-board engine that is a spark ignition engine or a compression ignition engine. The starting fuel may have a residence time in the on-board reactor from 0.001 second to 1 second. The process may include feeding steam to the on-board reactor, and the on-board reactor is heated with waste heat from the on-board engine. The on-board reactor may have an operating temperature from 350 to 1000°C and a pressure from 1 to 15 ATM, or an operating temperature is from 350 to 650°C and the pressure is from 1 to 5 ATM. The present process invention provides an on-demand fuel supply to the on-board engine.

[0039] The process of converting the saturated hydrocarbons in the starting fuel to one or more unsaturated hydrocarbons may be achieved in the present invention through the partial oxidation process, which is achieved by partially oxidizing the saturated hydrocarbons with a gas containing oxygen over the catalyst in the on-board reactor to form the final fuel. The gas containing oxygen may be ambient air, an exhaust gas from the on-board engine, or a combination thereof, and the catalyst for partial oxidation may be a supported metal catalyst comprising at least one of rhodium and/or platinum.

[0040] The present invention can also convert hydrocarbons through thermal cracking. All known techniques of thermal cracking of hydrocarbons have yet to resolve long-felt problems associated with thermal cracking, which make such known processes and systems less effective and efficient than desired. The present invention includes a process of converting

the saturated hydrocarbons in the starting fuel to one or more unsaturated hydrocarbons in a thermal cracking process achieved by feeding an exhaust gas from the on-board engine to an on-board reactor in the presence of the catalyst under conditions to thermally crack the starting fuel to form the final fuel. The process may also comprise feeding a gas containing oxygen to the on-board reactor with the exhaust gas, and the catalyst for thermal cracking may be an alkali earth metal, an alkaline earth metal or a zeolite.

[0041] Further, the present invention includes a process for operating an engine, comprising the steps of: (1) providing an on-board reactor having a catalyst capable of catalyzing saturated hydrocarbons to one or more unsaturated hydrocarbons, wherein said on-board reactor is able to convert saturated hydrocarbons to one or more unsaturated hydrocarbons on-demand, (2) providing a starting fuel of a gasoline fuel or a diesel fuel to the engine when the engine is operating at a first load, where the starting fuel may be saturated hydrocarbons having 2 to 25 carbons comprising at least one of paraffins, cycloparaffins, and iso-paraffins, and the starting gasoline fuel has a first RON or the starting diesel fuel has a first cetane number (CN).

[0042] At least a portion of the starting fuel is converted in the on-board reactor to a final fuel having one or more unsaturated hydrocarbons, where the final fuel has a second RON that is higher than the first RON or a second CN that is lower than the first CN in the starting fuel. The final fuel may be port injected to the engine; and, the engine may be operated at a second load that is greater than the first load.

[0043] The present invention includes a process for operating an engine where the conversion of the saturated hydrocarbons in the starting fuel to one or more unsaturated hydrocarbons in the final fuel occurs by a partial oxidation. The partial oxidation process may be achieved by partially oxidizing the saturated hydrocarbons with a gas containing oxygen over a supported metal catalyst that may comprise rhodium and/or platinum in the on-board reactor to form the final fuel, and the gas containing oxygen may be ambient air, exhaust gas from the on-board engine or combinations thereof.

[0044] The present invention is also directed to a process for operating an engine where the conversion of the saturated hydrocarbons in the starting fuel to one or more unsaturated hydrocarbons in the final fuel occurs by thermal cracking. This process may be achieved by feeding an exhaust gas from the on-board engine and steam to the on-board reactor in the

presence of the catalyst, which may be an alkali earth metal, an alkaline earth metal or a zeolite, under conditions to thermally crack the starting fuel to form the final fuel.

[0045] The details of one or more embodiments of the present invention are set forth in the description below. The detailed description provided herein is not intended to limit the invention to the particular forms disclosed. On the contrary, the intention is meant to cover all modifications, equivalents, and alternatives falling within the spirit and scope of the invention as defined by the appended claims.

BRIEF DESCRIPTION OF THE DRAWINGS

[0046] The above, and other objects and advantages of the present invention will be understood upon consideration of the following detailed description taken in conjunction with the accompanying drawings, in which like reference characters refer to like parts throughout, and in which:

[0047] FIG. 1 shows a flow-chart configuration for on-board conversion of saturated hydrocarbons to unsaturated hydrocarbons via thermal cracking and or partial oxidation.

[0048] FIG. 2 shows a flow-chart configuration for on-board conversion of saturated hydrocarbons to unsaturated hydrocarbons via partial oxidation.

[0049] FIG. 3 shows a comparison of ignition delay times of various gasoline surrogate fuels and possible products from the present reactor over a range of temperatures.

[0050] While the invention is susceptible to various modifications and alternative forms, specific embodiments thereof have been shown by way of example in the drawings and are herein described in detail.

DETAILED DESCRIPTION

[0051] An octane number is a standard measure of the performance of an engine fuel, and the octane rating number is used to denote an engine fuel's resistance to end-gas auto-ignition. The most common type of octane number measure is a Research Octane Number (RON). A recommended RON value for any given engine depends on a variety of factors, including the compression ratio of the engine; whether the vehicle is supercharged or turbocharged; whether the vehicle is being used for heavy duty operations, such as towing or carrying heavy loads; and, other driving or operating conditions such as high temperatures, steep hills, acceleration, or running at increased RPMs.

[0052] While the RON value used and/or recommended in various vehicles can vary, one theory is that operators should use a RON valued fuel that is sufficient to avoid, at least, knocking and pinging of the engine so as to avoid engine damage. For example, a higher RON valued fuel is recommended when the engine is operating at higher loads; and, when the engine is not operating at such loads, a lower RON valued fuel can be used while still avoiding engine damage or engine knocking or pinging. This situation may be balanced against using too much octane fuel when it is not required for the condition or use of the engine. When an engine is fed with a fuel having a higher RON than needed, a situation arises called octane "give away," which is considered to be inefficient engine operations.

[0053] The present systems and processes avoid, minimize and largely eliminate the condition of octane "give away" by providing an appropriate octane-rated fuel to an engine under appropriate conditions. For instance, the present invention provides the engine with a fuel having a minimal RON value (e.g., just enough of a RON valued fuel) to operate without engine knocking or pinging during basic operation, but the present invention provides a process for converting the fuel having a relatively low RON to a fuel having a higher RON when the engine need arises for the operating conditions or vehicle's use.

[0054] For instance, an idling automobile may operate without engine knocking or pinging at a RON value of 64, but once the automobile is being driven up a hill or in high load conditions, the required RON value for its fuel may need to be increased up to 90 to avoid knocking and pinging of the engine, which would avoid associated engine damage in those conditions. In accordance with the present systems and processes, at least a portion of the fuel having a relatively low RON would be converted via an on-board reactor to a fuel having a higher RON required for the greater load on the engine. When the vehicle is not operated under this higher load condition any longer, the initial fuel having the lower RON may again be directed to the engine.

[0055] The present invention accomplishes this "on-demand" higher RON valued fuel through an on-board reactor capable of converting saturated hydrocarbons to unsaturated hydrocarbons, with its associated processes and systems for the conversion of saturated hydrocarbons to unsaturated hydrocarbons in an on-board reactor. In the present invention, a fuel comprising saturated hydrocarbons is provided to an on-board reactor, and the hydrocarbon fuel is converted to a fuel comprising unsaturated hydrocarbons.

[0056] The fuel comprising unsaturated hydrocarbons has a higher Research Octane Number (RON) than the fuel comprising saturated hydrocarbons. Because the reactor is an on-board reactor, the process may be conducted on-board the vehicle and on-demand when needed by the vehicle engine, which reduces or eliminates octane "give away" and maximizes efficiency of the engine because the higher RON fuel is only converted in the on-board reactor when there is a need for a higher RON octane rated fuel in the vehicle engine. The present invention results in an associated saving of space for fuel capacity on the vehicle over known systems requiring multiple tanks on the vehicle, which is inefficient and ineffective to resolve the long-felt problems associated with octane "give away."

[0057] As used herein, the term on-board reactor refers to a reactor that is an integrated part of a transport vehicle, which means it is a part of the vehicle and is not located at a separate facility or physical location. Similarly, the term on-board engine refers to an engine that is an integrated part of a transport vehicle, which is part of the vehicle and is not located at a separate facility or physical location. A transport vehicle includes any vehicle that is motorized by a fuel engine; and, such vehicles would include, but are not limited to, automobiles, buses, trucks, motorcycles, recreation vehicles, construction vehicles, scooters, boats, and material handling vehicles (such as forklifts).

[0058] The RON of the starting fuel is dependent on the composition of the fuel. The starting fuel may be selected to have a relatively low RON, e.g., a RON of less than 87, less than 85, less than 80, less than 75, or less than 70. This starting fuel generally comprises saturated hydrocarbons, as described herein.

[0059] In addition to RON, another measurement used to quantify fuel octane quality is Motor Octane Number (MON). The MON measurement is generally carried out at 900 rpm with a variable spark advance of 19 to 26°C before top-dead center (BTDC) and an intake air temperature of 149°C. The Octane Index (OI) of a fuel for modern engines can be calculated as follows:

$$OI = RON - (K*(RON - MON)),$$

where K is a constant that depends on the engine operating conditions and (RON-MON) is referred to as fuel sensitivity. Modern engines have been shown to have negative K values; and, thus, as RON increases and the MON decreases, the OI increases and enables higher engine efficiency.

[0060] High sensitivity fuels increase the octane index of the final fuel as compared to the starting fuel when the engine is operated at a K value below 0. A positive K value signifies that anti-knock performance correlates better with fuel MON, while a K value of 0 is indicative of the RON conditions. A negative K value implies that the octane index is beyond the RON conditions; and, therefore, a lower value of MON is preferred.

[0061] The K value of modern engines is lower than older engines, and a negative K value causes the effective octane index to increase as fuel sensitivity increases for a fuel with a given RON. Accordingly, anti-knock performance of modern engines generally correlated better with RON than MON.

[0062] It is relevant to note that that anti-knock index (AKI), which is the average of RON and MON, is generally reported on fuels sold at the fuel pump, at least in the United States. For example, in the United States, fuels for automobiles are generally marketed as regular (having an AKI of 87), mid-grade (having an AKI of 88-90), or premium (having an AKI of 91-94). Because the RON correlates better with anti-knock performance in modern engines, for the present systems and processes the starting fuel and final fuel are quantified in terms of RON, rather than MON, octane index, or AKI.

[0063] In the present invention, the systems and processes may refer to RON and gasoline engines, but the present systems and processes may also apply to diesel fuels and diesel engines by reducing cetane values. Cetane number (CN) has been used as an indicator of the combustion speed of diesel fuel, and cetane numbers are usually the inverse of the similar octane rating for gasoline. The standard for measuring cetane number is ASTM D-613 (2015).

[0064] Lower cetane number fuels are better for high load operations, as this lower cetane rates fuels increase combustion resulting in engines handling greater engine operating loads. Thus, higher cetane numbers limit the load of the engine, but high cetane numbers are required for operating the engine at other operational points. Thus, modifying the cetane is beneficial for increasing the engine load.

Fuel Comprising Saturated Hydrocarbons

[0065] As described herein, the systems and processes in the present invention relate to supplying saturated hydrocarbons to an on-board reactor for conversion on-demand to the on-board vehicle engine. The saturated hydrocarbons, also referred to herein as alkanes and

paraffins, are generally supplied as part of a fuel; and, are often found in an abundant amount in fuel. The fuel may comprise at least about 40 wt% saturated hydrocarbons, e.g., from 40% to 99%. The fuel may also comprise unsaturated hydrocarbons (up to about 10%), naphthenes (up to about 30%), aromatics (up to about 30%), and oxygenates (such as ethanol, up to about 20%). In some aspects, the fuel is a naphtha, which includes paraffins, naphthenes (cyclic paraffins), and aromatic hydrocarbons. The naphtha may be a light naphtha, generally containing C2-C7 hydrocarbons, or may be a heavy naphtha, containing C7-C25 hydrocarbons.

[0066] The saturated hydrocarbons may contain from 2 to 25 carbon atoms. Saturated hydrocarbons include, but are not limited to, straight chain hydrocarbons, branched hydrocarbons, and/or cyclic hydrocarbons. Straight chain hydrocarbons may include, but are not limited to, ethane, propane, butane, pentane, hexane, heptane, octane, nonane, decane, undecane, dodecane, tridecane, tetradecane, pentadecane, hexadecane, heptadecane, octadecane, nonadecane, eicosane, heneicosane, docosane, tricosane, tetracosane and pentacosane.

[0067] Branched hydrocarbons may include from 3 to 25 carbon atoms that include, but are not limited to, all isomers of mono-, di-, tri-, and tetra-methylpropane, methylbutane, methylpentane, methylhexane, methylheptane, methyloctane, methylnonane, methyldecane, methylundecane, methyldodecane, methyltridecane, methyltetradecane, methylpentadecane, methylhexadecane, methylheptadecane, methyloctadecane, methylnonadecane, methyleicosane, methylheneicosane, methyldocosane, methyltricosane, methyltetracosane and methylpentacosane.

[0068] Cyclic hydrocarbons may include, but are not limited to, cyclopropane, cyclobutane, cyclopentane, cyclohexane, cycloheptane, cyclooctane, cyclodecane, cycloundecane, cyclododecane, cyclotridecane, cyclotetradecane, cyclopentadecane, cyclohexadecane, cycloheptadecane, cyclooctadecane, cyclononadecane, cycloeicosane, cycloheneicosane, cyclodocosane, cyclotricosane, cyclotetracosane and cyclopentacosane.

[0069] The saturated hydrocarbons can contain 2 to 12 carbon atoms. Generally, the octane quality of alkanes increases with a reduction in chain length. For vehicles with greater octane requirements under normal loads and operating conditions, the fuel comprising saturated hydrocarbons may contain predominantly C4-C10 saturated hydrocarbons; and, of the saturated hydrocarbons, at least 50% are C4-C10 saturated hydrocarbons. For vehicles with

lower octane requirements under normal loads and operating conditions, the fuel comprising saturated hydrocarbons may contain predominantly C₁₁-C₂₅ saturated hydrocarbons; and, of the saturated hydrocarbons, at least 50% are C₁₁-C₂₅ saturated hydrocarbons.

[0070] As described further herein, the processes convert the saturated hydrocarbons to one or more unsaturated hydrocarbons in an on-board reactor. The conversion may occur by cracking, isomerization, and/or reforming. Cracking refers to converting long chain alkanes to shorter alkanes, and to converting alkanes into alkenes/alkynes of the same or lower number of carbon atoms. Isomerization refers to converting straight chain alkanes to branched alkanes. And, reforming refers to converting alkanes to cycloalkanes, and then converting cycloalkanes to aromatics.

[0071] The converted unsaturated hydrocarbons may be of the same chain length as the saturated hydrocarbons from which they were converted or may have a shorter carbon chain length. For example, butane may be converted to butene or to propene. The conversion and selectivity, which are described further herein, are a function of numerous process parameters, including temperature, pressure, residence time, catalyst, fuel to air feed ratio, and composition of the fuel. These parameters may be controlled to achieve a desired conversion and selectivity based on the demand of the engine and desired RON.

[0072] In addition to the conversion of saturated hydrocarbons to one or more unsaturated hydrocarbons thereby increasing the RON, the sensitivity of the final fuel comprising the one or more unsaturated hydrocarbons is also increased due to the fuel sensitivity being dependent on the molecular structure of the fuel.

Partial Oxidation Process

[0073] In the system and process of the present invention for converting saturated hydrocarbons (paraffins) to unsaturated hydrocarbons (olefins), a fuel comprising saturated hydrocarbons is provided to an on-board reactor. The fuel comprising saturated hydrocarbons is then partially oxidized in the on-board reactor with an oxygen-containing gas. After partial oxidation, the final fuel has a RON that is higher than the RON of the starting fuel, or a lower cetane number than the starting fuel. The final fuel may then be delivered to an on-board engine. The partial oxidation may occur in the presence of a catalyst, and the partial oxidation reaction may occur in the presence of steam. The partial oxidation process may also provide heat for the conversion reactions.

[0074] The fuel provided to the on-board reactor may be provided in liquid or gas form. The on-board reactor may be operated at a temperature from 350 to 1000°C; from 350 to 650°C, or from 700 to 900°C, or any range there between; and, at a pressure from 1 to 15 ATM, from 1 to 5 ATM, or any range there between. In some aspects, the on-board reactor is operated at atmospheric pressure, and the gas hourly space velocity of the reactor is selected depending on the size of the vehicle and the size of the fuel tank.

[0075] The residence time of the fuel comprising saturated hydrocarbons is relatively short, which means it is less than 1 second, less than 0.5 seconds, or less than 0.1 seconds. In terms of ranges, residence time of the fuel comprising saturated hydrocarbons is from 0.001 seconds to 1 second, from 0.001 seconds to 0.5 seconds, or from 0.001 seconds to 0.1 seconds.

[0076] Partial oxidation may occur in the presence of a catalyst. Any reactor capable of containing a catalyst, capable of accepting a fuel flow from a fuel injector, and capable of containing the reactants at selected temperatures is appropriate for use in the present systems and processes. The reactor material can be quartz; however, any material, such as ceramic, is appropriate for use in a reactor provided it can withstand the reaction temperatures. The reactor can be of any shape, provided contact time with the catalyst is maintained, and a tube shaped reactor is one possible shape option. Additionally, a tube shaped reactor can be of any length desired, provided catalyst contact time is maintained.

[0077] Catalysts for use in the present systems and processes include at least one metal selected from metals defined under the CAS system as Group VIII and Group IB of the Periodic Table. These groups are also known as Groups 8-11 under alternative nomenclature. Group VIII and Group IB include iron, ruthenium, osmium, cobalt, rhodium, iridium, nickel, palladium, platinum, copper, silver and gold, and these metals are referred to as Group VIII and Group IB metals. The catalyst may include at least one Group VIII and Group IB metal disposed on a support. Catalysts can also include tin, which is Group IVA of the Periodic Table (also known as Group 14 under alternative nomenclature).

[0078] Catalysts of the present systems and processes can also include platinum, rhodium, and combinations thereof. The Group VIII and Group IB metals and tin can be deposited in an amount of at least about 0.5 weight percent (wt%), at least about 1 weight percent, or at least about 3 weight percent, based on total weight of the support and catalyst. The Group VIII and Group IB metals and tin can be deposited in an amount of no greater than about 10

weight percent, no more than about 8 weight percent, or no more than about 6 weight percent, based on total weight of the support and catalyst.

[0079] Typically, a metal catalyst can be deposited on a support from a metal salt solution. Any organic liquid having the metal salt soluble therein may be used to deposit metals onto selected supports. The metals may also be deposited from aqueous solution using water soluble salts, or the metal may also be deposited on the support by, for example, chemical vapor deposition.

[0080] Supports for use with catalysts in the present systems and processes include a monolithic carrier, which is a carrier of the type including one or more monolithic bodies having a plurality of finely divided gas flow passages extended therethrough. Such monolithic carrier members are often referred to as honeycomb type carriers. A carrier can be made of a refractory, substantially inert, rigid material that is capable of maintaining its shape and a sufficient degree of mechanical strength at temperatures of, for example, about 1500°C. Typically, a material is selected for the support that exhibits a low thermal coefficient of expansion, good thermal shock resistance, and low thermal conductivity.

[0081] Another support that may be used with a catalyst is a ceramic foam monolith. The foam structure is characterized by the number of pores per linear inch (ppi). Ceramic foam monoliths include those with at least about 10 ppi (approximately 394 pores per meter). The monolith that may be used in the on-board reactor includes a monolith with no greater than about 100 ppi (approximately 3937 pores per meter). For example, the ceramic foam monolith can be about 80 ppi (approximately 3110 pores per meter).

[0082] Supports for catalysts further include those made from metals and metal oxides selected from the group of α -alumina and magnesium aluminum silicate (cordierite). The monolith support is wash-coated to increase the surface area of the catalyst and to reduce the pore size of the monolith, which increases the surface area of the catalyst and decreases the probability that a species will pass through the catalyst without reacting on the surface. The wash-coat can be applied by coating an aqueous solution of γ -alumina on the monolith substrate, and then allowing the aqueous solvent to evaporate off the substrate.

[0083] The oxygen-containing gas that is fed to the on-board reactor may be ambient air. The exhaust gas can be mixed with ambient air as a function of oxygen required. The quantity of air is controlled through a throttle plate or a mass flow controller to regulate stoichiometry of

the fuel/oxidizer mixture. The gas hourly space velocity can be maintained without increasing oxygen quantity. The ratio of fuel to oxygen in the on-board reactor is maintained depending on the reactant stoichiometry, but it can range from equivalence ratios of 1 to 4 in the present invention.

Thermal Cracking Process of Conversion

[0084] In the system and process of the present invention for converting saturated hydrocarbons to one or more unsaturated hydrocarbons, a starting fuel comprising saturated hydrocarbons is provided to an on-board reactor and an exhaust gas is fed to the on-board reactor from an on-board engine. The starting fuel is thermally cracked, in the presence of a catalyst, to form the final fuel comprising unsaturated hydrocarbons.

[0085] Thermal cracking generally refers to decomposition by heating, and the thermal cracking can occur in the presence of steam. The saturated hydrocarbons in the present invention may be cracked into shorter chain saturated hydrocarbons and into alkenes/alkynes of the same or lower number of carbon atoms. After thermal cracking, the final fuel has a RON that is higher than the RON of the starting fuel, and the final fuel may then be delivered to an on-board engine.

[0086] The fuel provided to the on-board reactor may be provided in liquid or gas form. The on-board reactor in the present invention may be operated at a temperature from 350 to 1000°C, or from 350 to 650°C, or 700 to 900°C, or any range there between; and, at a pressure from 1 to 15 ATM, or from 1 to 5 ATM in the present invention, or any range there between. In some aspects, the on-board reactor is operated at atmospheric pressure, and the gas hourly space velocity of the reactor is selected depending on the size of the vehicle and the size of the fuel tank.

[0087] The residence time of the fuel comprising saturated hydrocarbons is relatively short in the present invention, which is less than 1 second, less than 0.5 seconds, or less than 0.1 seconds. In terms of ranges, residence time of the fuel comprising saturated hydrocarbons in the present invention is from 0.001 seconds to 1 second, from 0.001 seconds to 0.5 seconds, or from 0.001 seconds to 0.1 seconds. Any suitable type of reactor may be used as the on-board reactor, and the on-board reactor can be a fixed bed reactor, a fluidized bed reactor, or a moving bed reactor.

[0088] For purposes of the present systems and processes, the term conversion refers to the amount of saturated hydrocarbons in the starting fuel that is converted to a compound other than the saturated hydrocarbon. Conversion is expressed as a percentage based on saturated hydrocarbon in the starting fuel. The conversion in the present invention may range from about 10% to about 70%, and the conversion may be at least 10%, at least 40%, or at least 70%. Although catalysts that have high conversion ratios are desirable, such as at least 70%, a low conversion ratio may be acceptable at high selectivity for unsaturated hydrocarbons. It is possible to compensate for lower conversion ratios through the use of larger reactors, but it is more difficult to compensate for poor selectivity.

[0089] Selectivity is expressed as a mole percent based on converted saturated hydrocarbons. Each compound converted from the saturated hydrocarbon has an independent selectivity, and that selectivity is independent from conversion. For example, if 40 mole % of the converted saturated hydrocarbon is converted to unsaturated hydrocarbons, the unsaturated hydrocarbon selectivity is referred to herein as 40%. Catalyst selectivity to unsaturated hydrocarbons in the present invention is at least 10%, at least 30%, or at least 60%.

[0090] The catalyst used in the present invention may be any catalyst known to be used in thermal cracking, isomerization and reforming of saturated hydrocarbons and is selected based on the desired conversion and selectivity. The catalyst may be a supported metal catalyst comprising at least one metal, and the metal may be selected from the group consisting of rhodium, platinum, and mixtures thereof.

[0091] The catalyst for thermally cracking the starting fuel in the present invention may further comprise an alkali or alkaline earth (alkali(ne-earth)) metal or metal oxide that converts, at least in part, upon calcination to alkali(ne-earth) oxides and that have been calcined at elevated temperatures. The alkali(ne-earth) metal oxides or compounds of alkali(ne-earth) metals can be deposited on porous oxidic carriers.

[0092] Compounds of alkali(ne-earth) metals are, for example, those that contain oxygen and those that decompose at least in part upon calcination to produce oxides. When the alkali(ne-earth) metal compound cannot be decomposed upon calcination to produce an oxide, it is necessary that the compound either can be oxidized at least in part in an oxygen-containing atmosphere to provide an alkali(ne-earth) metal oxide or, alternatively, can be dissolved in a suitable solution, precipitated with a suitable oxyanion and subsequently calcined to decompose at least in part to produce an oxide.

[0093] As used herein, the term oxide as applied to alkali(ne-earth) metal, refers to inorganic metal compounds which contain alkali(ne-earth) metal bound to oxygen, and the oxygen being bound to the alkali(ne-earth) metal is not bound to any other element (but not elements in oxidic carriers when the alkali(ne-earth) metal oxide is dispersed in an oxidic carrier which forms a new compound with the oxidic carrier at the temperature adopted in catalyst preparation). The alkali(ne-earth) metal oxide catalyst can occur in several forms when utilized in the present systems and processes is dispersed on an oxidic carrier. For example, the alkali(ne-earth) metal oxide catalyst may retain its chemical identity with the carrier acting as a dispersing agent, or it may dissolve in the carrier to give a solid solution, or it may form a new stoichiometric compound with the carrier.

[0094] The term compound as applied to alkali(ne-earth) metal refers to the combination of alkali(ne-earth) metal with one or more elements by chemical and/or physical and/or surface bonding, such as ionic and/or covalent and/or coordinate and/or Van Der Waals bonding. Illustrative examples of suitable alkali(ne-earth) metal compounds include, by way of non-limiting examples, carbonates, bicarbonates, hydroxides, nitrates, nitrites, sulfates, hydrogen sulfates, sulfites, dithionates, thiosulfates, alkoxides, carboxylates, sulfonates, oxyhalides, iodates, halides and the like.

[0095] The term oxyanionic or oxyanion refers to a negatively charged moiety containing at least one oxygen atom in combination with another element. An oxyanion is thus an oxygen atom in combination with another element. Ions that do not exist *in vacuo* can nonetheless be found in combination with charge-balancing counter ions.

[0096] The term oxidic as applied to a carrier refers to a carrier where an element such as aluminum, silicon, and magnesium is bound to oxygen, and possibly one or more different elements, by surface and/or chemical bonding to provide an oxygen-containing moiety (e.g., Al-O-, Si-O-, Mg-O, etc.). Illustrative examples of suitable porous oxidic carriers are alumina, silica, and silica-alumina, magnesia, keiselguhr (diatomaceous earth), ceramics, and combinations thereof.

[0097] The term salt as used herein is meant to encompass a single salt, as well as mixtures of two or more salts. The term alkali(ne-earth) metal refers to any alkali metal or alkaline-earth metal. The term alkali metal is used herein as a descriptor of the elements of Group IA of the Periodic Table of the Elements (Li, Na, K, Rb, Cs). The term alkaline earth metal is

used herein as a descriptor of the elements of Group IIA of the Periodic Table of the Elements (Be, Mg, Ca, Sr, Ba).

[0098] The term basic refers to having the characteristic of a base; e.g., when placed in a solution, a basic material will have a pH consistent with a base rather than an acid; and, if a catalyst, will catalyze chemical reactions that are catalyzed by bases.

[0099] The saturated hydrocarbons in the starting fuel can be cracked and dehydrogenated over a catalyst comprising oxides of alkali(ne-earth) metals, or mixtures thereof, which contain primarily only oxygen and alkali(ne-earth) metals, and are substantially free of other elements. In a specific aspect, the oxides are dispersed in a porous oxidic carrier, such as alumina, silica, silica-alumina, keiselguhr, magnesia, or other ceramics, or mixtures thereof.

[00100] The oxides, either with or without supporting carriers, can be calcined prior to the commencement of the catalytic cracking step, but they can also be used without the calcination step. When a carrier is used, the alkali(ne-earth) metal oxide may retain its chemical identity (with the carrier only acting as a dispersing agent), or it may dissolve in the carrier to give a solid solution, or it may form a new stoichiometric compound with the carrier upon calcination.

[00101] In the present systems and processes, compounds of alkali(ne-earth) metals which contain oxygen and which decompose at least in part upon calcination to produce alkali(ne-earth) metal oxides are utilized. These compounds include carbonates, carboxylates, nitrates, hydroxides, or sulfates. Decomposition can be indicated by the evolution of gases such as carbon oxides, nitrogen oxides, sulfur oxides, or water.

[00102] Decomposition will also be indicated by disappearance, at least in part, of the particular anionic form associated with the alkali(ne-earth) metal. When carboxylates and alkoxides are calcined, the carboxylate and alkoxide moiety associated with the alkali(ne-earth) metal will decompose giving off carbon oxides and/or water and/or hydrocarbons, thereby disappearing at least in part. Compounds to be used as the catalyst in the present systems and processes can be (alkali) carbonates, nitrates and carboxylates. The oxygen-containing alkali(ne-earth) metal compounds may also be supported on a porous oxidic carrier as described above and it may form a new stoichiometric compound with the carrier upon calcination.

[00103] An alkali(ne-earth) metal compound, either supported or unsupported, that can be oxidized to an oxide upon calcination is employed in the present invention as a catalyst. Suitable alkali(ne-earth) compounds include metals, alloys, amalgams, hydrides, amides, sulfides, polysulfides, carbides, naphthlides, salts of cyclopentadiene, and other compounds with similar properties. The alkali(ne-earth) compound is oxidized, at least in part, upon calcination to provide alkali(ne-earth) metal oxide, which if not supported, may be subsequently deposited on a suitable carrier.

[00104] In certain aspects, the catalyst for thermally cracking the saturated hydrocarbons in the starting fuel may comprise a zeolite. A suitable zeolite includes a penta-sil type zeolite, such as ZSM-5 or ZSM-11 type zeolites. In further aspects, the mole ratio of silica to alumina of the zeolite may range from 25 to 800, from 40 to 600 or from 80 to 300. The zeolite may also contain a rare earth element, which may include, lanthanum, cerium, praseodymium, neodymium, samarium, gadolinium, or dysprosium.

[00105] Each rare earth element may be employed alone or in combination of two or more kinds thereof. Modification of rare earth elements into a catalyst employs the use of various kinds of salt, such as acetate, nitrate, halide, sulfate, carbonate or alkoxide, acetylacetonato; and, such modification may be conducted by means of an ion exchange method, an impregnation method, a hydrothermal crystallization method, or another similar modification method. The zeolite may also contain manganese and/or zirconium, or compounds or oxides thereof.

[00106] For process of the present invention that include air as the oxygen-containing gas, nitrogen is present in the air in an atomic ratio of no greater than about 6:1 (nitrogen to oxygen). Alternatively, nitrogen is present in the air in an atomic ratio of no greater than about 4:1 (nitrogen to oxygen). Reduced oxygen levels as compared to ambient air may also be used.

[00107] The carbon to oxygen (C/O) atomic ratio of the fuel and oxygen source mixture reacted is important to the determination of the reaction products. For example, good selectivities of syngas are typically produced using C/O atomic ratios of at least about 0.5 (or, alternatively, at least about 0.7). Also, C/O atomic ratios for the production of syngas are no greater than about 1.5 (or, alternatively, no greater than about 1.2). Furthermore, a decrease in the C/O ratio, with the flow rate held constant, typically will cause a decrease in syngas production and an increase in production of the combustion products (CO₂ and H₂O).

Additionally, in combination with the selected flow rate, the C/O atomic ratio of the reactants determines the reaction temperature.

[00108] To produce shorter chain unsaturated hydrocarbons (such as ethylene and propylene), the C/O atomic ratio used should be at least about 0.8 (or, alternatively, at least about 1). Additionally, to produce unsaturated hydrocarbons, the C/O atomic ratio should be no greater than about 5 (or, alternatively, no greater than about 2; or, alternatively, no greater than about 1.5). Using these selected C/O ratios and under the selected conditions of the present invention, ethylene is selectively produced. At these C/O atomic ratios, ethylene is produced at a selectivity of at least 35 percent (or, alternatively, at least 50 percent).

[00109] Under the selected conditions for production of ethylene, propylene may also be produced. Propylene can be produced at a selectivity of at least about 15 percent (or, alternatively, at least about 20 percent). The selectivity of propylene under these conditions is no greater than about 50 percent (or, alternatively, no greater than about 40 percent).

[00110] To produce α -olefins (particularly α -olefins having 4 or more carbon atoms), the fuel source is present in a C/O atomic ratio of at least about 2 (or, alternatively, at least about 2.5) carbon to oxygen. To produce these α -olefins, the fuel source is present in a C/O atomic ratio of no greater than about 10 (or, alternatively, no greater than about 5, no greater than about 4, or no greater than about 3.5) carbon to oxygen. Using these C/O ratios and under selected conditions of the present systems and processes, the selectivity of α -olefin reaction products is at least 20 percent (or, alternatively, at least 50 percent).

[00111] The hydrogen content of the final fuel can be increased using the present invention. The hydrogen content of the final fuel can be increased in the same on-board reactor or in a separate on-board reactor. Because the partial oxidation reaction is an exothermic reaction, the heat from the partial oxidation reaction may be used for a secondary reaction, such as a water-gas shift reaction. The water-gas shift reaction can be characterized by the reaction of carbon monoxide and water vapor to form carbon dioxide and hydrogen, and this water-gas reaction may be catalyzed by a water-gas shift catalyst.

[00112] The water-gas shift can use a high-temperature shift catalyst that comprises one or more iron oxides stabilized with chromia and/or alumina, as well as zinc oxide and one or more copper compounds. Chromia-promoted magnetite catalysts may also be used. Iron oxide/chromia shift catalysts are made by precipitation of iron and chromium compounds

(that decompose to the oxides upon heating) from a solution of iron and chromium salts by the addition of a suitable alkaline reactant, such as sodium hydroxide or carbonate.

[00113] The resulting precipitate of iron and chromium is washed, dried, and calcined and tableted to form catalyst precursor pellets. The precursor possesses an iron oxide content (expressed as Fe_2O_3) of 60 to 95% by weight, and the iron to chromium atomic ratio in the precursor is in the range 6 to 20 (or, alternatively, 8 to 12). The precursor contains oxides of other metals, such as, aluminum, manganese, or copper, and such precursors have an iron to copper atomic ratio of 10:1 to 100:1. Prior to use for the shift reaction, the pellets are subjected to reduction conditions wherein the iron oxide is reduced to magnetite (Fe_3O_4) and any chromium trioxide present is reduced to the sesquioxide, chromia (Cr_2O_3). This reduction is carried out in the reactor wherein the shift reaction is to be effected.

[00114] The activity of the catalyst may be significantly increased by incorporating into the catalyst precursor particles with an aspect ratio of at least 2 and with a maximum dimension of at least 5000Å (500nm) (or, alternatively, less than 15000Å (1500nm)) into the catalyst precursor pellets. The chromia-promoted magnetite catalyst comprises acicular iron oxide particles. It may be desirable to partially replace the chromia with alumina or another stabilizing oxide, and zinc oxide and copper may also be present in the catalyst precursor particles.

[00115] The water-gas shift catalyst is a sour shift catalyst comprising 1-5 wt% cobalt and 5-15 wt% molybdenum, and it can also include additional oxides such as magnesia and/or titanium dioxide, on a suitable support such as alumina or calcium aluminate. Such catalysts are often made by impregnating an oxidic support composition with cobalt and molybdenum compounds and heating the resulting composition to convert the cobalt and molybdenum compounds to their respective oxides.

[00116] In use, or before use if desired, the cobalt and molybdenum oxides may be sulphided with a suitable sulphur compound such as hydrogen sulphide. Where the water-gas shift reaction occurs in a second on-board reactor, heat exchangers may be included between the on-board reactors to recuperate or recapture the heat being expended in the processing systems. Such heat exchangers would allow the use of low temperature shift catalysts, which may be more effective. Waste heat from the on-board engine may be used to heat the second on-board reactor.

On-Demand On-board Fuel Supply

[00117] The octane requirements of an engine depend on the load under which the engine is working. Under normal or low-load operating conditions (such as idling, driving on flat roads, and driving at a constant pace), a fuel with a relatively low RON may be used. When the engine has to operate at a higher load condition, a fuel with a higher RON is needed to avoid engine knocking, loss in fuel economy, and/or loss in engine performance. But, providing this higher octane fuel to the engine during low-load conditions will result in inefficient engine operations and octane give away.

[00118] To minimize the inefficiencies associated with octane "give away," the present systems and processes allow for an on-demand fuel supply of a fuel with an increased RON when the engine is operating under an increased load condition, while allowing the engine to operate with lower RON fuel during low-load conditions. Examples of an increased load operation include when the pressure on the engine is increased by a supercharger or turbocharger; when the vehicle is used for heavy duty operations, such as towing or carrying heavy loads; and other driving conditions such as high temperatures, steep hills, or significant acceleration. In such cases, the starting low RON fuel would not meet the needs of the engine. In accordance with the present systems and processes, when a fuel with a higher RON is needed, the starting low RON fuel is converted on-board to a final fuel having a higher RON than the starting fuel, and such conversion includes the conversion of saturated hydrocarbons in the fuel to unsaturated hydrocarbons in the fuels (which inherently increases the RON octane rating of the fuel).

[00119] FIG. 1 shows the process in the present invention for addressing an engine's need for a fuel with an increased RON using an on-demand on-board vehicle reactor. Fuel tank 110 is supplied with starting fuel via line 101, and the starting fuel is stored in fuel tank 110 until needed. The starting fuel then exits fuel tank 110 via line 111, and under normal load conditions, the starting fuel is then fed through a fuel pump and directed to intake port 115 via line 113. Intake port 115 then directs the starting fuel to on-board engine 160 either via direct in-cylinder injection or via port injection. On-board engine 160 may be a spark ignition engine or compression engine.

[00120] Exhaust gas 161 exits on-board engine 160 through exhaust ports, and a portion of the exhaust gas may be directed to the environment via line 162. Some or all of exhaust gas 161 may be directed via line 163 to other parts of the process, such as evaporator 140 via line 165

or on-board reactor 150 via line 164. The system of the present invention includes valves, coupled to sensors, to control the feed of exhaust gases to the evaporator 140 and/or on-board reactor 150.

[00121] When the engine begins to operate under an increased load, the on-demand function of the process begins with the starting fuel in line 111 being redirected to a separate fuel pump, which is then directed to fuel injector 124 via line 112. Valves can control when starting fuel in line 111 is directed to fuel injector 124 or intake port 115, and such valves can be coupled with sensors that sense the need for the on-demand function. The starting fuel is then directed from fuel injector 124 to evaporator 140 via line 125.

[00122] By "on-demand", the invention contemplates that the engine, on-board reactor and valves can be set and operated in a manner to accommodate predetermined specifications and criteria for a "high load" or "increased load" condition that would selectively activate the conversion of fuel from the starting fuel to a higher octane (or lower cetane) rated fuel. This selective "on-demand" activation of the fuel conversion, which occurs on-board the vehicle, under predetermined conditions enhances the efficiency of the engine, reduces the possibility of engine damage, and increases the economic operation of the engine by reducing (or eliminating) octane "give away."

[00123] Under normal load, ambient air is provided to turbocharger 130 via line 126, and is then directed to engine 160 via lines 131 and 132. Under an increased load condition, ambient air in line 131 is diverted to evaporator 140 via line 133. Valves control when ambient air is directed to engine 160 or evaporator 140, and such valves may be coupled with sensors.

[00124] When a thermal cracking process is used for conversion of the starting fuel to the final fuel, water may be provided via line 116 to tank 120, where it is stored until needed. Under increased load conditions, the water is directed to water injector 122 via line 121. The water is then injected into evaporator 140 via line 123, as seen in FIG. 1. FIG. 2 is a flow diagram of the on-board conversion process for partial oxidation without the water injection features used for thermal cracking.

[00125] Under increased engine load conditions, the starting fuel undergoes conversion to a final fuel by either partial oxidation or thermal cracking in the system described above. In the case of partial oxidation, the starting fuel provided to evaporator 140 may be combined with exhaust gases via line 165 and/or waste heat and with ambient air via line 133. In the

case of thermal cracking, the starting fuel (provided via line 125) is combined with water via line 123 (which is evaporated to steam), and exhaust gas via line 165 to the evaporator 140. When used, the ambient air and/or water can be preheated prior to being fed to evaporator 140. Valves may be coupled to sensors so as to control the feed of the ambient air, water, exhaust gas, and starting fuel into the evaporator 140.

[00126] Evaporator 140 can have a heating plate to provide the heating required to vaporize the starting fuel, and/or heat from the exhaust gas may be used to vaporize the fuel and to form steam. Evaporator 140 may contain a catalyst to assist with partial oxidation of the starting fuel to generate heat to sustain the thermal cracking, isomerization and reforming reactions that occur in on-board reactor 150.

[00127] The mixture formed in evaporator 140 is then directed to on-board reactor 150 via line 141. The type of on-board on-demand reactor may vary based on whether the process for conversion of the starting fuel to the final fuel is a partial oxidation process or a thermal cracking process. As described herein, the type of catalyst may also vary depending on whether the process for conversion of the starting fuel to the final fuel is a partial oxidation process or a thermal cracking process. Additionally, an additional on-board reactor may be included, in series with on-board reactor 150 for the production of additional hydrogen.

[00128] The final fuel exits reactor 150 via line 151 and is directed to engine 160 at port 115. The final fuel will continue to be formed and directed to on-board engine 160 until the engine load decreases and the RON required decreases.

[00129] When the on-board engine is operating under a normal load, the starting fuel is direct injected into on-board engine 160; and, when the engine operates under an increased load, the final fuel is port injected into on-board engine 160. The example below is intended to further illustrate certain aspects of the processes described herein.

EXAMPLES

Example 1:

[00130] The ignition delay response for possible gas composition output as a function of temperature was compared for several fuels. As shown in FIG. 3, the ignition delay time 301 (ms) was plotted against the temperature (in Kelvin) on the top x-axis and against $1000/T$ (1/K) 302. Naphtha (n-pentane is used as a surrogate) with RON of 60 is fed into a platinum coated monolith reactor. The fuel is fed along with air into the reactor.

[00131] The intake feed is pre-heated to 200 °C using the exhaust gas. The C_5H_{12}/O_2 ratio is maintained at 0.5. The residence time is 6.5×10^{-3} s. The major products species with 80% of fuel conversion are C_2H_4 , C_3H_6 , C_4H_8 , CO, CH_4 , and H_2O . The composition at the outlet denoted as Product 1 is:

Chemical Species	Mole Fraction
NC_5H_{12}	0.2
C_2H_4	0.32
C_3H_6	0.08
C_4H_8	0.04
CO	0.16
CH_4	0.08
H_2O	0.12

[00132] The simulated ignition delay times of Product 1 (305), Naphtha (306) with RON 60, and gasoline (306) with RON 90 is presented in Fig 2. The increase in ignition delay times is an indication of increasing RON. Product 1 (305) produced according to the process described herein showed a significant delay in ignition time over unconverted Naphtha (306) indicating an increase in RON for Product 1 following conversion. Product 1 (305) showed ignition delay times approximately equal to or exceeding that for the gasoline (304) with RON 90.

[00133] The foregoing description is by way of example only, and is not intended to limit the invention. While the systems and processes have been described in detail, modifications of those detailed descriptions are within the spirit and scope of the invention. It should be understood that aspects of the systems and processes and portions of various embodiments and various features recited above and/or in the appended claims may be combined or interchanged either in whole or in part. In the foregoing descriptions of the various embodiments, those embodiments which refer to another embodiment may be appropriately combined with other embodiments.

WHAT IS CLAIMED IS:

1. A process for conversion of saturated hydrocarbons to unsaturated hydrocarbons in an on-board reactor, the process comprising.
 - a) providing saturated hydrocarbons having 2 to 25 carbons comprising at least one of paraffins, cycloparaffins, and iso-paraffins, said saturated hydrocarbons being a starting gasoline fuel having a first Research Octane Number (RON) or a starting diesel fuel having a first Cetane Number (CN) for an associated engine, said starting gasoline fuel or starting diesel fuel being satisfactory for the operation of said associated engine under normal operating conditions;
 - b) providing an on-board reactor having a catalyst capable of catalyzing saturated hydrocarbons to one or more unsaturated hydrocarbons;
 - c) directing selectively the saturated hydrocarbons in the starting fuel to the on-board reactor on-demand when a second operating condition arises that requires the engine to use a higher octane-rated fuel or lower cetane-rated fuel;
 - d) converting selectively the saturated hydrocarbons in the starting fuel in the on-board reactor over the catalyst to form on-demand a final fuel comprising one or more unsaturated hydrocarbons, wherein the final fuel has a second RON that is higher than the starting gasoline fuel or a second CN that is lower than the starting diesel fuel;
 - e) delivering the final fuel having the second RON value or second CN value to the on-board engine on-demand only when the engine is operating under the second operating conditions so that the engine can operate more effectively with the higher octane-rated or lower cetane-rated fuel; and,
 - f) delivering the starting gasoline fuel or diesel fuel to the associated engine during normal operating when the engine does not require the higher octane-rated or lower cetane-rated fuel so as to efficiently operate the associated engine while minimizing octane give away inefficiencies.
2. The process of claim 1, wherein converting the saturated hydrocarbons in the starting fuel to one or more unsaturated hydrocarbons is a partial oxidation process achieved by partially oxidizing the saturated hydrocarbons with a gas containing oxygen over the catalyst in the on-board reactor to form the final fuel.

3. The process of claim 2, wherein the gas containing oxygen is ambient air, an exhaust gas from the on-board engine, or a combination thereof.
4. The process of claims 2 or 3, wherein the catalyst is a supported metal catalyst comprising at least one of rhodium and platinum.
5. The process of claim 1, wherein converting the saturated hydrocarbons in the starting fuel to one or more unsaturated hydrocarbons is a thermal cracking process achieved by feeding an exhaust gas from the on-board engine to the on-board reactor in the presence of the catalyst under conditions to thermally crack the starting fuel to form the final fuel.
6. The process of claim 5 further comprising: feeding a gas containing oxygen to the on-board reactor with the exhaust gas.
7. The process of claim 5 or 6, wherein the catalyst comprises an alkali earth metal, an alkaline earth metal or a zeolite.
8. The process of any one of claims 1-7, further comprising: feeding steam to the on-board reactor.
9. The process of any one of claims 1-8, wherein the on-board engine is a spark ignition engine or a compression ignition engine.
10. The process of any one of claims 1-9, wherein the starting fuel has a residence time in the on-board reactor from 0.001 second to 1 second.
11. The process of any one of claims 1-10, wherein the on-board reactor has an operating temperature from 350 to 1000°C and a pressure from 1 to 15 ATM.
12. The process of claim 11, wherein the operating temperature is from 350 to 650°C and the pressure is from 1 to 5 ATM.
13. The process of any one of claims 1-12, wherein the on-board reactor is heated with waste heat from the on-board engine.
14. The process of any one of claims 1-13, wherein the process provides an on-demand fuel supply to the on-board engine.

15. A process for operating an engine, comprising:
- a) providing an on-board reactor having a catalyst capable of catalyzing saturated hydrocarbons to one or more unsaturated hydrocarbons selectively on-demand when a higher octane-rated or lower cetane-rated fuel is needed by the engine, wherein said on-board reactor converts saturated hydrocarbons to one or more unsaturated hydrocarbons selectively on-demand when the engine requires the higher octane-rated or lower cetane-rated fuel;
 - b) providing a starting fuel of a gasoline fuel or a diesel fuel to the engine when the engine does not require the higher octane-rated or lower cetane-rated fuel, said starting fuel comprising saturated hydrocarbons having 2 to 25 carbons comprising at least one of paraffins, cycloparaffins, and iso-paraffins, and said starting gasoline fuel has a first RON or the starting diesel fuel has a first cetane number (CN);
 - c) converting selectively on-demand a first portion of the starting fuel to a final fuel comprising one or more unsaturated hydrocarbons in the on-board reactor by the process of any one of claims 1-14, wherein the final fuel has a second RON that is higher than the first RON or a second CN that is lower than the first CN in the starting fuel;
 - d) port injecting the final fuel to the engine selectively on-demand only when the higher octane-rated or lower cetane-rated fuel is needed by the engine;
 - e) operating the engine at a second load that is greater than the first load using the higher octane-rated or lower cetane-rated fuel in the engine; and,
 - f) providing the starting fuel to the engine when the engine is operating in the first load condition so as to efficiently operate the associated engine while minimizing octane give away inefficiencies.
16. A process for conversion of saturated hydrocarbons to unsaturated hydrocarbons in an on-board reactor, the process comprising:
- a) providing to an engine saturated hydrocarbons having 2 to 25 carbons comprising at least one of paraffins, cycloparaffins, and iso-paraffins, said saturated hydrocarbons being a starting gasoline fuel having a first Research Octane Number (RON) or a starting diesel fuel having a first Cetane Number (CN), said a saturated hydrocarbons being included in a starting fuel of a gasoline fuel or a diesel fuel;

b) delivering the starting fuel to the engine when the engine does not need a higher octane-rated or lower cetane-rated fuel so as to efficiently operate the associated engine while minimizing octane give away inefficiencies;

c) partially oxidizing selectively on-demand the saturated hydrocarbons in the on-board reactor with a gas containing oxygen over a catalyst to form a final fuel comprising one or more unsaturated hydrocarbons, wherein the final fuel has a second RON that is higher than the starting gasoline fuel or a second CN that is lower than the starting diesel fuel, said oxidizing occurs selectively on-demand when a higher octane-rated or lower cetane-rated fuel is needed by the engine; and,

d) delivering the final fuel to an on-board engine on-demand only when a higher octane-rated or lower cetane-rated fuel is needed by the engine.

17. The process of claim 16, wherein the on-board engine is a spark ignition engine or a compression ignition engine.

18. The process of claim 16, wherein the gas containing oxygen is ambient air, exhaust gas redirected from the on-board engine, or a combination thereof.

19. The process of any one of claim 16, wherein the starting fuel has a residence time in the on-board reactor from 0.001 second to 1 second.

20. The process of claim 16, wherein the on-board reactor has an operating temperature from 350 to 1000°C and a pressure from 1 to 15 ATM.

21. The process of claim 16, wherein the on-board reactor is heated with waste heat from the on-board engine.

22. The process of claim 16, wherein the catalyst is a supported metal catalyst comprising at least one of rhodium and platinum.

23. The process of claim 16, wherein the process provides an on-demand fuel supply to the on-board engine.

24. A process for conversion of saturated hydrocarbons to unsaturated hydrocarbons in an on-board reactor:

a) providing a starting fuel of a starting gasoline fuel or a starting diesel fuel to an engine, said starting fuel comprising saturated hydrocarbons having 2 to 25 carbons comprising at least one of paraffins, cycloparaffins, and iso-paraffins to an on-board

reactor, wherein the starting gasoline fuel has a first RON or the diesel fuel has a first cetane number (CN), and said starting fuel being provided to the engine when the engine does not require the higher octane-rated or lower cetane-rated fuel so as to efficiently operate the associated engine while minimizing octane give away inefficiencies;

b) feeding an exhaust gas from an on-board engine to the on-board reactor in the presence of a catalyst under conditions to thermally crack the starting fuel on-demand to selectively form a final fuel, said final fuel has a higher RON than the starting gasoline fuel or a lower CN than the starting diesel fuel; and

c) delivering the final fuel to the on-board engine selectively on-demand only when the higher octane-rated or lower cetane-rated fuel is needed by the engine.

25. The process of claim 24, further comprising: feeding steam to the on-board reactor with the exhaust gas.

26. The process of claim 24, further comprising: feeding a gas containing oxygen to the on-board reactor with the exhaust gas.

27. The process of claim 24, wherein the on-board engine is a spark ignition engine or a compression ignition engine.

28. The process of claim 24, wherein the starting fuel has a residence time in the on-board reactor from 0.001 second to 1 second.

29. The process of claim 24, wherein the on-board reactor has an operating temperature from 350 to 650°C and a pressure from 1 to 5 ATM.

30. The process of claim 24, wherein the catalyst comprises an alkali earth metal, an alkaline earth metal, or a zeolite.

31. The process of claim 24, wherein the process provides an on-demand fuel supply to the on-board engine.

32. A process for operating an engine, comprising:

a) providing an on-board reactor having a catalyst capable of selectively converting saturated hydrocarbons to one or more unsaturated hydrocarbons on-demand when the engine requires the higher octane-rated or lower cetane-rated fuel to operate at a second load condition, wherein said on-board reactor is able to convert saturated

hydrocarbons to one or more unsaturated hydrocarbons on-demand, said reactor having an operating temperature of 350 to 1000°C and a pressure from 1 to 15 ATM;

b) providing a starting fuel of a starting gasoline fuel having a first (Research Octane Number) RON or a starting diesel fuel having a first cetane number (CN) to the engine when the engine is operating at a first load condition, said starting fuel comprising saturated hydrocarbons having 2 to 25 carbons comprising at least one of paraffins, cycloparaffins, and iso-paraffins, said starting fuel is sufficient for engine operation when the engine does not require the higher octane-rated or lower cetane-rated fuel so as to efficiently operate the associated engine while minimizing octane give away inefficiencies;

c) delivering the starting gasoline fuel or diesel fuel to the associated engine during normal operating so as to efficiently operate the associated engine while minimizing octane give away inefficiencies.

d) converting selectively a portion of the starting fuel to a final fuel comprising one or more unsaturated hydrocarbons in the on-board reactor, wherein the final fuel has a second RON that is higher than the first RON or a second CN that is lower than the first CN so that the engine can operate at the second load condition using the final fuel, said starting fuel having a residence time in the on-board reactor from 0.001 second to 1 second;

e) port-injecting the final fuel to the engine only when the engine requires fuel with a second RON that is higher than the first RON or a second CN that is lower than the first CN; and,

f) operating the engine at a second load that is greater than the first load.

33. The process of claim 32, wherein converting the saturated hydrocarbons in the starting fuel to one or more unsaturated hydrocarbons in the final fuel is a partial oxidation process achieved by partially oxidizing the saturated hydrocarbons with a gas containing oxygen over the catalyst in the on-board reactor to form the final fuel, wherein said gas containing oxygen is ambient air, exhaust gas from the on-board engine or combinations thereof, and the catalyst is a supported metal catalyst comprising at least one of rhodium and platinum.

34. The process of claim 32, wherein converting the saturated hydrocarbons in the starting fuel to one or more unsaturated hydrocarbons in the final fuel is a thermal cracking process achieved by feeding an exhaust gas from the on-board engine and steam to the on-board reactor in the presence of the catalyst under conditions to thermally crack the starting fuel to form the final fuel, wherein the catalyst comprises an alkali earth metal, an alkaline earth metal or a zeolite.

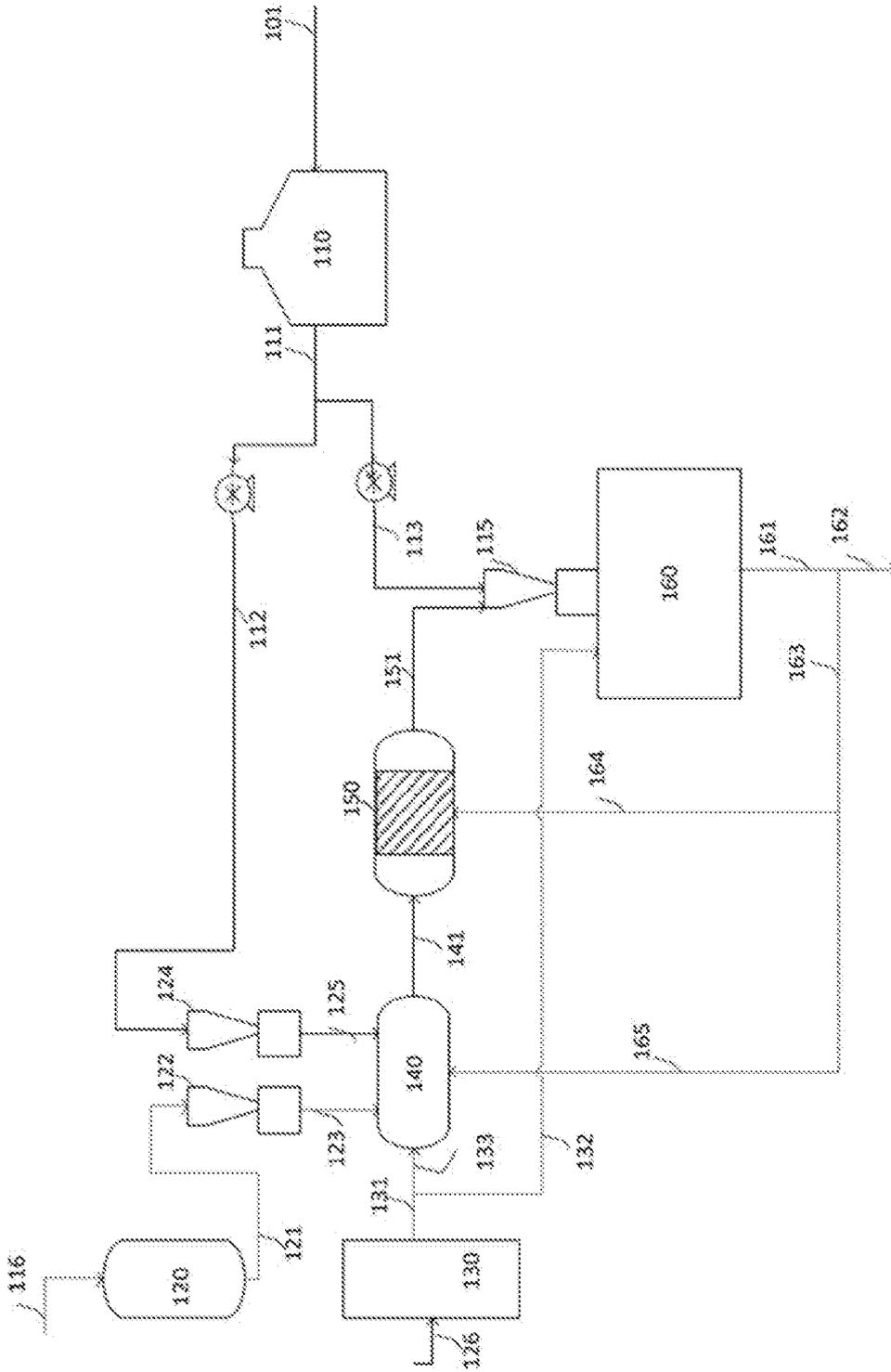


FIG. 1

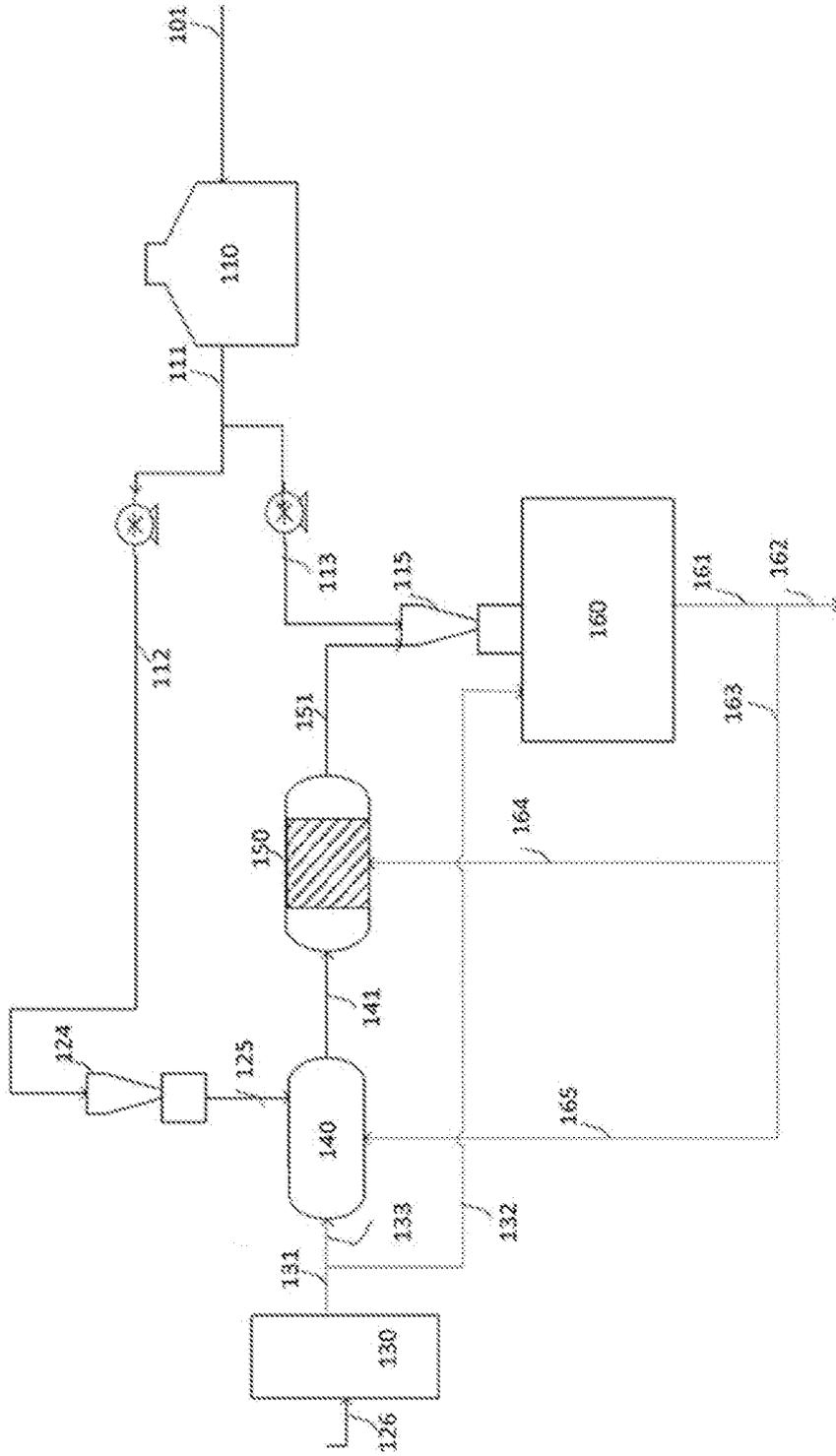


FIG. 2

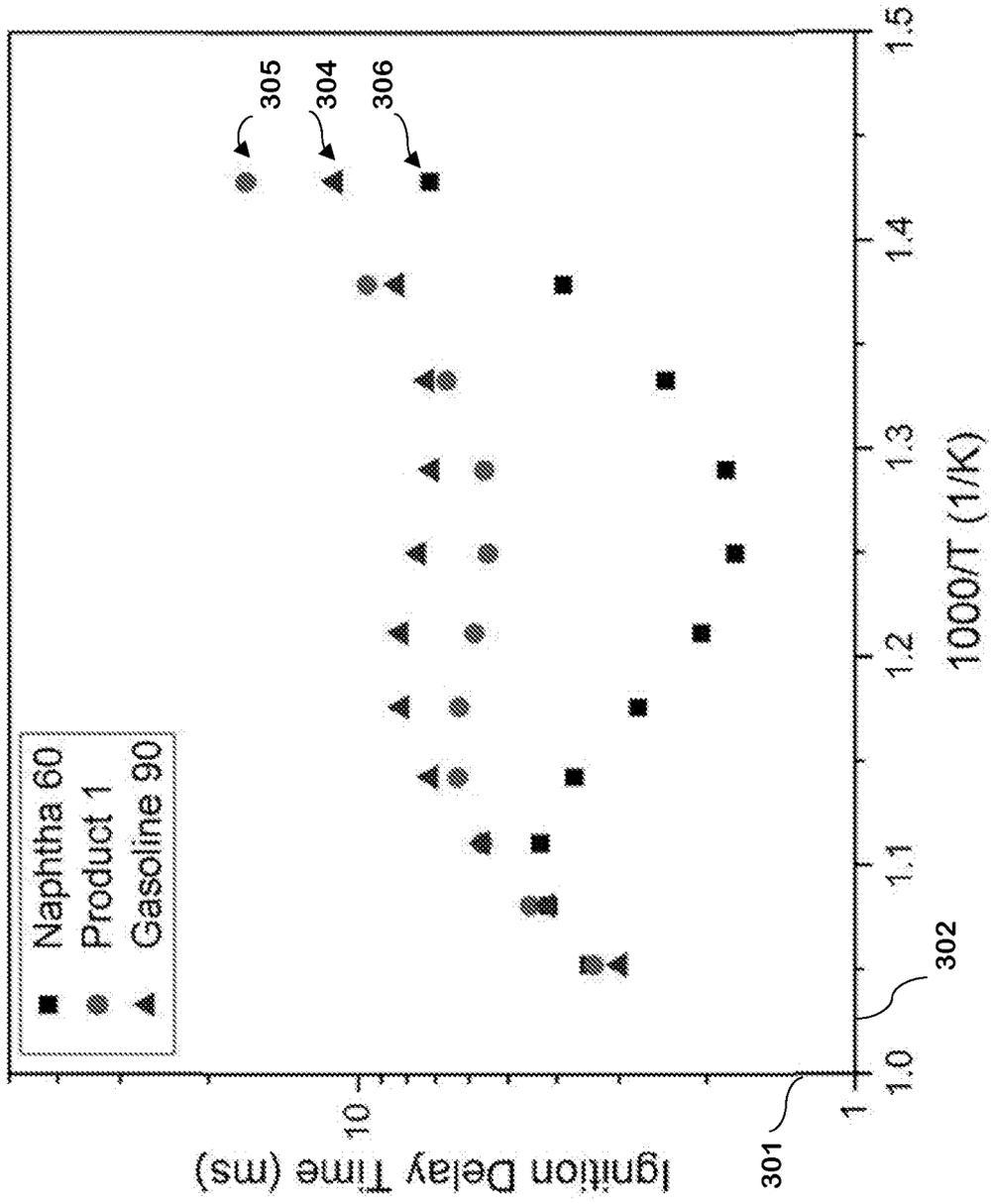


FIG. 3

INTERNATIONAL SEARCH REPORT

International application No
PCT/IB2017/054851

A. CLASSIFICATION OF SUBJECT MATTER
 INV. C10G35/04 C10G9/36 CIOGII/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)
 CIOG

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	US 4 070 993 A (CHEN NAI YUEN) 31 January 1978 (1978-01-31) col umn 1, line 17 - line 20 col umn 2, lines 13-15,50-62 col umn 3, line 42 - line 48 col umn 7, lines 28-36,67-68 -----	1-34
X	US 4 884 531 A (DEGNAN JR THOMAS F [US] ET AL) 5 December 1989 (1989-12-05) col umn 1, line 19 - line 24 col umn 2, line 56 - line 65 col umn 3, line 23 - line 35 col umn 5, line 30 - line 32 example 2 ----- -/- .	1-34

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 9 October 2017	Date of mailing of the international search report 17/10/2017
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Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Chau, Thoi Dai
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INTERNATIONAL SEARCH REPORT

International application No
PCT/IB2017/054851

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
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