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(54) Title: IMPROVING THE IGNITION QUALITY OF FUELS

(57) Abstract: Provided herein are compounds and methods of producing compounds for improving ignition quality and combustion efficiency of fuels, for example fossil fuels. In various aspects we generate highly oxygenated compounds from hydrocarbon feedstocks. The feedstock can be a branched alkane or n-alkane having a chain length greater than or equal to 6, a cycloalkane with a 5 or 6 membered ring structure, or a alkylated cycloalkane with 5 or more carbon atoms. The reactant can be fed in the gas-phase to a partial oxidation reactor (with or without a catalyst), and at a fixed temperature, mixture composition, and residence time. The reactant can be converted to a mixture of products including keto hydroperoxides, diketo hydroperoxides, keto dihydroperoxides, hydroperoxyl cyclic ethers, and alkenyl hydroperoxides. The compounds are inherently unstable and can quickly decompose to highly reactive radical species that can be used to improve the ignition quality of a fuel and advance ignition in an engine.



## IMPROVING THE IGNITION QUALITY OF FUELS

### CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application claims priority to, and the benefit of, co-pending U.S. provisional application entitled "IGNITION QUALITY OF FUELS" having serial no. 62/261,516 filed December 1, 2015 the contents of which are incorporated by reference in their entirety.

### TECHNICAL FIELD

[0002] The present disclosure generally relates to improvement of combustion efficiency of fossil fuels and reduction of pollutant emission.

### BACKGROUND

[0003] Among real fuels (e.g., gasoline, diesel and jet fuels), straight-chain (normal) and branched (iso) paraffins are common species, and thus selected as important components in surrogate fuels. The iso-paraffins in typical diesel fuels are lightly substituted with one or two methyl groups on a long (C<sub>10</sub>-C<sub>24</sub>) chain<sup>44</sup>. Similarly, jet fuel GC-MS data indicates that most of the identified iso-paraffins have one, or at most two, methyl substitutions<sup>57</sup>. A study on Fischer-Tropsch Jet A-1 (S-8), a synthetic jet fuel, also found similar results<sup>58</sup>.

[0004] Recent research has focused on the combustion study of mono-methylalkanes and di-methylalkanes. Sarathy et al.<sup>41</sup> investigated the combustion of a series of 2-methylalkanes from C<sub>7</sub>-C<sub>20</sub>. The reaction classes and their corresponding rate rules were proposed. The comprehensive studies on 2-methylheptane and 3-methylheptane<sup>39, 41, 42, 58, 60</sup> have found that the combustion properties of mono-methylated paraffins are notably different than those of their straight-chain isomers (n-

octane), i.e., they exhibit decreased low-temperature reactivity and lower premixed laminar flame speeds.

**[0005]** Experimental and modeling investigations on di-methylalkanes have also been carried out. Ji et al.<sup>61</sup> studied the laminar flame speeds of five octane isomers, showing that increased methyl substitutions decreases reactivity. Sarathy et al.<sup>60</sup> found that 2,5-dimethylhexane has an increased propensity towards flame extinction and decreased tendency towards flame ignition compared to the mono-methylated hexane and normal octane isomers. Similar trends were observed by Liu et al.<sup>62</sup> during counterflow flame ignition of C<sub>8</sub> and C<sub>10</sub> di-methylalkanes in non-premixed flames. More recently, Sarathy et al.<sup>40</sup> further investigated 2,5-dimethylhexane combustion in a range of homogenous reaction systems, and developed a comprehensive kinetic model. Furthermore, Li et al.<sup>63</sup> studied 2,7-dimethyloctane pyrolysis and oxidation using shock tube species time-histories and ignition delay analysis. Rotavera et al.<sup>21</sup> studied the initial reaction pathways of 2,5-dimethylhexane using Cl-atom initiated oxidation in a flow reactor using the multiplexed photoionization mass spectrometry.

**[0006]** Coupling of jet-stirred reactor (JSR) with synchrotron vacuum ultra-violet photo-ionization molecular beam mass spectrometry (SVUV-PI-MBMS) is a state-of-the-art approach to investigate the low-temperature gas-phase oxidation chemistry<sup>47</sup>. Stable intermediates such as cyclic ethers, alkenes, aldehydes, ketones, acids and also unstable peroxides and keto-hydroperoxides were detected and identified during hydrocarbon low-temperature oxidation<sup>26-28</sup>.

**[0007]** Recent work by Wang et al.<sup>27</sup> investigated the low-temperature oxidation of five hexane isomers, in which cyclic ethers with various ring sizes (i.e., from three to six) were detected, as well as C<sub>2</sub>-C<sub>3</sub> monocarboxylic acids, ketohydroperoxides, and species with two carbonyl groups. At low-temperatures, increasing the methyl substitution decreases reactivity, which is in agreement with the observation by Ji et al.<sup>61</sup>, Sarathy et al.<sup>60</sup>, and Liu et al.<sup>62</sup>.

[0008] Despite the progress towards understanding the combustion kinetics of iso-paraffins combustion, a detailed characterization of their low-temperature oxidation is still lacking. Compounds and methods for improving combustion efficiency and reduction of pollutant emission are still desired.

#### SUMMARY

[0009] Provided herein are compounds and methods of producing compounds for improving ignition quality and combustion efficiency of fuels, for example fossil fuels.

[0010] In an embodiment, improved ignitability of a fuel by the production of highly oxidized hydrocarbons is provided. These compounds can decompose rapidly under low temperatures, such that they lead to the production of radicals which lead to ignition. Thus, this technology can be used to improve the ignition quality of a fuel before it enters into an engine.

[0011] In an aspect, highly oxygenated compounds can be generated from hydrocarbon feedstocks. A reactor can be used for the homogeneous gas-phase production of keto hydroperoxides, diketo hydroperoxides, keto dihydroperoxides, hydroperoxyl cyclic ethers, alkenyl hydroperoxides, etc. In an aspect, a perfectly-stirred reactor can be used. The feed reactant can be a branched alkane, an n-alkane having a chain length greater than or equal to 6 for example a C6-C20 n-alkane, or a cycloalkane. The branched alkane can be, for example, a C6-C20 mono-methylalkane, dimethylalkane, tri-methylalkane, multi-substituted alkane, or any mixture comprising the aforementioned species. The cycloalkane can have a carbon number of 5 or greater, for example a C5 or C6 ring. The cycloalkane can also have alkylated side chains such as cyclopentane, methylcyclopentane, cyclohexane, methylcyclohexane, dimethylcyclohexane, ethylcyclohexane, propylcyclohexane, and butylcyclohexane, or any mixture of the aforementioned species. The reactant can be fed in the gas-phase to a partial oxidation reactor (with or without a catalyst), and at a fixed temperature,

mixture composition, and residence time. The reactant can be converted to a mixture of products comprising keto hydroperoxides, diketo hydroperoxides, keto dihydroperoxides, hydroperoxyl cyclic ethers, and alkenyl hydroperoxides. These compounds are inherently unstable and can quickly decompose to highly reactive radical species, which can be used to advance ignition in, for example, an engine. We are unaware of any existing technology that selectively produces the active compounds (e.g., keto hydroperoxides, diketo hydroperoxides, keto dihydroperoxides, hydroperoxyl cyclic ethers, alkenyl hydroperoxides) using the feed reactant.

**[0012]** In various embodiments, methods of producing highly oxygenated compounds from hydrocarbon feedstocks and highly oxygenated compounds produced thereby are provided. The methods can include the steps of: providing a feed reactant in gas phase, the feed reactant being a branched alkane, or an n-alkane having a carbon chain length greater than 6; mixing the feed reactant with an oxidant; and carrying out a low temperature reaction, including a low temperature oxidation, of the feed reactant to convert the feed reactant to a product including a keto hydroperoxide, a diketo hydroperoxide, a keto dihydroperoxide, a hydroperoxyl cyclic ether, or a alkenyl hydroperoxide, or combinations thereof.

**[0013]** In any one or more aspects of any one or more of the various embodiments, the feed reactant can be selected from the group consisting of a C6-C20 n-alkane, C6-C20 mono-methylalkane, dimethylalkane, tri-methylalkane, or multi-substituted alkane, C5-C6 cycloalkanes, C6-C10 alkylated cycloalkanes, or any combination thereof. The low temperature oxidation reaction can be carried out in a partial oxidation reactor (with or without a catalyst). The partial oxidation reactor can be a perfectly stirred reactor for the homogeneous gas-phase production of the product. The feed reactant can be fed in the gas-phase to the partial oxidation reactor, and at a fixed temperature, mixture composition, and residence time. The temperature can be in the range of 200° to 800°K. The pressure can be in the range of 1 to 100 bar (atm). The residence time can be a fixed residence time in the range of about 0.1 to about 10 seconds. The low temperature

reaction can include the steps of: a radical initiation of the feed reactant to form an alkyl radical followed by oxidation of the alkyl radical to form an alkyl peroxy radical; intramolecular hydrogen-atom migration to form a hydroperoxy alkyl radical; and oxidation of the hydroperoxy alkyl radical to form an  $\alpha$ -hydroperoxyalkyl hydroperoxy radical (OOQOOH). The method can further include the steps of any of Scheme 2(a), 2(b), 2(c), 3(a), 3(b), 4(a), 4(b), 4(c) or 4(d).

**[0014]** In further aspects, the formation of keto-dihydroperoxides can be initiated by alternative isomerization of OOQOOH radicals to P(OOH)<sub>2</sub> radicals (Note: Q=C<sub>n</sub>H<sub>2n</sub>, P=C<sub>n</sub>H<sub>2n-1</sub>) via intramolecular H-atom migration reactions. The P(OOH)<sub>2</sub> radicals can decompose to a hydroperoxyl cyclic ether or a scission of the P(OOH)<sub>2</sub> radicals can produce an HO<sub>2</sub> radical and an alkenylhydroperoxide. Subsequent O<sub>2</sub> addition to the P(OOH)<sub>2</sub> radicals followed by intramolecular H-atom migration and decomposition can form the keto-dihydroperoxides. The aforementioned decomposition step can also produce an OH radical, which together with further homolytic O-O dissociation of the keto-dihydroperoxide to release another OH radical, behaves as a radical chain-branching pathway. Another chain branching process can occur during the formation of diketo-hydroperoxides, which can result from subsequent reactions of keto-hydroperoxide and keto-dihydroperoxide species.

**[0015]** Other systems, methods, features, and advantages of the present disclosure will be or become apparent to one with skill in the art upon examination of the following drawings and detailed description. It is intended that all such additional systems, methods, features, and advantages be included within this description, be within the scope of the present disclosure, and be protected by the accompanying claims.

## DETAILED DESCRIPTION

[0016] Described below are various embodiments of the present systems and methods for improving ignition quality of fuels. Although particular embodiments are described, those embodiments are mere exemplary implementations of the system and method. One skilled in the art will recognize other embodiments are possible. All such embodiments are intended to fall within the scope of this disclosure. Moreover, all references cited herein are intended to be and are hereby incorporated by reference into this disclosure as if fully set forth herein. While the disclosure will now be described in reference to the above drawings, there is no intent to limit it to the embodiment or embodiments disclosed herein. On the contrary, the intent is to cover all alternatives, modifications and equivalents included within the spirit and scope of the disclosure.

### Discussion

[0017] Before the present disclosure is described in greater detail, it is to be understood that this disclosure is not limited to particular embodiments described, as such may, of course, vary. It is also to be understood that the terminology used herein is for the purpose of describing particular embodiments only, and is not intended to be limiting, since the scope of the present disclosure will be limited only by the appended claims.

[0018] Where a range of values is provided, it is understood that each intervening value, to the tenth of the unit of the lower limit (unless the context clearly dictates otherwise), between the upper and lower limit of that range, and any other stated or intervening value in that stated range, is encompassed within the disclosure. The upper and lower limits of these smaller ranges may independently be included in the smaller ranges and are also encompassed within the disclosure, subject to any specifically excluded limit in the stated range. Where the stated range includes one or both of the limits, ranges excluding either or both of those included limits are also included in the disclosure.

[0019] Unless defined otherwise, all technical and scientific terms used herein have the same meaning as commonly understood by one of ordinary skill in the art to which this disclosure belongs. Although any methods and materials similar or equivalent to those described herein can also be used in the practice or testing of the present disclosure, the preferred methods and materials are now described.

[0020] All publications and patents cited in this specification are herein incorporated by reference as if each individual publication or patent were specifically and individually indicated to be incorporated by reference and are incorporated herein by reference to disclose and describe the methods and/or materials in connection with which the publications are cited. The citation of any publication is for its disclosure prior to the filing date and should not be construed as an admission that the present disclosure is not entitled to antedate such publication by virtue of prior disclosure. Further, the dates of publication provided could be different from the actual publication dates that may need to be independently confirmed.

[0021] As will be apparent to those of skill in the art upon reading this disclosure, each of the individual embodiments described and illustrated herein has discrete components and features which may be readily separated from or combined with the features of any of the other several embodiments without departing from the scope or spirit of the present disclosure. Any recited method can be carried out in the order of events recited or in any other order that is logically possible.

[0022] Embodiments of the present disclosure will employ, unless otherwise indicated, techniques of chemistry, synthetic inorganic chemistry, analytical chemistry, and the like, which are within the skill of the art. Such techniques are explained fully in the literature.

[0023] The following examples are put forth so as to provide those of ordinary skill in the art with a complete disclosure and description of how to perform the methods and use the compositions and compounds disclosed and claimed herein. Efforts have been



made to ensure accuracy with respect to numbers (*e.g.*, amounts, temperature, *etc.*), but some errors and deviations should be accounted for. Unless indicated otherwise, parts are parts by weight, temperature is in °C, and pressure is in bar. Standard temperature and pressure are defined as 0 °C and 1 bar.

**[0024]** It is to be understood that, unless otherwise indicated, the present disclosure is not limited to particular materials, reagents, reaction materials, manufacturing processes, or the like, as such can vary. It is also to be understood that the terminology used herein is for purposes of describing particular embodiments only, and is not intended to be limiting. It is also possible in the present disclosure that steps can be executed in different sequence where this is logically possible.

**[0025]** It must be noted that, as used in the specification and the appended claims, the singular forms "a," "an," and "the" include plural referents unless the context clearly dictates otherwise. Thus, for example, reference to "a support" includes a plurality of supports. In this specification and in the claims that follow, reference will be made to a number of terms that shall be defined to have the following meanings unless a contrary intention is apparent.

**[0026]** The term "alkane," as generally used herein, refers to saturated aliphatic groups, including straight-chain alkanes, branched-chain alkanes, cycloalkanes, alkyl-substituted cycloalkanes, and cycloalkyl-substituted alkanes. In some embodiments, a straight chain or branched chain alkane has 30 or fewer carbon atoms in its backbone (*e.g.*, C1-C30 for straight chains, C3-C30 for branched chains), 20 or fewer, or 12 or fewer. Likewise, in some embodiments cycloalkanes have from 3-10 carbon atoms in their ring structure, *e.g.* have 5, 6 or 7 carbons in the ring structure. The term "alkane" (or "lower alkane") as used throughout the specification, examples, and claims is intended to include both "unsubstituted alkanes" and "substituted alkanes", the latter of which refers to alkanes having one or more substituents replacing a hydrogen on one or more carbons of the hydrocarbon backbone. As used herein, the term "mono-

methylalkane" refers to an alkane where a hydrogen on exactly one carbon atom is replaced with a methyl substituent, "di-methylalkane" refers to an alkane where a hydrogen atom on exactly two carbon atoms are replaced with a methyl substituent, "tri-methylalkane" refers to an alkane where a hydrogen atom on exactly three carbon atoms are replaced with a methyl substituent, and "multi-substituted alkane" refers to an alkane where a hydrogen atom on four or more carbon atoms are replaced with a methyl substituent.

### **Description**

[0027] The low-temperature auto-oxidation of hydrocarbons occurs in many natural and engineered systems. For example, linear alkanes (i.e., n-alkanes) and those with one or more methyl substitutions (i.e., methylalkanes) are important components of conventional petroleum jet and diesel fuels, as well as alternative Fischer-Tropsch (FT) and hydrotreated renewable jet (HRJ) fuels. Understanding the fundamental combustion (oxidation) mechanism of these fuels is required for improving their use in practical combustion applications. Oxidation mechanisms also occur in the atmosphere.

[0028] The process begins with radical initiation and proceeds by a series of O<sub>2</sub> addition and intramolecular H-atom migration reactions that eventually lead to radical chain branching, propagation, or termination<sup>1</sup>. Fundamental gas-phase auto-oxidation mechanisms provide the foundations for chemical kinetic simulations used to improve the efficiency and emissions of combustion systems<sup>2-4</sup>. In the atmosphere, gas-phase auto-oxidation mechanisms govern the chemical nature and concentrations of pollutants both spatially and temporally<sup>5</sup>. Simulations attempting to predict the ignition properties of a hydrocarbon fuel in engines or the distribution of atmospheric pollutants should accurately represent the various auto-oxidation pathways and branching ratios to various products<sup>13,16</sup>.

[0029] **Scheme 1** below presents, in part, the typical low-temperature auto-ignition mechanism for alkanes. The typical mechanism is annotated with solid arrows to identify the pathways that have been confirmed by rigorous experimental measurements. The reaction of alkyl radicals (R) with molecular oxygen ( $O_2$ ) to form alkylperoxy radicals (ROO) is central to this auto-oxidation chemistry. The reaction of alkylperoxy radicals with NO to form peroxy radical (RO) largely governs tropospheric oxidation of organic species, except in low NO conditions.

[0030] However, the fate of ROO displays more complex behavior under combustion conditions. One possible channel is the bimolecular reaction of ROO with  $HO_2/RH$  to form an alkylhydroperoxide (ROOH), which further decomposes to RO and OH radicals. ROO could also undergo a concerted elimination to produce a conjugated alkene and a hydroperoxy ( $HO_2$ ) radical. This second reaction channel is effectively chain-terminating at low temperatures (i.e., releasing  $HO_2$  radical).

[0031] An interesting reaction channel for the ROO radical is intramolecular H-atom migration, resulting in the formation of a hydroperoxyalkyl radical (QOOH). The cyclization of a hydroperoxyalkyl radical to form a cyclic ether and an OH radical is important for radical chain propagation. More importantly, the reaction of molecular oxygen with QOOH (the second  $O_2$  addition) leads to an OOQOOH radical, which undergoes intramolecular H-atom migration to form an HOOQ'OOH (Note:  $R=C_nH_{2n+1}$ ,  $Q=C_nH_{2n}$ ,  $Q'=C_nH_{2n-1}$ ) radical. In the conventional low temperature oxidation scheme, only the hydrogen atom from the carbon bonded to the hydroperoxy group is abstracted, which is plausible since it has a lower C-H bond strength than a corresponding normal primary, secondary, and tertiary C-H bond. The HOOQ'OOH is an  $\alpha$ -hydroperoxyalkylhydroperoxy radical, which is unstable and easily decomposes to a keto-hydroperoxide and an OH radical<sup>17</sup>. Moreover, the keto-hydroperoxide has a weak O-O bond which can break to generate more OH radicals, thereby acting as a chain branching intermediate leading to eventual auto-ignition.

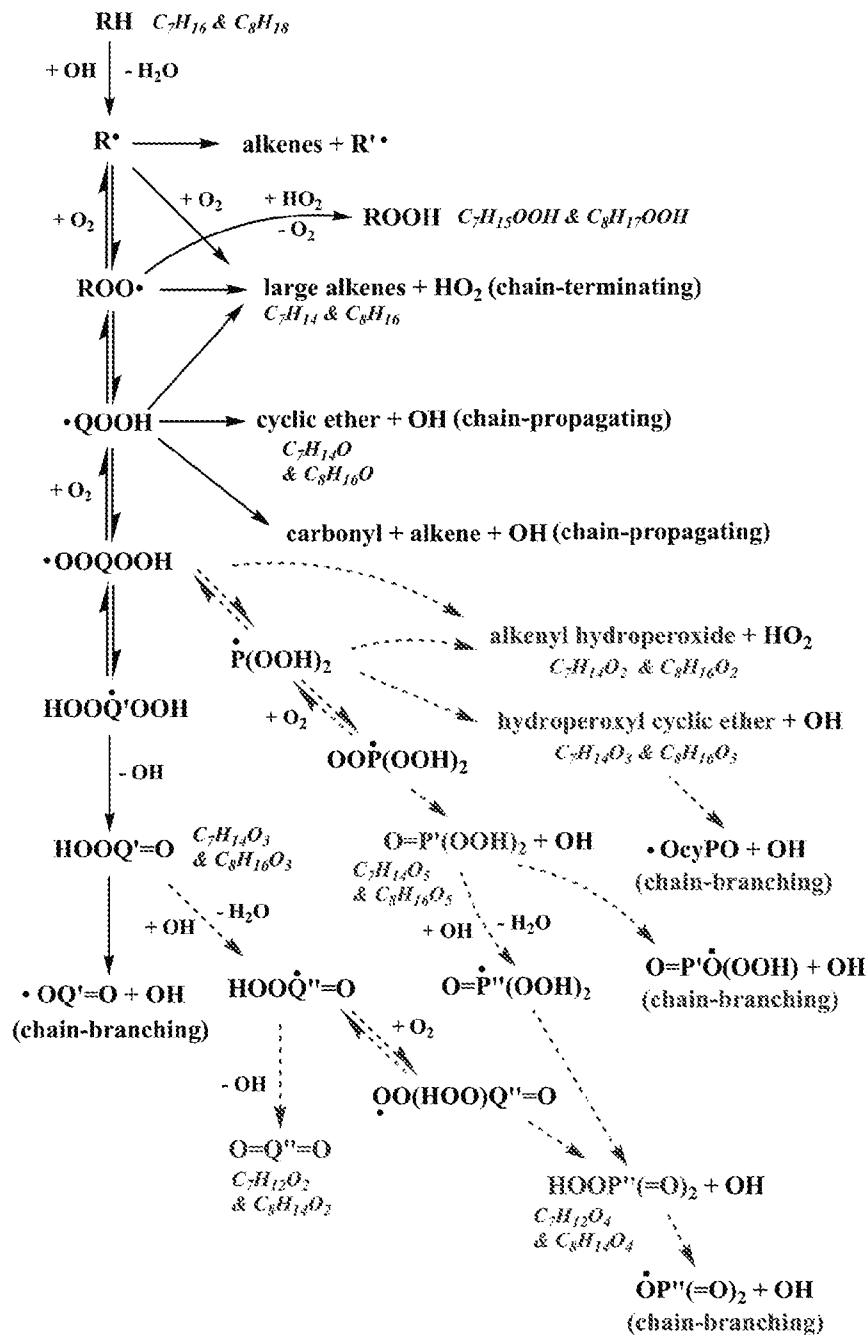
[0032] The aforementioned reaction scheme, i.e., first and second O<sub>2</sub> addition, has been confirmed via gas-phase measurements of the key intermediates such as hydroperoxyalkyl radicals (QOOH)<sup>18</sup>, alkylhydroperoxides<sup>19,20</sup>, conjugate alkenes<sup>21-23</sup>, cyclic ethers<sup>19,21,24</sup>, and keto-hydroperoxides<sup>25-31</sup>. However, as shown herein, the conventional low-temperature reaction scheme is incomplete considering the following two cases.

[0033] Firstly, the OOQOOH radical can undergo intramolecular H-atom migration involving a C-H bond not adjacent to the C-OOH site (denoted as an alternative isomerization here); a pathway competitive to the intramolecular H-atom migration leading to keto-hydroperoxide. Theoretical calculations by Sharma and coworkers on the intramolecular hydrogen migration in hydroperoxyalkylperoxy radicals concluded that "alternative" isomerizations are competitive with the pathways leading to keto-hydroperoxides, and thus cannot be neglected<sup>17</sup>. A recent kinetic modeling study further demonstrated the importance of including alternative isomerization pathways to simulate the ignition delay time of pentane isomers<sup>38</sup>.

[0034] Furthermore, previous work on slightly branched alkanes<sup>39-42</sup> has shown that OOQOOH radicals with an OOH group bonded to the tertiary carbon can only undergo alternative isomerizations. Despite previous computational works indicating alternative fates of OOQOOH radicals, the experimental focus in recent times has been on measuring products from the conventional isomerization pathways, i.e., keto-hydroperoxides. A lone study by Elin-Simiand and coworkers<sup>43</sup> on the low-temperature gas-phase oxidation of n-dodecane detected keto-hydroperoxides with two or more carbonyl groups, which could have resulted from alternative isomerizations of OOQOOH radicals.

[0035] **Scheme 1** below also includes an extended scheme for the low-temperature oxidation of hydrocarbons presented herein. The reaction network annotated with solid arrows is the conventional reaction scheme, while the reaction network annotated with

dashed arrows denotes new pathways disclosed herein. The annotated species were detected during the oxidation of 2-methylhexane and 2,5-dimethylhexane.



Scheme 1

[0036] To further determine the fate of OOQOOH radicals, the low-temperature oxidation of three branched alkanes (2-methylhexane, 2,5-dimethylhexane, and 2,7-

dimethyloctane), two n-alkanes (n-hexane and n-dodecane), and one cycloalkane (cyclohexane) were investigated as presented herein. These structures were chosen because the probabilities of alternative isomerization of OOQOOH radicals are favored. We report herein the direct measurement of species with multiple carbonyl and hydroperoxyl groups, such as the diketo-hydroperoxides and keto-dihydroperoxides, produced during the low-temperature gas-phase oxidation of the aforementioned fuels. The experimental observations confirm the presence of extended auto-oxidation reaction mechanisms at conditions of relevance to auto-ignition in engines. It should be noted, however, that the feed reactant is not limited to these two compounds. The feed reactant can be a branched alkane or an n-alkane as described further herein.

**[0037] Scheme 2a** below, presented herein, provides O<sub>2</sub> addition to the primary fuel radical and the subsequent chain branching reaction network. The species' notation is based on the scheme proposed by Sarathy et al.<sup>40</sup>, wherein carbon sites are labeled such that the position of the methyl substitution is minimized. Briefly, a lower case letter at the end of the string denotes the position of a radical, while a number denotes the position of a functional group (e.g., -OOH and -OO). The ROO radical undergoes intramolecular H-migration through five-, six-, seven-, and eight-membered-ring transition states (TS), and leads to β-QOOH, γ-QOOH, δ-QOOH, and ε-QOOH, respectively (hereafter, the position of a carbon bonded to an -OOH group in a QOOH radical is designated as α, β, δ, ε, respectively; α position is the carbon site with the radical). As calculated by the rate rules of Villano et al.<sup>53</sup>. The most feasible isomerization route is via a six-membered-ring TS abstracting the secondary C-H to form C<sub>8</sub>H<sub>15</sub>-OOH<sub>1-c</sub> (γ-QOOH), which further adds another O<sub>2</sub> to produce C<sub>8</sub>H<sub>15</sub>-OOH<sub>1-OO<sub>3</sub></sub>, a γ-OOQOOH (hereafter, the position of a carbon bonded to an -OOH group in an OOQOOH radical is designated as α, β, δ, ε, respectively; α position is the carbon site with the -OO group). In the conventional low-temperature oxidation scheme, this γ-OOQOOH radical (C<sub>8</sub>H<sub>15</sub>-OOH<sub>1-OO<sub>3</sub></sub>) abstracts an H-atom from the C-H bonded to the OOH group, thereby releasing an OH and forming a keto-hydroperoxide (KHP-1); the

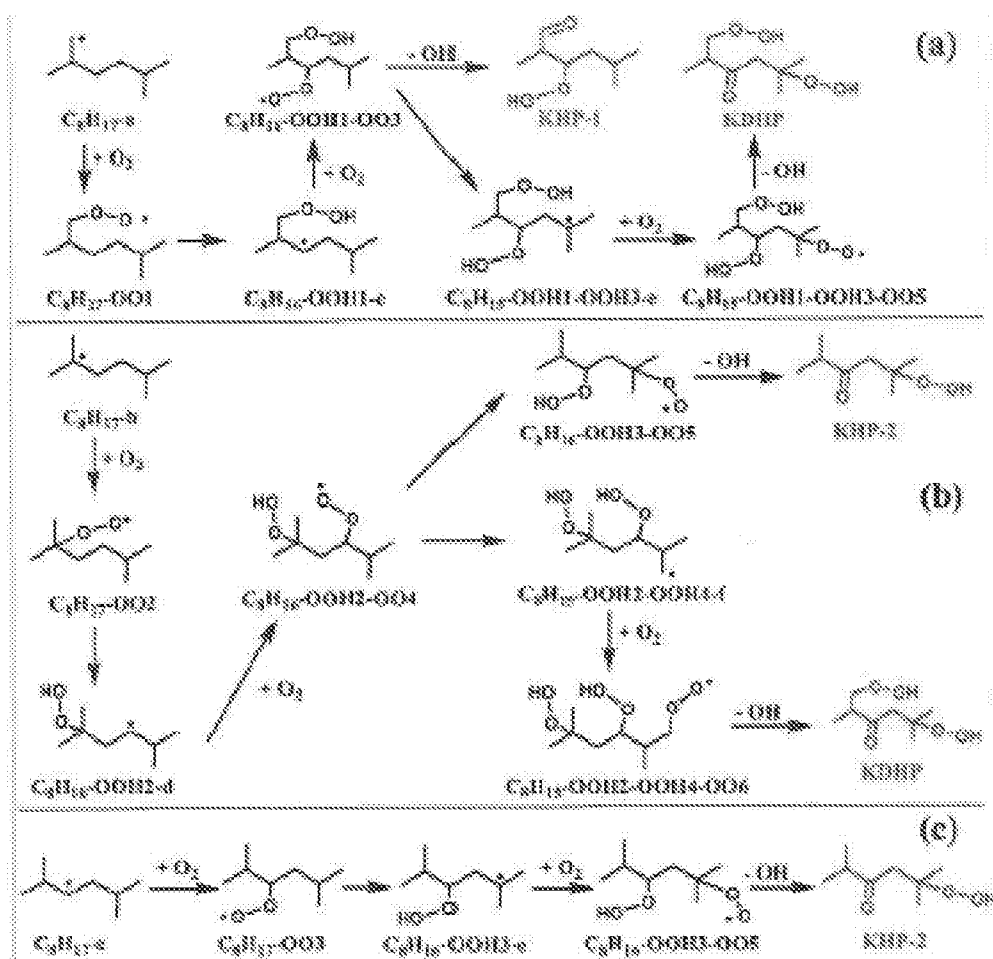
latter further decomposes to another OH radical and completes the low-temperature chain branching process.

**[0038]** However, for 2,5-dimethylhexane at 500 K, the rate constant of the channel to KHP-1 ( $6.6 \times 10^1 \text{ s}^{-1}$ )<sup>17</sup> is considerably lower than abstracting an H-atom from the tertiary C-H site to form  $\text{C}_8\text{H}_{15}\text{-OOH1-OOH3-e}$  ( $\text{P}(\text{OOH})_2$ ) ( $6.2 \times 10^3 \text{ s}^{-1}$ )<sup>53</sup>. Thus, the formation of  $\text{C}_8\text{H}_{15}\text{-OOH1-OOH3-e}$  is plausible, which is an  $\gamma,\epsilon\text{-P}(\text{OOH})_2$  radical (hereafter, the position of a carbon bonded to an  $\text{-OOH}$  group in a  $\text{P}(\text{OOH})_2$  radical is designated by  $\alpha$ ,  $\beta$ ,  $\delta$ ,  $\epsilon$ , respectively;  $\alpha$  position is the carbon site with the radical). According to Miyoshi<sup>54</sup>, this radical can undergo  $\text{O}_2$  addition at lower temperatures (e.g., 500 K in this work). The third  $\text{O}_2$  addition intermediate,  $\text{C}_8\text{H}_{15}\text{-OOH1-OOH3-OO5}$  ( $\text{OOP}(\text{OOH})_2$ ), further undergoes intramolecular H-atom migration from the  $\gamma\text{-C-H}$  bonded to the  $\text{OOH}$  group, via a six-membered-ring TS, and produces a keto-dihydroperoxide (KDHP) and an OH radical. The decomposition of KDHP releases another OH radical, thereby acting as an additional chain branching pathway.

**[0039]** **Scheme 2b** below, presented herein, provides  $\text{O}_2$  addition to the tertiary fuel radical to form another ROO radical, which can undergo intramolecular H-atom migration via a six-membered-ring TS<sup>53</sup> to produce  $\text{C}_8\text{H}_{16}\text{-OOH2-d}$  ( $\gamma\text{-QOOH}$ ). Further  $\text{O}_2$  addition to this  $\gamma\text{-QOOH}$  radical leads to  $\text{C}_8\text{H}_{16}\text{-OOH2-OO4}$  ( $\text{OOQOOH}$ ), which is also a  $\gamma\text{-OOQOOH}$  radical. The conventional scheme indicates that this radical cannot produce a  $\text{C}_8$  keto-hydroperoxide since there are no available H-atoms available on the tertiary site bonded to the  $\text{OOH}$  group. However, the study by Miyoshi<sup>54</sup> suggests that the hydrogen exchange between the  $\text{-OOH}$  and  $\text{-OO}$  group in the  $\gamma\text{-OOQOOH}$  radical is a rapid process, and will be important if there is no hydrogen on the carbon with  $\text{-OOH}$  group. This reaction leads to another  $\gamma\text{-OOQOOH}$  ( $\text{C}_8\text{H}_{15}\text{-OOH3-OO}_\delta$ ), whose 1,5-H shift from the carbon with the  $\text{-OOH}$  group, and the subsequent decomposition to a keto-hydroperoxide (KHP-2) and an OH radical is dominant. On the other hand, intramolecular H-atom migration from the primary C-H site via a six-membered-ring TS

forms  $C_8H_{15}-OOH_2-OOH_4-f$  ( $\gamma,\epsilon$ -P(OOH)<sub>2</sub>). A third  $O_2$  addition to this radical, and subsequent reactions, release an OH radical and also produce a KDHP.

[0040] The present **Scheme 2** generally depicts a reaction network for the formation of keto-dihydroperoxide and keto-hydroperoxide from 2,5-dimethylhexane low-temperature oxidation. The naming of the species is referred to in Sarathy et al.<sup>40</sup>



Scheme 2

[0041] The ROO radical resulting from initial abstraction from a secondary C-H site predominantly undergoes intramolecular H-atom migration from the tertiary C-H via a six-membered-ring TS<sup>53</sup>. This ROO radical undergoes further  $O_2$  addition leading to the  $\gamma$ -OOQOOH ( $C_8H_{15}-OOH_3-OO_5$ ). As discussed above, subsequent reaction of this  $\gamma$ -OOQOOH radical generates a keto-hydroperoxide (KHP-2) shown in **Scheme 2c**. This



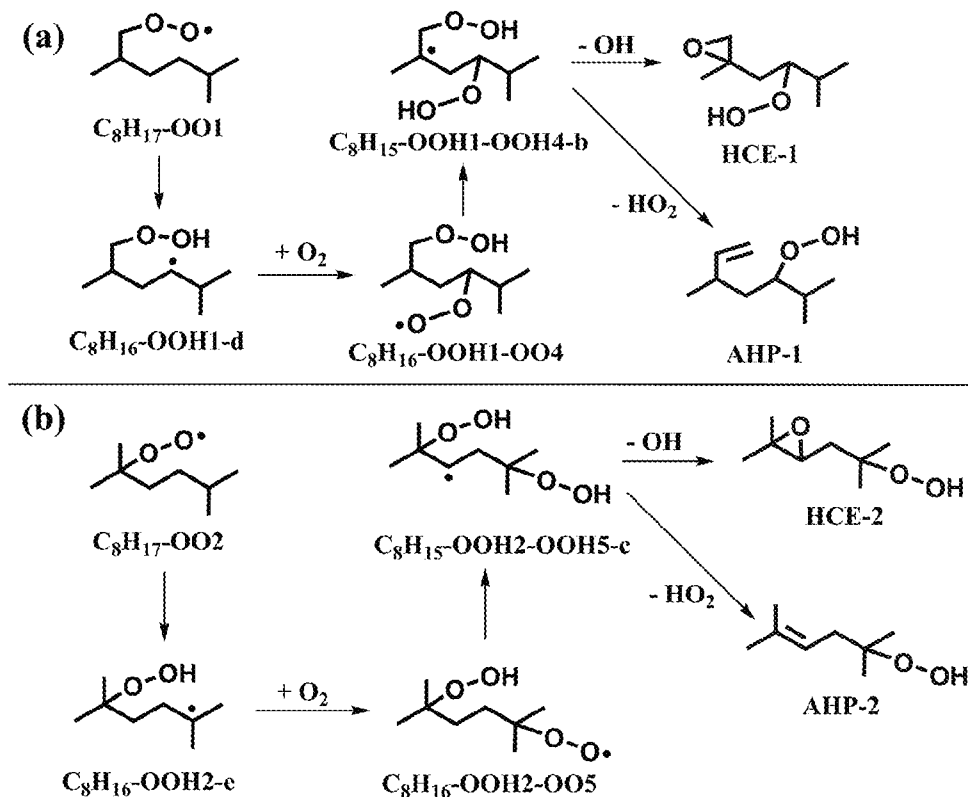
keto-hydroperoxide is predicted as the most significant isomer produced during 2,5-dimethylhexane low-temperature oxidation<sup>40</sup>.

**[0042]** For ROO radicals initiated the O<sub>2</sub> addition on the primary and tertiary fuel radicals, i.e., C<sub>8</sub>H<sub>17</sub>-OO<sub>1</sub> and C<sub>8</sub>H<sub>17</sub>-OO<sub>2</sub>, there are other important isomerization pathways. As discussed above, the most feasible intramolecular H-atom migration of C<sub>8</sub>H<sub>17</sub>-OO<sub>1</sub> abstracts the secondary C-H via a six-membered-ring transition state. The theoretical calculations by Villano et al.<sup>53</sup> suggest that intramolecular H-atom migration abstraction from the other secondary C-H site via a seven-membered-ring TS can be important. In this process, presented herein, the C<sub>8</sub>H<sub>16</sub>-OOH<sub>1-d</sub> radical produced (**Scheme 3a**) undergoes a second O<sub>2</sub> addition to generate C<sub>8</sub>H<sub>16</sub>-OOH<sub>1</sub>-OO<sub>4</sub>. For this OOQOOH radical, the most feasible intramolecular H-atom migration occurs from the tertiary C-H site via a six-membered-ring transition state<sup>17,53</sup>. This alternative isomerization produces a β,γ-P(OOH)<sub>2</sub> radical, C<sub>8</sub>H<sub>15</sub>-OOH<sub>1</sub>-OOH<sub>4-b</sub>. Miyoshi<sup>54</sup> suggests that the β,γ-P(OOH)<sub>2</sub> radical mainly decomposes to a hydroperoxyl cyclic ether (HCE-1) and an OH radical, as shown in **Scheme 3a**. On the other hand, the β-scission of the β,γ-P(OOH)<sub>2</sub> radical's C-O bond produces an HO<sub>2</sub> radical and an alkenylhydroperoxide, AHP-1.

**[0043]** For the C<sub>8</sub>H<sub>17</sub>-OO<sub>2</sub> radical, the rate constant of C<sub>8</sub>H<sub>17</sub>-OO<sub>2</sub> H-atom migration from the tertiary C-H site via a seven-membered-ring TS (**Scheme 3b**) is close to that of H-atom migration from the secondary C-H site via a six-membered-ring TS (**Scheme 2b**). The subsequent reactions from the former, as shown in **Scheme 3b** presented herein, leads to an hydroperoxyl cyclic ether isomer (HCE-2) and/or alkenylhydroperoxide isomer (AHP-2). From a kinetic perspective, the pathways leading to formation of hydroperoxyl cyclic ethers and alkenylhydroperoxides in **Scheme 3** are competitive to the formation of keto-dihydroperoxides in **Scheme 2**. The fate of hydroperoxyl cyclic ethers is expected to be similar to that of a keto-hydroperoxide, wherein decomposition leads to to release an OH radical and acts as radical chain

branching pathway. It is also noted that the concerted elimination of  $\text{OOQOOH}$  can lead to the formation of alkenylhydroperoxides

[0044] The present **Scheme 3** depicts a reaction network for the formation of hydroperoxyl cyclic ether and alkenylhydroperoxide from 2,5-dimethylhexane low-temperature oxidation. The naming of the species is referred to Sarathy et al.<sup>40</sup>



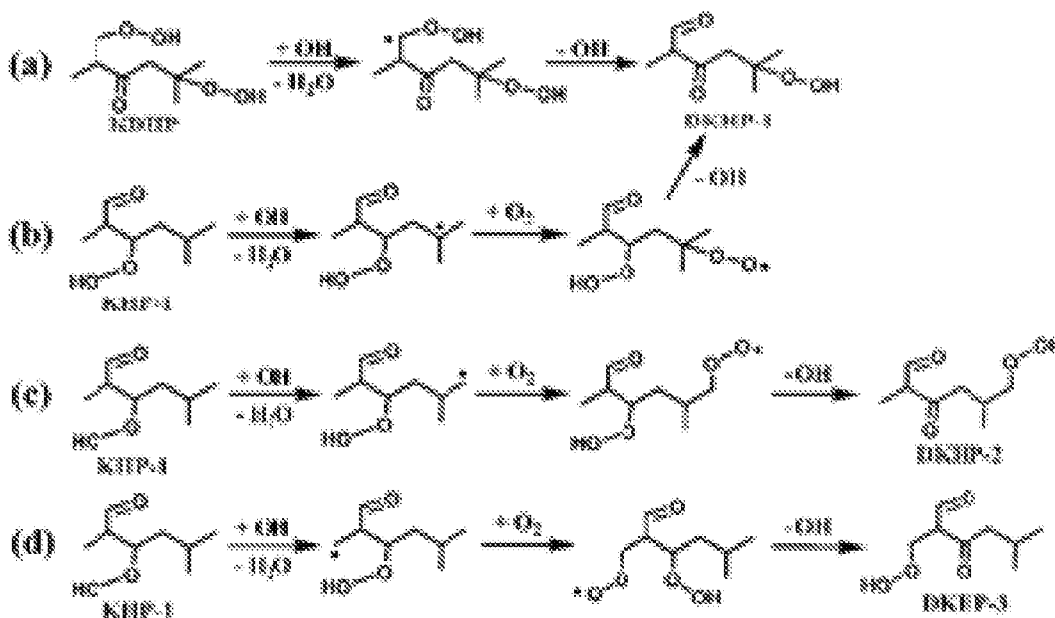
**Scheme 3**

[0045] Previous studies have shown that keto-hydroperoxides undergo H-abstraction from the C-H attached to the OOH group, and then dissociate easily to the diketo-compounds, such as 2,4-heptadione in n-heptane oxidation<sup>28,55</sup>. Diketo-compounds with formulas of  $\text{C}_7\text{H}_{12}\text{O}_2$  and  $\text{C}_8\text{H}_{14}\text{O}_2$  were also observed during 2-methylhexane and 2,5-dimethylhexane oxidation. Similarly, H-atom abstraction from keto-dihydroperoxides results in the formation of diketo-hydroperoxides.

[0046] Also provided herein is another pathway to a diketo-hydroperoxide that begins with a keto-hydroperoxide. H-atom abstraction from a normal C-H site, followed

by a third  $O_2$  addition, then intramolecular H-atom migration from the C-H site attached to the OOH group, and finally release of an OH radical produces a diketo-hydroperoxide. Similar to the keto-dihydroperoxides, the decomposition of diketo-hydroperoxides generates another OH radical, acting as another radical chain branching step. **Scheme 4** presents the reaction mechanism for the formation of diketo-hydroperoxides (DKHP-1, DKHP-2 and DKHP-3).

[0047] **Scheme 4** presented herein depicts a reaction network for the formation of diketo-hydroperoxide from 2,5-dimethylhexane low-temperature oxidation




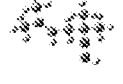
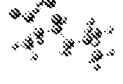
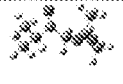

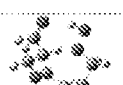
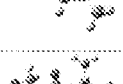
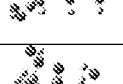
**Scheme 4**

[0048] Additional supporting evidence of these new species was performed by measuring the PIE spectra to obtain the threshold of ionization energies (IEs). Furthermore, the adiabatic ionization energies were calculated for the probable isomers of keto-dihydroperoxides, keto-hydroperoxides, alkenylhydroperoxides, diketo-hydroperoxides produced in **Schemes 2-4**.

[0049] The geometries and IEs of the probable isomers of these species are presented in Table 1. The measured onsets at  $\sim 8.8 \pm 0.05$ ,  $8.5 \pm 0.05$ ,  $8.8 \pm 0.05$ , and  $8.7 \pm 0.05$  eV agree well with the calculated IEs (eV) of APH-1 ( $8.72 \pm 0.05$ ), APH-2

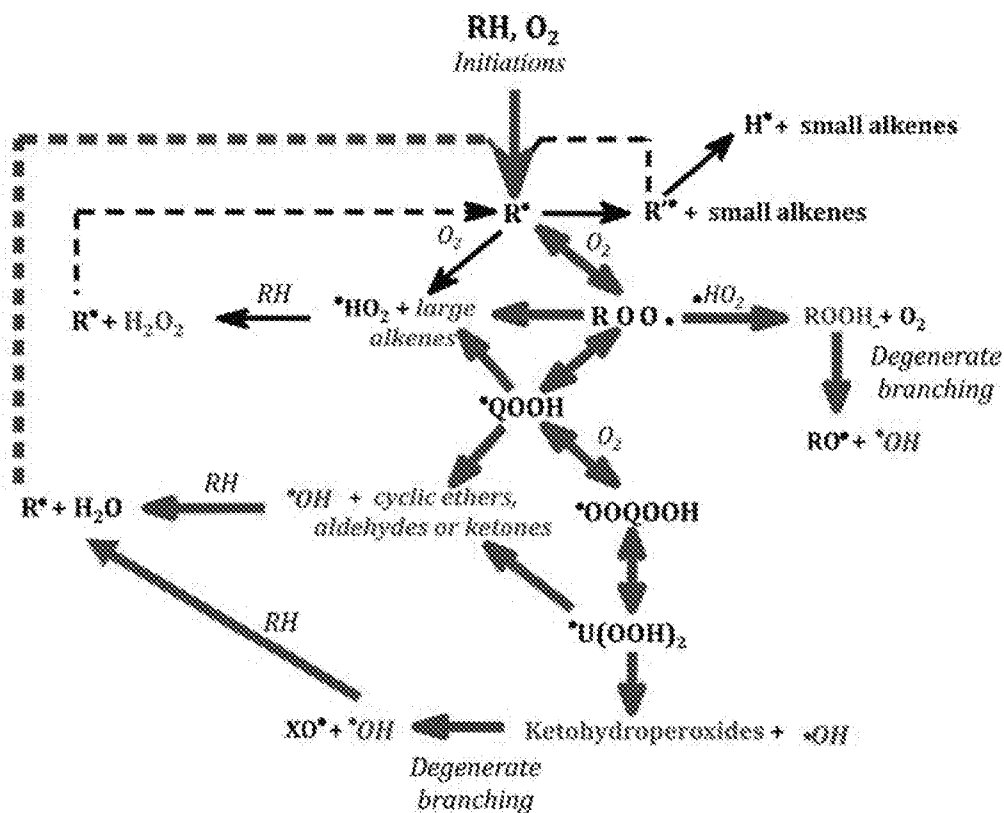
( $8.58 \pm 0.05$ ), KHP-2 ( $8.75 \pm 0.05$ ), and DKHP-2 ( $8.70 \pm 0.05$  eV). The IE of KHP-1 ( $9.60 \pm 0.05$  eV) is not evident in the PIE curve, while those of DKHP-1 ( $9.14 \pm 0.05$  eV) and DKHP-3 ( $9.42 \pm 0.05$  eV) are not so clear. For KDHP, the IE of  $9.33 \pm 0.05$  eV lies above the onset of 9.0 eV from experiment. It should be noted that there can be other probable isomers for these intermediates, making the interpretation of the PIE spectra difficult. The overlap of PIE curves of possible isomers and/or conformers makes the identification of IE onsets unobvious<sup>48</sup>. On the other hand, the inconsideration of all probable conformers increases the errors in the calculated IEs<sup>46</sup>. The identification of hydroperoxyl cyclic ethers (HCE<sub>1</sub> and HCE<sub>2</sub>, etc) is not attempted here due to the significant overlap in PIE curves with keto-hydroperoxides. Nevertheless, the computational chemistry calculations compared with PIE curves together with the probable mechanistic pathways show that the species observed are of the suggested isomeric structures.

Table 1

Formula	Species	Structure	IE/eV
C <sub>8</sub> H <sub>16</sub> O <sub>3</sub>	APH-1		8.72
	APH-2		8.58
C <sub>8</sub> H <sub>16</sub> O <sub>3</sub>	KPH-1		9.60
	KPH-2		8.75
C <sub>8</sub> H <sub>14</sub> O <sub>4</sub>	DKPH-1		9.14
	DKPH-2		8.70
	DKPH-3		9.42
C <sub>8</sub> H <sub>16</sub> O <sub>3</sub>	KDPH		9.33

[0050] Thus, presented herein, in particular, is a scheme for the low-temperature oxidation of 2-methylhexane and 2,5-dimethylhexane. A series of oxygenated species with one to five oxygen atoms were detected and identified. The observation of conjugated alkenes, cyclic ethers, and keto-hydroperoxides are supporting evidence of the conventional low-temperature oxidation mechanism (first and second O<sub>2</sub> addition). Moreover, the observation of alkenylhydroperoxides, keto-dihydroperoxides, diketo-hydroperoxides, and potentially hydroperoxyl cyclic ethers provides evidence of the extended low-temperature hydrocarbon oxidation scheme under ignition-relevant conditions. These experimentally measured species can be formed by a series of steps including alternative isomerization of OOQOOH radicals, a third O<sub>2</sub> addition process, and subsequent decomposition. The reactions of keto-dihydroperoxides, diketo-hydroperoxides, and hydroperoxyl cyclic ethers can be chain branching pathways during hydrocarbon low-temperature oxidation.

[0051] The following discussion focuses on the identification of several intermediates, confirming the existing low-temperature oxidation mechanism, and furthermore, providing new insights into the present reaction pathways. **Scheme 5** provides the simplified low-temperature oxidation mechanism developed in the past decades for alkanes. As discussed by Herbinet et al.<sup>19</sup>, the reaction is initiated by H-atom abstraction from the alkane (RH, C<sub>7</sub>H<sub>16</sub> in this work) by O<sub>2</sub>, to give the alkyl (C<sub>7</sub>H<sub>15</sub>) and hydroperoxy (HO<sub>2</sub>) radicals. At low temperatures, such as the 560 K applied herein, the alkyl radical reacts with O<sub>2</sub>, and follows several types of reactions, as shown in **Scheme 5**, leading to the occurrence of auto-ignition and the abundance of low-temperature intermediates.



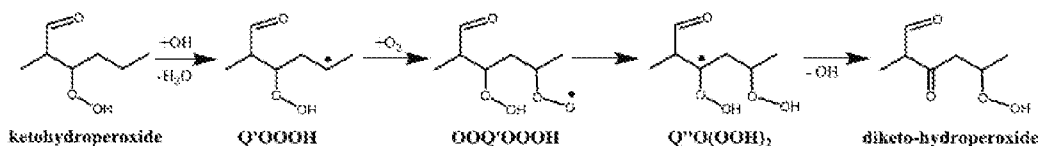
[0052] The initial step in low-temperature oxidation usually involves the formation of an alkylperoxy complex,  $RO_2$ . By low temperature, in one or more, aspects, we mean temperature(s) in the range of 400-800°K. The bimolecular reaction of  $RO_2$  with  $HO_2$  leads to a alkylhydroperoxide ( $ROOH$ ), which further decomposes to  $RO$  and  $OH$  radicals; while the concerted elimination of  $RO_2$  leads to a large alkene and a hydroperoxy ( $HO_2$ ) radical<sup>41</sup>. The first reaction channel is the chain propagation step while the second channel is the chain termination step. In this work, both the large alkenes  $C_7H_{14}$  and alkylhydroperoxides  $C_7H_{15}OOH$  were detected at  $m/z$  of 98.11 and 132.10, respectively.

[0053] The intramolecular H-migration of the alkylperoxy radical forming a hydroperoxyalkyl radical (i.e.,  $QOOH$ ) is the second step in the low-temperature chain branching process. The cyclization of the hydroperoxyalkyl radicals to form a cyclic ether and  $OH$  radical is another important chain propagation step, which competes with

the critical chain branching channel<sup>41</sup> (second O<sub>2</sub> addition, as discussed later). According to the reaction classes and rate rules proposed by Sarathy et al.<sup>41</sup>, the cyclic ethers with 3-6 membered-rings were selected for calculation. The IE range of 15 possible isomers is 9.02-9.87. In particular, the IEs of the five- and six-member-ring cyclic ethers are in the range of 9.02-9.14 eV, which are close to the measured IE onset (8.97 eV). The profile of C<sub>7</sub>H<sub>14</sub>O with temperature is very similar to the cyclic ethers measured in alkane oxidation<sup>27, 28</sup>.

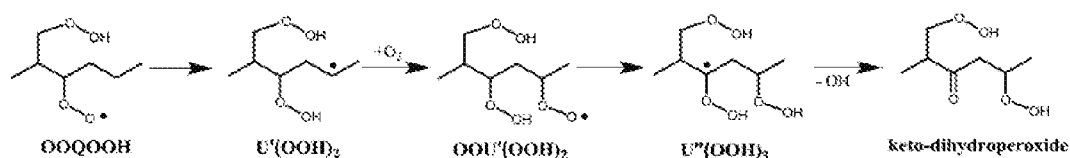
**[0054]** The addition of O<sub>2</sub> to hydroperoxyalkyl radical (i.e., QOOH) is the third step in the low-temperature chain branching process, where OOQOOH is produced. Further intramolecular H-migration of OOQOOH leads to formation of U(OOH)<sub>2</sub>, as shown in **Scheme 5**. Generally, the hydrogen atom being abstracted is bound to the carbon atom bonded to the hydroperoxy (OOH) group, which has a lower C-H bond strength than a normal C-H bond and makes it easier to abstract<sup>41</sup>. The decomposition of U(OOH)<sub>2</sub> releases OH radicals and forms ketohydroperoxides (**Scheme 5**). Ketohydroperoxides can easily decompose to generate more OH radicals, and thus complete the low-temperature chain branching sequence.

**[0055]** For C<sub>7</sub>H<sub>12</sub>O<sub>4</sub>, a pathway comes from the ketohydroperoxides (C<sub>7</sub>H<sub>14</sub>O<sub>3</sub>). H-abstraction from the ketohydroperoxide forms Q'OOH, which is followed by O<sub>2</sub> addition to form OOQ'OOH (O<sub>2</sub>C<sub>7</sub>H<sub>13</sub>O<sub>3</sub>). This radical further undergoes intramolecular H-abstraction of the C-H bond connected to the hydroperoxy (OOH) group and leads to Q''O(OOH)<sub>2</sub>. The subsequent decomposition of Q''O(OOH)<sub>2</sub> releases an OH radical and forms a diketo-hydroperoxide (C<sub>7</sub>H<sub>12</sub>O<sub>4</sub>). One example of the process is illustrated below.



[0056] Depending on the proposed mechanism and the structures of the ketohydroperoxides, 43 possible isomers of the diketo-hydroperoxides were selected for IE calculation. The IE range is 8.60 to 9.54 eV. The lowest energy of 8.60 eV is in agreement with the experimental measurement, where the first onset appears around 8.6 eV. Another clear onset appears at 8.97 eV. For the diketo-hydroperoxides, there are 18 isomers with the IEs between 8.6 and 9.0 eV, while the rest lie between 9.1 and 9.54 eV. The temperature dependence of the signal of  $C_7H_{12}O_4$  is similar to that of ketohydroperoxides, further confirming the existence of diketo-hydroperoxides.

[0057] For  $C_7H_{14}O_5$ , the pathway can come from the  $OOQOOH$  radical. As in the discussion above, the mechanism in the literature<sup>41</sup> only considers the intramolecular H-abstraction of the hydrogen atom bound to the carbon atom bonded to the hydroperoxy (OOH) group and leads to  $U'(OOH)_2$ , which further decomposes to release an OH radical and then form a ketohydroperoxide. However, there are other possible intramolecular H-abstractions of the hydrogen atoms of the normal C-H bonds when the chain of the fuel is long enough, in the case of 2-methylhexane presented herein. These alternative isomerizations were first studied by Sharma et al.<sup>17</sup>. The intermediates in this process, denoted as  $U'(OOH)_2$ , can further undergo  $O_2$  addition ( $OOU'(OOH)_2$ ), and then intramolecular H-abstraction of the C-H bonds bonded to the hydroperoxy (OOH) group producing  $U''(OOH)_3$ . The mechanism finally releases an OH radical and forms a keto-dihydroperoxide ( $C_7H_{14}O_5$ ). One example of the process is given below.



[0058] In the IE calculation, 56 possible isomers were considered, and their IEs range from 8.4 to 9.69 eV. There are 10 isomers with the IEs below 8.8 eV, while the rest lies around 8.8 eV or higher. The profile of the  $C_7H_{14}O_5$  is similar to those of ketohydroperoxides and diketo-hydroperoxide.



[0059] As shown herein, the low-temperature oxidation of 2-methylhexane was investigated using the synchrotron vacuum ultra-violet photoionization molecular beam mass spectrometry (SVUV-PI-MBMS). Several key intermediates controlling the auto-ignition process were identified with the combination of exact mass calibration, energy scans of the ionization threshold, and ionization energy calculation. The identification of intermediates such as methylhexenes ( $C_7H_{14}$ ), 2-methyl-hydroperoxy-hexanes ( $C_7H_{15}OOH$ ), cyclic ethers ( $C_7H_{14}O$ ) and ketohydroperoxides ( $C_7H_{14}O_3$ ) confirms the first and second  $O_2$  addition process. The identification of diketo-hydroperoxides ( $C_7H_{12}O_4$ ) and keto-dihydroperoxides ( $C_7H_{14}O_5$ ) provides evidence of a third  $O_2$  addition process in 2-methylhexane low-temperature oxidation. The third  $O_2$  addition process presented herein provides new insights into a low-temperature oxidation mechanism.

[0060] Ratios, concentrations, amounts, and other numerical data may be expressed in a range format. It is to be understood that such a range format is used for convenience and brevity, and should be interpreted in a flexible manner to include not only the numerical values explicitly recited as the limits of the range, but also to include all the individual numerical values or sub-ranges encompassed within that range as if each numerical value and sub-range is explicitly recited. To illustrate, a concentration range of "about 0.1% to about 5%" should be interpreted to include not only the explicitly recited concentration of about 0.1 % to about 5 %, but also include individual concentrations (e.g., 1%, 2%, 3%, and 4%) and the sub-ranges (e.g., 0.5%, 1.1%, 2.2%, 3.3%, and 4.4%) within the indicated range. In an embodiment, the term "about" can include traditional rounding according to significant figure of the numerical value. In addition, the phrase "about 'x' to 'y'" includes "about 'x' to about 'y'".

[0061] It should be emphasized that the above-described embodiments are merely examples of possible implementations. Many variations and modifications may be made to the above-described embodiments without departing from the principles of the

present disclosure. All such modifications and variations are intended to be included herein within the scope of this disclosure and protected by the following claims.

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**CLAIMS**

Therefore, the following is claimed:

1. A method of producing highly oxygenated compounds from hydrocarbon feedstocks, the method comprising the steps of:
  - providing a feed reactant in gas phase, the feed reactant comprising a branched alkane having a carbon number of 6 or greater, an n-alkane having a carbon number of 6 or greater, a cycloalkane having a carbon number of 5 or greater, an alkyl cycloalkane having a carbon number of 6 or greater, or a combination thereof;
  - mixing the feed reactant with an oxidant; and
  - carrying out a low temperature reaction, including a low temperature oxidation, of the feed reactant to convert the feed reactant to a product comprising a keto hydroperoxide, a diketo hydroperoxide, a keto dihydroperoxide, a hydroperoxyl cyclic ether, an alkenyl hydroperoxide, or a combination thereof.
2. The method of claim 1, wherein the feed reactant is selected from the group consisting of a C6-C20 n-alkanes, a C6-C20 mono-methylalkane, a C6-C20 dimethylalkane, a C6-C20 tri-methylalkane, a C6-C20 multi-substituted alkane, a C5-C6 cycloalkane, a C6-C10 alkylcycloalkane, and a combination thereof.
3. The method of claim 1 or 2, wherein the low temperature oxidation reaction is carried out in a partial oxidation reactor.
4. The method of claim 3, wherein the partial oxidation reactor is a perfectly stirred reactor for the homogeneous gas-phase production of the product.
5. The method of claim 4, wherein the feed reactant is fed in the gas-phase to the partial oxidation reactor, and at a fixed temperature, mixture composition, and residence time.
6. The method of claim 5, wherein the temperature is in the range of 200° to 800°K.
7. The method of claim 5, wherein the pressure is in the range of 1-100 atm.

8. The method of claim 5, wherein, the residence time is a fixed residence time in the range of about 0.1 to about 10 seconds.
9. The method of claim 1, wherein the low temperature reaction comprises the steps of:
  - radical initiation of the feed reactant to form alkyl radicals followed by oxidation of the alkyl radicals to form alkyl peroxy radicals;
  - intramolecular hydrogen-atom migration in the alkyl peroxy radicals to form hydroperoxy alkyl radicals; and
  - oxidation of the hydroperoxy alkyl radicals to form an OOQOOH radicals.
10. The method of claim 9, further including the steps of isomerization of the OOQOOH radicals to form P(OOH)<sub>2</sub> radicals via an intramolecular hydrogen-atom migration reactions, wherein the P(OOH)<sub>2</sub> radicals decompose to a hydroperoxyl cyclic ether or a scission of the P(OOH)<sub>2</sub> radicals produces an HO<sub>2</sub> radical and an alkenylhydroperoxide or both, and subsequent addition of oxygen to the P(OOH)<sub>2</sub> radicals followed by intramolecular hydrogen-atom migration and decomposition forms the keto-dihydroperoxide.
11. The method of claim 9, further including the steps of Scheme 2(a).
12. The method of claim 9, further including the steps of Scheme 2(b).
13. The method of claim 9, further including the steps of Scheme 2(c).
14. The method of claim 9, further including the steps of Scheme 3(a).
15. The method of claim 9, further including the steps of Scheme 3(b).
16. The method of claim 9, further including the steps of Scheme 4(a).
17. The method of claim 9, further including the steps of Scheme 4(b).
18. The method of claim 9, further including the steps of Scheme 4(c).
19. The method of claim 9, further including the steps of Scheme 4(d).
20. The method of any of claims 1-19, used to improve the combustion efficiency of a fossil fuel.



**INTERNATIONAL SEARCH REPORT**

International application No  
PCT/IB2016/057231

**A. CLASSIFICATION OF SUBJECT MATTER**  
 INV. C10L1/02 C10G27/00 C10G5/00 C07C27/14 C07C27/10  
 F02M21/02 F23C99/00  
 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)  
 C10L C10G C07C F02M F23C F02B

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	ZHANDONG WANG ET AL: "Experimental Investigation of the Low Temperature Oxidation of the Five Isomers of Hexane", JOURNAL OF PHYSICAL CHEMISTRY. A, MOLECULES, SPECTROSCOPY, KINETICS, ENVIRONMENT AND GENERAL THEORY, vol. 118, no. 30, 31 July 2014 (2014-07-31), pages 5573-5594, XP055344038, US ISSN: 1089-5639, DOI: 10.1021/jp503772h figure 1 paragraph [0002] paragraph [0003] ----- -/--	1-20

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	"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
"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  10 February 2017	Date of mailing of the international search report  24/02/2017
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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  Bernet, Olivier
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## INTERNATIONAL SEARCH REPORT

International application No  
PCT/IB2016/057231

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	<p>BATTIN-LECLERC ET AL: "Detailed chemical kinetic models for the low-temperature combustion of hydrocarbons with application to gasoline and diesel fuel surrogates", PROGRESS IN ENERGY AND COMBUSTION SCIENCE, ELSEVIER SCIENCE PUBLISHERS, AMSTERDAM, NL, vol. 34, no. 4, 1 August 2008 (2008-08-01) , pages 440-498, XP022713360, ISSN: 0360-1285, DOI: 10.1016/J.PECS.2007.10.002 [retrieved on 2008-01-04] paragraphs [0002], [02.1], [02.3] tables 3-5 paragraphs [0004], [04.1], [04.2]; figure 21 paragraph [0006]</p> <p style="text-align: center;">-----</p>	1-20
X	<p>KUIWEN ZHANG ET AL: "An experimental and kinetic modeling study of n-hexane oxidation", COMBUSTION AND FLAME, vol. 162, no. 11, 1 November 2015 (2015-11-01), pages 4194-4207, XP055344398, AMSTERDAM, NL ISSN: 0010-2180, DOI: 10.1016/j.combustflame.2015.08.001 paragraphs [0002], [0003], [03.2], [0004], [04.3]; figures 6, 11</p> <p style="text-align: center;">-----</p>	1-20
X	<p>US 2003/040650 A1 (BUTLER GRAHAM [GB] ET AL) 27 February 2003 (2003-02-27) examples 1-10 paragraphs [0032] - [0037]</p> <p style="text-align: center;">-----</p>	1-20

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Information on patent family members

International application No  
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