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(54) **SOLVATED METAL FUEL COMBUSTION
SYSTEM AND METHOD**

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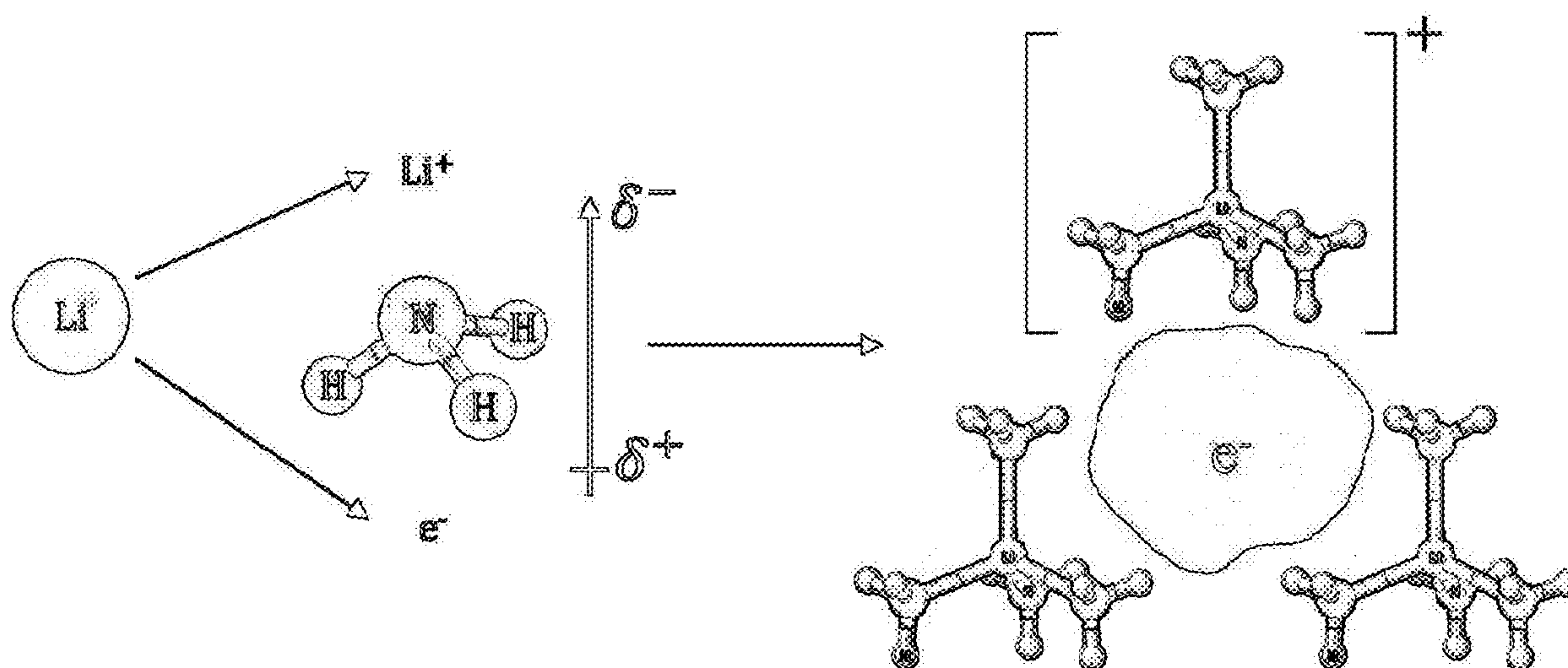
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(57) **ABSTRACT**

The combustion system includes a metal additive and a polar outer-sphere electron transferring solvent. The metal additive is solvated in the polar outer-sphere electron transferring solvent. The polar outer-sphere electron transferring solvent may include liquid ammonia, methylamine, and/or hexamethylphosphoramide. The metal additive may include an alkali metal and/or an alkaline earth metal. For instance, the metal additive may include lithium, sodium, aluminum, zirconium, titanium, yttrium, hafnium, and/or magnesium.



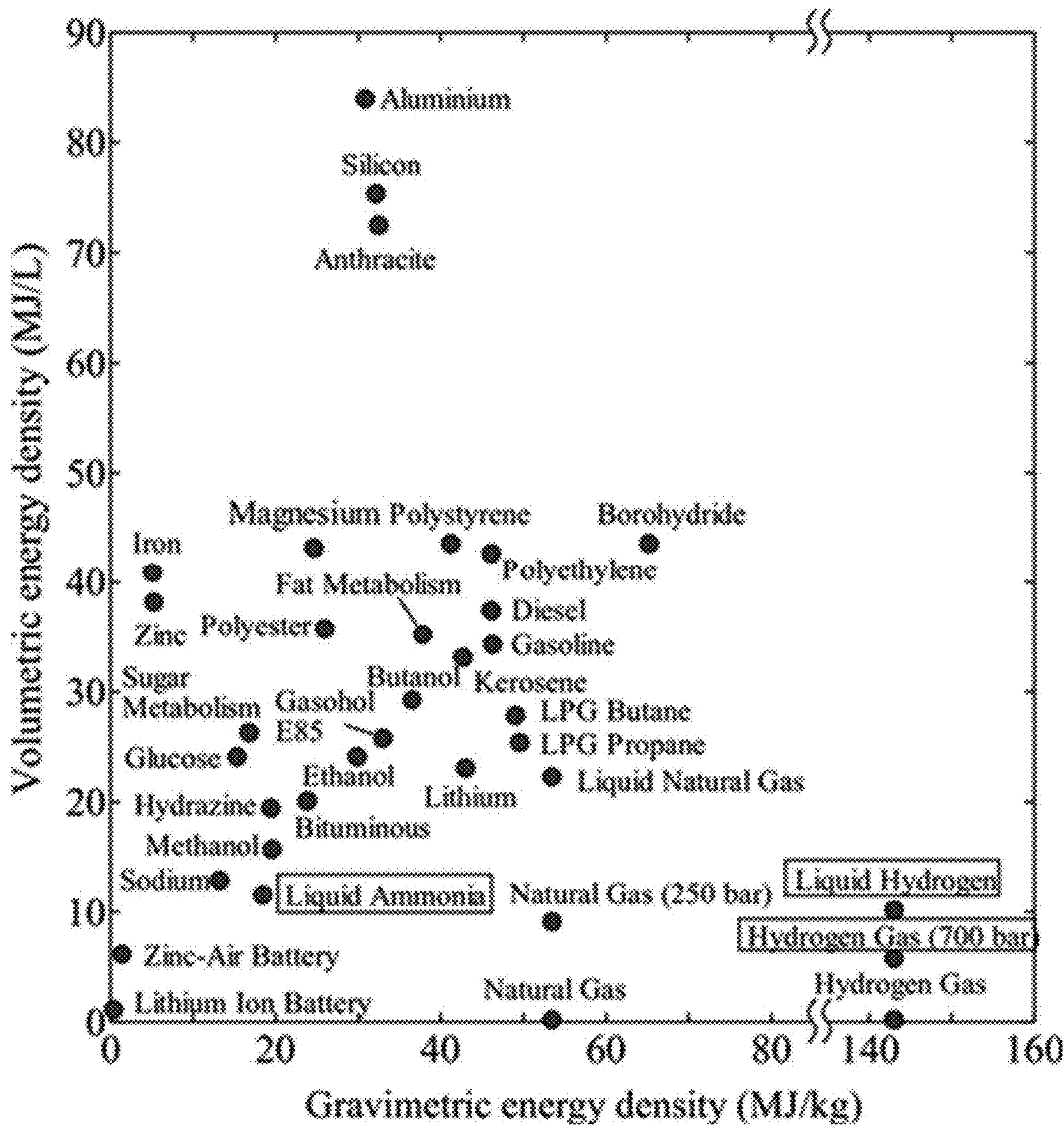


FIG. 1

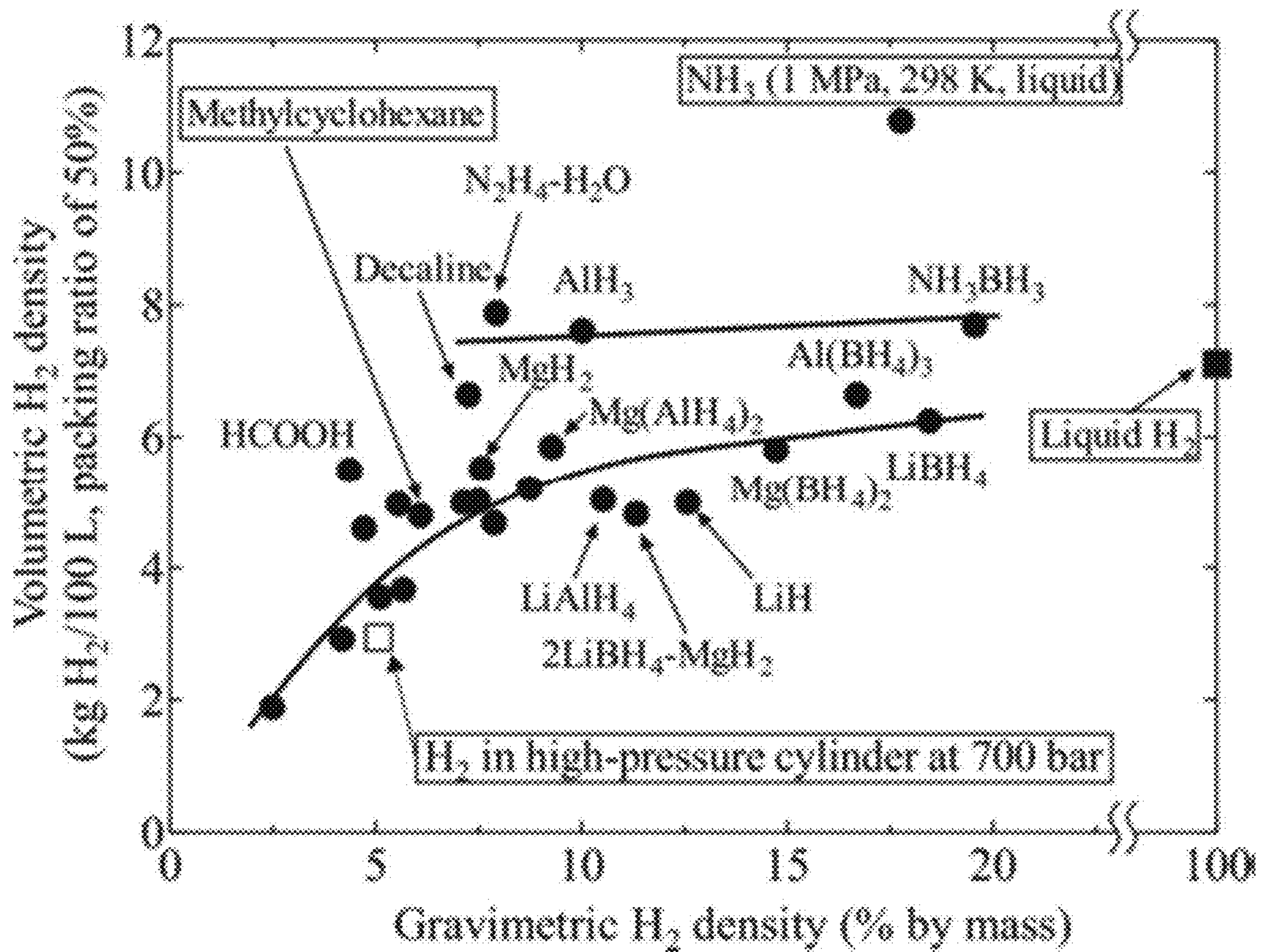


FIG. 2

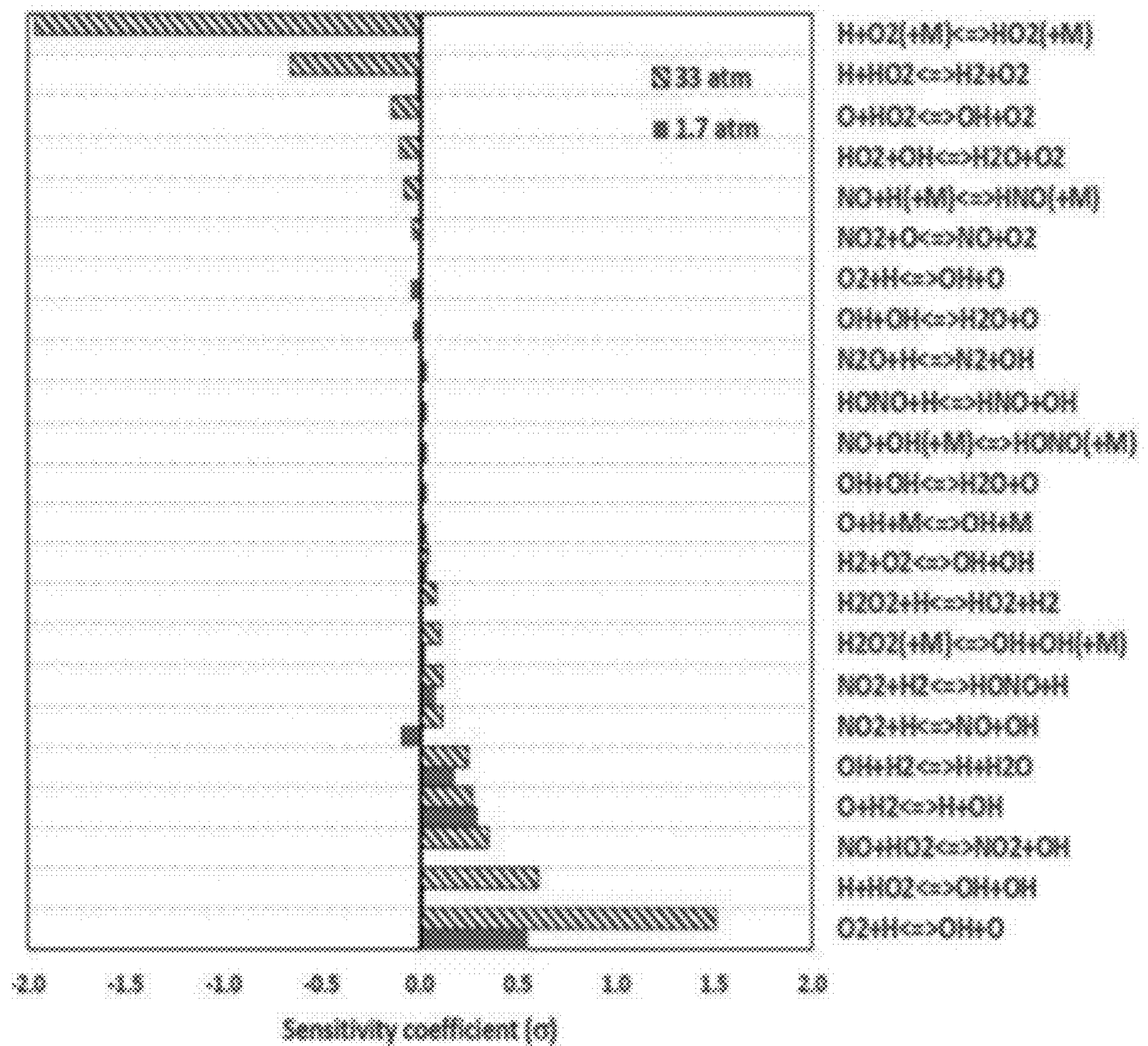


FIG. 3

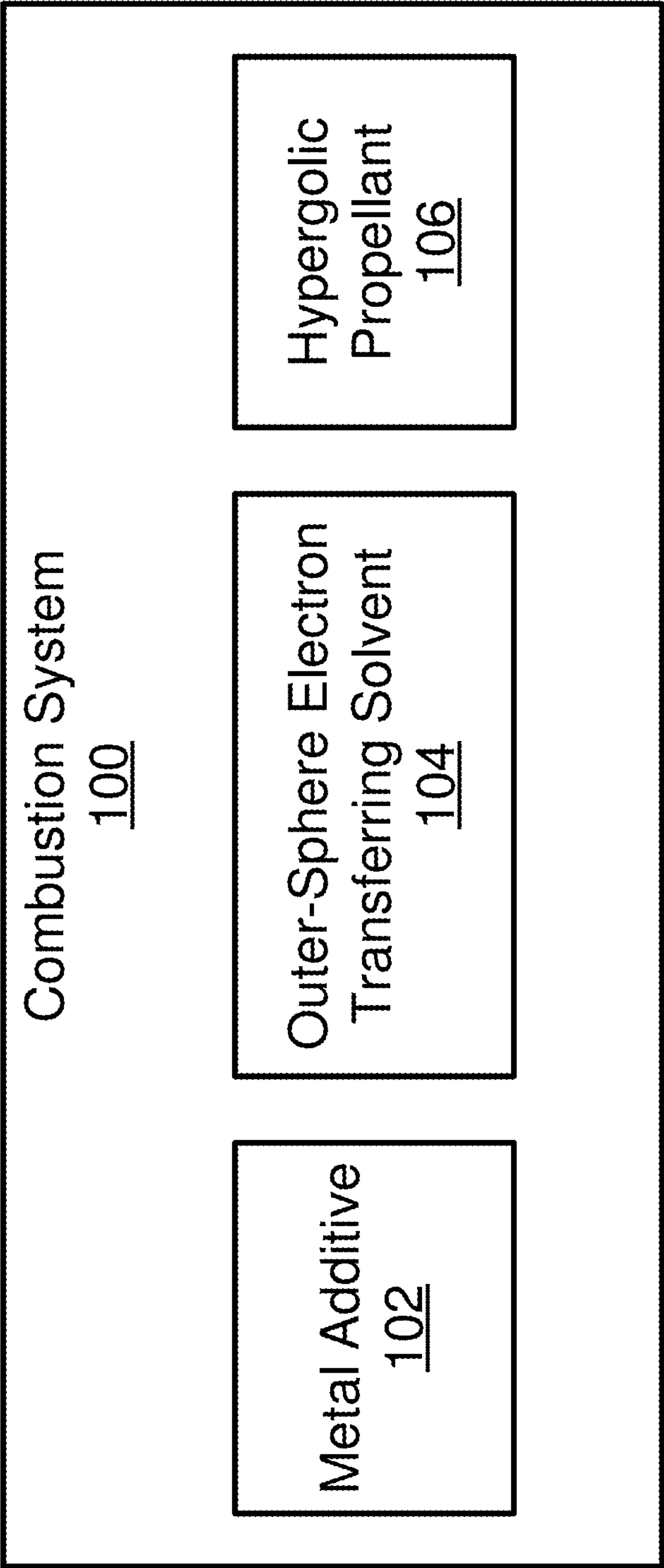


FIG. 4

Isp vs O/F with LOX

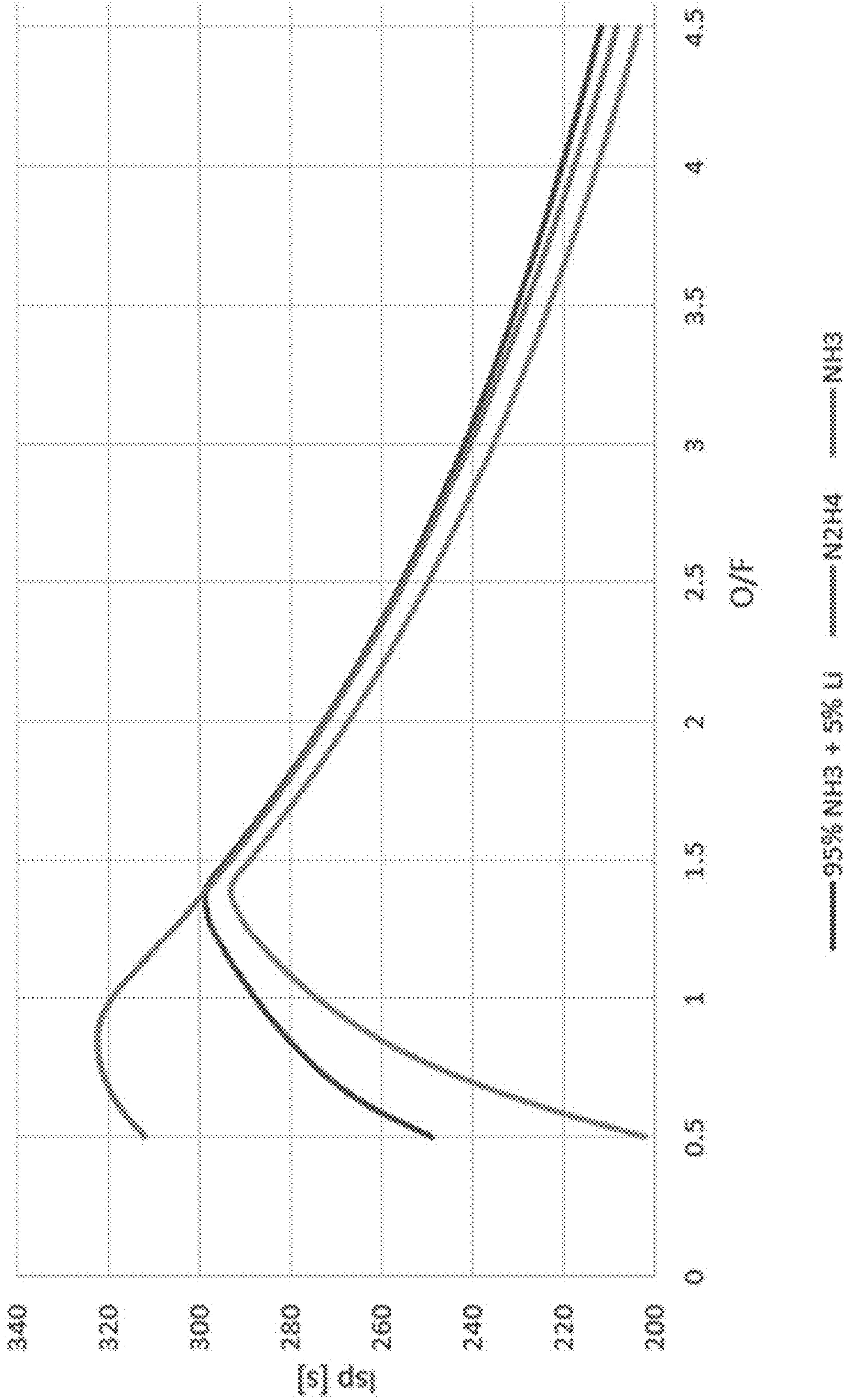


FIG. 5

Isp vs O/F with Nitric Acid

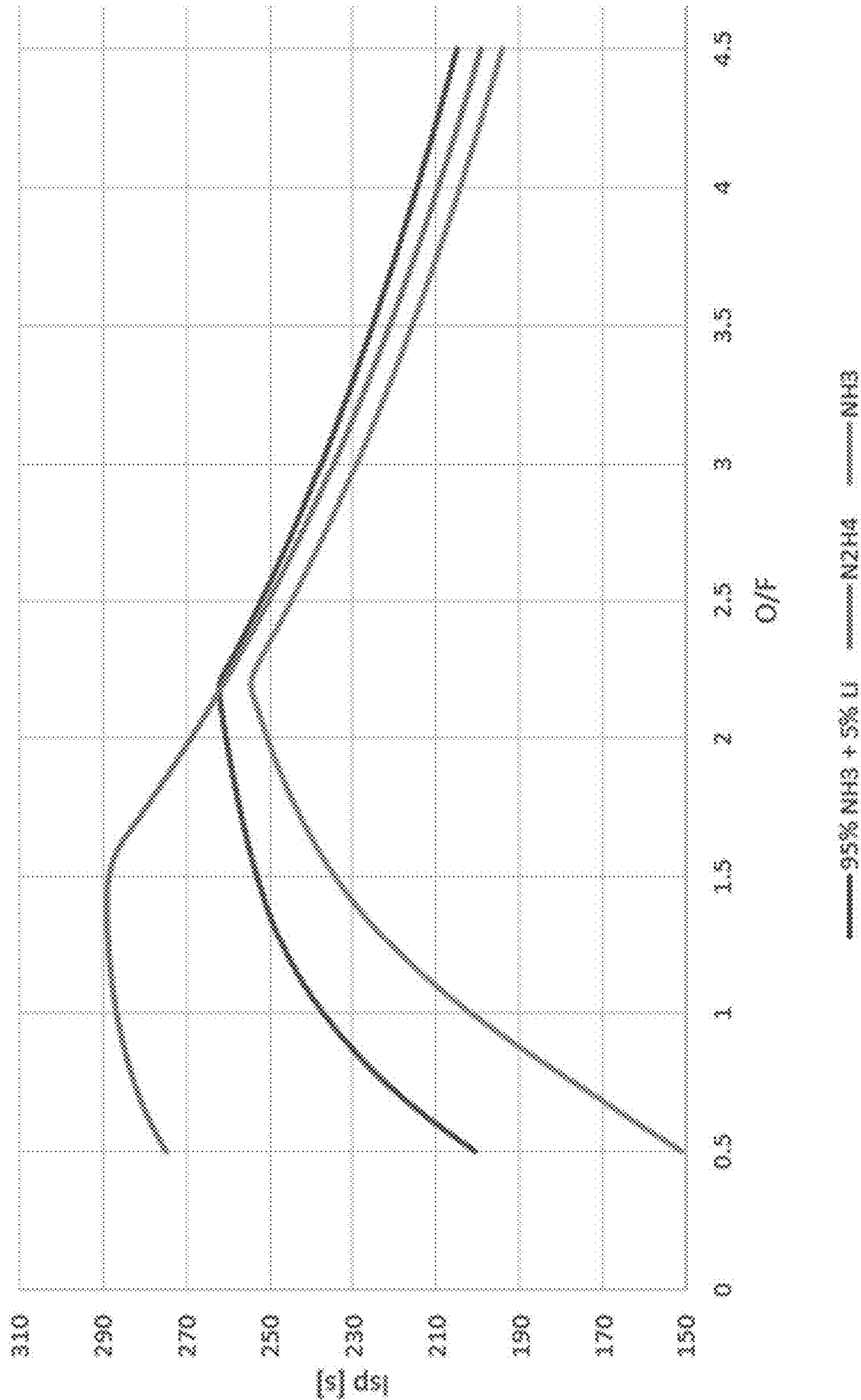


FIG. 6

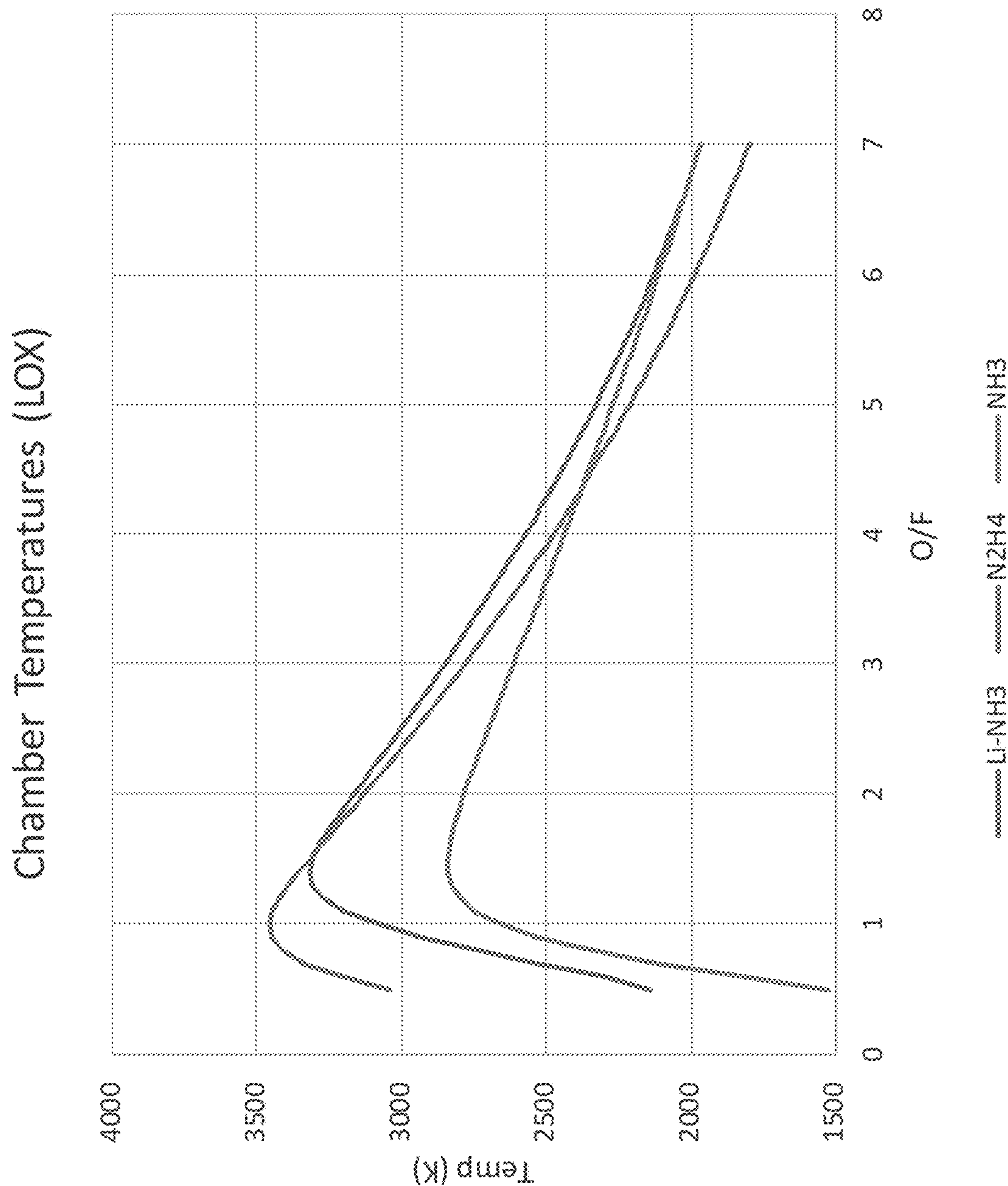


FIG. 7

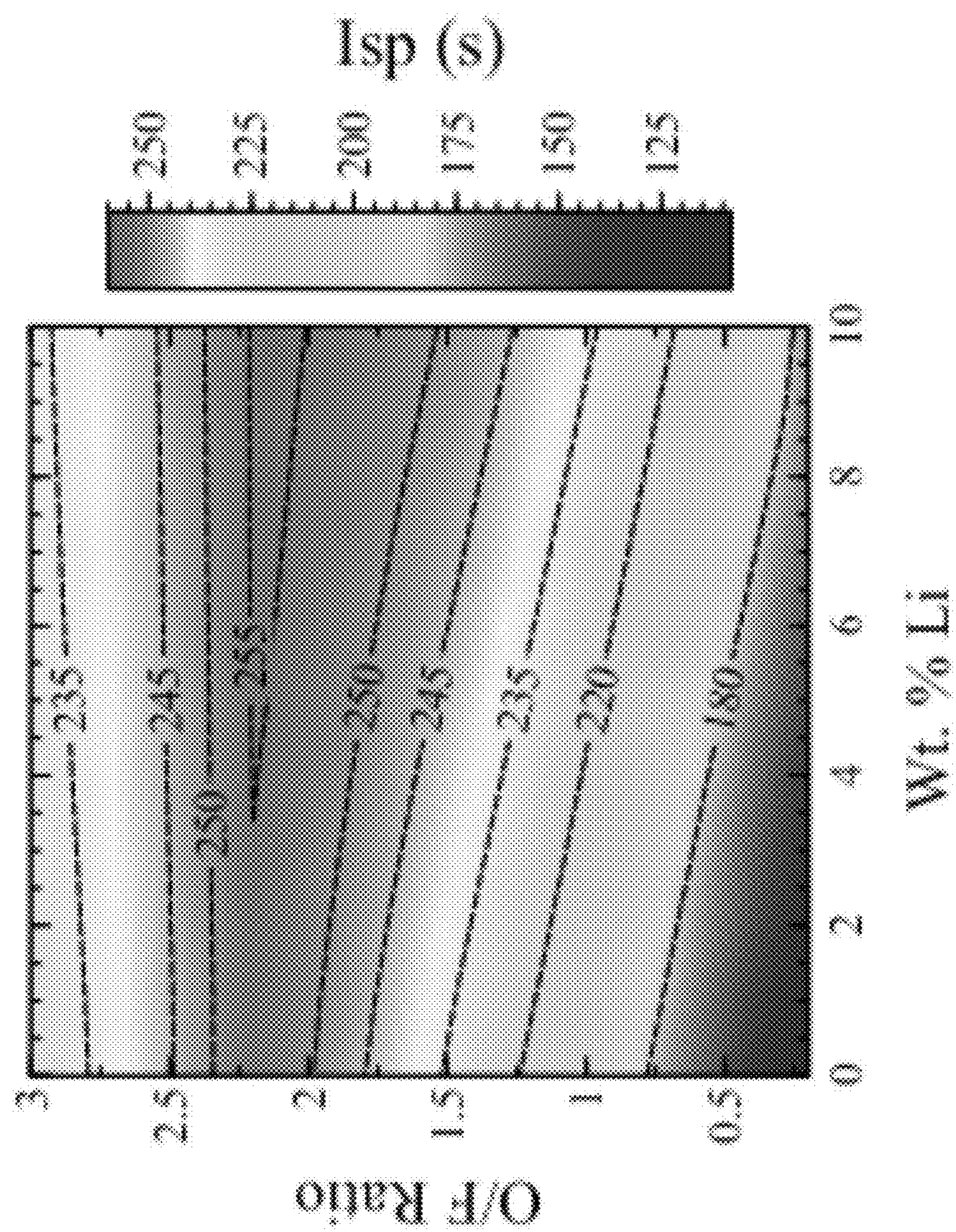


FIG. 8

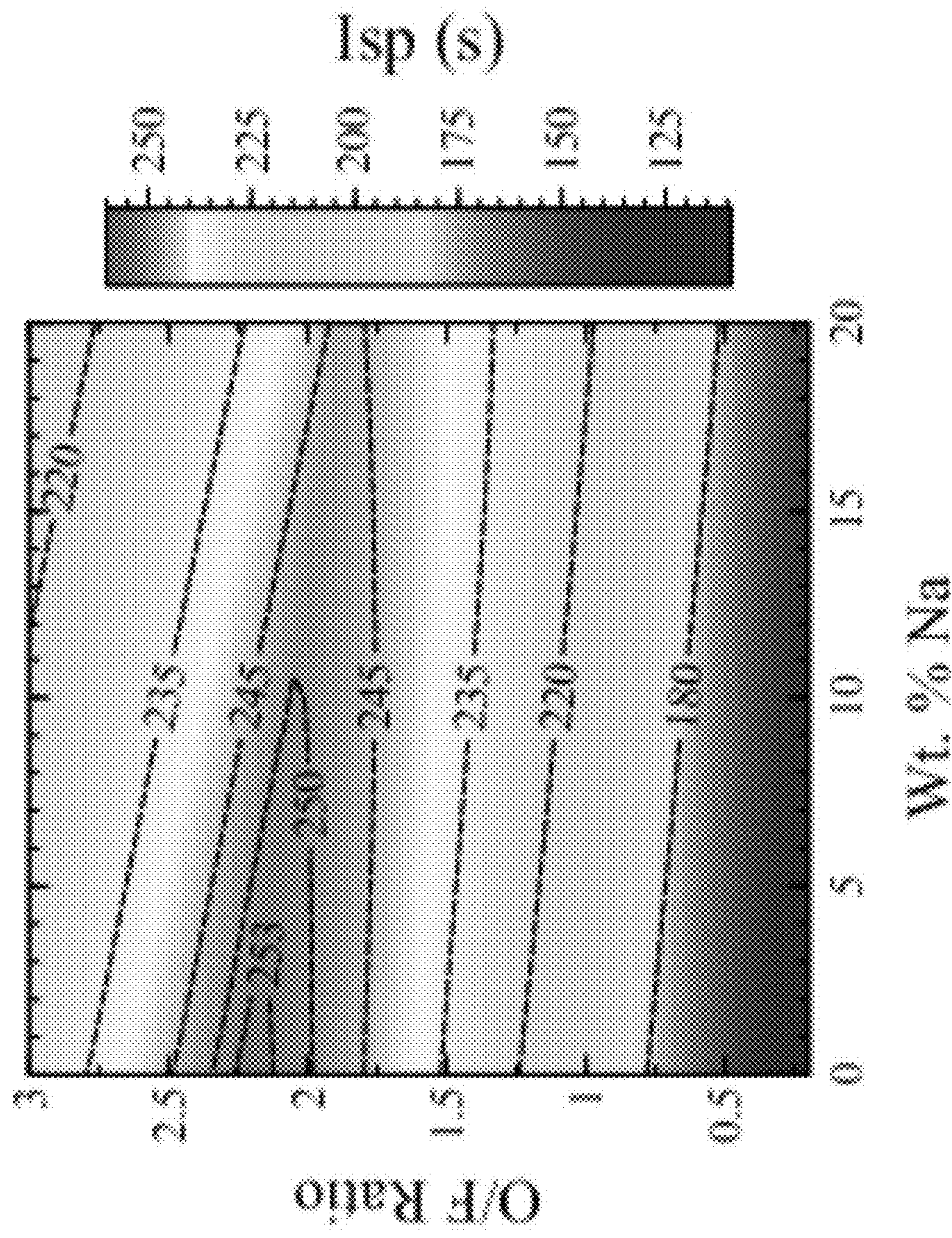


FIG. 9

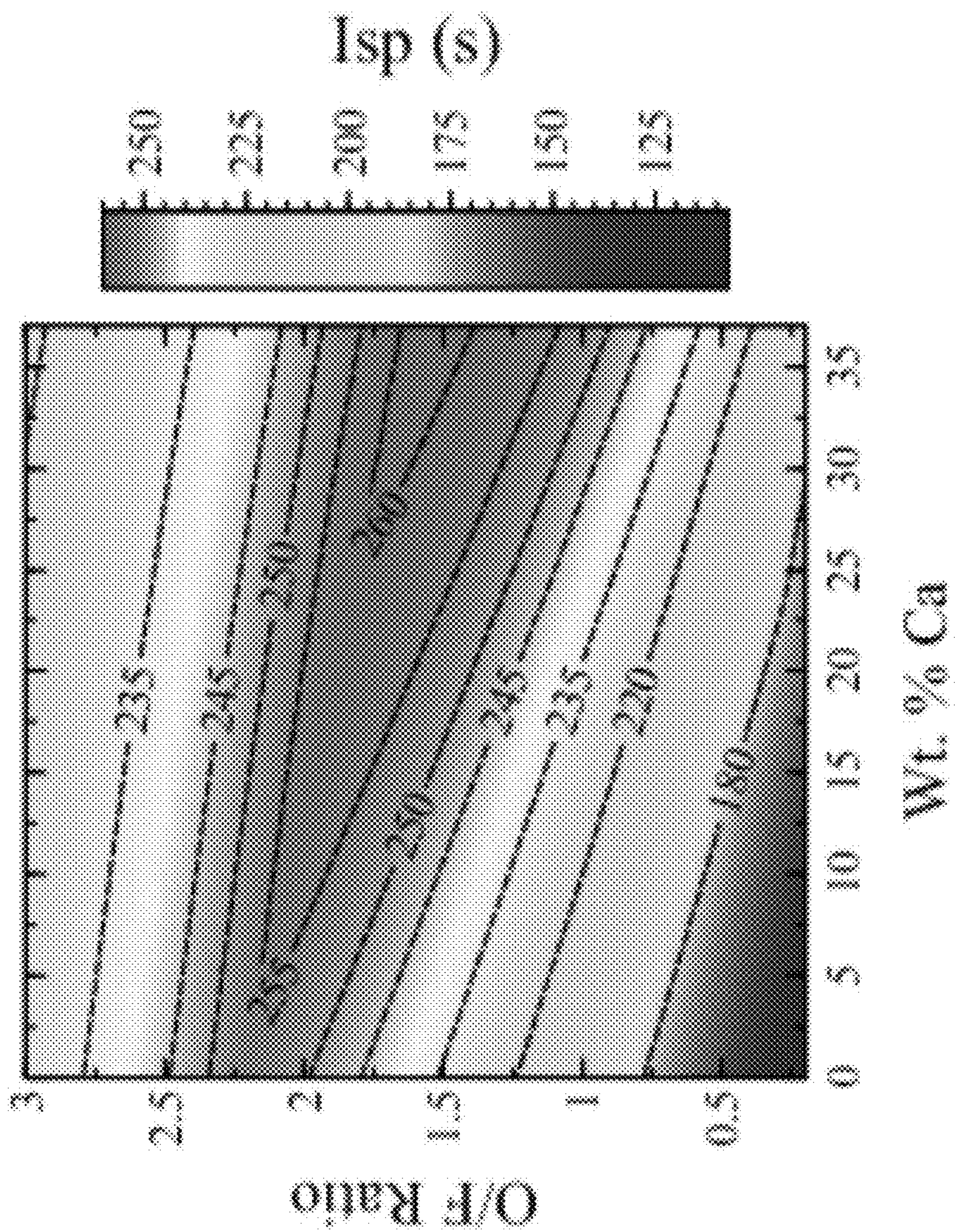


FIG. 10

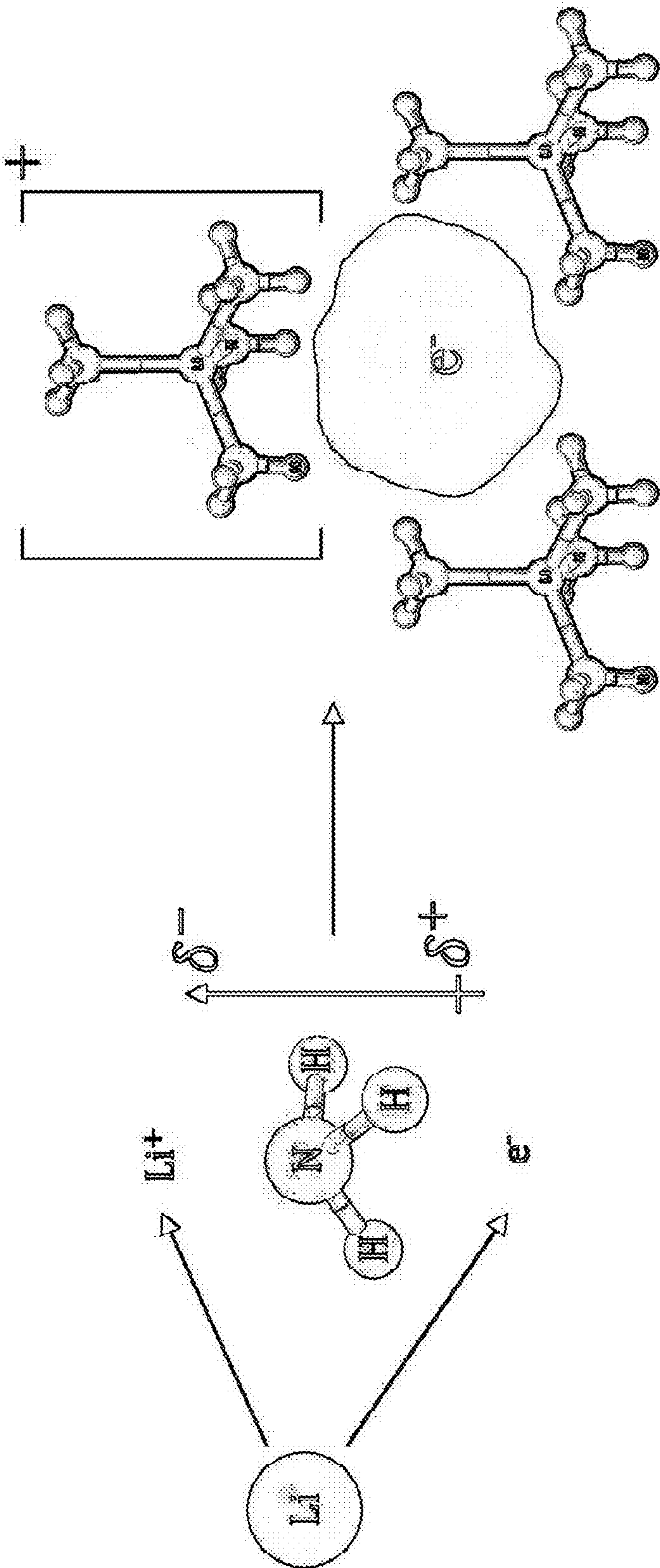


FIG. 11

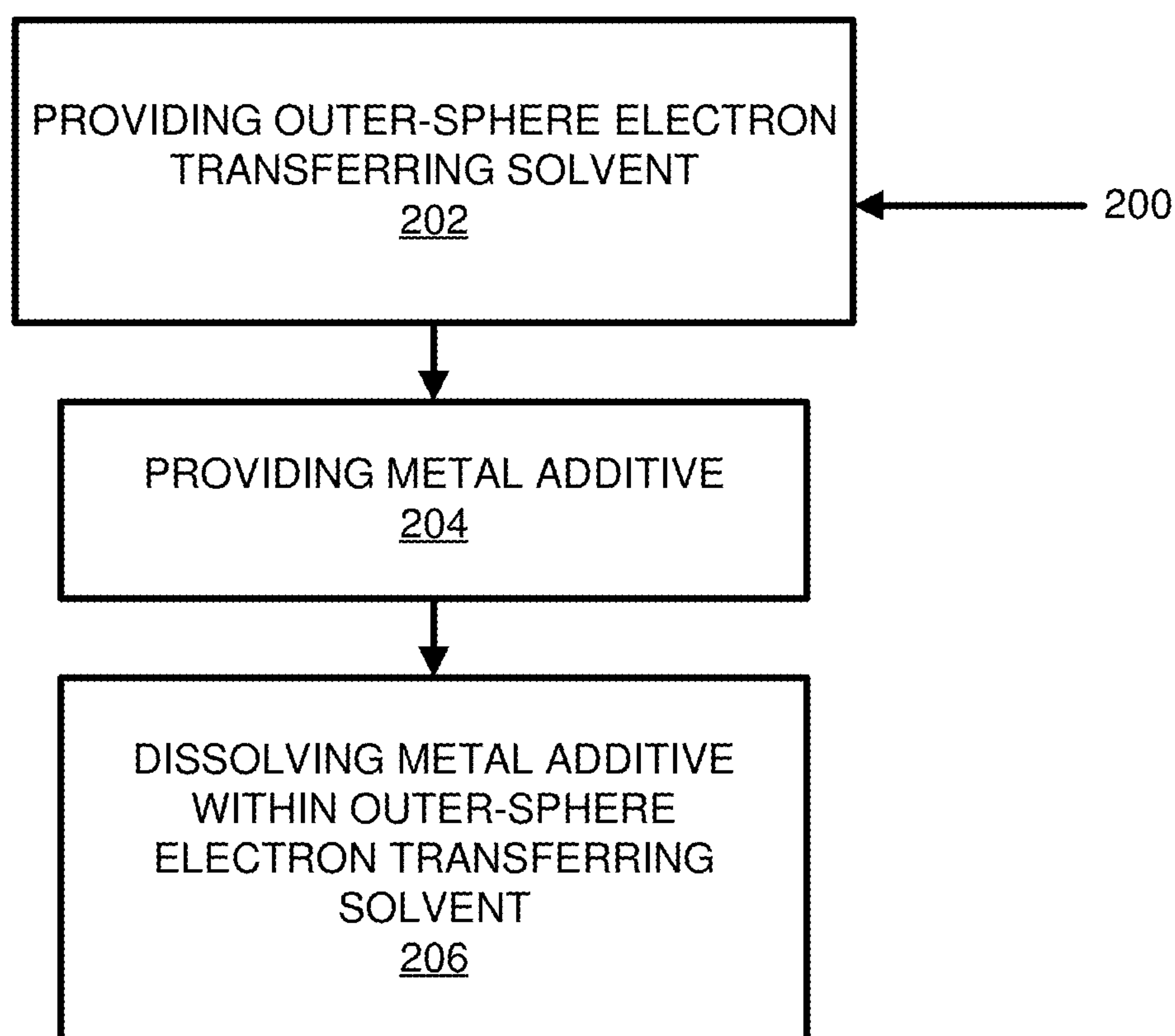


FIG. 12

SOLVATED METAL FUEL COMBUSTION SYSTEM AND METHOD

CROSS REFERENCE TO RELATED APPLICATIONS

[0001] The present application is a U.S. non-provisional application which claims the benefit of U.S. provisional application Ser. No. 63/347,191, filed May 31, 2022, the content of which is incorporated by reference herein in its entirety.

GOVERNMENT SUPPORT CLAUSE

[0002] This invention was made with government support under W911NF2020189 awarded by the United States Army. The government has certain rights in the invention.

FIELD

[0003] The disclosure generally relates to combustion systems and, more particularly, to ammonia combustion systems.

INTRODUCTION

[0004] This section provides background information related to the present disclosure which is not necessarily prior art.

[0005] More sustainable green energy alternatives are needed to address the increasing global pollution caused by fossil fuel emissions. As part of this effort, the United Nations General Assembly has proposed an agenda to double global energy efficiency and disseminate greener energy sources worldwide by the year 2030.

[0006] In accordance with this agenda and to address the global pollution issue, numerous methods of generating more sustainable green energy have been proposed and attempted. Several of these methods, namely wind, solar, nuclear, and hydroelectric power show promise, but are ultimately limited by our ability to efficiently store their energy for later use. A solution to this problem is through the use of energy carriers that can optimize the complex interaction between supply and demand chains. However, current “green” energy carriers, such as batteries, have poor gravimetric and volumetric energy densities compared to fossil fuels. This poor energy density inherent in modern batteries poses a challenge to replace fossil fuels and is one of the principal obstacles preventing the use and production of battery-powered aircraft.

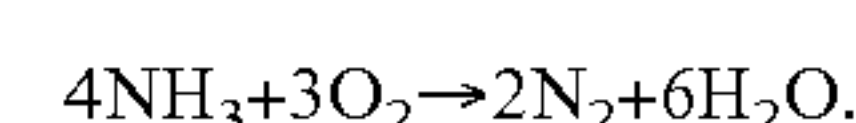
[0007] To continue to maintain the world’s increasing energy demands while simultaneously decreasing global atmospheric pollution, the search for more efficient and energy dense fuels is needed. Liquid hydrogen is one potential green fuel alternative; however, it is difficult to store, transport, and has many other challenges that are currently preventing it from being widely used as a fuel today. While addressing these challenges are beyond the scope of this review, liquid hydrogen may be utilized as a comparative green fuel.

[0008] Ammonia has garnered particular attention as an attractive energy carrier and green fuel due to its zero-carbon content, stability, availability, and relatively low toxicity compared to other pnictogen hydrides such as hydrazine. As shown in the plot graph of FIG. 1, from Kobayashi et al., “Science and technology of ammonia combustion,” Proceedings of the Combustion Institute, Vol. 37, No. 1, pp.

109-133, 2019., the gravimetric and volumetric energy densities of various fuels are compared to liquid ammonia and liquid hydrogen. While liquid ammonia is not as gravimetrically energy dense as liquid hydrogen, it has a higher volumetric energy density than liquid hydrogen. Chatterjee, et al., “Limitations of Ammonia as a Hydrogen Energy Carrier for the Transportation Sector,” ACS Energy Letters, Vol. 6, No. 12, pp. 4390-4394, 2021. Liquid ammonia also has higher volumetric and gravimetric energy density compared to traditional batteries. Additionally, liquid ammonia is easier to store, transport, and handle in comparison with its liquid hydrogen counterpart. These characteristics are a driving factor behind the research interest in using ammonia as a fuel.

[0009] Efforts have been made in the past to use ammonia as a fuel, but many of these projects have suffered challenges due to ammonia’s poor combustion properties. For example, due to its high specific heat (even higher than water), liquid ammonia was chosen to be a fuel for the X-15 hypersonic aircraft using an XLR-99 engine. This thermal property allowed liquid ammonia to be an efficient coolant on the X-15’s nozzle before entering the combustion chamber. Despite these advantages of using liquid ammonia, it was eventually discontinued due to how difficult it was to maintain combustion and avoid dangerous flame-out conditions.

[0010] More specifically, pure ammonia is the simplest pnictogen hydride with the formula NH_3 . Industrially, ammonia as a precursor accounts for approximately 40% of the world’s fertilizer and is an important compound used in the synthesis of explosives. Because ammonia holds such importance in the global industry, methods of manufacturing, handling, and transporting ammonia are well known. Many of anhydrous ammonia’s physical and thermal properties make it attractive as a hydrogen or energy carrier over other green fuel alternatives. As mentioned previously, ammonia has garnered attention because it is a zero-carbon pnictogen hydride with ideal combustion products of nitrogen and water,



[0011] In terms of boiling points and condensation pressures, ammonia’s thermal properties are comparable to propane, as presented in Table 1 below.

TABLE 1

Thermal properties of ammonia, propane, methane, and hydrogen. Data are from the NIST database				
Fuel	NH_3	C_3H_8	CH_4	H_2
Boiling point at 1 atm (° C.)	-33.4	-42.1	-161	-253
Condensation Pressure at 25° C. (atm)	9.90	9.40	N/A	N/A

[0012] These physical properties make liquid ammonia reasonably easy to store and transport compared to its cryogenic hydrogen counterpart. Additionally, liquid ammonia has one of the highest volumetric H_2 densities; even higher than liquid hydrogen itself, as represented in the plot diagram shown in FIG. 2, from Kobayashi et al. With such a high volumetric hydrogen density, liquid ammonia may also find applications as a hydrogen carrier.

[0013] Therefore, in addition to ammonia’s availability and ease of manufacture, its thermal properties make it easy

to store and transport. However, despite these promising inherent properties, using anhydrous ammonia as a fuel is difficult due to its very poor combustion properties.

[0014] Pure ammonia combustion has a very low flame speed, a low combustion temperature, high auto-ignition temperatures, and a very narrow flammability range. These characteristics are well known in the combustion industry and have led to many challenges in using ammonia as a fuel. Several models for ammonia combustion have been proposed; such as the Bian et al., “Experimental study of the formation of nitrous and nitric oxides in h₂-o₂-ar flames seeded with no and/or nh₃,” Vol. 23, No. 1, pp. 379-386, mechanism in 1991 that focuses on H₂/O₂/Ar flames and ammonia/NO flames. Lindstedt et al. “Detailed kinetic modelling of chemistry and temperature effects on ammonia oxidation,” Vol. 99, No. 4, pp. 253-276. developed a more detailed model in 1994 for ammonia combustion in laminar premixed flames. Another notable model that is still used today is the Konnov and De Ruyck model “Implementation of the NCN pathway of prompt-NO formation in the detailed reaction mechanism,” Vol. 156, No. 11, pp. 2093-2105, proposed in 2001 that accurately predicts the pyrolysis, oxidation, ignition, and overall flame structure of many H/N/O compounds including ammonia, hydrogen, hydrazine, and various nitrogen oxides.

[0015] Despite the efforts of these and many other legacy models developed for ammonia combustion, none of these models were able to accurately predict laminar flame speeds for both fuel-lean and fuel-rich mixtures simultaneously. Due to this apparent discrepancy, many modifications are being made to the legacy ammonia combustion models. Several of these modifications include the Shrestha et al., “Detailed kinetic mechanism for the oxidation of ammonia including the formation and reduction of nitrogen oxides,” Vol. 32, No. 10, pp. 10202-10217, model that focuses on the formation and reduction of nitrogen oxides in ammonia flames, the Xiao et al. “Study on reduced chemical mechanisms of ammonia/methane combustion under gas turbine conditions,” Vol. 30, No. 10, pp. 8701-8710, model that attempts to reduce the chemical mechanisms for ammonia/methane flames, and the Duynslaegher et al. “Modeling of ammonia combustion at low pressure,” vol. 159, no. 9, pp. 2799-2805, model that predicts the effects of ammonia combustion at low pressures.

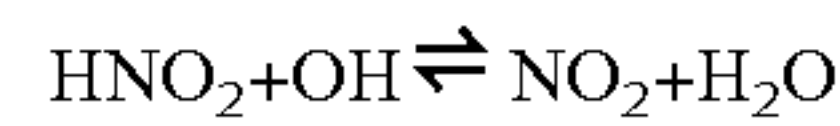
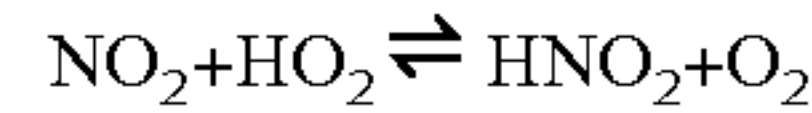
[0016] Through simple dimensional derivations, it can be shown that laminar flame speed is a function of the overall reaction rate as follows:

$$S_L \propto \sqrt{2\alpha w}$$

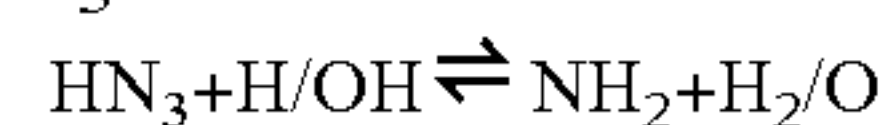
where α is the thermal diffusivity and w is the overall reaction rate. From this simple relationship derived by Turns, “An Introduction to Combustion: Concepts and Applications.” McGraw Hill, 1996, it can be shown that the laminar flame speed is proportional to the overall reaction rate. Compared to hydrocarbons, ammonia combustion has relatively slow reaction rates and large radical sinks that reduce the flame speed and decrease adiabatic flame temperatures. Increasing the flame temperature would increase the reaction rate and thus the laminar flame speed.

[0017] Hydrogen-oxygen chemistry play a very important role in determining the radical pool size in hydrocarbon combustion systems. Because of this, reactions involving H, O, OH, HO₂, H₂O, and H₂O₂ can greatly affect the overall reaction rate and flame temperatures of the system. Rasmus-

sen et al. “Experimental measurements and kinetic modeling of CO/H₂/O₂/NO_x conversion at high pressure,” Vol. 40, pp. 454-480, proposed the following reaction mechanisms:

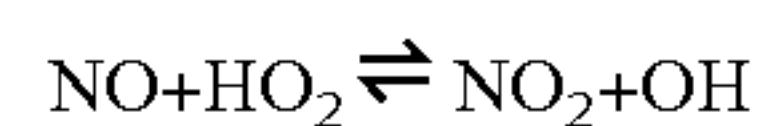
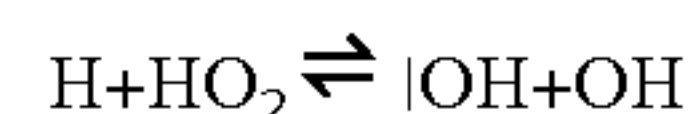
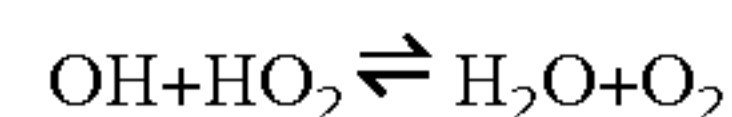
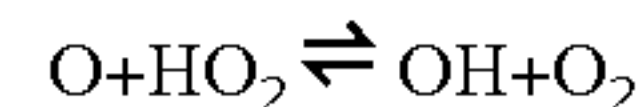
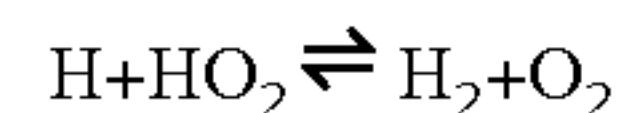
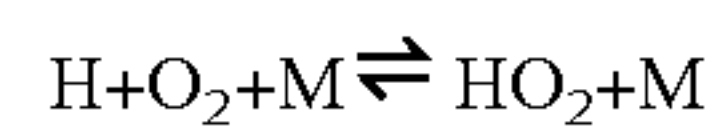


[0018] They concluded that NO₂ readily reacts with the radical HO₂ to form HNO₂ (HONO) during combustion. HNO₂ then acts as an OH sink, which greatly decreases the radical pool and inhibits the system’s overall reactivity. Shrestha et al. took this information from Rasmussen and demonstrated the negative effect of these reactions on ignition delay times. This effect is shown through the important reaction of OH radicals on the initial thermal decomposition of NH₃:



[0019] Therefore, with decreased OH and HO₂ radicals caused by HNO₂ production, the initiation step is significantly retarded. The bar graph shown in FIG. 3 presents the most influential reactions as calculated by Shrestha et al. on ignition sensitivity. From this sensitivity analysis, it was shown that introducing NO₂ to the flame readily proceeds to stifle the radical pool and increase ignition delay times.

[0020] The most sensitive reactions with respect to ignition delay are the reactions involving the HO₂ radical, as outlined on the following page:



[0021] These reactions involving HO₂ indicate the large dependence on the OH and HO₂ radicals on ignition. Therefore, when reactions stifle the OH radical pool, the ability of the mixture to ignite is severely hampered. Other sources indicate a similar competition between chain-propagation and chain-termination steps involving H and NH₂ radicals rather than OH and HO₂ radicals. Ergo, ammonia combustion has difficulty proceeding due to this close competition between radical propagation and termination.

[0022] In addition to important chain-termination steps that readily occur in ammonia combustion, many of the reactions involving nitrogen occur much slower than their hydrogen counterparts—i.e., many nitrogen reactions have higher activation energies—. This indicates a plethora of rate-limiting steps that ultimately reduce the overall reaction rate of the system. This combination of fast chain-termination reactions and slow chain-propagation reactions yields relatively slow overall reaction rates. Therefore, via the relationship provided by Turns, “An Introduction to Combustion: Concepts and Applications.” McGraw Hill, 1996, these reduced overall reaction rates of pure ammonia yield slower laminar flame speeds compared to typical hydrocarbons.

[0023] The relationship between flame speed and flame thickness is presented by Turns “An Introduction to Combustion: Concepts and Applications.” McGraw Hill, 1996, as:

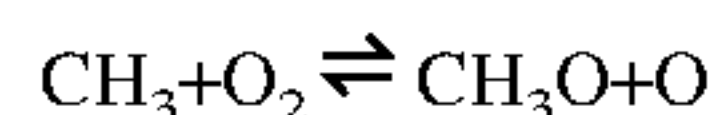
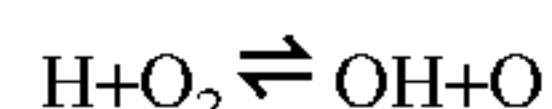
$$S_L \propto \frac{1}{\delta_r}$$

where r is the flame thickness. With laminar flame speeds typically less than 7 cm/s for ammonia (≈ 50 cm/s for hydrocarbons), flame thicknesses are generally larger than 2.85 mm (< 1 mm for hydrocarbons). This thick reaction zone consequently has more surface area for heat loss and potentially extinguish the flame. This results in the observed narrow flammability range of ammonia combustion at equivalence ratios between 0.63 and 1.40 (comparatively, H_2 combustion occurs between equivalence ratios of 0.1 and 7.1). Increasing the reaction rate would be expected to expand the flammability range also.

[0024] Noting the inherently poor combustion characteristics of ammonia, many efforts have been made to enhance ammonia's combustion with various additives. Unfortunately, these efforts have had various success. Many of ammonia's poor combustion properties are likely due to the combination of several rate-limiting steps and major radical sinks. One attempt to address this was to introduce hydrocarbons to the flame to replenish diminished radical pools and overcome the major radical sinks of the system by slowing radical chain-termination steps. While these attempts have shown some promising results in improving ammonia combustion, the addition of hydrocarbons can negatively affect ammonia's more attractive properties (e.g. zero carbon content, high heat capacity, etc.) For instance, adding propane to ammonia may increase performance, but the mixture with propane would then contain carbon and advantageous thermal properties (such as its high heat capacity, its ease of transportation, etc.) of ammonia are reduced. A secondary proposed attempt is the use of catalysts.

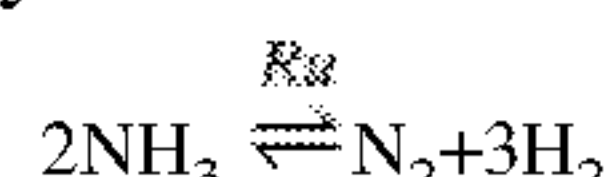
[0025] In an attempt to model ammonia/methane combustion in a gas turbine, Xiao et al. proposed five simplified mechanisms from the original legacy Konnov model. By comparing these reduced mechanisms to the legacy model, Xiao et al. were able to demonstrate the importance of several key reactions on the flame behavior of ammonia/methane flames.

[0026] Two of the most sensitive reactions on ignition delay from this study were the following:



[0027] Both of these reactions are chain-branching steps that help overcome the major radical sinks proposed by Shrestha et al. Therefore, by replenishing the radical pool size in the flame with these hydrocarbon additives, the overall reaction rate is increased and allows faster laminar flame speeds.

[0028] In an attempt to further improve the combustion characteristics of ammonia, Ryu et al. "Performance enhancement of ammonia-fueled engine by using dissociation catalyst for hydrogen generation," Vol. 39, No. 5, pp. 2390-2398, studied the effect of alumina pellets coated with ruthenium as a catalyst in ammonia decomposition. This catalyst acts as follows:



[0029] Catalytic additives do not greatly affect thermal properties and carbon content, but they are only effective at low to medium flow rates. The longer the ammonia is with

the catalytic additive, the higher the conversion rate to N_2 and H_2 . Therefore, for high-speed engine applications, this can become a major problem as the catalytic additive cannot keep up with the flow demand.

[0030] Accordingly, there is a continuing need for a more efficient and energy dense fuel that maintains combustion and militates against flame-out conditions. Desirably, the more efficient and energy dense fuel may also militate against global pollution.

SUMMARY

[0031] In concordance with the present disclosure, a combustion system that provides a more efficient and energy dense fuel source that maintains combustion and militates against flame-out conditions, has surprisingly been discovered. Desirably, the combustion system preserves and may enhance the thermal properties of ammonia, and allows for high flow rate combustion to occur while preserving zero carbon content fuel.

[0032] The combustion system includes a metal additive and a polar solvent capable of outer-sphere electron transfer. The metal additive is solvated in the polar outer-sphere electron transferring solvent. The polar outer-sphere electron transferring solvent may include liquid anhydrous ammonia, methylamine, other primary amines, and/or hexamethylphosphoramide. The metal additive may include an alkali metal and/or an alkaline earth metal. More specifically, the metal additive may include aluminum, zirconium, titanium, yttrium, hafnium, and/or magnesium if electrolysis is used. The metal additive and the outer-sphere electron transferring solvent may include various other materials and/or components, within the scope of the present disclosure. Limits for what metal additives may be solvated are given by Lagowski, "Solution phenomena in liquid ammonia" *Pure and Applied Chemistry*, Vol. 25, No. 2, 1971, pp. 429-456, through the following inequality:

$$\Delta H_s + IP < \Delta H_m^+ + \Delta H_e^-$$

[0033] where ΔH_s is the heat of sublimation of the metal, IP is the ionization potential of the metal, ΔH_m^+ is the heat of solvation of the metal ion, and ΔH_e^- is the heat of solvation of the electron. If this inequality does not hold for a particular metal and solvent combination, solvation is not spontaneous. However, if the required energy can be supplied from an external source through electrolysis or radiolysis, then the solvation of other metals may be possible.

[0034] Various ways of manufacturing the combustion system are provided. For instance, a first method may include a step of providing a polar outer-sphere electron transferring solvent. The first method may include a step of also providing a metal additive. The metal additive may be dissolved within the outer-sphere electron transferring solvent. It is also contemplated that the combustion system may be manufactured on demand by passing the outer-sphere electron transferring solvent through a porous metal. One skilled in the art may select other suitable ways of manufacturing the combustion system, within the scope of the present disclosure.

[0035] Further areas of applicability will become apparent from the description provided herein. The description and specific examples in this summary are intended for purposes of illustration only and are not intended to limit the scope of the present disclosure.

DRAWINGS

[0036] The drawings described herein are for illustrative purposes only of selected embodiments and not all possible implementations and are not intended to limit the scope of the present disclosure.

[0037] FIG. 1 is a plot diagram illustrating the gravimetric and volumetric energy densities of various fuels compared to liquid ammonia and liquid hydrogen;

[0038] FIG. 2 is a plot diagram illustrating the volumetric and gravimetric densities of various fuels, further depicting liquid ammonia having one of the highest volumetric H_2 densities, even higher than liquid hydrogen itself;

[0039] FIG. 3 is a bar graph illustrating influential reactions on ignition sensitivity, further depicting that introducing NO₂ to the flame readily proceeds to stifle the radical pool and increase ignition delay times;

[0040] FIG. 4 is a box diagram of a combustion system, further depicting the combustion system having a metal additive, an outer-sphere electron transferring solvent, and a hypergolic propellant, according to one embodiment of the present disclosure;

[0041] FIG. 5 is a line graph comparing the combustion system to hydrazine and neat ammonia, further depicting the specific impulse of the combustion system outperforming the hydrazine and neat ammonia at a high oxidizer-to-fuel mass flow ratio, according to one embodiment of the present disclosure;

[0042] FIG. 6 is a line graph comparing the combustion system, as shown in FIG. 2, to hydrazine and neat ammonia, further depicting the specific impulse of the combustion system outperforming the hydrazine and neat ammonia at a high oxidizer-to-fuel mass flow ratio, according to one embodiment of the present disclosure;

[0043] FIG. 7 is a line graph comparing the combustion system, to hydrazine and neat ammonia, further depicting the combustion system having higher flame temperatures than neat liquid ammonia, which indicates the combustion system has more radicals and faster reactions to overcome poor combustion characteristics of neat liquid ammonia, according to one embodiment of the present disclosure;

[0044] FIG. 8 is a graph depicting a specific impulse calculation a function of oxidizer-to-fuel ratio and weight percent of lithium as the metal additive, further depicting an optimal O/F ratio between 2 and 2.5 for all weight percent values, according to one embodiment of the present disclosure;

[0045] FIG. 9 is a graph depicting a specific impulse calculation a function of oxidizer-to-fuel ratio and weight percent of sodium as the metal additive, according to one embodiment of the present disclosure;

[0046] FIG. 10 is a graph depicting a specific impulse calculation a function of oxidizer-to-fuel ratio and weight percent of calcium as the metal additive, further depicting an optimal O/F ratio around 2.25 for low concentrations of the metal additive 102 and around 1.5 for high concentrations of the metal additive 102, according to one embodiment of the present disclosure;

[0047] FIG. 11 is a schematic diagram of a solvation process for the combustion system, further depicting a quasi-free electron of lithium dissolving into solution, according to one embodiment of the present disclosure; and

[0048] FIG. 12 is a flowchart of a method for manufacturing the combustion system, according to one embodiment of the present disclosure.

DETAILED DESCRIPTION

[0049] The following description of technology is merely exemplary in nature of the subject matter, manufacture, and use of one or more inventions, and is not intended to limit the scope, application, or uses of any specific invention claimed in this application or in such other applications as may be filed claiming priority to this application, or patents issuing therefrom. Regarding methods disclosed, the order of the steps presented is exemplary in nature, and thus, the order of the steps can be different in various embodiments, including where certain steps can be simultaneously performed. “A” and “an” as used herein indicate “at least one” of the item is present; a plurality of such items may be present, when possible. Except where otherwise expressly indicated, all numerical quantities in this description are to be understood as modified by the word “about” and all geometric and spatial descriptors are to be understood as modified by the word “substantially” in describing the broadest scope of the technology. “About” when applied to numerical values indicates that the calculation or the measurement allows some slight imprecision in the value (with some approach to exactness in the value; approximately or reasonably close to the value; nearly). If, for some reason, the imprecision provided by “about” and/or “substantially” is not otherwise understood in the art with this ordinary meaning, then “about” and/or “substantially” as used herein indicates at least variations that may arise from ordinary methods of measuring or using such parameters.

[0050] Although the open-ended term “comprising,” as a synonym of non-restrictive terms such as including, containing, or having, is used herein to describe and claim embodiments of the present technology, embodiments may alternatively be described using more limiting terms such as “consisting of” or “consisting essentially of.” Thus, for any given embodiment reciting materials, components, or process steps, the present technology also specifically includes embodiments consisting of, or consisting essentially of, such materials, components, or process steps excluding additional materials, components or processes (for consisting of) and excluding additional materials, components or processes affecting the significant properties of the embodiment (for consisting essentially of), even though such additional materials, components or processes are not explicitly recited in this application. For example, recitation of a composition or process reciting elements A, B and C specifically envisions embodiments consisting of, and consisting essentially of, A, B and C, excluding an element D that may be recited in the art, even though element D is not explicitly described as being excluded herein.

[0051] As referred to herein, disclosures of ranges are, unless specified otherwise, inclusive of endpoints and include all distinct values and further divided ranges within the entire range. Thus, for example, a range of “from A to B” or “from about A to about B” is inclusive of A and of B. Disclosure of values and ranges of values for specific parameters (such as amounts, weight percentages, etc.) are not exclusive of other values and ranges of values useful herein. It is envisioned that two or more specific exemplified values for a given parameter may define endpoints for a range of values that may be claimed for the parameter. For example, if Parameter X is exemplified herein to have value A and also exemplified to have value Z, it is envisioned that Parameter X may have a range of values from about A to about Z. Similarly, it is envisioned that disclosure of two or

more ranges of values for a parameter (whether such ranges are nested, overlapping, or distinct) subsume all possible combination of ranges for the value that might be claimed using endpoints of the disclosed ranges. For example, if Parameter X is exemplified herein to have values in the range of 1-10, or 2-9, or 3-8, it is also envisioned that Parameter X may have other ranges of values including 1-9, 1-8, 1-3, 1-2, 2-10, 2-8, 2-3, 3-10, 3-9, and so on.

[0052] When an element or layer is referred to as being “on,” “engaged to,” “connected to,” or “coupled to” another element or layer, it may be directly on, engaged, connected, or coupled to the other element or layer, or intervening elements or layers may be present. In contrast, when an element is referred to as being “directly on,” “directly engaged to,” “directly connected to” or “directly coupled to” another element or layer, there may be no intervening elements or layers present. Other words used to describe the relationship between elements should be interpreted in a like fashion (e.g., “between” versus “directly between,” “adjacent” versus “directly adjacent,” etc.). As used herein, the term “and/or” includes any and all combinations of one or more of the associated listed items.

[0053] Although the terms first, second, third, etc. may be used herein to describe various elements, components, regions, layers and/or sections, these elements, components, regions, layers and/or sections should not be limited by these terms. These terms may be only used to distinguish one element, component, region, layer or section from another region, layer, or section. Terms such as “first,” “second,” and other numerical terms when used herein do not imply a sequence or order unless clearly indicated by the context. Thus, a first element, component, region, layer, or section discussed below could be termed a second element, component, region, layer, or section without departing from the teachings of the example embodiments.

[0054] Spatially relative terms, such as “inner,” “outer,” “beneath,” “below,” “lower,” “above,” “upper,” and the like, may be used herein for ease of description to describe one element or feature’s relationship to another element(s) or feature(s) as illustrated in the figures. Spatially relative terms may be intended to encompass different orientations of the device in use or operation in addition to the orientation depicted in the figures. For example, if the device in the FIG. is turned over, elements described as “below,” or “beneath” other elements or features would then be oriented “above” the other elements or features. Thus, the example term “below” can encompass both an orientation of above and below. The device may be otherwise oriented (rotated 90 degrees or at other orientations) and the spatially relative descriptors used herein interpreted accordingly.

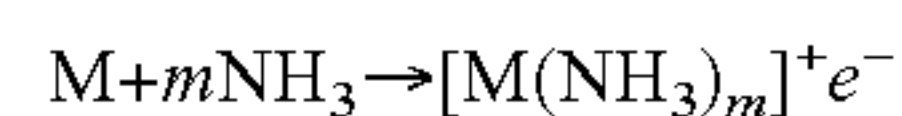
[0055] As shown in FIG. 4, the combustion system 100 includes a metal additive 102 and a polar outer-sphere electron transferring solvent 104. The metal additive 102 is solvated in the polar outer-sphere electron transferring solvent 104. In a specific example, the metal additive 102 may be solvated in the polar outer-sphere electron transferring solvent 104 via simple dissolution or electrolysis. By dissolving the metal additive 102 within the polar outer-sphere electron transferring solvent 104, the metallic-bonding system of the metal additive 102 may be uniquely combined with the covalent bonding system of the polar outer-sphere electron transferring solvent 104. It should be appreciated that by dissolving the metal additive 102 within the polar outer-sphere electron transferring solvent 104, the dissolved

metal additive 102 may have more surface area exposed for potential combustion. Without being bound to any particular theory, it is believed this combination may advantageously increase flame temperatures and militate against flame-out conditions. Desirably, the combustion system 100 may offer greater performance compared to known environmentally-friendly fuel sources while operating at a high oxidizer to fuel mass ratio. The polar outer-sphere electron transferring solvent 104 may include liquid anhydrous ammonia, methylamine, and/or hexamethylphosphoramide. The metal additive 102 may include an alkali metal and/or an alkaline earth metal. More specifically, the metal additive 102 may include lithium, sodium, aluminum, zirconium, titanium, yttrium, hafnium, and/or magnesium. A skilled artisan may select other suitable materials for the metal additives 102 and/or the polar outer-sphere electron transferring solvent 104, within the scope of the present disclosure.

[0056] In certain circumstances, the combustion system 100 may be provided with various ratios of the metal additive 102 and the polar outer-sphere electron transferring solvent 104. In a specific example, the combustion system 100 may include up to around twenty percent of the metal additive 102 by weight. For instance, where sodium is provided as the metal additive 102 and liquid anhydrous ammonia is provided as the polar outer-sphere electron transferring solvent 104, the combustion system 100 may include up to around twenty percent sodium by weight. In a more specific example, the combustion system 100 may include up to around ten percent of the metal additive 102 by weight. For instance, where lithium is provided as the metal additive 102 and liquid anhydrous ammonia is provided as the polar outer-sphere electron transferring solvent 104, the combustion system 100 may include up to around ten percent lithium by weight. One skilled in the art may select other suitable ratios for providing the metal additive 102 and the polar outer-sphere electron transferring solvent 104, within the scope of the present disclosure.

[0057] In certain circumstances, a solvated electron solution may be formed by dissolving the metal additive 102 within the polar outer-sphere electron transferring solvent 104. Solvated electrons are quasi-free electrons in solution and are the smallest possible anion. In the present disclosure, solvated electrons may be formed in solvents that exhibit outer-sphere electron transfer via radiation chemistry, electrolysis, and/or by simple dissolution of specific metals. A skilled artisan may select other suitable ways to provide the solvated electron, within the scope of the present disclosure.

[0058] The simplest representation of the solvated electron in liquid anhydrous ammonia (LAA) takes the general form:



[0059] Where M is a soluble metal and e^- is a quasi-free electron dissolved into solution. Depending on the solvated metal, a stable number of ammonia molecules (denoted m) will coordinate with the metal cation to form a complex. Provided as a non-limiting example, in the case of lithium, four ammonia molecules coordinating with one lithium cation may give the most stable coordination. With continued reference to the non-limiting example, a simplification of the solvation process of lithium in liquid anhydrous ammonia is shown in FIG. 11.

[0060] In reality, the number of solvated states is quite complex, with each state having unique physical and chemi-

cal properties. Due to the reactive nature of many of these solvation states, the solution slowly reacts with itself to form a metal amide:



[0061] Despite this side reaction, solvated electron solutions can be stable for days, depending on the metal additive **102** and the polar outer-sphere electron transferring solvent **104**.

[0062] In certain circumstances, the combustion system **100** may have enhanced specific impulse and oxidizer-to-fuel mass flow ratio. As shown in FIGS. 5-6, the compulsion system outperformed hydrazine at higher oxidizer-to-fuel mass flow ratios. With reference to FIG. 7, the compulsion system had higher flame temperatures than neat NH_3 . Advantageously, it should be appreciated that more radicals and faster reactions may be obtained with the combustion system **100** to overcome the poor combustion characteristics of neat NH_3 . As shown in FIGS. 8-10, specific impulse calculations are provided for various metal additives **102**. FIGS. 8-10 are both a function of oxidizer-to-fuel ratio and weight percent metal additive **102**. Estimated ranges depend on the metal additive **102**. For example, as shown in FIG. 8, lithium has an optimal O/F ratio between 2 and 2.5 for all weight percent values. As shown in FIG. 10, calcium has an optimal O/F ratio around 2.25 for low concentrations of the metal additive **102** and around 1.5 for high concentrations of the metal additive **102**.

[0063] In certain circumstances, as shown in FIG. 4, the combustion system **100** may include a hypergolic propellant **106**. In a specific example, the hypergolic propellant **106** may include white fuming nitric acid. In a more specific example, the combustion system **100** coupled with a hypergolic propellant **106** may be provided as a propellant fuel. In a more specific example, the combustion system **100** coupled with a hypergolic propellant **106** may be provided as a non-carbonaceous propellant fuel. Additionally, the combustion system **100** coupled with a hypergolic propellant **106** may be provided as a propellant fuel that is less toxic than hydrazine. One skilled in the art may select other suitable uses for the combustion system **100**, within the scope of the present disclosure.

[0064] Various ways of manufacturing the combustion system **100** are provided. For instance, as shown in FIG. 12, a method **200** may include a step **202** of providing a polar outer-sphere electron transferring solvent **104**. The method **200** may include a step **204** of also providing a metal additive **102**. The metal additive **102** may be dissolved within the polar outer-sphere electron transferring solvent **104**. In a specific example, a hypergolic propellant may be provided. In a more specific example, the metal additive **102** dissolved in within the polar outer-sphere electron transferring solvent **104** may be ignited. One skilled in the art may select other suitable ways of manufacturing the combustion system **100**, within the scope of the present disclosure.

[0065] In certain circumstances, the method **200** may include a way to provide the combustion system **100** on demand. For instance, the metal additive **102** may be specifically provided as a porous metal. In a specific example, the porous metal may have a pore size large enough to allow NH_3 to flow therethrough. The step **206** of dissolving the metal additive **102** within the polar outer-sphere electron transferring solvent **104** may more particularly include selectively passing the polar outer-sphere electron transfer-

ring solvent **104** through the porous metal. It is also contemplated to provide the metal additive **102** as a powder bed or tubes to provide the same or similar function as the porous metal. A skilled artisan may select other suitable ways of manufacturing the on-demand combustion system **100**, within the scope of the present disclosure.

[0066] Advantageously, the combustion system **100** may provide a more efficient and energy dense fuel source that maintains combustion by providing temporary oxidation protection of the metal additive **102**, militates against flame-out conditions, and is less toxic than known combustion materials such as hydrazine. Desirably, the combustion system **100** may also militate against global pollution. For instance, in a specific example, the combustion system **100** may produce zero-carbon emissions.

[0067] Example embodiments are provided so that this disclosure will be thorough and will fully convey the scope to those who are skilled in the art. Numerous specific details are set forth such as examples of specific components, devices, and methods, to provide a thorough understanding of embodiments of the present disclosure. It will be apparent to those skilled in the art that specific details need not be employed, that example embodiments may be embodied in many different forms, and that neither should be construed to limit the scope of the disclosure. In some example embodiments, well-known processes, well-known device structures, and well-known technologies are not described in detail. Equivalent changes, modifications and variations of some embodiments, materials, compositions, and methods can be made within the scope of the present technology, with substantially similar results.

What is claimed is:

1. A combustion system, comprising:
a metal additive; and
an outer-sphere electron transferring solvent, wherein the metal additive is solvated in the outer-sphere electron transferring solvent.
2. The combustion system of claim 1, wherein the outer-sphere electron transferring solvent includes liquid anhydrous ammonia.
3. The combustion system of claim 1, wherein the outer-sphere electron transferring solvent includes at least one of methylamine and hexamethylphosphoramide.
4. The combustion system of claim 1, wherein the metal additive includes at least one of an alkali metal and an alkaline earth metal.
5. The combustion system of claim 4, wherein the metal additive includes at least one of aluminum, zirconium, titanium, yttrium, hafnium, and magnesium.
6. The combustion system of claim 4, wherein the metal additive includes lithium.
7. The combustion system of claim 4, wherein the metal additive includes sodium.
8. The combustion system of claim 1, further comprising a hypergolic propellant.
9. The combustion system of claim 8, wherein the hypergolic propellant includes white fuming nitric acid.
10. A propellant fuel comprising a combustion system of claim 1.
11. A method of manufacturing a combustion system, the method comprising the steps of:
providing an outer-sphere electron transferring solvent;
providing a metal additive; and

dissolving the metal additive within the outer-sphere electron transferring solvent.

12. The method of claim **11**, further comprising a step of providing a hypergolic propellant.

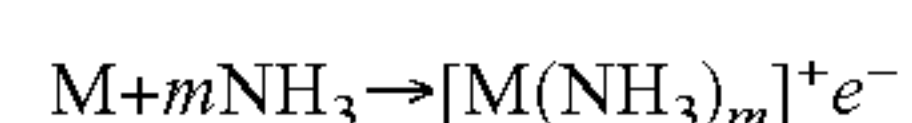
13. The method of claim **12**, further comprising a step of igniting the dissolved metal additive within the outer-sphere electron transferring solvent.

14. The method of claim **11**, wherein the step of dissolving the metal additive within the outer-sphere electron transferring solvent utilizes an electrolysis process.

15. The method of claim **11**, wherein the step of dissolving the metal additive within the outer-sphere electron transferring solvent utilizes a dissolution process.

16. The method of claim **11**, wherein the step of dissolving the metal additive within the outer-sphere electron transferring solvent utilizes a radiation chemistry process.

17. The method of claim **11**, wherein the step of dissolving the metal additive within the outer-sphere electron transferring solvent includes a reaction having the formula:



18. The method of claim **11**, wherein the metal additive is a porous metal.

19. The method of claim **18**, wherein the step of dissolving the metal additive within the outer-sphere electron transferring solvent includes passing the outer-sphere electron transferring solvent through the porous metal.

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