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Effects of water content and diluent pressure on the ignition of aqueous ammonia/ammonium nitrate and urea/ammonium nitrate fuels

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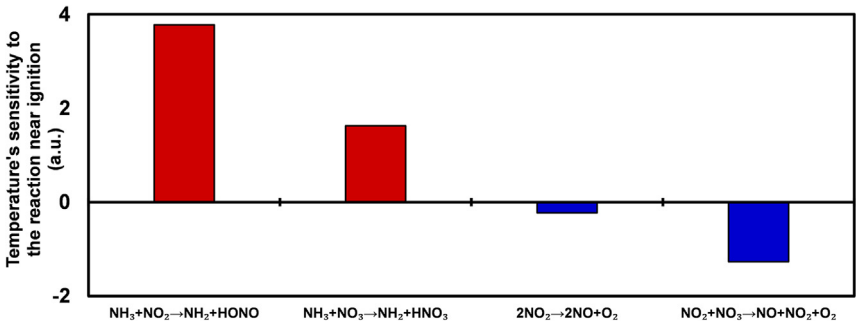
HIGHLIGHTS

- Thermal autoignition of two nitrogen-based aqueous monofuels is studied.
- Diluents increase the autoignition temperature due to the heat sink effect.
- Isocyanic acid hydrolysis dominates its decomposition prior to the ignition.
- Ignition is promoted by NH_2 generation from NH_3 by reaction with NO_3/NO_2.
- Reduction of high oxidation NO_x species inhibits the thermal autoignition.

GRAPHICAL ABSTRACT



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ABSTRACT

Two aqueous monofuels composed of aqueous solutions of ammonia/ammonium nitrate and urea/ammonium nitrate have been suggested as feasible nitrogen-based hydrogen carriers. Such synthetic fuels can serve as long-term energy storage media, providing back-up power generation for intermittent renewable energy sources. The effects of diluents such as helium and water on the thermal behavior of these fuels are mostly unexplored. Experimental results indicated the fuels' autoignition temperature increases with diluent content due to the heat sink effect of the inert water and helium. Simulations were performed using an updated mechanism to study the reaction pathways leading to thermal autoignition. Isocyanic acid underwent hydrolysis generating NH_3 and most of the CO_2. Ammonia was oxidized by either NO_3 or NO_2 to form NH_2 and either HNO_3 or HONO. Nitric acid reacted with HONO producing N_2O_4 and most of the H_2O. Molecular nitrogen was mostly produced by the termination reaction between NH_2 and NO. Sensitivity analyses indicated the ignition of these fuels is promoted by the generation of NH_2 from NH_3 by high oxidation NO_x, and inhibited by the reduction of NO_3 and NO_2 to NO_2 and NO, respectively. This work demonstrates for the first time the effect of aqueous ammonia/ammonium nitrate water content on its auto-ignition temperature and the crucial role of isocyanic acid hydrolysis in aqueous urea/ammonium nitrate pre-ignition pathways.

1. Introduction

By 2040, worldwide energy consumption is predicted to increase by 30% [1,2], with renewable energy sources providing 40% of this increase [1,2]. However, the intermittency sources such as solar and wind limits their integration [3,4]. Overcoming fluctuations in power generation necessitates short- and long-term energy storage media [5,6]. Specifically, storage using synthetic fuels offers high energy density values and long-term storage stability [6,7]. While hydrogen offers the highest specific energy of any fuel (HHV 142 MJ kg^{-1}) [8], its low

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volumetric energy density (HHV 12.7 MJ m^{-3}) [8] and incompatibility with steel infrastructure [9] inhibit its application. Therefore, hydrogen carriers are necessary for utilizing renewable hydrogen for energy storage [10,11]. In contrast, synthetic carbon- and nitrogen-based fuels offer superior energy densities [12] and full compatibility with the steel infrastructure. Ammonia has been researched recently for gas turbine [13] and internal combustion engine [14] applications. While ammonia is compatible with steel and offers a higher energy density (13.6 GJ m^{-3}) than methane (10.4 GJ m^{-3}) [12], it is incompatible with copper [15] and a toxicant [16]. In this work, the thermal autoignition of aqueous solutions of ammonia and ammonium nitrate (AAN), as well as urea and ammonium nitrate (UAN) were studied for energy-based applications. These liquid fuels can complement an ammonia economy for applications in which ammonia's limitations hinder its use. Both fuels are safe to store and transport, non-toxic, compatible with current infrastructure [17], and combust to produce mainly water, nitrogen, and in the case of UAN, carbon dioxide (R1-R2).

$$3NH_4NO_{3(aq)} + 2NH_{3(aq)} + XH_2O_{(l)} \rightarrow 4N_{2(g)} + (X+9)H_2O_{(g)} \quad \text{(R1)}$$

$$3NH_4NO_{3(aq)} + CO(NH_2)_{2(aq)} + XH_2O_{(l)} \rightarrow 4N_{2(g)} + CO_{2(g)} + (X+8)H_2O_{(g)} \quad \text{(R2)}$$

Previous studies indicated adding nitrogen or water to the combustion of AAN and UAN inhibits their ignition [18,19]. Studying this effect is vital to implement these fuels successfully in power-generating systems and elucidating the reaction mechanism responsible for their combustion.

Altering the water content in these aqueous solutions affects their solubility. For instance, increasing AAN water content from 25 wt% to 45 wt% H_2O decreases the solubility temperature from 23 °C to −10 °C [20]. This relation enables the use of AAN in cold environments by adding water. A similar study on UAN indicated that its autoignition temperature (AIT) increases with water [18]. Specifically, the AIT rose from 598 K to 605 K as UAN water content increased from 25 wt% to 45 wt% [18]. However, the effect of AAN water content on its ignition has not been investigated previously and is therefore studied herein.

Diluent gases can be added to combustion processes to lower the adiabatic combustion temperature, thereby decreasing pollutant generation and heat loss [21]. The effect of adding helium to UAN has been studied previously [22]. Results indicated that AIT increased from 565 K to 581 K as the helium pressure rose from 0.10 MPa to 1.31 MPa [22]. This change was attributed to condensed-phase processes inhibiting reactive species released to the gas-phase. An attempt to model similar experiments [23] resulted in disagreement between experiment and simulation AIT values [23]. Therefore, this effect was investigated using an improved simulation model in this work.

In this paper, the effect of AAN water content on its thermal autoignition is explored for the first time using an AIT measurement system. An updated reaction mechanism with fitted parameters is used for the simulations. Modeling tools are applied to simulate the effects of AAN water content and UAN helium pressure on AIT. Rates of production analyses are performed to investigate the reaction pathways leading to thermal autoignition and the effect mechanism on them. Finally, sensitivity analyses are applied to identify the ignition-promoting and inhibiting reactions.

2. Materials and methods

2.1. Experimental

Monofuel samples were prepared using ammonium hydroxide (28%, Merck), ammonium nitrate (≥99%, Sigma-Aldrich), urea (≥99.5%, Sigma-Aldrich) and ultrapure water (Milli-Q®). Samples were filtered using a 0.45 µm syringe filter (SLHV033RS, Millex). Septa-mounted vials (PTFE/silicone, Agilent) were used for AAN storage with a valve-equipped syringe (500R-V-GT, Restek) for extraction.

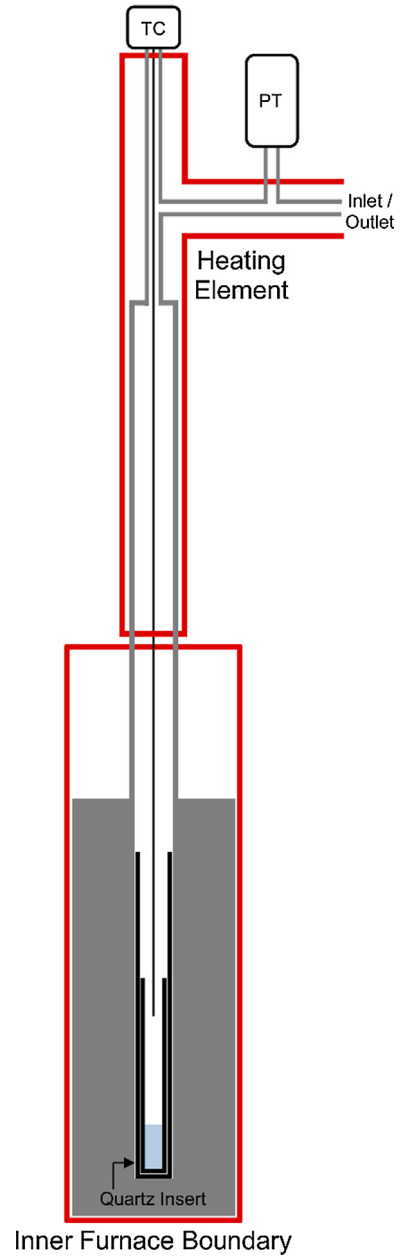

Fig. 1. Schematic of the experimental system used in the AAN water content effect experiments (TC-Thermocouple, PT-Pressure transducer).

Two separate batch systems were used in the experiments described herein. The first was used to investigate the effect of AAN water content on its AIT, and was designed according to the ASTM G72 standard (Fig. 1) [24]. A 48 ml reactor was constructed from SS316L. The reactor and gas inlet/outlet line were heated by a 500 W furnace and a 250 W heating element, respectively. Woven fiberglass was used to insulate lines protruding from the furnace. In each experiment, the reactor was first heated and soaked at 323 K for 35 min, and then heated at 5 K min^{-1} to 723 K. Pressure and temperature measurements were taken at 1 Hz by a type-K thermocouple (CT-TCKB, Controtech) and a pressure transducer (G27M0105M15000#G, Ashcroft), respectively. Sample weights of 1.00–1.36 g corresponding to 25–45 wt% H_2O were injected into a double-lined quartz insert (Table 1). Each water concentration was tested at least four times to determine the experimental error. Ammonia and AN masses were kept constant in all samples while increasing only the water mass. Sealed air was displaced by nitrogen