



# Pressure effect on the combustion of aqueous urea ammonium nitrate alternative fuel



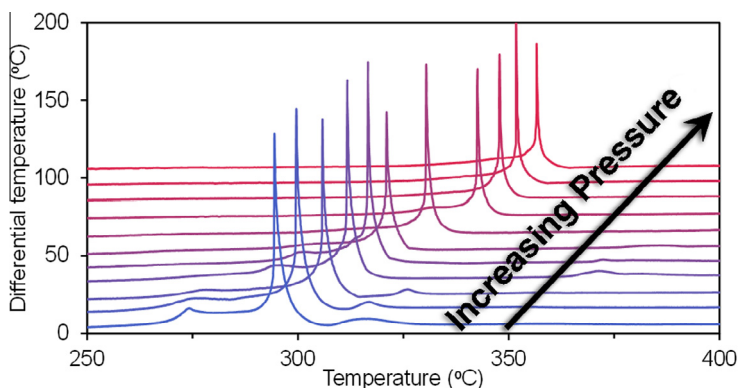
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## GRAPHICAL ABSTRACT



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## ABSTRACT

Differential Thermal Analysis (DTA) and Differential Barometric Analysis (DBA) were used to study the combustion of aqueous urea ammonium nitrate alternative fuel, a low carbon nitrogen-based hydrogen storage medium, under varied pressures (up to 27 MPa) in a constant volume analyzer. The thermal processes governing the fuel combustion under applied pressure were investigated at elevated temperatures (up to 500 °C). Three distinct exothermic effects were observed during reaction, and all three shifted towards higher temperatures with increased pressure. A change in combustion mechanism was suggested to occur at 5 MPa, and the calculated activation energy of the low pressure region ( $P < 5$  MPa) was  $209 \text{ kJ mol}^{-1}$ , in agreement with the literature value for radical ammonium nitrate decomposition. Deduction of the reaction pathway is crucial for a basic understanding of the fuel's combustion mechanism.

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## 1. Introduction

Energy from renewable sources can be harvested readily by advanced technologies, yet economical, convenient, and safe

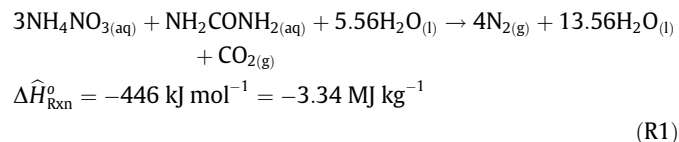
delivery of this energy remains a challenge [1,2]. Renewable energy sources are often unavailable at the site of end-usage, since they are intermittent, undependable, and limited to specific geographies. The urgent effort to shift our energy dependency from pollution-emitting and finite fossil fuels to clean and renewable energy sources requires the development of a means for storing and transporting energy. Given the current liquid fuel paradigm

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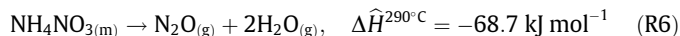
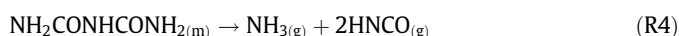
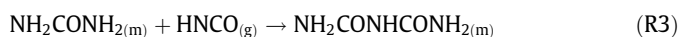
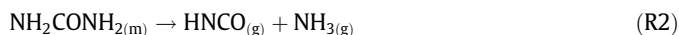
and the existing worldwide infrastructure, it is favorable to synthesize liquid alternative fuels as chemical hydrogen storage media and energy carriers. Such fuels could be key enabling elements for renewable energy utilization and deliverability.

Previously, a carbon neutral nitrogen-based alternative fuel in the form of an aqueous urea and ammonium nitrate (UAN) solution was suggested for chemical hydrogen storage [3]. Ammonium nitrate (AN), a net oxidizing species, and urea, a reducer, are common global fertilizer commodities [4,5]. Aqueous UAN solution is also being used directly as a fertilizer, though at concentrations different from that of the fuel [6]. Ideal combustion of this fuel yields an environmentally friendly effluent gas consisting of 73.0% H<sub>2</sub>O, 21.6% N<sub>2</sub>, and 5.4% CO<sub>2</sub>, on a per mole basis (Reaction (R1)).



In case the desired Reaction (R1) is incomplete, this nitrogen-based fuel is bound to emit pollutants such as NO<sub>x</sub> species (i.e., NO<sub>2</sub>, NO, and N<sub>2</sub>O) and ammonia. In standard carbon-based fuels the NO<sub>x</sub> species originate from high temperature side reactions of atmospheric nitrogen and oxygen (thermal NO<sub>x</sub>). However, unlike conventional fuels, NO<sub>x</sub> species formed during the combustion of a nitrogen-based fuel are essential combustion intermediates. In other words, their formation is mandatory for the combustion propagation [3]. Hence, significant NO<sub>x</sub> abatement must be achieved by optimizing the combustion parameters so that the desired Reaction (R1) occurs to a higher extent. Further NO<sub>x</sub> abatement could be achieved by catalytic processes. In previous studies we presented the principal chemical reactions during continuous combustion of aqueous UAN fuel at high pressures. In addition, we reported that at 25 MPa NO<sub>x</sub> pollutant species were reduced well below US Environmental Protection Agency regulation for stationary natural gas power generation turbines, and that the N<sub>2</sub> yield approached 99.9% [3]. It is noted that the aqueous UAN fuel does not require an external oxidizer (Reaction (R1)) since it is a monofuel. Clearly, the combustion technology of such fuels needs to be further developed to minimize pollutant emissions.

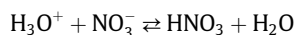
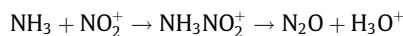
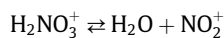
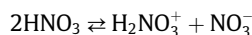
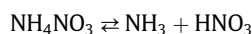
The dominant condensed phase chemical processes during aqueous UAN thermal decomposition at ambient pressure under argon flow were also characterized, and four distinct endothermic stages were identified [7]: (a) In the first stage (83–156 °C) about 75% of the water in the solution vaporizes. (b) In the second stage (156–210 °C), in addition to water vaporization completion, some of the urea endothermically decomposes into isocyanic acid and ammonia (Reaction (R2)), while the remaining urea forms biuret (Reaction (R3)). (c) In the third stage (210–269 °C) biuret decomposes (Reaction (R4)). (d) The fourth and final endothermic stage (269–315 °C) is dominated by the dissociation reaction of AN (Reaction (R5)). In addition, it was shown that urea hydrolysis and urea isomerization into ammonium cyanate (NH<sub>4</sub>CNO) are inhibited in the presence of high AN concentration. While aqueous UAN decomposition at ambient pressure under flow is endothermic, it becomes exothermic when confined and when pressure is applied (e.g., 5 and 10 MPa) [7].



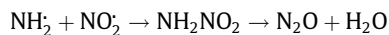
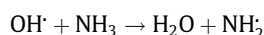
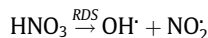
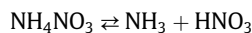
The exothermic thermal decompositions of AN is described by the global Reaction (R6) [8,9]. The reaction is irreversible and has a detectable rate only at temperatures slightly above the AN melting point [9,10]. It was previously shown that due to thermal coupling of Reactions (R5) and (R6), pure molten AN maintains a predictable limiting temperature that is dependent on the pressure and the heat supplied to or removed from the reacting mass [11].

The chemical routes of AN decomposition (Reaction (R6)) gradually change with temperature: An ionic pathway (Mechanism 1) [10] is overtaken at high temperatures by a radical pathway (Mechanism 2) [12] with a higher activation energy than that of Mechanism 1. The two mechanisms became isokinetic around 290 °C [12]. The Rate Determining Step (RDS) of high temperature AN decomposition via the radical mechanism is the homolysis of nitric acid [12]. Pressure decomposition studies concluded that there is no significant change in AN decomposition pattern up to 3 MPa [13], yet the decomposition temperature increases at elevated pressures [14].

Mechanism 1 (Ionic pathway)



Mechanism 2 (Radical pathway)



The decomposition behavior of aqueous UAN has not been previously systematically studied under high pressure conditions. The thermal data under such conditions are of immense importance for understanding the aqueous UAN combustion mechanism; understanding the high-pressure mechanism is particularly necessary since the environmentally friendly continuous combustion of this fuel requires high pressures [3]. Therefore, the main objective of this work is to investigate the chemical processes that dominate aqueous UAN decomposition at elevated temperatures under high applied pressures up to 27 MPa.

## 2. Experimental

The fuel solution was prepared using AN (≥99%, Sigma-Aldrich), urea (≥99.5%, Sigma-Aldrich), and water (Milli-Q® ultrapure water), and was subsequently filtered using a 0.45 μm filter. The fuel composition was AN/urea/water 12:3:5 by weight. Ultra high purity helium (99.9995%) was used throughout the experiments as carrier and pressurizing gas.

The combustion experiments were conducted in a thermal analyzer designed based on the Differential Thermal Analysis (DTA) concept, equipped with two isolated 30 ml stainless steel (SS) 316L compartments and a single zone 500 W furnace (Scheme 1). The temperature controller (Eurotherm, model 3216) was equipped with a K-type thermocouple mounted near the middle

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