Validation of an Aqueous UAN Alternative Fuel Combustion Mechanism

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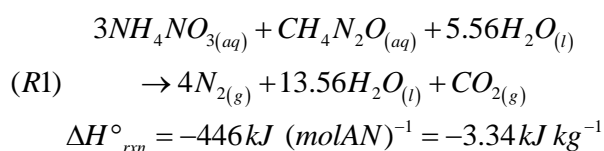
Abstract

A novel nitrogen-based fuel consisting of a urea and ammonium nitrate aqueous solution (UAN) has been previously suggested as a hydrogen carrier that can undergo efficient combustion into N_2, H_2O and residual CO_2, with minimal NOx emissions. Using CHEMKIN-PRO a new combustion kinetic database is suggested and validated relative to previous experiments in the pressure range of 1-25 MPa. Excellent agreement was found for nitrogen-based species at high pressures and for carbon-based products at all pressures. This confirms the suitability of the new kinetic database for the simulation of high pressure UAN combustion.
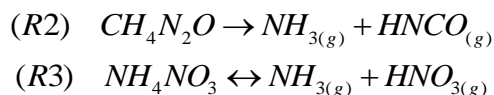
Introduction

Many sources of renewable energy production suffer from fluctuations in production. To implement such sources on a global scale, an energy storage medium is necessary. One option available is to produce fuels that can be stored and then used upon demand.

Hydrogen has shown great promise but its use in a pure form is plagued by low volumetric energy density and safety issues [1-2]. To overcome these obstacles, hydrogen can be converted into a fuel molecule, which in turn could serve as a hydrogen carrier. Such fuels can be carbon-based as well as nitrogen-based [3]. A nitrogen-based fuel has been studied previously in the form of an aqueous solution of urea and ammonium nitrate (UAN) [4-5]. Continuous and stable combustion of this fuel has been demonstrated under high pressures with low levels of pollutants [5].

The full combustion of UAN (Reaction R1) is by itself environmentally friendly:

$$3NH_4NO_{3(aq)} + CH_4N_2O_{(aq)} + 5.56H_2O_{(l)}$$
$$(R1) \rightarrow 4N_{2(g)} + 13.56H_2O_{(l)} + CO_{2(g)}$$
$$\Delta H°_{rxn} = -446kJ \ (molAN)^{-1} = -3.34kJ \ kg^{-1}$$

It is facilitated by the thermal decomposition of both urea (Reaction R2) and ammonium nitrate (Reaction R3):

$$(R2) \quad CH_4N_2O \rightarrow NH_{3(g)} + HNCO_{(g)}$$
$$(R3) \quad NH_4NO_3 \leftrightarrow NH_{3(g)} + HNO_{3(g)}$$

During urea thermal decomposition NH_3 and HNCO are continuously produced, though their production goes through intermediates as well. At high temperatures molecules such as biuret, ammelide and cyanuric acid (CYA) are formed in the condensed phase and decompose to NH_3 and HNCO [6]. Both urea and ammonium nitrate have been shown to undergo complete evaporation [7-8]. The thermal decomposition of an aqueous UAN solution has also been studied in detail by TGA/DTA/MS and the same products as for separated urea and ammonium nitrate were detected [9].

Combustion of nitrogen-based fuels can potentially lead to the production of pollutants such as NO, NO_2, N_2O and NH_3. To minimize these undesirable products, the combustion parameters need to be optimized. Using previous experimental data on UAN combustion as a reference [5], computational modeling could provide the key to a better understanding of this complex combustion process.

Here we present the results for detailed simulations of UAN combustion and compare them to experimental results. A kinetic gas-phase simulation software (CHEMKIN-PRO) [10] was used with a new kinetic database of our creation. This database was assembled by integrating the Additivi 2002 and Goswami et al. 2008 kinetic databases [11-12]. The model simulated a PFR reactor with a gaseous inlet mass flow rate of 0.18 gr s^{-1}. A gas composition of NH_3 : HNO_3 : HNCO : H_2O = 4 : 3 : 1 : 5.56 (molar ratio) was used, complying with the stoichiometry of Reactions R1-R3,. The temperature profile was uniformly set to 1000 K and the pressures were set in the range of 1-25 MPa.

While previous CHEMKIN simulations exist for urea and ammonium nitrate separately [12-13], to the best of our knowledge, our work is the first simulation study involving both reactants. Moreover, the above cited works were performed at pressures under 2 MPa – considerably lower than the current study which is at an order of magnitude higher pressure.

Results

In order to evaluate the pollutant emissions the experimental yields of both CO_2 and N_2 were calculated according to Reaction R1 using an atomic mass balance [5]. Yields are presented for both simulation and experimental results in Figure 1a,b.

Simulation results for N_2 showed improved agreement with increasing pressure (Figure 1a).

Agreement between simulation and experimental results for CO_2 was excellent at all pressures tested (Figure 1b).
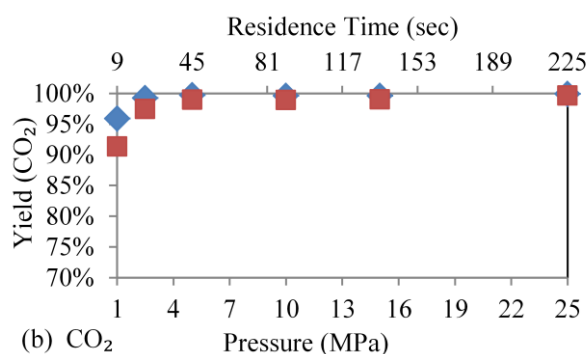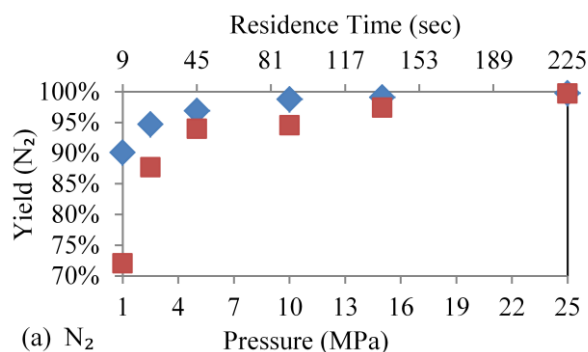

(a) N_2

(b) CO_2

Figure 1. Comparison of experimental (◆) and simulation (■) results at pressures between 1-25 MPa and overall residence times between 9-225 seconds for: (a) N_2 and (b) CO_2.

A maximal difference of 4.54% in CO_2 yield was observed at 1 MPa and declined to 0.23% at 25 MPa. Both products showed increased agreement and yield at increasing pressure, with excellent correlation for both above 15 MPa.

In order to explain the increased yield for both CO_2 and N_2, the conversion of the inlet gasses was calculted from simualtion (Figure 2). Since conversion for HNO_3 was observed to be close to 100% at all pressures, it was omitted from Figure 2.
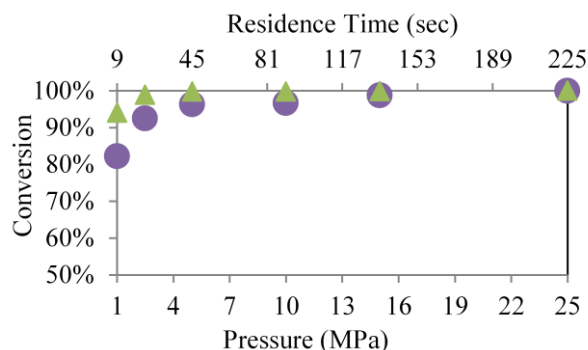

Figure 2. Simulated conversions: NH_3 (●) and HNCO (▲) at pressures of 1-25 MPa and overall residence times of 9-225 seconds.

Conversion for NH_3 is shown to increase with pressure. The low conversion of NH_3 at short residence

times, partially explains the low N_2 simulation yield seen in Figure 1a. However, formation and slow decomposition of intermediary pollutants such as NO and N_2O is also responsible for this result. In the case of HNCO, conversion can be seen to be high (over 90%) at all pressures studied. This corresponds to the high yield of CO_2 in Figure 1b. The same trend, of increasing conversion with pressure, is observed in both HNCO and NH_3, with close to 100% at 25 MPa.

In order to evaluate the effect of residence time on the changes in yield (Figure 1), the evolving nitrogen-based species concentrations at both 1 and 25 MPa were plotted in Figure 3a,b. A residence time of 9 seconds was chosen since at 1 MPa it is the overall residence time under these experimental conditions.
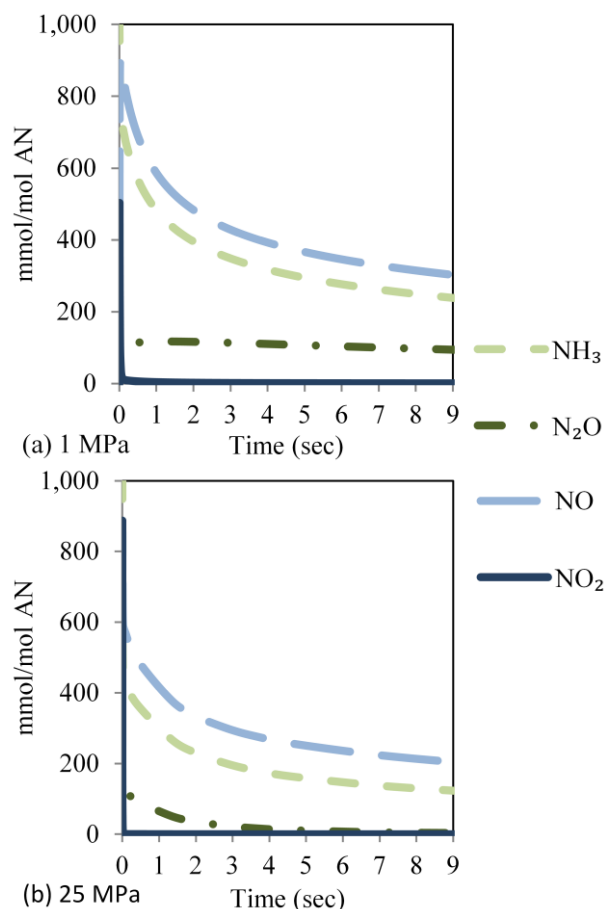

(a) 1 MPa

(b) 25 MPa

Figure 3. Pollutant and CO_2 concentrations in the reactor at: (a) 1 MPa and (b) 25 MPa.

As can be seen from comparing Figure 3a and Figure 3b, the NO concentration is considerably higher at low pressures. Although NO_2 levels were considerably high during the first 0.1 seconds, they fell sharply to 0.58 millimole per AN mole and 10^{-4} millimole per AN mole at 1 MPa and 25 MPa, respectively. The concentration of N_2O as well can be seen to plummet at 25 MPa. These results, along with those of NH_3, help explain why N_2 yield is relatively low at low pressures. This data also confirms the strong effect of pressure on the combustion process and thus

the effluent concentrations both in experimental and simulation results.

Conclusions

This work presented and validated a kinetic database for the combustion simulations of UAN at high pressures in a PFR model. Pollutants were shown to decrease considerably with pressure as yield and conversion increased. Along with the higher residence times used, the effect of pressure on the combustion was shown to be responsible for the achieved process improvements. Thus, the kinetic databse was able to predict the experimentally observed trends. In agreement with experimental results, simulations point toward the use of high pressures for a cleaner combustion process of this fuel.

Acknowledgments

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