

# Thermal decomposition of nitromethane: Experiments and model validation

Meng Yang, Zhaohua Xu, Zhenhua Gao, Chenglong Tang, Erjiang Hu, and Zuohua Huang  
State Key Laboratory of Multiphase Flow in Power Engineering, Xi'an Jiaotong University  
Xi'an, Shaanxi, China

## 1 Introduction

Nitromethane ( $\text{CH}_3\text{NO}_2$ ) is the simplest energetic fuel with a nitro group and generally considered a suitable prototype to understand monopropellant in detail [1, 2]. Kinetic and mechanistic information on decomposition pathways of nitromethane are important for comprehending its physical and chemical properties. The first kinetic model of the decomposition was investigated via shock heating by Glänzer and Troe [3]. The concentration profiles of  $\text{CH}_3\text{NO}_2$  and  $\text{NO}_2$  were recorded over the temperature range 900-1400 K. And other products were not determined. The pyrolysis of nitromethane at the temperature range of 676-771 K was studied by Perche et al. [4] in a static reaction vessel. They found numerous species in the pyrolysis, like CO, NO,  $\text{CH}_4$ ,  $\text{H}_2$ ,  $\text{C}_2\text{H}_6$ ,  $\text{CH}_3\text{OH}$  and so on. A mechanism of nitromethane, involving 28 reactions, was proposed and validated using the experimental data. Hsu and Lin [5] carried out the decomposition of highly diluted nitromethane in Ar over the temperature range of 940-1520 K through a shock tube, at the pressures of 0.4-2.0 atm. Two most important product concentration profiles: NO and CO were measured. They suggested a mechanism of 37 reactions that was an extension of the mechanism of Perche et al. Then Zhang and Bauer [6] reported on the decomposition of nitromethane developed in reflected shock waves. The rate of disappearance of nitromethane and on the production rates of several light hydrocarbons over the temperature range of 1000-1100 K. To account fully for the available data, a reaction mechanism of 99 reactions was proposed and validated with experimental data.

Based on these experimental data, which covers the temperature range 1000-1400 K and pressures from 0.5 to 6.0 bar, Glarborg et al. [7] developed a detailed chemical kinetic model of nitromethane dissociation. In the recent, Mathieu et al. [8] measured the ignition delay times for nitromethane behind reflected shock waves over wide ranges of temperature (875-1595 K); pressure (2.0-35 atm); equivalence ratio (0.5, 1.0 and 2.0) and dilution (99, 98, 95 and 90% Ar by volume). The mechanism involving 166 species and 1204 reactions was presented. And many experimental data of nitromethane decomposition have been validated and discussed.

Compared with the decomposition kinetic studies of nitromethane, these models were mainly validated from experimental results on shock tube at higher temperature or in a static reaction vessel. In order to get

experimental data in a different type of reactor and for a broader temperature range condition, the new study presented here has been performed using a jet-stirred reactor (JSR). In addition, the detailed mechanism of Mathieu et al. also was validated using the experimental data in this work.

## 2 Experimental Setup

The study of the thermal decomposition of nitromethane was conducted in a jet-stirred reactor facility. Figure 1 shows the schematic diagram of experimental facility. The system consists of the mixture preparation assembly, the jet stirred reactor and the sampling analysis facilities. The liquid nitromethane with 99% purity is evaporated in a vaporizer at 408 K, 35 K higher than its boiling point. In order to ensure that the temperature environment of the nitromethane remains the same as the vaporizer, gas pipes are also heated to 408 K. The flow rate of the fuel is controlled by a high pressure infusion pump (AP0010, HPLC) with the uncertainty of 0.1%. The flow rates of argon (99.995% purity) are controlled by MKS mas-flow controller. And the gases are mixed together before the entrance of JSR.

The JSR consists of a fused silica sphere (volume of 106 cm<sup>3</sup>) and an injection cross with 4 nozzles of 0.3 mm inner diameter located in the center. One important issue of the jet stirred reaction is it resembles a 0-D reactor such that the temperature and concentration of species should be homogenous within the reactor. As such, sufficient stirring is realized by turbulent jets flowing from the carefully arrayed nozzles. The reactor is put into a stove (SK-G05123K, ZH) which can provide a rapid heating process and maintain a stable target temperature. In addition, there is a K-type thermocouple located inside the center of the sphere.

As to the sampling system, the outlets are analyzed online by GC (Agilent 7890B) and GC-MS (Agilent 7890B-5977A). The GC is equipped with 3 packed columns (2 Haysep Q and 1 Molecular Sieve 5A). The thermal conductivity detector (TCD) is used to detect the light species concentration such as CO, CO<sub>2</sub>, O<sub>2</sub> and H<sub>2</sub>. The GC-MS is fitted with two flame ionization detectors (FID) and two capillary columns (HP-5 and Plot Q) to analyze hydrocarbons and lighter oxygenated compounds, respectively.

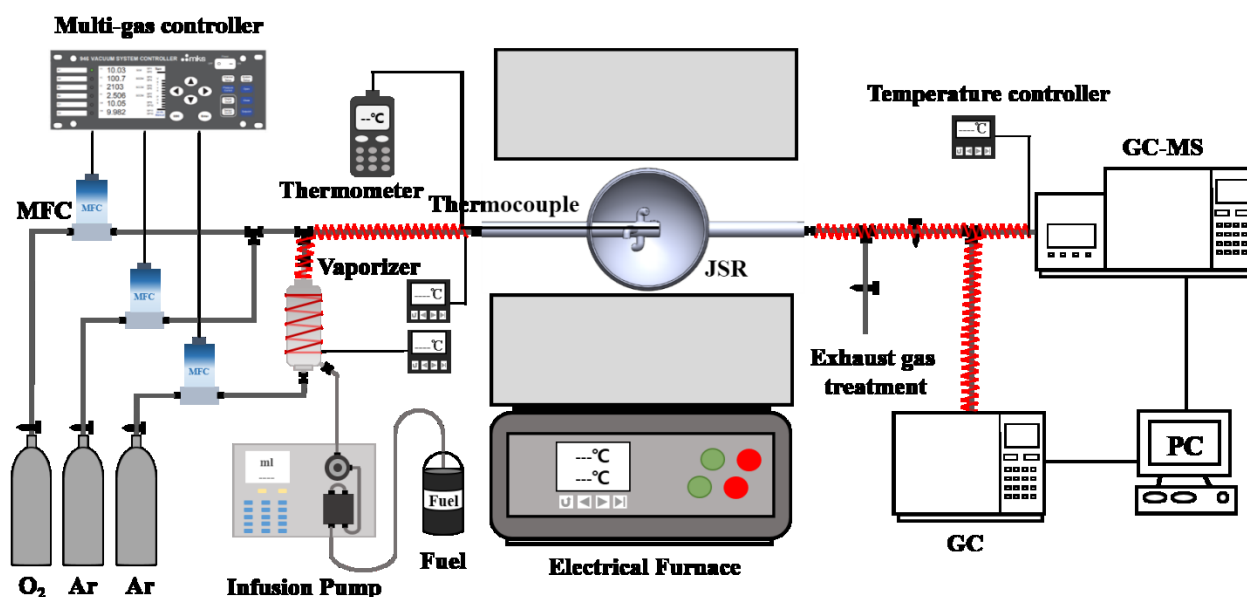


Figure 1. The schematic diagram of JSR.

The pyrolysis experiment was conducted at atmospheric pressure and temperature range of 675-1225 K with a fixed initial nitromethane mole fraction of 1%. The residence time is set to 2.0 s. Each experimental data point was repeated at least three times and good repeatability was observed for all conditions. Species concentration is calibrated using the standard gas mixture purchased from AIR PRODUCTS. The uncertainties of major species and intermediates were about  $\pm 5\%$  and  $\pm 10\%$ .

### 3 Experimental Results and Discussion

In this work, 8 species were detected and measured with GC and GC-MS. Results are given in Figure 2, Figure 3 and Figure 4, which show the measured species concentration profiles for the fuel, CO, H<sub>2</sub>, CH<sub>4</sub> and the main hydrocarbon intermediate species produced.

In Figure 2, the mole fraction of nitromethane is presented at temperature from 675 K to 1225 K. At  $T = 750$  K, the nitromethane begins to decompose. Then it decomposes sharply as the temperature increasing. At  $T = 900$  K, the pyrolysis of nitromethane finishes completely.

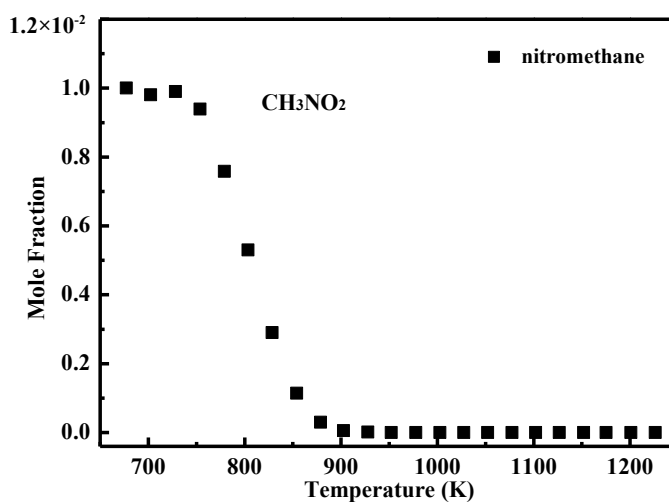


Figure 2. Mole fraction profile of nitromethane.

In Figure 3, the mole fraction profiles of hydrogen, carbon monoxide and methane are shown. It can be seen that the mole fraction profile of H<sub>2</sub> has two different rates of rise. At  $T < 900$  K, due to the decomposition of nitromethane the amount of H<sub>2</sub> increases. However, at  $T = 900$  K, the decomposition is complete, and H<sub>2</sub> concentration keeps increase slowly. Up to  $T > 1000$  K, the concentration of H<sub>2</sub> increases again, because at that temperature the main hydrocarbon intermediate species like C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>6</sub> reach temperature to generate C1 and H<sub>2</sub> species. The mole fraction profile of CO has a similar trend with H<sub>2</sub>. The concentration increase of CO at low temperature is mainly due to the decomposition of the fuel itself. While the decomposition of nitromethane is completed at high temperature, and the intermediate species gradually react to form small molecular species, mainly CO and H<sub>2</sub>. For the CH<sub>4</sub> species, at  $T > 900$  K, it stays the same.

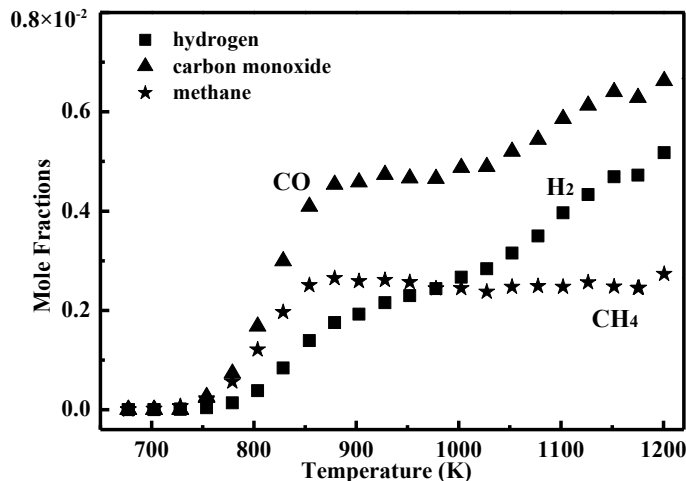


Figure 3. Mole fraction profiles of hydrogen, carbon monoxide and methane.

Figure 4 shows the main hydrocarbon intermediate species profiles. As can be seen at  $T > 825$  K,  $\text{CH}_3\text{OH}$  concentration begins to decrease. And at  $T = 1200$  K, it is almost completely consumed. For the mole fractions of  $\text{C}_2\text{H}_6$  and  $\text{C}_2\text{H}_4$  species begin to decrease at 1050 K and 1200 K, respectively. In addition, the  $\text{C}_2\text{H}_2$  is difficult to form at low temperature and begins to appear at  $T > 1100$  K.

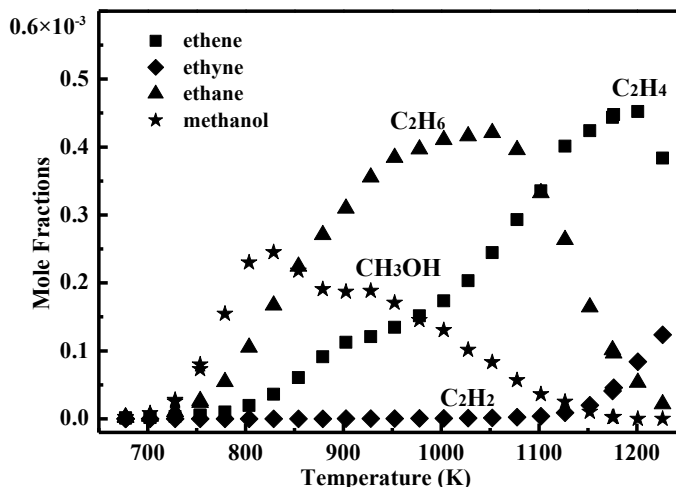


Figure 4. Mole fraction profiles of ethene, ethyne, ethane and methanol.

#### 4 Validation of the Mathieu-model

The model of Mathieu et al. [8] is based on the work of  $\text{H}_2/\text{N}_2\text{O}$  [9],  $\text{H}_2/\text{NO}_2$  [10],  $\text{NH}_3/\text{NO}/\text{N}_2\text{O}$  [11], and  $\text{CH}_4/\text{NO}_2/\text{N}_2\text{O}$  [12]. That work has been extended with the nitromethane sub-mechanisms from Brequigny et al. [13] and some reactions from the recent study of Annesley et al. [14]. Especially, the decomposition reactions for nitromethane ( $\text{CH}_3\text{NO}_2 = \text{CH}_3 + \text{NO}_2$  and  $\text{CH}_3\text{NO}_2 = \text{CH}_3\text{O} + \text{NO}$ ) are adopted from Annesley et al. [14]. The simulation on JSR data was conducted on CHEMKIN-PRO using PSR code [15].

Comparison between the simulation results of Mathieu et al. [8] and experimental data is conducted. As shown in Figure 5(a), the model of Mathieu et al. could capture the concentration profile of the fuel both qualitatively and quantitatively. In Figure 5(b), at  $T < 900$  K, there is a reasonable fitting result between the experimental data and simulations. While, at  $T > 900$  K, the concentration profiles of  $H_2$  and  $CO$  continue to raise and  $CH_4$  profile keeps constant, the predictions of Mathieu et al. keeps basically the same, even slight drop. Especially, for the  $CO$  and  $H_2$ , the mechanism may need to be considered at related reactions.

In Figure 5(c) and (d), the simulations of  $C_2H_4$ ,  $CH_3OH$  and  $C_2H_6$  reach the maximum concentrations at 1050 K, 825 K and 850 K, respectively. While the corresponding experimental maximum concentration points are at 1200 K, 825 K and 1050 K, respectively. The predicted mole fraction of  $C_2H_2$  is higher than the experimental data.

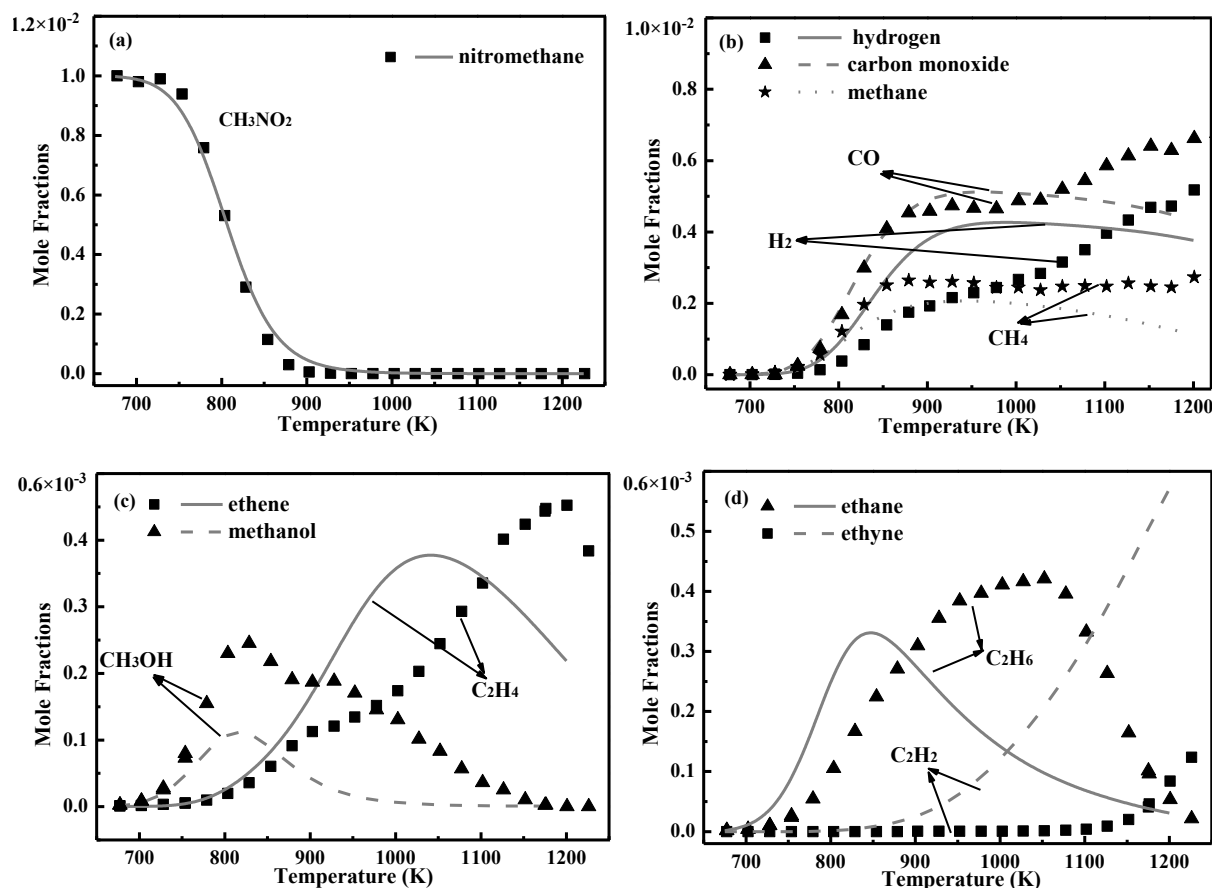


Figure 5. Comparison between JSR data and the predictions of the model from Mathieu et al. [8].

## 5 Conclusion

To summarize, this work, in the first time, develops the thermal decomposition experiment of nitromethane using a well validated jet-stirred reactor (JSR). 8 important species concentrations are obtained at the temperature range 675–1225 K. In addition, the detailed discussions about the mole fraction profiles also are presented. The recent model of Mathieu et al. [8] has been validated using the

JSR experimental data in the work. In further studies, the important N-containing species like NO will be measured and compared. Then based on the experimental data, the existing mechanism will be improved.

## 6 Acknowledgement

This work is supported by the Science Challenge Project (No. TZ2016001).

## References

- [1] S. Kelzenberg, N. Eisenreich, W. Eckl, V. Weiser, Modelling nitromethane combustion, *Propell. Explos. Pyrot.* 24 (1999) 189–194.
- [2] R. Guirguis, D. Hsu, D. Bogan, E. Oran, A mechanism for ignition of high-temperature gaseous nitromethane—The key role of the nitro group in chemical explosives, *Combust. Flame* 61 (1985) 51-62.
- [3] K. Glänzer, J. Troe, Thermische zerfallsreaktionen von nitroverbindungen I: Dissoziation von nitromethane, *Helv. Chim. Acta* 55 (1972) 2884.
- [4] A. Perche, J.C. Tricot, M. Lucquin, Pyrolysis of nitromethane.1. Experimental-study- nitromethane alone and in the presence of additives, *J. Chem. Res.* 4 (1979) 116–117.
- [5] D.S.Y. Hsu, M.C. Lin, Laser probing and kinetic modeling of NO and CO production in shock-wave decomposition of nitromethane under highly diluted conditions, *J. Energ. Mat.* 3 (1985) 95-127.
- [6] Y.X. Zhang, S.H. Bauer, Modeling the decomposition of nitromethane, induced by shock heating, *J. Phys. Chem. B* 101 (1997) 8717-8726.
- [7] P. Glarborg, A.B. Bendtsen, J.A. Miller, Nitromethane dissociation: Implications for the  $\text{CH}_3 + \text{NO}_2$  reaction, *Int. J. Chem. Kinet.* 31 (1999) 591-602.
- [8] O. Mathieu, B. Giri, A.R. Agard, T.N. Adams, J.D. Mertens, E.L. Petersen, Nitromethane ignition behind reflected shock waves: Experimental and numerical study, *Fuel* 182 (2016) 597-612.
- [9] O. Mathieu, A. Levacque, E.L. Petersen, Effects of  $\text{N}_2\text{O}$  addition on the ignition of  $\text{H}_2 - \text{O}_2$  mixtures: Experimental and detailed kinetic modeling study, *Int. J. Hydrogen Energ.* 37 (2012) 15393-15405.
- [10] O. Mathieu, A. Levacque, E.L. Petersen, Effects of  $\text{NO}_2$  addition on hydrogen ignition behind reflected shock waves, *Proc. Combust. Inst.* 34 (2013) 633-640.
- [11] O. Mathieu, E.L. Petersen, Experimental and modeling study on the high-temperature oxidation of Ammonia and related  $\text{NO}_x$  chemistry, *Combust. Flame* 162 (2015) 554-570.
- [12] O. Mathieu, J.M. Pemelton, G. Bourque, E.L. Petersen, Shock-induced ignition of methane sensitized by  $\text{NO}_2$  and  $\text{N}_2\text{O}$ , *Combust. Flame* 162 (2015) 3053-3070.
- [13] P. Brequigny, G. Dayma, F. Halter, C. Mounaïm-Rousselle, T. Dubois, P. Dagaut, Laminar burning velocities of premixed nitromethane/air flames: An experimental and kinetic modeling study, *Proc. Combust. Inst.* 35 (2015) 703-710.
- [14] C.J. Annesley, J.B. Randazzo, S.J. Klippenstein, L.B. Harding, A.W. Jasper, Y. Georgievskii, B. Ruscic, R.S. Tranter, Thermal dissociation and roaming isomerization of nitromethane: Experiment and theory, *J. Phys. Chem. A* 119 (2015) 7872-7893.
- [15] R. Design, CHEMKIN-PRO 15151. Reaction Design San Diego, 2016.