Experimental and Theoretical Investigations on the Burning Behaviour of Liquid and Gelled Nitromethane Monopropellants

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Abstract

Recently gelled propellants are in the scope of rocket propulsion interest as energy source for missiles with controlled thrust and save handling. Purpose of this study was to characterise the influence of the gellification of nitromethane (NM) as monopropellant on the combustion behaviour under rocket motor conditions. Experiments were performed using NM gelled with Aerosil and an organic gelling agent. For characterizing the burning behaviour liquid and gelled NM was combusted in test tubes in a window bomb under pressure up to 13 MPa. The burning rate and visible flame structure was measured optically, the flame temperature was analyzed using a rapid NIR emission spectrometer. The main reaction products were studied in atmospheric pool fire of the same propellants. For a better understanding of the combustion phenomena a one dimensional combustion model was applied that calculates transient burning of mono-propellants under pressure regarding heat and mass flow in the condensed and gaseous phase, evaporation according to Clausius-Clapeyron and a simplified overall chemical kinetics in the gas phase as a 2-step chain reaction. The kinetic parameters were derived from CHEMKIN calculations. All material properties were set to liquid NM only the reaction order and pre-exponential factor of the 2nd reaction step were wangled to adapt the calculated values to the measurements. Gellification was simulated by varying boiling point and the heat of evaporation.

1. Introduction

Gelled propellants are of recent interest in the scope of rocket propulsion as energy source for missiles with controlled thrust and save handling [1]. The gellification of liquid propellants alters not only the physical state, surface tension and viscosity or rheology which mainly affects storage and atomization [2] but has also a considerable influence on the ignition and combustion behaviour of the energetic material.

While the usually low amount of gelling agent vary the combustion chemistry only by catalytic effects physicochemical qualities like evaporation and heat flow inside the propellant are changed completely through a higher vapour pressure and different boiling point as well as an inhibited internal convection.

Purpose of this study was to characterise the influence of the gellification of nitromethane on the combustion behaviour under rocket motor conditions.

2. Experimental

2.1 Propellants

Nitromethane (CH_3NO_2, NM) is a high energetic liquid monopropellant with a theoretical specific impulse of 2400 N s kg^{-1} and is a promising substance to be used as a gelled monopropellant [3], [4]. NM is regarded as a green propellant with low vulnerability and can be produced well-priced and handled easily. For this investigation pure liquid NM was compared with two gelled samples. NMG-0-10 was gelled with 10% of an energetic organic gelling agent not more specified. The second gel NMG-5-5 was gelled with 5% of the same gelling agent and 5% Aerosil. Aerosil is a trade mark from Degussa [5] for a fumed silica with the general formula $[SiO_x(OH)_{4-2x}]_n$. Table 1 summarises some characterising parameter of the samples. The heat of combustion of the gels is slightly higher than that of pure NM. But most interesting is the flash point that shows the gelled samples are easier to ignite than the liquid.

Table 1: Parameter of used samples

	NM	**NMG-5-5**	**NMG-0-10**
Density	1.120 g cm^{-3}	1.130 g cm^{-3}	1.162 g cm^{-3}
Viscosity (Shear rate 10^{-3} s^{-1})	0.9 Pa s	10^5 Pa s	500 Pa s
Viscosity (Shear rate 10^{3} s^{-1})	0.9 Pa s	0.2 Pa s	0.2 Pa s
Heat of combustion	11600 kJ/kg	11950 kJ/kg	13000 kJ/kg
Flash point	37°C (35°C*)	26-27°C*	26°C*
Shock sensitivity	3.0 Nm	10.0 Nm	15.0 Nm
Friction sensitivity	108 N	80 N	96 N
Mass specific impulse (7 MPa)**	2396 Ns/kg	2247 Ns/kg	2258 Ns/kg
Vol. specific impulse (7 MPa)**	2729 Ns/dm^3	2612 Ns/ dm^3	2623 Ns/ dm^3
Adiabatic flame temperature**	2467 K	2173 K	2194 K
Mean molecular weight of reaction products**	20.332 g/mol	19.980 g/mol	18.763 g/mol

* Pensky-Martens method, received without stirring
**calculated with ICT-Thermodynamic Code [15]

Thermogravimetric measurements with different heating rates of 1, 5 and 20 K/min result in a significantly delayed evaporation process when NM is gelled. The delay increases with increasing heating rate. E.g. at a heating rate of 20 K/min liquid NM was completely evaporated at 40°C. Under the same conditions the evaporation process of NMG-5-5 lasts up to 130°C.

2.2 Set-Ups

To investigate chemical reactions at ignition conditions pool fire investigations were performed in a porcelain pan of 60 mm diameter and 5 mm height under atmospheric conditions. At the beginning of each experiment the pan was filled up to 1 mm below the rim. Fuel temperature was initially about room temperature (20 to 25°C). A blowtorch was used to ignite the fuel.

Pressurised combustion was observed in a chimney type window bomb equipped with two quartz windows under 3, 4, ... 13 MPa (nitrogen) (comp. [6]). The samples of pure and gelled NM were filled into test tubes (7 mm diameter, 70 mm length) of quartz glass using a syringe with a 2 mm canola. It was specially attended to avoid bubbles inside the tubes filled with gel. The test tubes were fixed vertically inside the bomb according to strand burner experiments with solid propellants [6]. Ignition was performed with a small cylindrical peace of a solid propellant equipped with a melting wire.

2.3 Measurement Techniques and Analysis

The combustion progress was recorded using a DV-Camcorder (Panasonic NV-DX110) to receive a visual impression of the reaction zone and the burning rate. An exposure time of 1/1000 s at full aperture was used. Using a PC the frame rate was increased to 50 fps by separating of the even and odd interlaced frames. The burning rate was received applying the AVICOR picture analysis tool evaluating the regression of the propellant surface [7].

For the acquisition of emission spectra in the UV/Vis-range a commercial diode array spectrometer from LOT was available. The chosen monochromators allowed detecting a wavelength range from 170 to 1000 nm (focal length 250 mm, entrance slit 50 µm). The detector is equipped with a 1024 element Si-diode array. Minimum time resolution of the system is 10 ms. Wavelength calibration is performed by standard lamps of Hg and Ne.

To receive NIR-spectra a Plane Grating Spectrometer PGS-NIR 2.2 from Carl ZEISS GmbH was used. The wavelength of this monolithic miniature spectrograph (MMS) ranges from 1 to 2.17 µm with 300 lines/mm and is blazed for 1.4 µm. This results in a spectral resolution of 16 nm. Integration time varies from 100 µs to 1.6 s with a shortest interval of about 13 ms. The diode array consists in an InGaAs-sensor manufactured by Hamamatsu with 256 lines of 50 µm x 250 µm. As optical entrance a 600 µm glass fibre is used, equipped with a 100 µm pin hole which limits the acceptance angle to 7°. The evaluation of NIR spectra uses the ICT-BaM code to model spectra of gaseous reaction products, soot and continuum radiation. The procedure is described in more details in [8]. For the recent application the water bands at 1.1 to 1.2 µm, 1.3 to 1.6 µm and 1.7 to 2.1 µm were evaluated. Continuum radiation was regarded as a black body with constant emissivity (grey-body radiation).

3. Experimental Results

3.1 Pool Fire

A pool fire burning in ambient atmosphere enables to analyse flame species in UV/Vis range that allow conclusions to the reaction mechanism. Under pressure conditions this species live to short and could not be detected in the window bomb. The experiments result in spectra of numerous emitting species especially in UV range like CO, NO, OH, NH, CN and CH. These molecules belong mainly to the type of intermediary combustion species and hot flame gas radicals [9][10]. An example is presented in Figure 1. In visible and NIR range mainly water bands were detected. A very week continuum was detected indicating that only few particles were evolved into the gas phase. Under this conditions nearly all Aerosil remained in the condensed phase without melting. This effect is investigated in more details in [11]. Additional investigations in IR range results in combustion products like water, CO_2, CO, NO [12]. In all pool fire investigations of the emitting flames absolutely no significant difference in species or intensity distribution (that would qualify different concentrations or temperatures) could be observed between pure and gelled NM (compare black and red line in Figure 1). So these investigations suggest that at least under ignition conditions at low pressure liquid and gelled NM react with similar reaction kinetics.

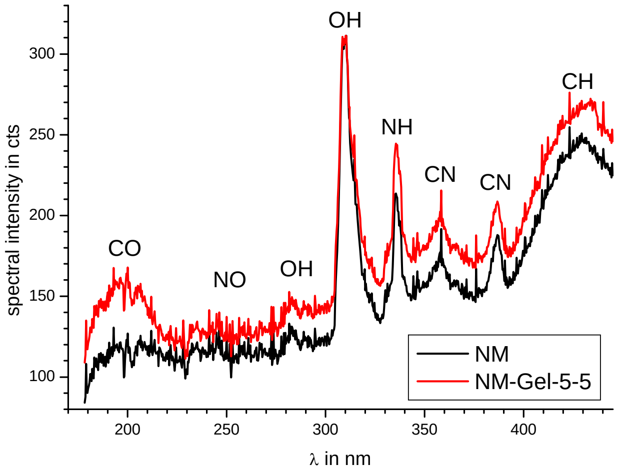

Figure 1: UV spectra of nitromethane in liquid and gelled state.

3.2 Combustion under Pressure

Under pressure conditions the visible flame structures of all samples differ in a meaningful way as shown in Figure 2. Pure NM burns with a smooth flame weakly lighting in yellow to red colour. No significant reaction zones can be distinguished. No bubbles were observed in the liquid phase. The flame structure of NMG-0-10 with organic binder is much more inhomogeneous and emits in a more yellow colour. The recorded NIR-spectra feature a continuum radiation that probably indicates burning soot particles. The pictures also denote that most soot radiation is emitted several millimetres above the propellant surface and might not have a significant influence to the burning rate that usually is dominated from the flame gas reaction less than 500 µm above the fuel level [13]. NMG-5-5 also including Aerosil exhibits a similar flame than liquid NM but show distinct yellow glowing structures of a solid material starting directly at the surface. These structures remain as vitreous residues after the total reaction in the test tube. Like investigated in [11] they consist in residues of Aerosil molten by the heat of NM combustion.

The total flame length of all samples is increasing with pressure. Compared to most solid propellants (e.g. double base [14]) where flame length usually decreases with pressure the flame is exceptional long. This indicates that the kinetics of the total burn out reactions of NM are relatively slow and depends only minor on pressure.

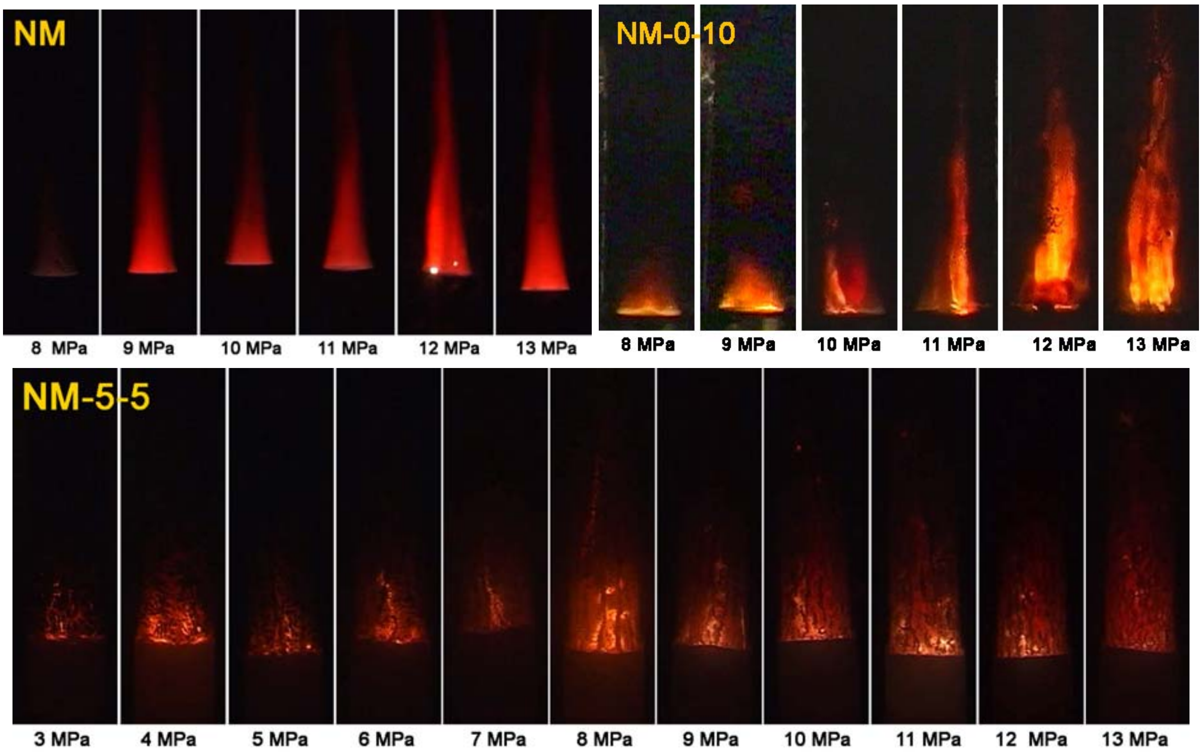

Figure 2: Frames of the combustion of pure nitromethane and gelled NM propellants at different pressure.

NM and NMG-0-10 did not ignite below 8 MPa. NMG-5-5 ignited at a lowest pressure of 3 MPa. After ignition the burning progress of all NM propellants is strongly linear and enables to determine repeatable regression rates that are summarised in Figure 3. At 10 MPa the regression rates are in the order of 1 to 2 mm s^{-1}. The burning velocities of pure NM and the organic gel NMG-0-10 are congruent. The values of NMG-5-5 also including Aerosil are about 30% lower. The pressure dependence of all samples can perfectly be described using the potential Vieille’s law resulting in pressure exponents close to 1, also inscribed in Figure 3. In scope that NM and NMG-0-10 are only investigated between 8 to 13 MPa the small deviations should not be overstated.

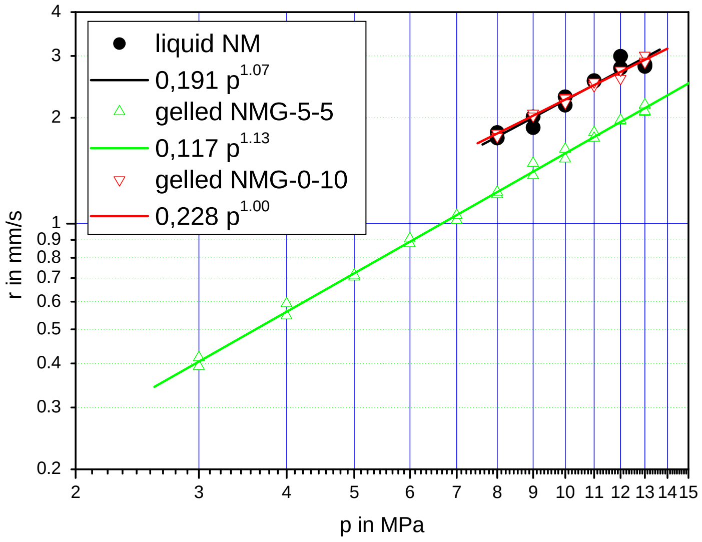

Figure 3: Regression rates measured by DV movies

In Figure 4 the measured maximum and mean flame temperatures of all samples received from the ICT-BaM analysis of NIR-spectra are presented as function of pressure. The analysis was dominated by evaluating the water bands emitted by nitromethane combustion product. At NMG-5-5 the influence of the weak continuum emitted from Aerosil exerted only a minor influence, so these values describes only the flame gases but not the molten Aerosil residues.

Between 8 and 13 MPa the mean temperature of all samples are constant at a level between 1900 and 2000 K. The values for NMG-5-5 at lower pressure decrease linearly to 1200 K at 3 MPa. The maximum temperatures are measured in the flame zone some millimetres above the propellant surface. The maximum values of all samples follow a similar function but are about 200 K higher than the mean values. The maximum temperatures between 8 and 13 MPa are about 300 K lower than the adiabatic flame temperature of NM calculated with ICT-Code and also plotted in Figure 4. This is a typical margin observed in hundreds of non-metallised solid and liquid propellant analysed in the same window bomb caused by convective heat loss to the pressure gas and radiative heat loss from the emitting flame to the bomb walls. So the measurements validate a total conversion rate of the propellants. The values of NMG-5-5 at pressure below 8 MPa are much lower than the adiabatic flame temperature and indicate an incomplete combustion.

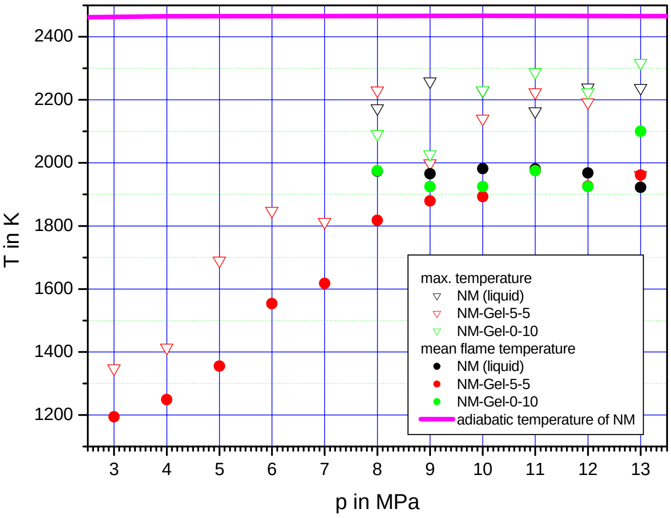

Figure 4: Maximum and mean flame temperatures received from ICT-BaM analysis and compared with adiabatic flame temperature of nitromethane calculated with ICT-Code [15]

4. Discussion including Modelling Calculations

Glarborg, Bendtsen and Miller developed a chemical reaction mechanism for nitromethane combustion including 77 species and 484 elementary reactions for use in CHEMKIN software package [16]. CHEMKIN II package developed at Sandia National Laboratories allow calculating the reaction progress of such a mechanism under isotherm or adiabatic and isobar conditions varying initial conditions and concentrations [17]. In Figure 5 some exemplary results for the isotherm decomposition and reaction of NM are presented. About 30 calculations were conducted for different boundary conditions on initial temperature and pressure under isotherm or adiabatic conditions. All calculations result in a 2-step mechanism how it is best obvious from the temperature development in Figure 5 (left). The most reasonable conditions concerning to our investigations are isotherm calculations with initial temperatures of 1000 to 1500 K. In this regime temperature rise in two steps where the first step release a heat that yield to a temperature increase that is about 20% than that of the second step. Results like presented in Figure 5 (right) describing the evolution of chemical species indicate that the first step is mainly dominated from the decomposition of NM that is given in the mechanism as:

$$\mathbf{CH_3NO_2 \longrightarrow CH_3 + NO_2} \qquad \mathbf{(1)}$$

The second step is dominated by the reaction of NO that seems to be responsible for the oxidation of most species. NO is mainly formed from the reaction

$$\mathbf{NO_2 \longrightarrow NO + \tfrac{1}{2}\,O_2} \qquad \mathbf{(2)}$$

The consumption of CH_3 is much faster and contributes by its heat release but less on its chemical kinetics on these two reaction steps. For following calculations the reactions (1) and (2) were considered as dominant.

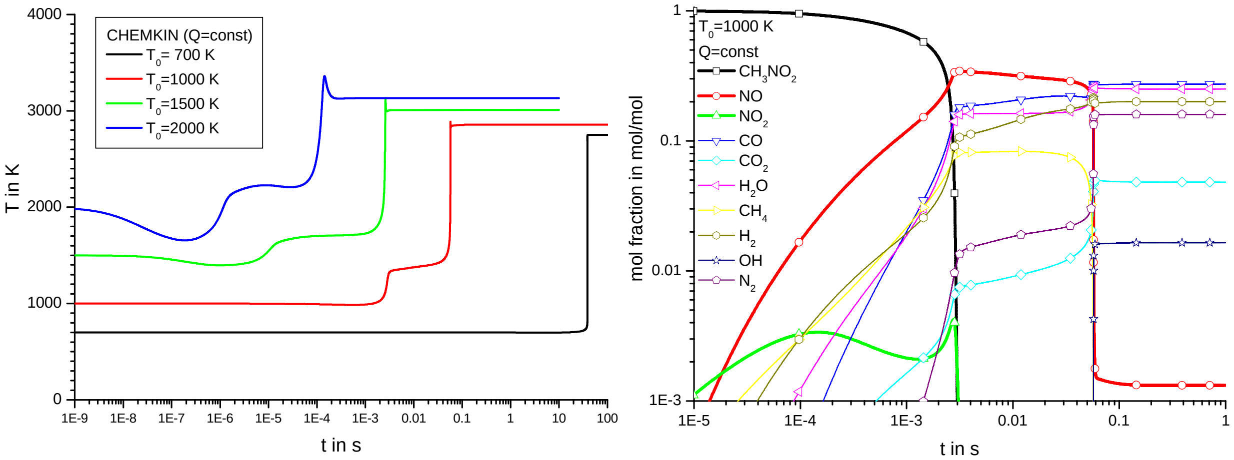

Figure 5: Adiabatic CHEMKIN calculations for NM combustion using reaction mechanism of Glarborg et al. [16]; left : temperature evolution for various initial temperatures T_0 ; right: evolution of main reacting species for T_0=1000 K.

For further investigations of the influence of these findings and the experimental results to the burning characteristic of NM and NM-gels a model named CTEM (Combustion Transients of Energetic Materials) was applied originally developed by Gusachenko, Zarko and Rychkov [18]-[20] and later modified in cooperation with ICT [21]-[24].

CTEM is a 1-dimensional computer code which simulates the transient burning of heterogeneous energetic materials. It takes into account time-dependent phenomena of condensed propellants subjected to time-variable heat flux and under varying pressure conditions. It allows studying the combustion response under modulated irradiation, varied pressure and under heat flux and pressure variation to investigate the stability of ignition and combustion. CTEM can include a solid and a liquid phase allowing the solid propellant to melt and evaporate at the surface using Clausius-Clapeyron relation. Depending on the optical properties of the propellant the radiant flux is absorbed in the depth of radiation penetration. In the condensed phase the heat flow equation is solved numerically. Also Chemical conversions can occur both in the condensed and gas phase as simplified overall reactions of n^{th} order. In the gaseous phase, in addition to the heat flow, the diffusion of three species is assumed which can undergo a two-step consecutive reaction.

All available chemical and physical constants like specific heat capacity, heat of evaporation, thermal conductivity, density etc. of nitromethane were include like summarised in Table 2 received from diverse data bases and ICT-Code calculations (Table 1). For chemical kinetic scheme a 2-step consecutive reaction with reaction (1) and (2) was chosen. Both reactions were assumed to obey an Arrhenius law. The heat release of both reactions was divided as 1 to 4 following Figure 5 (left) and receiving a final temperature of about 2200 K that is in coincidence with the measurements (Figure 4). The order, activation energy and pre-exponential factor of the decomposition of NM (1) was taken from [25] as E_A=225 kJ/mol; log k_0 = 14.6; 1st order. The activation energy of NO_2 to NO (2) was taken from the same source (original: E_A=113 kJ/mol; log k_0=9.9; 2nd order). The order of this reaction was changed to 3 and the pre-exponential factor was chosen as only parameter to wangle the experimental results to the measured ones. Both seems to be permitted as one has to keep in mind that the chosen 2-step reaction scheme is a strong simplification and much more species and reactions included in the 2nd step will have a contribution to the burning behaviour of NM. Like presented in Table 2 the resulting values of the pre-exponential factors are still in a very reliable order and the change from 2nd order to 3rd order is plausible for the total reaction of NM to H_2O, H_2, CO and N_2 (comp. Figure 5 right). Figure 6 shows the measured burning rate of Figure 3 in comparison with some of the modelling calculations including the pressure exponent n. As shown by the calculation NMSim56 (dark blue curve) performed with a 2nd order reaction like Eq. (2) is characterised in [25] the pressure exponent can not be described correctly. But NMSim60 (light blue curve) calculated with a 3rd order reaction fits the regression rates of NM and NMG-0-10 nearly perfectly. To investigate if the lower burning rate of NMG-5-5 could be explained by a heat loss from the melting of Aerosil calculation NMSim63 was performed with an increased heat of evaporation. By such method it was succeeded to describe the lower burning rate without changing the pressure exponent. In calculation NMSim64 additionally the boiling point was increased like found in TGA measurement for gelled propellants (see chapter 2.1). This did not affect the modelled burning rates very much.

Table 2: Parameter for calculations with CTEM model

Condensed phase:	
Heat conductivity	0.21 W m^{-1} K^{-1}
Heat capacity	1.7500 kJ kg K^{-1}
Density	1139 kg m^{-3}
Initial temperature	293 K
Heat of evaporation	556.80 kJ kg^{-1}
Boiling point	374.5 K
Molar weight	61 kg $kmol^{-1}$

Gas_phase:	**Reaction 1**	**Reaction 2**
Molar weight	30.5 kg $kmol^{-1}$	20.3 kg $kmol^{-1}$
Enthalpy of reaction	1100 kJ mol^{-1}	4400 kJ mol^{-1}
Activation energy	225 MJ mol^{-1}	113 MJ mol^{-1}

Reaction 2:	**Pre-exponential factor**	**Reaction order**	**Heat of evaporation**	**Boiling point**
NMSim56	2.5 10^{11}	2	556.8 kJ kg^{-1}	374.5 K
NMSim60	8 10^{13}	3	556.8 kJ kg^{-1}	374.5 K
NMSim63	8 10^{14}	3	1000 kJ kg^{-1}	374.5 K
NMSim64	8 10^{14}	3	1000 kJ kg^{-1}	424.5 K

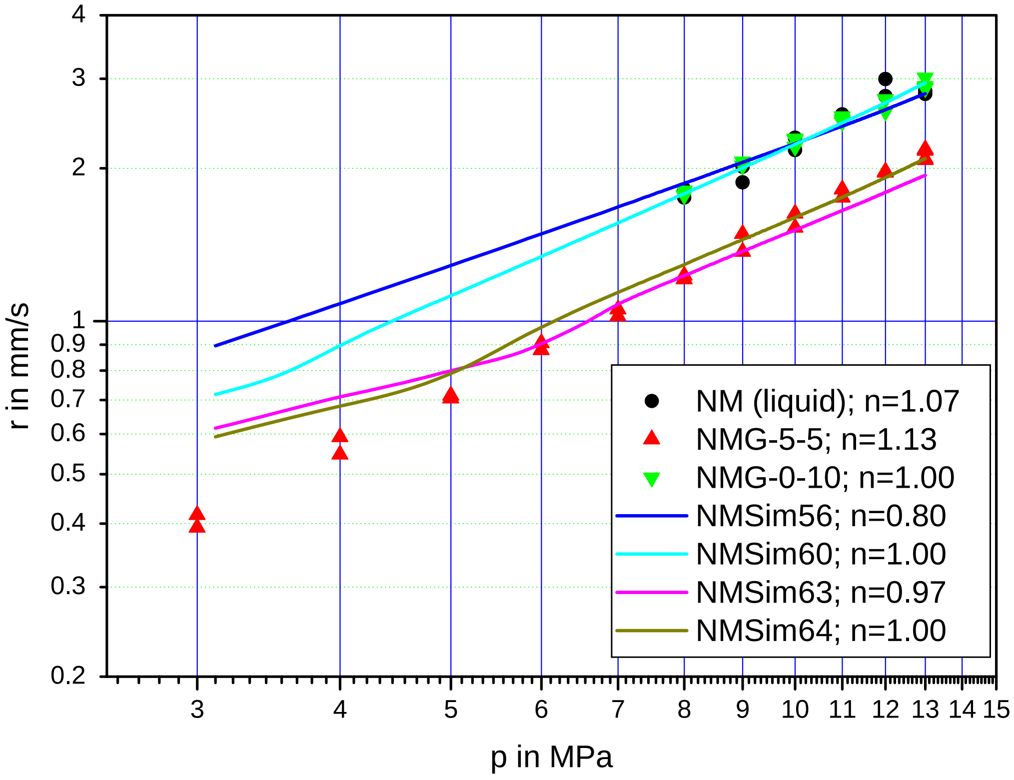

Figure 6: Burning rates of liquid and gelled NM (full dots) compared with CTEM calculation of NM combustion; in the agenda additionally the pressure exponent n of the reactions is given.

5. Conclusions

The burning behaviour of pure and gelled nitromethane was investigated under pressure. No influence of gellification to the reaction mechanism could be demonstrated. The experiments show only a minor influence to the burning rate, pressure exponent and flame temperatures. With the help of CHEMKIN calculations parameter for a simplified reaction mechanism were derived that allow describing the pressure dependence of NM combustion. A parameter study resulted in a pressure exponent mainly influenced by the reaction order of the overall gas reaction.

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