Experimental and numerical study of 1-Pentanol pyrolysis in a shock tube at high pressure and high temperature

D. Nativel, R. Grosseuvres, A. Comandini, S. Abid, N. Chaumeix
ICARE, CNRS-INSIS, Orléans, France

1 Introduction

Due to the increase of greenhouse gases and the finite sources of fossil energies, alternative fuels are the focus of many current research programs. Moreover, European regulation imposes a proportion of 20 % of biofuel in conventional fuels. Currently, ethanol is widely used as a biofuel but it has several drawbacks such as a low energy density and source of supply related to food-stock. Heavier alcohols are foreseen since they have higher energy densities and are less hygroscopic. Among all the heavier alcohols, 1-pentanol seems to be a good candidate. A better understanding of its decomposition, at engine-like combustion conditions, is a requirement, as a first step, in order to construct a detailed kinetic mechanism that will describe its combustion. In the present study, new experimental data on 1-pentanol decomposition are acquired using a heated high pressure shock tube coupled to a Gas Chromatograph equipped with different detectors (FID, MS). This analytical system allowed an on-line sampling of the gases behind reflected shock waves via a high speed valve. As a first step, this new method was assessed through the study of the n-heptane pyrolysis behind reflected shock waves. N-heptane was chosen because its chemistry is well established. Indeed, it has been subject to numerous experimental and modeling studies which led to a comprehensive and detailed understanding of the associated chemistry. The methodology validation is presented, then the results obtained for the decomposition of 1-pentanol pyrolysis was undertaken. A comparison with simulated results based on Togbé et al. mechanism and Heufer et al. mechanism are also presented.

2 Experimental

The heated shock tube has been described in detail in a previous publication [1]. Briefly, experiments were carried out behind reflected shock waves in a stainless steel shock tube with a 2 m long driver section and a 4.70 m driven section with a 52.4 mm internal diameter (Figure 1). This tube is designed for initial pressures up to 40 bars and initial temperatures up to 403 K. Both of the two shock tube portions were evacuated using two primary vacuum pumps. Mixtures of helium and argon were used as driver gas, and the shock wave was initiated by the bursting of a double diaphragm. Four piezoelectric pressure transducers (Chimie Metal, Model A25L05B) with a sensitive surface area of 0.75 mm^2 and a rise time of 0.4 µs were used to measure the shock velocity over the last section (0.7 m long) and were mounted flush with the inner surface of the tube, the last one being at 10 mm from the end-wall. The very small surface area coupled with a short rise time allows precise determination of the shock wave passage and, consequently, more accurate evaluation of the temperature and pressure behind reflected shock waves (reflected shock pressure, P_5, and temperature,

Correspondence to: damien.nativel@cnrs-orleans.fr

T_5, were calculated using the classical shock tube equations [2]). Additionally, a Kistler pressure transducer (model 603B1) is mounted at the end-wall, provided quantitative reaction pressure and reaction times measurements. The outputs from the pressure transducers were recorded using two numerical oscilloscopes (Tektronix TDS5034B). The reactive gas mixtures were prepared manometrically using four capacitance manometer MKS Baratron type 631 in a 30 L stainless steel reservoir equipped with magnetic fans to ensure homogeneous composition prior to experiments being performed. A typical reagent mixtures contained 100ppm fuel (purity ≥99.5% if n-heptane, ≥99% if 1-pentanol, both Sigma Aldrich) with balance Argon (Air Liquide 99,999%). The whole setup (shock tube, tubing and reservoir) has been heated up to an initial temperature of 90 °C in order to avoid any condensation or adsorption on the walls. The analytical apparatus utilized in the present study consist of a Thermo Ultra Trace gas chromatograph coupled to a mass spectrometer (GC-MS). The GC part is equipped with a flame ionization detector (FID) and a thermal conductivity detector (TCD). The mass spectrometer is also used as a detector. Two HP-PLOT Q columns were used in this study, one 30m x 0.53mm x 40.0µm for the n-heptane study and one 30m x 0.32mm x 20.0µm for the 1-pentanol study.

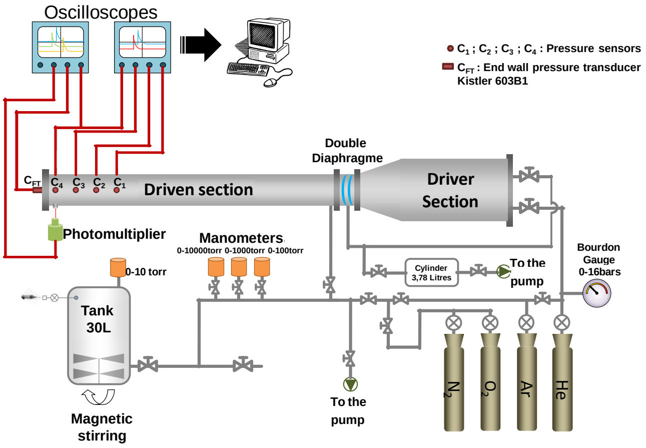

Figure 1: Schematic of the high pressure heated shock tube used for this study

3 Results and discussion

3.1 Calibration and validation of the experimental set-up

After the implementation of the analytical apparatus and coupling with the shock tube it was necessary to validate its ability to sample efficiently behind reflected shock waves for a known residence time and calibrated reaction pressure and temperature. The methodology adopted is hereafter detailed: (i) decompose n-heptane behind a reflected shock wave ; (ii) characterize the stable intermediate species with GC-MS ; (iii) modeling of the decomposition of n-heptane with the LLNL detailed kinetic model [3] ; (iv) comparison between simulation and experiments. N-heptane was a good candidate since its chemistry is well established. Indeed, n-heptane has been subject to numerous experimental and modeling studies which led to a comprehensive and detailed understanding of the associated chemistry [3-12]. The current n-heptane chemical kinetic models, which have been continuously optimized over the last few decades by many research groups, are capable of accurately simulate a large number of experimental results. Thus, n-heptane was an excellent choice as a target species for the verification of a new experimental set-up such as the one implemented at ICARE, for the measurement of stable intermediates from shock tube experiments through gas chromatographic techniques.

3.1.1 Decomposition of n-heptane

N-heptane decomposition experiments were performed over a wide temperature range of 800-1600 K and at a nominal pressure P_5 of 10 bars. Good repeatability was observed in this series of experiments, and a good carbon balance of 100 ± 3% was determined between 800 and 1200K and 100 ± 10% between 1200 and 1600K. This 10% is due to the fact that after 1200K other products were formed but not identified and measured. The major stable species formed in these experiments (>20ppm) were: acetylene, ethylene, methane, ethane and propylene. Propane, propadiene, propyne, 1-butene, n-butane, 1-butyne, 2-butyne, 1-pentene and pentane were observed and quantified at a concentration <10ppm. As can be seen in Figure 2, the consumption of the fuel occurs at ~1020 K with a corresponding beginning of formation of ethylene, ethane, propylene, propylene, methane and butane. The beginning of formation of acetylene, propyne and propadiene is observed 70 K later. A maximum of concentration of the products is observed between 1230 and 1330 K, except for 1-butene (maximum at 1120 K), methane (maximum at 1450 K) and for acetylene the maximum of concentration was not observed since at the final temperature of this study the total formation of acetylene was not achieved. After 1200 K, approximately 90% of the fuel has been consumed.

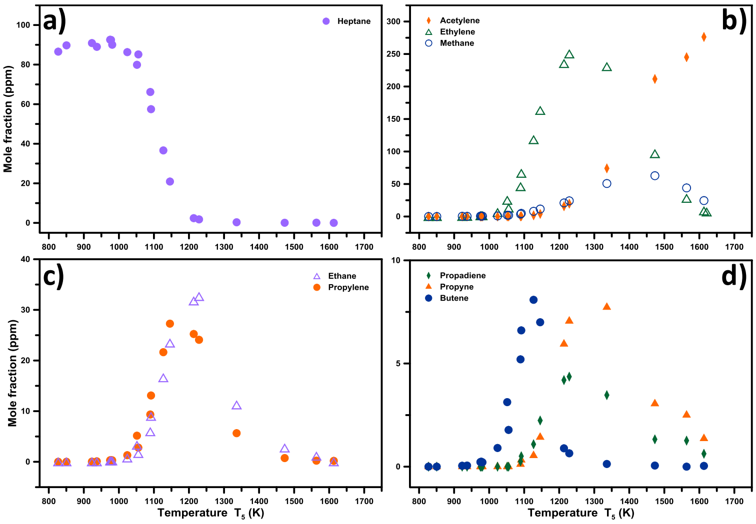

Figure 2: n-heptane decomposition experiments at 10 bar showing fuel decay a); acetylene, ethylene and methane formation c); ethane and propylene formation c); propadiene, propyne and butene formation d) as a function of the tecflected shock temperature, T_5.

3.1.2 Modeling of the decomposition of n-heptane

The experimental data from the decomposition of n-heptane have been simulated using the LLNL model [3]. This model is composed of 654 species and 2827 reversibles reactions and is capable to accurately simulate a large domain of experimental results at high and low temperature. Simulations were performed using COSILAB software with the Transient Homogeneous Systems code. To perform the simulation, the reaction time of each experiment was necessary. A series of experiments were conducted between 800K and 1600K with a pressure transducer (Kistler 603B1) at the end-wall instead of the automated valve. The driven section was filled with argon owing to the fact that highly diluted mixtures are used for speciation profiles experiments. The initial temperature was 90°C and the nominal pressure P_5 was 10 bars. With this new series of experiments, a calibration of the shock tube was done in order to have the evolution of the pressure with time and to have an estimation of the reaction time for various number of mach.

- **Pressure and reaction time**

From the pressure transducer trace the reaction time was determined by the method described by Hidaka et al. [13]. After the reaction time, the temperature in the reaction zone rapidly drops at a rate approximately 2.0 x 10^5 K/s. Figure 3a shows how to estimate the reaction time and on Figure 3b the evolution of the reaction time is represented against the temperature T_5 where one point represents one experiment. This last figure was used to determine the reaction time for each n-heptane experiments knowing the temperature T_5 of each experiment (and for the next part, n-pentanol experiments). Figure 3a also shows two important phenomena: first, a variation in the pressure history due to non ideal behavior (like boundary layer growth or diaphragm bursting mechanics) and secondly, a bump. An explanation for the apparition of that bump is given on the paper of Hong et al. [14]. During the experiments, the shocks were “tailored” by adding argon on the driver section to prevent interaction between the reflected shock wave and the contact surface. The issue here is that even if the shocks are tailored or almost tailored, the interface between the driver and driven gases is not ideal (not infinitely thin and flat) and a bump is formed. Thus, the evolution of the pressure is not constant and the use of the pressure evolution with time directly on the simulation was necessary to be more realistic.

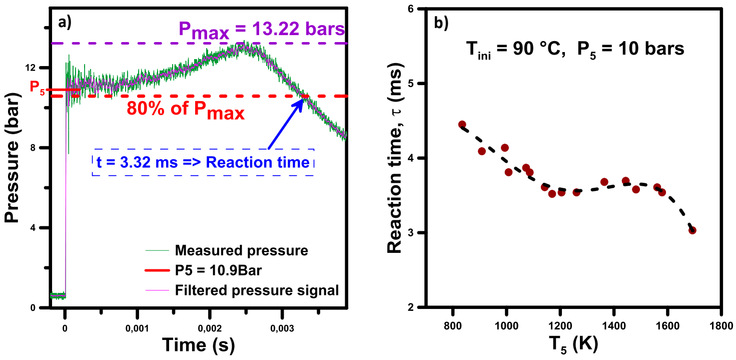

Figure 3: Definition of the reaction time on a pressure trace a); Evolution of the reaction time with the temperature b)

- Comparison between experiments and simulation

Figure 4 show the LLNL model predictions for the fuel decay of n-heptane and corresponding major stable species formation (acetylene, ethylene, propylene) obtained from the pyrolysis experiments. Two different simulations were done : first at constant pressure (solid lines) and then with the real pressure profiles (dash lines). At constant pressure, the model predicts well the fuel decay and the products profiles but it is slightly shifted in temperature. On the other hand, at variable pressure, the LLNL model is able to match, very well, the experimental n-heptane decay profiles and the products profiles with minor under predictions observed for ethylene at the maximum of formation.

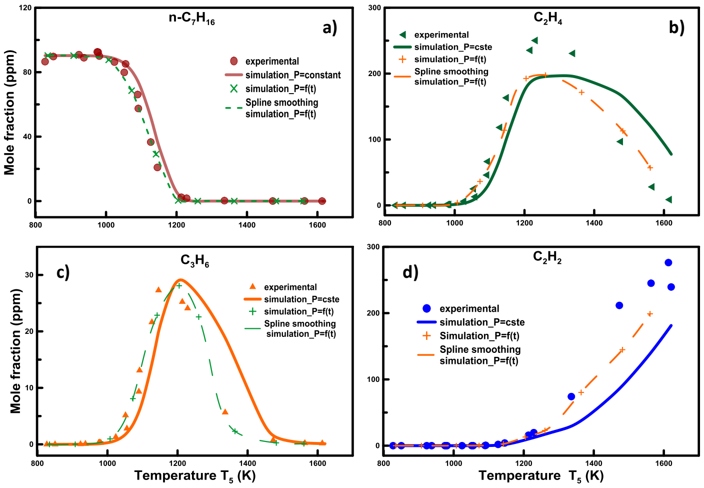

Figure 4: LLNL model predictions compared against experimental results at 10 bars for 100 ppm n-heptane decomposition. a) n-C_7H_{16} concentration profile; b) C_2H_4 concentration profile; c) C_3H_6 concentration profile; d) C_2H_2 concentration profile

The modeling results indicate that the LLNL model is able to make very good predictions for species profiles obtained at 10 bars for n-heptane decomposition over a broad temperature range. Consequently, the experimental set-up “high pressure heated shock tube + Gas Chromatography” is validated.

3.2 1-pentanol species profiles, experiments and modeling

The n-pentanol decomposition experiments were performed at 10 bars and over a wide range of temperature range 800-1400 K. Preliminary experiments were done to identify the major species obtained after decomposition. A good carbon balance of 100 ± 5% was found up to T_5 = 1200 K indicating that all the species have been accounted for. Above T_5 = 1200K, the carbon balance is reasonably good with 100 ± 17% which suggests that at the higher temperatures either not all the species are being recovered from the shock tube or that they are not being detected in the GC analytical system. The mass spectrometer was used and because of its low sensitivity limit compared to the FID detector, the experiments were conducted with 1000 ppm of fuel. The major species detected were : ethylene, ethane, acetylene, propylene, propane, propyne, propadiene, acetaldehyde, 1-butene, vinylacetylene, 1.3-butadiene, 1-pentene and diacetylene. The rest of the study was performed with 100 ppm of fuel and using the FID detector on the analytical set-up. Methane was also detected. All the species detected were quantified except diacetylene. As can be seen in figure 5, the consumption of the fuel occurs at ~1000 K accompanied with a rapid formation of ethylene, acetaldehyde and propylene. Ethylene, acetylene and methane are the main intermediate products formed.

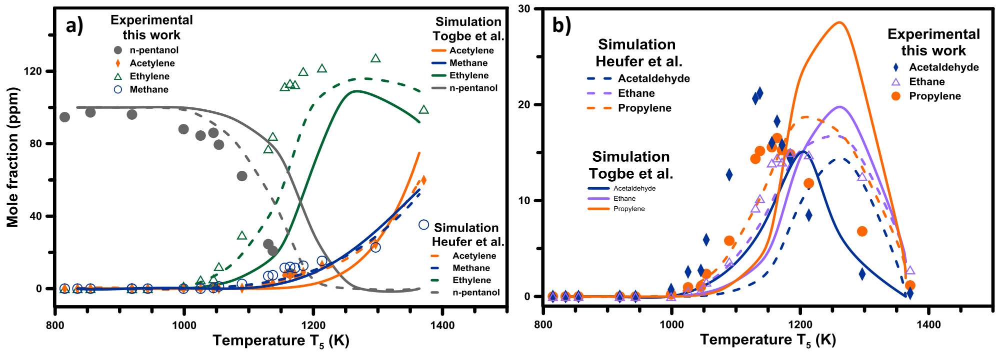

Figure 5: Togbe et al. and Heufer et al. model predictions compared against experimental results at 10 bars for 100 ppm n-pentanol decomposition

Figure 5 show also a comparison with the Togbe et al. [15] Heufer et al. [16] model predictions. The modeling study was done using the method described in section 3.1.2). These models are tested for the first time against highly diluted shock tube species profiles. The consumption of the fuel and the intermediate species formation are qualitatively reproduced even if a shift in the temperature is observed. It seems that the best prediction of intermediates concentration is achieved by Heufer et al. model.

4 Summary and conclusions

A high pressure heated shock tube has been coupled to a GC-MS analytical system. Further to the coupling, an online analysis of stable species from n-heptane pyrolysis behind a reflected shock wave was achieved. The experiments were conducted between 800 K and 1600 K at around 10 bars. The major stable species formed in these experiments (>20ppm) were: acetylene, ethylene, methane, ethane and propylene. Propane, propadiene, propyne, 1-butene, n-butane, 1-butyne, 2-butyne, 1-pentene and pentane were observed and quantified at a concentration <10ppm. A comparison with a detailed and extensively validated kinetic model (n-heptane, LLNL) allowed the validation of the technique. Indeed, a perfect prediction of the experimental results was observed with the modeling study. New values of species profiles concentration for n-pentanol pyrolysis at 10 bars and between 800K and 1400K were obtained. The simulation of the pentanol experimental profiles were performed using the model of Togbe et al. and Heufer et al.. The best agreement with the measurements was achieved by Heufer et al. model.

Acknowledgements

The authors are grateful for the financial support of this work provided by the French Ministry of Education and the French Labex CAPRYSSES (Cinétique chimique et aérothermodynamique pour des propulsions et des systèmes énergétiques propres et sûrs).

References

[1] Douce F, Djebaïli-Chaumeix N, Paillard C.-E, Clinard C. (2000). Proc. Combust. Inst. 28: 2523.

[2] Gaydon and Hurle. (1963). The shock-tube in high-temperature chemical physics. Chapman and Hall Ltd. London.

[3] Mehl M, Pitz WJ, Westbrook CK, Curran HJ. (2011). Proc. Combust. Inst. 33: 193.

[4] Garner S, Sivaramakrishnan R, Brezinsky K. (2009). Proc. Combust. Inst. 32: 461.

[5] Pilla GL, Davidson D. F, Hanson RK. (2011). Proc. Combust. Inst. 33: 333.

[6] Herbinet O, Husson B, Serinyel Z, Cord M, Warth V, Fournet R, Glaude P.-A, Sirjean B, Battin-Leclerc F, Wang Z, Xie M, Cheng Z, Qi F. (2012). Combustion and Flame. 159: 3455.

[7] Lenhert DB, Miller DL, Cernansky NP, Owens KG. (2009). Combustion and Flame. 156: 549.

[8] Chakraborty JP, Kunzru D. (2009). Journal of Analytical and Applied Pyrolysis. 86: 44.

[9] Berta P, Aggarwal SK, Puri IK. (2006). Combustion and Flame. 145: 740.

[10] Shen H.-P. S, Steinberg J, Vanderover J, Oehlschlaeger MA. (2009). Energy & Fuels, 23, (5), 2482-2489.

[11] Silke EJ, Curran HJ, Simmie JM. (2005). Proc. Combust. Inst. 30: 2639.

[12] Dirrenberger P, Glaude PA, Bounaceur R, Le Gall H, Da Cruz AP, Konnov AA, Battin-Leclerc F. (2014). Fuel. 115: 162.

[13] Hidaka Y, Shiba S, Takuma H, Suga M. (1985). Thermal decomposition of ethane in shock waves. Int. J. Chem. Kin. 17: 441.

[14] Hong Z, Davidson DF, Hanson RK. (2009). Shock waves. 19: 331.

[15] Togbé C, Halter F, Foucher F, Mounaim-Rousselle C, Dagaut P. (2011). Proc. Combust. Inst. 33: 367.

[16] Heufer KA, Sarathy SM, Curran HJ, Davis AC, Westbrook CK, Pitz WJ. (2012). Energy and fuel. 26: 6678.