Interpretation of Low-Temperature, High-Pressure Ignition Data from a Shock Tube with Significant Pre-Ignition Pressure Rise

Christopher J. Aul and Eric L. Petersen
Department of Mechanical Engineering, Texas A&M University
College Station, TX, USA

Henry Curran
Combustion Chemistry Centre, NUI Galway
Galway, Ireland

Mustapha Fikri and Christof Schulz
Institute for Combustion and Gasdynamics (IVG), University of Duisburg-Essen
Duisburg, Germany

1 Introduction

Shock-tube ignition delay times are faster than corresponding chemical kinetics model predictions for certain fuels at elevated pressures and temperatures below about 1100 K. This departure between model and experiment is apparent in some hydrocarbon- and hydrogen-based fuels and tends to increase as test temperature decreases. It was shown in the work by Petersen et al. [1] that shock-tube measurements from differing groups and facilities, for example in methane- and propane-based mixtures [2-4], agree with each other at these conditions whereas the ignition delay times predicted by current detailed kinetics mechanisms are higher by an order of magnitude or more. The impetus for the present work is to outline a procedure to more accurately interpret these conditions prior to ignition in an attempt to better understand the reasons for the discrepancy between model and experiment.

One common feature of the cases where shock-tube experiments show shorter ignition delay than the model prediction is the appearance of mild ignition accompanied by a considerable, often relatively slow pressure increase prior to the main ignition event. It is shown that when the ignition delay time data are plotted in a way that accounts for the corresponding increase in temperature due to this gas compression, good agreement is seen between data and model. An alternate and perhaps best way to compare model and data is to incorporate the measured pressure increase into the chemical kinetics model calculations, and the procedure for doing so is demonstrated herein. The pre-ignition pressure increases for the undiluted fuel-air shock-tube ignition delay time data are significantly larger than can be explained by traditional boundary layer effects. Chemical reaction occurs with and is likely the cause of this pressure rise as evidenced by the appearance of excited OH (or CH) prior to the main ignition. No new data are presented in this paper; rather, re-analyses of existing data from the authors are performed. Presented first is an overview of the original experimental approach, followed by the results of the analysis and some pertinent discussion.

2 Experiment and Approach

The shock-tube facility used for gathering the ignition delay time data of de Vries and Petersen [5] is described at length by Petersen et al. [6]. The representative experiments of their study at 800 K

incur an estimated temperature uncertainty in this method found to be less than 10 K, where the temperature refers to the initial temperature behind the reflected shock wave. Emission from CH* chemiluminescence was monitored at both the endwall and sidewall locations by using Hamamatsu 1P21 photomultiplier tubes with 430 ± 5 nm bandpass filters. Extended test times were achieved, where the arrival of the expansion or rarefaction fan was delayed, by varying the driver-gas composition with mixtures of CO_2, C_3H_8 and He. The exact mechanics of such a technique are explained in greater detail by Amadio et al. [7]. Test times of greater than 12 ms have been achieved using this method.

Table 1: Fuel blend composition by volume used in the pressure-rise modeling study, taken from de Vries and Petersen but renumbered herein for clarity [8].

Mix	CH_4	C_2H_6	C_3H_8	C_4H_{10}	H_2
1	0.751	0	0.249	0	0
2	0.75	0	0	0.25	0
3	0.5	0.5	0	0	0
4	0.5	0.25	0.25	0	0
5	0.493	0.257	0	0.25	0
6	0.5	0.251	0	0	0.249
7	0.498	0	0.251	0.251	0
8	0.489	0	0.252	0	0.259
9	0.501	0	0	0.245	0.254
10	0.503	0	0	0	0.497

Because of the low-temperature, high-pressure focus of the earlier alkane blend study by the Texas A&M University (TAMU) group and the occurrence of the pre-ignition pressure rise in most of those experiments [5], we have chosen those data for further analysis herein. A reduced matrix from the earlier study was selected, the qualities of which are presented in Table 1 with mixtures being renumbered for ease of identification in the present study. Chemical kinetics modeling was performed for the fuel mixtures in Table 1 at pressures and temperatures produced in the shock-tube experiment. Two models were used for prediction, the GRI-Mech 3.0 [9] and the C4 mechanism developed by Healy et al. [10] which is based on ignition delay time data with pressures up to 45 atm and temperatures between 550 and 1700 K. The thermochemical parameters and rate constant definitions are used with the closed homogeneous reactor element in the Chemkin software, version 4.1.1 [11]. As discussed below, the model calculations were performed in a way that incorporates the measured increase in pressure in a manner similar to that in Pang et al. [12]. Calculations were made constraining the volume and subsequently solving the energy equations with cases for constant-pressure input, as well as calculations where the pre-ignition pressure profile from respective experiments were included directly as a function of time. The parameters and implementation for such an input are described in the next section. Note that the present analysis is also similar to the work done earlier by Petersen and Hanson [13] wherein measured pressure time histories were imposed onto the chemical kinetics calculations; the main difference, however, is that in this earlier study, the emphasis was on boundary-layer-induced pressure increases of a much lower magnitude than the pre-ignition pressure changes observed herein.

3   Results and Discussion

The fuel blends selected for the original study were determined from a statistical design of experiments approach through a 21-mixture matrix, the development of which is presented elsewhere [8,14]. The matrix was tuned to studying parameters of blends similar to natural gas being burned at gas turbine engine premixer conditions, specifically 800 K, 20 atm, and fuel lean ($\phi = 0.5$).

Figure 2 shows results which are representative of many of the tests found at the low-temperature, high-pressure regime that exhibit the pre-ignition event for the tested mixtures. There is an initial period where there is minimal pressure rise (< 2% per ms) due to boundary layer effects, in contrast to the sudden change in pressure at the time denoted as τ_1. While the cause of this increase in pressure at τ_1 is not known at this time, it is not due to the facility-induced pressure rise seen from the boundary layer interaction with the bulk flow. To demonstrate this fact, also plotted in Fig. 2a is the pressure

profile obtained from similar conditions of temperature and pressure (845 K, 19.8 atm) but with a non-reactive test gas mixture comprised of only Argon and Oxygen at a volumetric ratio of 3.76. A slight pressure rise is noted in the cold flow case that originates from tailoring of the driver gas and is insignificant when compared with the recorded pressure rise before ignition in similar yet reactive cases.
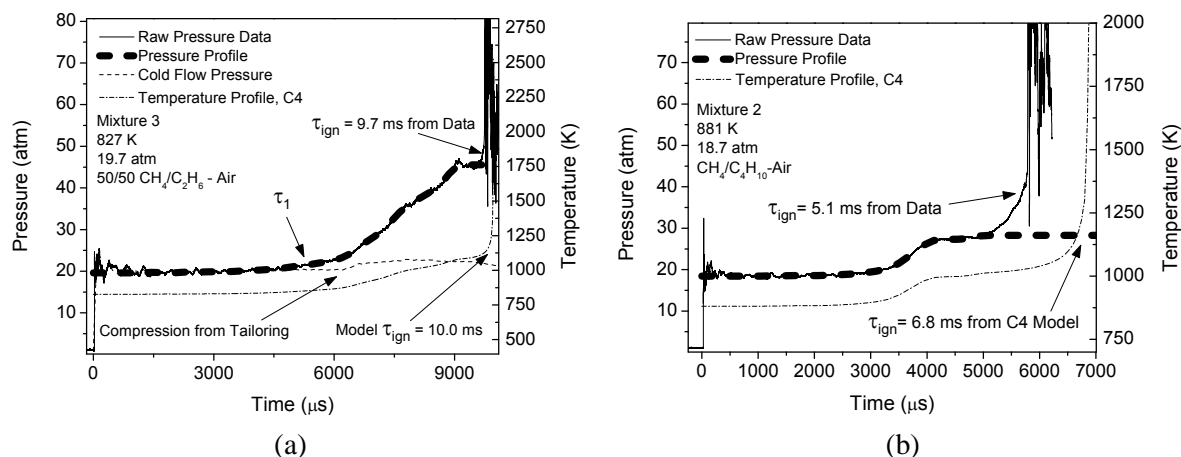

(a)   (b)

Figure 2. Pressure traces with associated pressure profile used in model simulation superimposed above raw data with predicted temperature profiles for (a) 50/50 CH_4/C_2H_6 fuel (by volume) argon-based "air" (0.21 O_2 + 0.79 Ar) in comparison with non-reactive cold flow experiment and (b) model simulation of 75/25 CH_4/C_4H_{10} fuel also with argon-based "air"

For analysis of this pre-ignition pressure rise, the raw pressure data were cleaned up by removing small fluctuations and making the trace smoother, noted by the thick dashed line in Figures 2a and 2b. We feel that such a treatment of the pressure trace accurately mimics the pressure increase found inside the shock tube. This profile is then input directly into the model to constrain the pressure to what is seen in the facility. The chemkin software allows the selection of a specified pressure input with the constant-volume, adiabatic solution of the chemistry and thermodynamics behind the reflected shock wave. As a result, the rise in pressure directly increases the temperature, from the isentropic temperature-pressure relationship, and the profile of which is also shown from the model.

Figure 2b outlines a case where ignition occurs at a relatively short test time but exhibits a scaled pressure increase from pre-ignition. This case is a representative data trace where there is a distinct "hump" in the pressure before main ignition. As is the case for some of the colder-ignition curves there is a tendency for complete and homogeneous combustion to not occur as the higher temperature kinetics could effectively burn out the fuel to a point where main ignition is not possible, as theorized by Fieweger et al. in similar instances [15]. For the situation in Fig. 2b, the model is able to predict reaction at a slower rate than what is observed physically, determining ignition from the associated pressure profile input at 6.8 ms. For Fig. 2a, the onset of τ_1 occurs at or around 7 ms, but for the experiment shown in Fig. 2b, the early pressure rise begins at approximately 3.5 ms. This distinction between longer and shorter pre-ignition events further illustrates that the early pressure increase may not be due to a time-dependant, facility-induced effect, such as boundary layer induced pressure rise, but from some heretofore unexplained reactivity ultimately leading to the main, or homogeneous, combustion.

Note that the presence of early reaction and the accompanying pressure increase shown above appears to be a different from what is described recently by Davidson and Hanson [16]. In that reference, the pressure rise is due solely to boundary layer effects that are manifest in a relatively slow pressure rise that occurs over several milliseconds. In the present paper, while there is an inevitable yet small pressure rise due to boundary layer effects, the major pressure rise of interest is much greater than that due to boundary layer effects and is accompanied by chemical reaction as evidenced by the

emission traces. The end result in either case is the same—the pressure and temperature increase in the facility leads to compression and early ignition of the mixture—but the initiating mechanism can differ and is yet unexplained in the case of the present work. Also both effects can occur in combination.

Table 2: Tabulated values for ignition, both from experiment and model. Model calculations utilize the GRI 3.0 mechanism where applicable and the present C4 mechanism

Mix	T, Post Reflected Shock (K)	p, Post Reflected Shock (atm)	τ_{ign} (ms)	GRI (ms)	GRI with p Profile (ms)	C4 (ms)	C4, with p Profile (ms)
1	817	20.2	**10.8**	2350.0	16.5	123.0	**11.0**
2	881	18.7	**5.1**	-	-	26.0	**6.8**
3	827	19.7	**9.7**	3795.0	12.9	395.0	**10.0**
4	815	20.5	**8.5**	936.0	9.5	154.0	**8.6**
5	792	18.4	**12.0**	-	-	49.0	**11.9**
6	802	20.6	**11.0**	-	-	819.0	**11.4**
7	797	20.3	**11.6**	-	-	36.0	**11.5**
8	786	20.0	**10.2**	-	-	187.0	**17.9**
9	797	18.7	**10.1**	-	-	35.5	**14.4**
10	803	20.1	**9.4**	-	-	998.0	**10.1**

Table 2 shows all of the results from the ignition calculations for the Table 1 mixtures. The ignition delay time values are compared with results from the GRI-Mech 3.0 mechanism (where applicable) and the C4 model [10] utilized herein. There is a clear difference between the calculated results for when just the constant T and p from 1-D shock relations are used and when the pressure profile is used to constrain a pressure relationship throughout the simulation. The closest agreement between data and calculated results comes from the C4 mechanism predictions for when the pressure profile is grafted onto the reaction. The use of the measured pressure traces for times before main ignition (rather than using the initial, post-shock pressure) leads to a good simulation of the results found within shock-tube experiments with pronounced pre-ignition occurrence.

In a recent paper by the authors [1], fuel-lean propane-air data from several facilities were used as an example for the discrepancies observed between shock-tube data and model data at lower temperatures and higher pressures. In light of the pressure increases seen prior to the main ignition event in the methane blends described and analyzed above, the propane-air data of Herzler et al. [3] were re-analyzed for the present study to determine if the data at the lower temperatures were also subject to extreme pre-ignition pressure increases. It was determined that such pressure rises were indeed present in the Herzler et al. [3] data, and the $\phi = 0.5$, 30-bar results were re-examined to quantify the pressure rise. The resulting pressure time histories look similar to those shown herein in Fig. 2 and were modeled in a similar fashion, serving as input to the chemical kinetics predictions. Figure 3 summarizes the results of the calculated ignition delay time when the measured pressure profiles are taken into account. As shown, there is excellent agreement between the adjusted model predictions and the experimental data for the propane-air experiments.

It should be mentioned here that Davidson and Hanson [16] presented a re-interpretation of the UDE propane data by assuming a linear pressure increase of 10% per ms over the whole ignition delay period. While this approach yielded a favorable comparison between model and experiment, the use of the 10%/ms dp/dt is inappropriate for these data since it assumes that the pressure rise is linear and, presumably, due to viscous facility effects alone. As mentioned above, a re-analysis of the data displays the extreme pre-ignition pressure increases more like those shown in Fig. 2. However, Davidson and Hanson [16] did not have access to the raw data, an important point for anyone attempting to interpret data with a very high pre-ignition pressure rise.

Although the focus of the present paper is on methane-blend and propane ignition delay times, similar discrepancies have been seen with shock-tube data for ignition delay times of hydrogen-based

mixtures as well with some flow reactor data [17-19]. Shock-tube ignition delay times for Hydrogen and syngas mixtures obtained by the TAMU group at elevated pressures and lower temperatures also exhibit unexplained early reaction accompanied by extreme pre-ignition pressure rises.

4   Summary and Conclusions

Discrepancies between shock-tube data and simulation results have been observed for methane, propane, and fuel blends with up to C_4 alkanes at temperatures below 1100 K. These discrepancies can in part be attributed to a significant rise in pressure (and correspondingly temperature) before main ignition behind the reflected shock wave. This early, significant increase in pressure is not predicted by chemical kinetics and is at present suspected to be due to early reactions in this facility and others alike, as evidenced by the accompanying appearance of excited intermediates such as OH* and CH*.
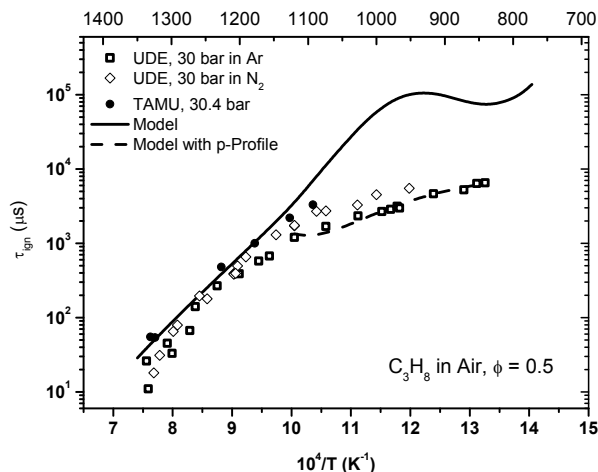
Figure 3. Propane-air shock-tube ignition delay time data showing comparison with pressure profile adaptation. The University of Duisburg-Essen (UDE) data were taken from the study of Herzler et al. [3], with a re-analysis of the data taking into account the pre-ignition pressure rise that was incorporated into the model calculation.

While the origin of this early reaction and subsequent pressure rise is not known at this time, it appears for the cases presented herein that it is not the result of a facility-induced pressure rise due to boundary layer interactions. Nonetheless, when the measured pressure rise is taken into account, the discrepancies between the shock-tube data and the simulation results are rectified. The pre-ignition pressure (and thus temperature) increase greatly accelerates the reactions in the gas mixture behind the reflected shock wave in a shock tube, leading to the earlier-than-expected strong ignition. A previous set of methane-blend ignition experiments near 800 K and 20 atm were used to demonstrate the approach, with excellent results. A similar comparison was shown for a fuel-lean propane-air set of experiments at 30 bar. A concluding point that should be made is that for shock-tube experiments showing extreme pressure increases such as those discussed herein, documenting the ignition delay time data by using the initial temperature and pressure behind the reflected shock wave is inadequate. Some representation of (at least) the measured pressure increase should be given, whether in the form of an equation or the actual time-dependent pressure measurement.

References

[1] Petersen E., Lamnaouer M., de Vries J., Curran H., Simmie J., Fikri M., Schulz C., Bourque G. (2007). Discrepancies between shock-tube and rapid compression machine ignition at low temperatures and high pressures. Paper No. 0911, 26th International Symposium on Shock Waves.

[2] Cadman P., Thomas G.O. (2000). The auto-ignition of propane at intermediate temperatures and high pressures. J. Phys. Chem. Chem. Phys. 2: 5411.

[3] Herzler J., Jerig L., Roth P. (2004). Shock-tube study of the ignition of propane at intermediate temperatures and high pressures. Combust. Sci. Tech. 176: 1627.

[4] Herzler J., Jerig L., Roth P., Schulz C. (2005). Shock tube study of the ignition of propane at intermediate temperatures and high pressures. Proc. Europ. Combust. Mtg. Louvain-la-Neuve.

[5] de Vries J., Petersen E.L. (2007). Autoignition of methane-based fuel blends under gas turbine conditions. Proc. Combust. Inst. 31: 3163.

[6] Petersen E.L., Rickard M.J.A., Crofton M.W., Abbey E.D., Traum M.J., Kalitan D.M. (2005). A facility for gas- and condensed-phase measurements behind shock waves. Meas. Sci. Technol. 16: 1716.

[7] Amadio A.R., Crofton M.W., Petersen E.L. (2006). Test-time extension behind reflected shock waves using CO_2-He and C_3H_8-He driver mixtures. Shock Waves 16: 157.

[8] Petersen E.L., de Vries J. (2005). Measuring the ignition of fuel blends using a design of experiments approach. AIAA Paper 2005-1165.

[9] Smith G.P., Golden D.M., Frenklach M., Moriarty N.W., Eiteneer B., Goldenberg M., Bowman C.T., Hanson R.K., Song S., Gardiner Jr. W.C., Lissianski V.V., Qin Z., http://www.me.berkeley.edu/gri-mech/

[10] Healy D., Curran H.J., Simmie J.M., Kalitan D.M., Zinner C.M., Barrett A.B., Petersen E.L., Bourque G. (2008). Methane/ethane/propane mixture oxidation at high pressures and at high, intermediate and low temperatures. Combust. Flame 155: 441.

[11] Kee R.J., Rupley F.M., Miller J.A., Coltrin M.E., Grcar J.F., Meeks E., Moffat H.K., Lutz A.E., Dixon-Lewis G., Smooke M.D., Warnatz J., Evans G.H., Larson R.S., Mitchell R.E., Petzold L.R., Reynolds W.C., Caracotsios M., Stewart W.E., Glarborg P., Wang C. and Adigun O., Chemkin Collection, Release 4.1.1, Reaction Design, Inc., San Diego, CA (2004)

[12] Pang G.A., Davidson D.F., Hanson R.K. (2009). Experimental study and modeling of shock tube ignition delay times for hydrogen-oxygen-argon mixtures at low temperatures. Proc. Combust. Inst. 32: 181.

[13] Petersen E.L., Hanson R.K. (2001). Nonideal effects behind reflected shock waves in a high-pressure shock tube. Shock Waves 10: 405.

[14] Petersen E.L., de Vries J. (2005). Design and validation of a reduced test matrix for the autoignition of gas turbine fuel blends. ASME Paper IMECE2005-80040.

[15] Fieweger K., Blumenthal R., Adomeit G. (1997). Self-ignition of S.I. engine model fuels: A shock tube investigation at high pressure. Combust. Flame 109: 599.

[16] Davidson D.F., Hanson R.K. (2009). Recent advances in shock tube/laser diagnostic methods for improved chemical kinetics measurements. Shock Waves 10: 271.

[17] Petersen E.L., Kalitan D.M., Barrett A., Reehal S.C., Mertens J.D., Beerer D.J., Hack R., McDonell V. (2007). New syngas/air ignition data at elevated pressure and comparison to current kinetics models. Combust. Flame 149: 244.

[18] Dryer F.L., Chaos M. (2008). Ignition of syngas/air and hydrogen/air mixtures at low temperatures and high pressures: Experimental data interpretation and kinetic modeling implications. Combust. Flame 152: 293.

[19] Chaos M., Dryer F.L. (2008). Syngas combustion kinetics and applications. Combust. Sci. Tech. 180: 1053.