Increasingly stringent regulations regarding CO₂ emissions, and the expectation that fossil fuel reserves will be exhausted within this century, have led to interest in the use of admixtures of hydrogen in natural gas as an alternative fuel in combustion devices. Combustion equipment is generally tuned for local fuel used, and clearly a change in fuel must not lead to deterioration in performance. Since the combustion properties of hydrogen differ in many respects from those of natural gas (Chapter 1), there are concerns regarding the possible negative response of combustion equipment such as gas engines, burners and turbines when fuelled with hydrogen-enriched natural gas. For example, the presence of hydrogen might increase pollutant emissions from combustion devices and cause knock (uncontrolled ignition) in gas engines. To understand these practical consequences properly, it is necessary to study the changes in the underlying physical and chemical processes that are responsible for changes in combustion behavior when hydrogen is added. The autoignition properties presented in this thesis provide new insight into the ignition characteristics of methane, hydrogen and methane/hydrogen fuel mixtures under conditions relevant to knock in gas engines. In addition, the spatial profiles of C₂H₂ and HCN (important precursors of soot and NOₓ, respectively) measured in atmospheric-pressure, one-dimensional CH₄/air and CH₄/H₂/air flames provide insight into changes in pollutant formation upon hydrogen addition. To test the accuracy of different chemical mechanisms, which could be used to predict the combustion behaviour of natural gas/hydrogen mixtures, the measurements presented in this thesis are compared with the results of numerical simulations.

To study autoignition under strictly controlled experimental conditions relevant to gas engines, a Rapid Compression Machine (RCM) was constructed in our laboratory based upon a design from MIT (Chapter 2). Test results showed that the RCM is able to compress the combustible gas-air mixture to final pressures up to ~70 bar and temperatures up to ~1100 K, where the majority of the pressure rise in the compression period takes place in a very short time (<3 ms). The temperature of the compressed mixture is calculated from the measured pressure by using the isentropic relations of an ideal gas, the uncertainty in the peak temperature after compression is better than ±3.5 K in the range of pressures of interest (10-70 bar).

Chapter 3 presents the experimental study of autoignition delay times of methane/hydrogen mixtures at high pressure (10-70 bar) and moderate temperatures.
Under stoichiometric conditions, the experimental results show that replacing methane by hydrogen results in a reduction in the measured ignition delay time. At moderately low concentrations of hydrogen (≤ 20%) only a weak effect on the measured ignition time is observed, while at 50% hydrogen content in the fuel a substantial reduction in ignition delay time is seen under all measured conditions. Moreover, the measurements show that the effects of hydrogen in promoting ignition increases with temperature and decreases with pressure. Experimental results for 50% hydrogen in the fuel at equivalence ratio $\phi = 0.5$ are essentially identical to those at $\phi = 1.0$. These results suggest that the adverse affects of hydrogen addition to natural gas on engine knock may be limited for hydrogen fractions of only a few tens of percent. Comparison between measured and calculated ignition delay times shows very good agreement for all fuel mixtures using the proposed mechanism of Petersen et al. (E. L. Petersen, D. M. Kalitan, S. Simmons, G. Bourgue, H. J. Curran and J. M. Simmie, *Proc. Combust. Inst.* 31 (2007) 447-454.)

Chapter 4 describes the experimental protocols for concentration measurements of HCN and C$_2$H$_2$ in one-dimensional flames using extractive probe sampling followed by analysis using *tunable diode laser absorption spectroscopy* (TDLAS) at $\sim$1.5 µm. The calibration procedure for acetylene is performed by measuring the absorption coefficient in a gas sample containing a known concentration of acetylene under the same experimental conditions as those existing for the flame samples. At mole fractions above 1000 ppm, the accuracy of the measured C$_2$H$_2$ is $\sim$5%; decreasing C$_2$H$_2$ mole fraction results in deteriorating accuracy, to 15% at 100 ppm. The same calibration procedure is performed for the HCN measurements. However, to increase the sensitivity wavelength modulation absorption spectroscopy (WMAS) with second harmonic detection is used. The accuracy of the measured HCN mole fraction in the sampled flame gases is better than 30% at concentrations above 3 ppm. Before examining the effects of hydrogen addition on the formation and consumption of these species, their profiles are first measured and analyzed in flames using pure methane as fuel.

Chapter 5 presents measurements of C$_2$H$_2$ concentration profiles in one-dimensional atmospheric-pressure rich premixed methane/air flames using spontaneous Raman scattering and an extractive probe sampling technique (Chapter 4). Excepting a shift of approximately 1.3 mm, resulting from the acceleration of the
Summary

Combustion products in the probe orifice, the axial Raman and probe profiles are in very good agreement. The measurements show that changing the equivalence ratio from $\phi = 1.4$ to 1.5 results in an increase of the peak C$_2$H$_2$ mole fraction by nearly a factor two. At fixed equivalence ratio, the maximum C$_2$H$_2$ mole fraction depends only slightly on the flame temperature, while the C$_2$H$_2$ oxidation in the post flame zone increases substantially in the flames with increasing flame temperature. Comparison of measured C$_2$H$_2$ profiles with those calculated, using the GRI-Mech 3.0 chemical mechanism, shows a much faster post-flame decay in the experimental results. Increasing the pre-exponential factor in the rate coefficient of reaction $C_2H_2 + OH \rightarrow CH_2CO + H$ to $1.7 \times 10^{12}$ cm$^3$mol$^{-1}$s$^{-1}$ in the range 1760 – 1850 K yields excellent agreement between computed and experimental results.

In Chapter 6 the formation and consumption of HCN in fuel-rich atmospheric pressure methane/air flames is discussed. Towards this end, axial HCN and temperature profiles have been measured at equivalence ratios $\phi = 1.3$, 1.4 and 1.5. For the richest flame studied ($\phi = 1.5$) very slow oxidation of HCN in the post flame zone is observed, demonstrating “residual” HCN in the post flame gases of fuel-rich methane/air flames. The HCN measurements show that increasing the flame temperature at fixed equivalence ratio does not result in significant changes in the HCN peak mole fraction, while the HCN oxidation in the post-flame gases increases substantially. Decreasing the equivalence ratio leads to faster HCN oxidation in the post flame zone. Large discrepancies are observed between measured and calculated HCN profiles using GRI-Mech 3.0. Attempts to bring the calculations using GRI-Mech 3.0 into agreement with the experimental observations by changing the rates of key formation and consumption reactions within the uncertainties in the literature were unsuccessful. Consideration of NCN as a primary product of the reaction between CH and N$_2$, based on recent theoretical studies, allows improvement in the agreement between measured and calculated HCN concentrations. However, the lack of information on the rate constants of the NCN reactions at high temperatures precludes unambiguous conclusions regarding this mechanism.

Chapter 7 is an extension of Chapters 5 and 6 and examines the effect of hydrogen addition on the formation and consumption of HCN and C$_2$H$_2$ in fuel-rich stabilized methane/air flames. The HCN measurements at $\phi = 1.4$ and 1.5 show that increasing the hydrogen fraction in the mixture at constant flame temperature results
in a substantial decrease in the HCN mole fraction. This decrease in HCN significantly exceeds the reduction of HCN caused by the dilution of hydrocarbon fuel when hydrogen is added to the mixture, indicating that hydrogen addition affects the chemistry related to the formation of HCN. As observed for pure methane flames (Chapter 6) at $\phi = 1.4$, the calculated HCN profiles using GRI-Mech 3.0 predict significantly higher HCN peak mole fractions and substantially slower decay in comparison to the measurements for all flames studied. Moreover, contrary to the experimental observations, the calculations show no substantial changes in the calculated peak HCN mole fraction when adding hydrogen to the fuel mixture and a strong reduction in the HCN mole fraction with decreasing flame temperature at constant hydrogen fraction. Good agreement between calculations and measurements is found for the flames at $\phi = 1.5$. However, the reduction in the calculated HCN mole fraction when hydrogen is added to the flame is probably the result of the computed reduction in flame temperature and not due to a “hydrogen” effect on the chemistry. No significant changes are observed in the measured C$_2$H$_2$ mole fractions for the flames with equivalence ratio $\phi=1.3$ and $1.5$ when hydrogen is added. This suggests that hydrogen addition does not have a significant effect on the chemistry responsible for C$_2$H$_2$ in CH$_4$/air flames. Replacing the rate coefficient of the reaction C$_2$H$_2$ + OH $\rightarrow$ CH$_2$CO +H used in the GRI 3.0 mechanism by the rate recommended in Chapter 6 resulted in good agreement between measured and calculated C$_2$H$_2$ profiles for all flames studied.