

Impact of the blending of n-butanol on the low and intermediate temperature heat release of a gasoline surrogate

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Introduction

Heat release analysis (HRA) is a useful tool that can be exploited in terms of improving our understanding of the exothermicity of a fuel under different thermodynamic conditions, for example during the process of ignition. Until recently, it has not been commonly applied to data sets from rapid compression machines (RCMs) due to challenges in obtaining robust transducer measurements and in dealing with physical phenomena taking place in the reaction chamber such as heat losses, growth of the boundary layer, heat and fuel transfer into piston crevices, etc. [1]. However, a recent paper by Goldsborough et al. proposed a methodology for exploiting pressure-time histories from RCMs for HRA [1]. This could potentially facilitate studies of the links between low/intermediate temperature heat release (LTHR/ITHR respectively) and ignition delay times of fuels and their blends, as well as providing additional data for the evaluation of chemical mechanisms. Information on the LTHR and ITHR of fuel blends can also potentially facilitate the design of advanced compression ignition conditions, by informing the control of combustion phasing through a better understanding of a fuel's low temperature exothermicity [2]. In this work we employ the method proposed in [1] for the HRA of a 3 component toluene reference fuel (TRF) gasoline surrogate containing n-heptane, iso-octane and toluene using pressure measurements obtained experimentally over a range of temperatures within an RCM at a compressed pressure of 20 bar. We then explore the influence of n-butanol blending with the TRF, on the low and intermediate temperature heat release of the mixtures. Experimentally derived heat release rates (HRR) are compared with those from a detailed model.

Methodology

Details on the set-up of the RCM have been described in the earlier papers of Agbro [3] and Gorbatenko [4] and are not reproduced here. Pressure records used in the HRA analysis were obtained at a compressed pressure of 20 bar and over a range of temperatures from (678–916 K) for stoichiometric fuel air mixtures. The TRF surrogate was developed in [3] to represent a research grade gasoline of RON 95 and MON 86.6. The influence of n-butanol addition at various blending ratios (10%, 20%, 40% and 85% vol n-butanol, referred to as B10, B20, B40 and B85 respectively) on its auto-ignition properties was studied in [4]. Here we further explore the impact of n-butanol blending on the LTHR and HTHR of the blends.

Following the method of Goldsborough et al. [1], the energy conservation equation is applied to the gas in the RCM reaction chamber:

$$\frac{dU_s}{dt} = \dot{Q}_{chem} - \dot{Q}_{wall} - \dot{W}_{piston} - \dot{H}_{out} + \dot{H}_{in} \quad (1)$$

where U_s is the total sensible internal energy, \dot{Q}_{chem} is the rate of heat released, \dot{Q}_{wall} is the rate of heat exchange with the chamber walls, \dot{W}_{piston} is the rate of work done by the piston on the gas and \dot{H}_{out} and \dot{H}_{in} are the rates of enthalpy flow out and in of the reaction chamber respectively. A simplified system is defined to represent the RCM experiments by applying the adiabatic core hypothesis, such that it contains a single volume consisting of both burnt and unburnt gases, and neglecting any reactivity in the boundary layer gas. It is assumed in this model that pressure is uniform throughout the gas, as well as assuming ideal gas behaviour. Heat loss from the system is accounted for empirically through the application of experimental non-reactive pressure histories. These are produced using the University of Leeds RCM, for all investigated reactive conditions, by replacing the oxygen present in reactive cases, with nitrogen due to the similar thermophysical properties of oxygen and nitrogen, thus allowing for the assumption of consistent heat loss behaviour between the non-reactive and reactive cases. The same technique is commonly applied to produce (variable volume) chemical kinetic simulations under RCM conditions [5].

By applying eqn. (1) under these conditions, and assuming that the piston trajectory is identical between both reactive and non-reactive cases, it can be shown that [1]:

$$HRR = \frac{\gamma}{\gamma - 1} \frac{dV}{dt} (P - P_{nr}) + \frac{1}{\gamma - 1} V \left(\frac{dP}{dt} - \frac{dP}{dt} \Big|_{nr} \right) - \frac{PV}{(\gamma - 1)^2} \left(\frac{d\gamma}{dt} - \frac{d\gamma}{dt} \Big|_{nr} \right) \quad (2)$$

where, HRR is the heat release rate, γ is the ratio of specific heats, V is the reaction chamber volume, P is the pressure in the chamber and the suffix ‘ nr ’ denotes properties of the non-reactive case. Using eqn. (2), it is possible to determine the HRR at any point during an RCM experiment, given the appropriate reactive and non-reactive pressure histories. Cantera is used to simulate the experiments using a reduced combined mechanism for n-butanol from [6] and for the TRF surrogate from [7], modified with the suggestions in [3], to calculate the temperature dependent specific heat ratios in eqn. (2), thus accounting for the changing composition of the gas during the experiments. The same model has also been used to fully calculate the pressure histories and HRRs based in this work on fixed volume simulations.

RCM pressure histories were collected using a Kistler 6045A dynamic pressure transducer, at a frequency of 20 kHz. Pressure traces are aligned for this model at the end of compression, as determined by piston displacement measurements, such that the end of compression is equivalent to piston top dead centre. A 2nd order fit, Savitzky-Golay algorithm is applied to pressure histories before processing, with a window of 2.55 ms. All presented HRRs are normalised against the lower heating value of the gas.

Results and Discussion

Figure 1 illustrates the trends in experimental LTHR and ITHR rates against the accumulated heat release (aHR) with increasing temperature for the three fuel blends TRF, B10 and B85. The gasoline TRF surrogate exhibits the expected low temperature heat release at temperatures above 700 K which reaches a maximum from the tested conditions at 761 K consistent with the minimum in ignition delays reported in [3]. At higher temperatures, the low temperature reactivity declines within the negative temperature coefficient (NTC) regime with mainly only high temperature HR shown by 916 K. As n-butanol is added to the blends, the LTHR is reduced, with B10 showing a peak HRR just over half of that for TRF in the low temperature region. B85 shows only low values of LTHR. N-butanol addition suppresses the low temperature reactivity of the system causing reduction in the

magnitude of the LTHR manifesting in longer ignition delays for B85 in lower temperature region compared to lower n-butanol percentage blends as shown in [3,4].

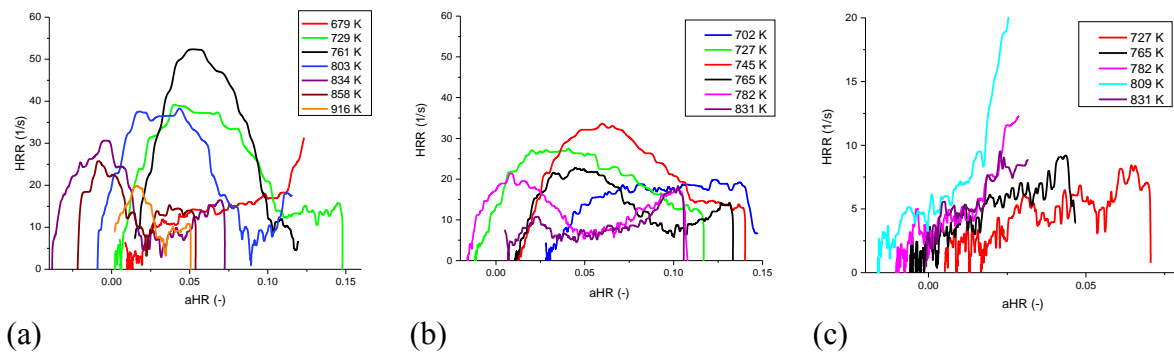


Figure 1: Comparisons of experimental HHR against accumulated heat release (aHR) at different temperatures for three fuel blends a) TRF b) B10 and c) B85.

Figure 2 shows a comparison of the HRRs for the different fuels against time for 3 selected temperature regions. Both experimentally derived and simulated HRRs are compared. The traces are aligned at the point of the maximum pressure rise for the main ignition in order to facilitate a comparison between the different fuel blends on the same axes. The simulations show a reasonable representation of the maximum LTHR rates at the lowest temperature (701 K), although the LTHR region from the simulations is slightly narrower in time than that shown by the experiments. The simulations also show higher LTHR/ITHR than the experimentally derived values for the two n-butanol blends, particularly for the B85 where no LTHR/ITHR was shown in the experiments.

At low temperatures ($T_c = 701$ K), heat release analysis for the TRF surrogate shows 3 stages of heat release. During the initial, lowest temperature heat release, exothermic fuel reactions slowly and continuously increase the gas temperature and pressure. Sensitivity analysis (not shown due to space) demonstrates that of particular importance are hydrogen abstraction reactions via the OH radical, for example, $iC_8H_{18} + OH = cC_8H_{17} + H_2O$ and $C_6H_5CH_3 + OH = C_6H_5CH_2 + H_2O$. Rising gas temperature and pressure influence the oxidation of fuel molecules, leading to an increasing decomposition of RO_2 to produce alkenes and HO_2 radicals (e.g. $bC_8H_{17}O_2 = iC_8H_{16} + HO_2$). At this point, these reactions are effectively chain terminating due to the low reactivity of HO_2 at low temperatures [8]. As the initial heat release slows, a decrease in OH concentration is observed as well as an increasing HO_2 concentration and the formation of a gradually increasing pool of H_2O_2 . A second peak in heat release rate is observed shortly after, indicating a second stage of heat release, which coincides with a local maximum of HO_2 radicals. Due to an increased reactivity as the gas temperature and pressure rise, reactions containing HO_2 radicals also become sensitive (such as the considerably exothermic reaction, $CH_3O_2 + HO_2 = CH_3O_2H + O_2$, which is highly sensitive during the second stage heat release), as does the recombination reaction of $2HO_2$ to form H_2O_2 , which becomes a dominant consumer of HO_2 . During this stage of heat release, non-branching exothermic reactions contribute significantly to the heat release rate, ultimately increasing temperature and pressure conditions to such a point that the accumulated quantities of H_2O_2 (largely formed during the second stage of heat release) decompose to produce large amounts of OH radicals, causing degenerate branching and, the third stage of heat release, ignition.

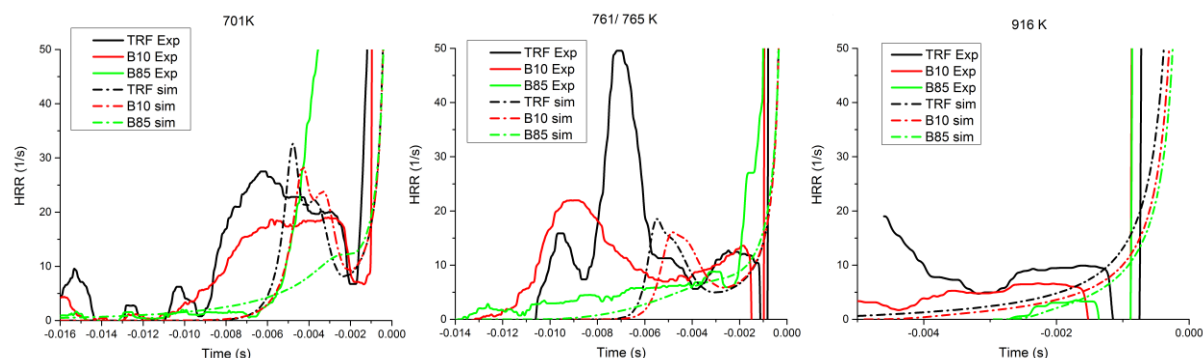


Figure 2: Comparisons of experimental and simulated HRR for three fuel blends a) TRF b) B10 and c) B85 and at three temperatures 701 K, 761 K (TRF) or 765 K (n-butanol/TRF blends), 916 K.

At the intermediate temperatures of 761/765 K, where the maximum LTHR/ITHR was seen for TRF in Figure 1, the simulations show a much smaller HRR for TRF than the derived experimental values. The experimental values show distinct peaks in LTHR and ITHER, whereas the simulations show merged peaks with an initial HR peak and a slightly later shoulder. Variable volume simulations should be carried out in order to determine whether this feature persists within the simulations when heat loss effects are accounted for. The addition of 10% n-butanol in the B10 is seen to increase the LTHR but to reduce the ITHER in the experimentally derived values. The simulations do not reproduce this feature and discrepancies between predicted and measured ignition delays were also noted for B10 in the NTC region in [4]. Further investigations are required to determine the source of these discrepancies, which persist up to B85, where the simulations show no LTHR/ITHR even though small amounts are seen in the experimentally derived HRRs.

Conclusions

HRR analysis appears to be a useful method for investigating the exothermicity of fuel blends over a range of temperatures and for evaluating the ability of chemical mechanisms to reproduce experimentally derived HRRs. Discrepancies were seen at intermediate and high temperatures here. Further work will explore the reasons for these and will explore the links between the extent of LTHR/ITHR and ignition delay times for the blends.

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