Effects of Nitrates on Hydrocarbon Flames and Detonations

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Hydrocarbon sensitization by nitrates has been of interest due to its application in promoting ignition. Borisov et al. (1983) investigated the ignition promotion for mixtures containing methane and nitrates. Studies of nitrate decomposition kinetics by Zaslonko et al. (1985, 1988) suggest that nitrates promote ignition of hydrocarbons through the formation of NO_2 which reacts with methyl radicals to produce OH radicals. Detonation experiments by Tiezen et al. (1991) show that, at stoichiometric concentrations, the detonation cell size for hexylnitrate vapor in air is close to that for a hydrogen-air mixture and is a factor of 5 less than that for a hexane vapor in air. The authors explained the results based on the sensitizing effect of the nitrate group. In fact, most nitrates can be considered as a fairly sensitive oxygenated fuel. The objective of the present paper is to determine whether the nitrates have a strong sensitizing effect at low concentrations or simply sensitize a hydrocarbon-air mixture based on an interpolation mixture rule of different-sensitivity fuels. The other objective is to determine whether the sensitizing effect is strongly dependent of the combustion mode (flame or detonation). Experiments performed included studies for flammability limits, flame velocities, ignition delays behind reflected shocks and detonation cell sizes.

Most nitrates are low-vapor-pressure liquids at normal ambient temperature and pressure. In order to avoid the influences caused by the multiphase transport time scales and heterogeneous reactions, experiments of flammability limits, flame velocities, ignition delays and detonations were conducted in the vapor state at an elevated temperature of 100 - 120 °C. Studies for lean flammability limits and flame velocities were performed in a stainless steel tube, 5 cm in internal diameter and 1.58 m in length. The tube was vertical and closed at both ends. Mixtures were ignited at the bottom of the tube and the flame propagation direction was upward. Ignition delay tests were conducted using a shock tube 8 cm in internal diameter. The driver section is 2 m in length filled with helium or nitrogen, and the driven section is 7.5 m long. The ignition delay was measured behind the reflected shock using a Kulite pressure transducer located on the end wall. Isopropyl nitrate was used as the representative nitrate additive ranging from 10, 20, and 50 to 100 mole % in total amount of fuel. Propane and hexane were used as the hydrocarbon fuel in the flame studies and hexane in the ignition delay studies. The results show that the lean flammability limit, the flame velocity and the ignition delay monotonically fall between the value for the fuel and the value for the pure nitrate (see Figs. 1 – 4). Experiments for detonations of fuel-additive-air mixtures are to be performed in a heated detonation tube, 0.3 m in internal diameter and 24 m in length. Smoke foils will be used to determine the detonation cell sizes. The detonation will be initiated by a hydrogen-oxygen detonation in a 4 m initiation section. Detonation cell sizes will be measured for hexane-air mixtures with the nitrate additive ranging from 10 to 100 mole percent in fuel.

The experimental results performed so far indicate that the nitrate does not act as a strong sensitizer at low concentrations. The sensitivity of a hydrocarbon-nitrate-air mixture monotonically increases when the nitrate additive is increased from 10 to 100 mole percent in its parent or higher-C alkane fuel. This fact demonstrates that the nitrate addition into hydrocarbon-air mixtures behaves like mixing of different-sensitivity fuels. These observations remain the same when the combustion mode is changed from the slow flame to the fast mode.

Acknowledgement

References

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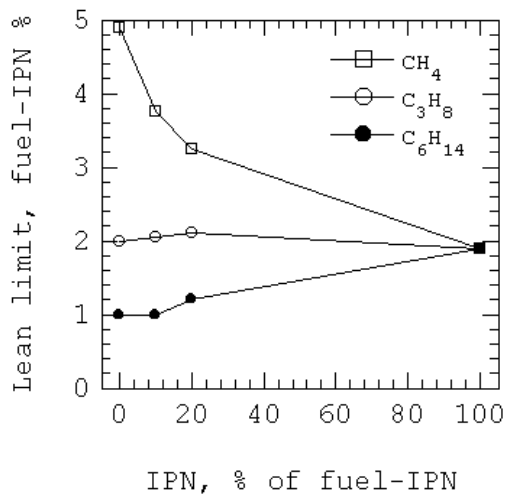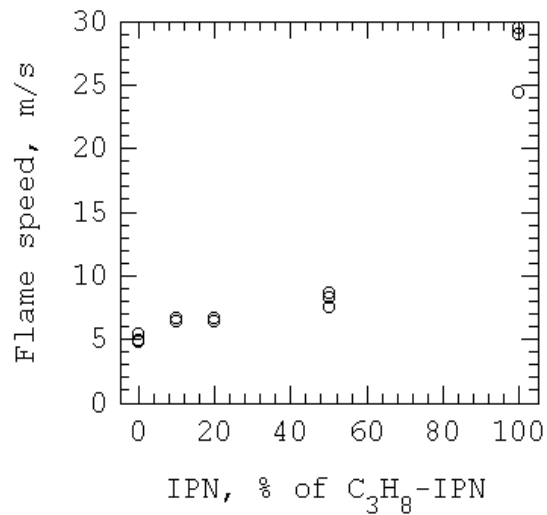
Figure 1. Lean flammability limit of fuel-IPN in air.

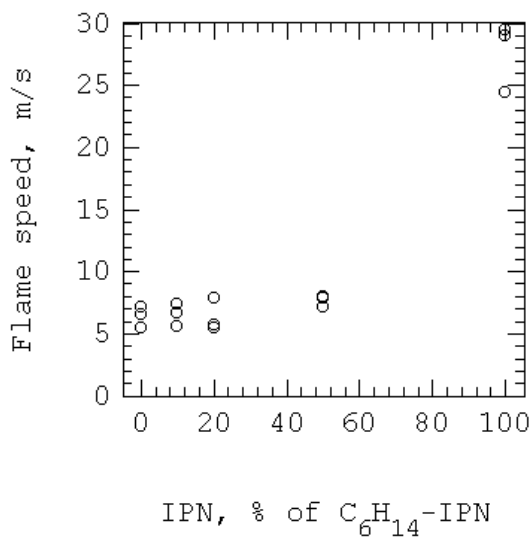Figure 2. Flame speed for stoichiometric C_3H_8-IPN-air mixtures.

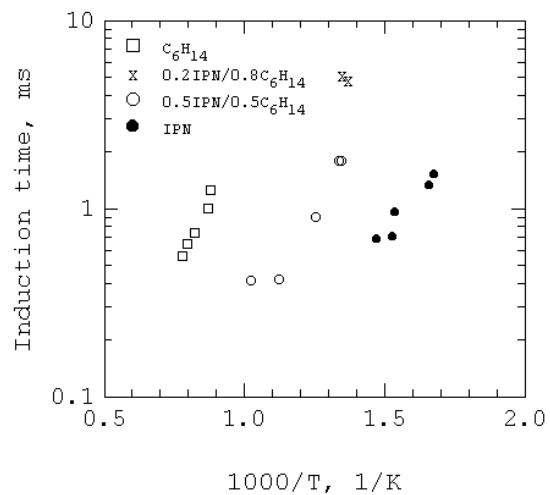Figure 3. Flame speed for stoichiometric C_6H_{14}-IPN-air mixtures.

Figure 4. Induction time after the reflected shock for stoichiometric C_6H_{14}-IPN-air mixtures.