ON THE MECHANISM OF ACTION OF A PROPYLENE ADDITIVE ON HYDROGEN SELF-IGNITION AT ATMOSPHERIC PRESSURE

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Abstract: Based on the analysis of theoretical principles and results of numerical simulation, the mechanism of action of unsaturated hydrocarbon additives (using propylene as an example) on hydrogen self-ignition in air at atmospheric pressure in a reactor with adiabatic and isothermal walls is investigated. Calculations are performed using ANSYS CHEMKIN software package and NUIGMech 1.1 (2020) kinetic mechanism. Fuel-lean and stoichiometric hydrogen–air mixtures (HAM) with 1 and 2 %(vol.) propylene additives are considered. It is shown that the mechanism of action of such additives is thermal, meaning that the development of a chain process can only be prevented by heat removal. With poor heat removal, even a significant addition of propylene does not suppress the self-ignition process. Moreover, both with poor heat removal, when self-ignition occurs, and with strong heat removal, when self-ignition does not occur, the process follows a qualitatively similar pattern and propylene additives have only a minor effect on the kinetic curves, either decreasing or increasing the self-ignition induction period. The results of calculations suggest that various combustible substances (e. g., H_2 and C_3H_6) in multicomponent mixtures with air oxidize interacting with each other primarily through heat which is released or absorbed at different stages of the process. Since the recombination reactions of atoms and radicals proceed with heat release and, therefore, lead to a more rapid occurrence of a chain avalanche, searching for reaction inhibitors that capture atomic hydrogen looks questionable. This conclusion applies to all unsaturated hydrocarbons.

Keywords: hydrogen; self-ignition; propylene; inhibitor; promotor; detailed kinetic mechanism; numerical simulation

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Figure Captions

Figure 1 Determination of the self-ignition induction period based on the calculated time history of process temperature for a stoichiometric H_2–air mixture at $T_0 = 800$ K and $p_0 = 0.1$ MPa: *1* — process temperature; *2* — HO_2 volume fraction; and *3* — H × 500 volume fraction

Figure 2 Comparison of calculated (curves) and measured (signs) dependences of the self-ignition delay time τ_i on the initial temperature for the stoichiometric ($p_0 = 0.1$ MPa, experiment: squares — data from [20], and circles — from [21]) (*a*) and fuel-lean (*1* — $p_0 = 0.1$ MPa, fuel-to-air equivalence ratio $\Phi = 0.25$, experiment [20]; *2* — $p_0 = 2$ MPa, $\Phi = 0.5$, experiment [22]; calculations: solid curves — [8] and dash-dotted curves — [13, 14]) (*b*) H_2–air mixtures

Figure 3 Comparison of calculated (solid curves — [8] and dash-dotted curves — [13, 14]) and measured (signs [25]) dependences of τ_i on the initial temperature for the stoichiometric propylene–air mixture at a pressure of 1 MPa

Figure 4 Calculated time histories of C_3H_6 volume fractions and process temperature T during self-ignition of the stoichiometric H_2–air mixtures without additives (0) and with propylene additives 1 %(vol.) (*1*) and 2 %(vol.) (*2*) at $p_0 = 0.1$ MPa and $T_0 = 800$ K

Figure 5 Calculated time histories of process temperature T and H, HO_2, and C_3H_6 volume fractions at the end of the self-ignition induction period for the stoichiometric H_2–air mixtures without additives (0) and with a propylene additive of 1 %(vol.) (1) at $p_0 = 0.1$ MPa and $T_0 = 800$ K

Figure 6 Calculated dependences of H, C_3H_6, and HO_2 volume fractions on the process temperature T during self-ignition of the stoichiometric H_2–air mixtures without additives (0) and with propylene additives 1 %(vol.) (*1*) and 2 %(vol.) (*2*) at $p_0 = 0.1$ MPa and $T_0 = 800$ K

Figure 7 Calculated dependences of H, C_3H_6, and H_2O (*a*) and H, HO_2, C_3H_6, CO, and CO_2 volume fractions (*b*) on the process temperature T during self-ignition of the stoichiometric H_2–air mixtures without additives (0) and with propylene additives 1 %(vol.) (*1*) and 2 %(vol.) (*2*) at $p_0 = 0.1$ MPa and $T_0 = 800$ K

Figure 8 Calculated dependences of H, C_3H_6, isomers i-C_3H_7 and n-C_3H_7, and HO_2 volume fractions on the process temperature T during self-ignition of the stoichiometric H_2–air mixtures without additives (0) and with the propylene additive 1 %(vol.) (*1*) at $p_0 = 0.1$ MPa and $T_0 = 800$ K

Figure 9 Calculated time histories of C_3H_6 volume fractions and process temperature T during self-ignition of the stoichiometric H_2–air mixtures without additives (0) and with propylene additives 1 %(vol.) (1) and 2 %(vol.) (2) at $p_0 = 0.1$ MPa and $T_0 = 1000$ K

Figure 10 Calculated dependences of H, C_3H_6, and HO_2 volume fractions on the process temperature T during self-ignition of the stoichiometric H_2–air mixtures without additives (0) and with propylene additives 1 %(vol.) (1) and 2 %(vol.) (2) at $p_0 = 0.1$ MPa and $T_0 = 1000$ K

Figure 11 Comparison of the calculated time histories of process temperature T during self-ignition of the stoichiometric ($[H_2]_0 = 29.6$ %(vol.)) and fuel-lean ($[H_2]_0 = 15$ %(vol.)) H_2–air mixtures without propylene additives at $p_0 = 0.1$ MPa and $T_0 = 850$ K

Figure 12 Calculated dependences of H and HO_2 volume fractions on the process temperature T during self-ignition of the stoichiometric ($[H_2]_0 = 29.6$ %(vol.)) and fuel-lean ($[H_2]_0 = 15$ %(vol.)) H_2–air mixtures without propylene additives at $p_0 = 0.1$ MPa and $T_0 = 850$ K

Figure 13 Calculated dependences of H and HO_2 volume fractions on the process temperature T during self-ignition of the stoichiometric ($[H_2]_0 = 29.6$ %(vol.)) and fuel-lean ($[H_2]_0 = 15$ %(vol.)) H_2–air mixtures without propylene additives at $p_0 = 0.1$ MPa and $T_0 = 1000$ K

Figure 14 Calculated dependences of H, C_3H_6, and HO_2 volume fractions on the process temperature T during self-ignition of the stoichiometric ($[H_2]_0 = 29.6$ %(vol.)) and fuel-lean ($[H_2]_0 = 15$ %(vol.)) H_2–air mixtures with propylene additive 1 %(vol.) at $p_0 = 0.1$ MPa and $T_0 = 1000$ K

Figure 15 Calculated dependences of the self-ignition induction period τ_i on the initial temperature T_0 for the stoichiometric ($[H_2]_0 = 29.6$ %(vol.)) (*a*) and fuel-lean ($[H_2]_0 = 29.6$ %(vol.)) (*b*) H_2–air mixtures without additives (0) and with propylene additives (1 — 1 %(vol.) and 2 — 2 %(vol.)) at $p_0 = 0.1$ MPa

Figure 16 Calculated time histories of process temperature T during self-ignition of the stoichiometric H_2–air mixture with different values of the heat loss coefficient α_S (*1* — 0 W/K; *2* —1.315; *3* — 4.543; *4* — 4.544; and *5* — 131.5 W/K) at $T_0 = T_a = 850$ K and $p_0 = 0.1$ MPa (T_a is the reactor wall temperature)

Figure 17 Calculated time histories of process temperature T (*a*), HO_2 volume fractions (*b*), and H volume fractions (*c*) for different values of the heat loss coefficient α_S (*1* — 0 W/K; *2* —1.315; *3* — 4.543; *4* — 4.544; and *5* — 131.5 W/K) at $T_0 = T_a = 850$ K and $p_0 = 0.1$ MPa; stoichiometric H_2–air mixture

Figure 18 Calculated time histories of process temperature T and HO_2 and H volume fractions (*a*) and the total rate of heat release (q_+) and heat removal (q_-) (*b*) at $\alpha_S = 4.543$ W/K, i. e., near the self-ignition limit of the stoichiometric H_2–air mixture; $T_0 = T_a = 850$ K and $p_0 = 0.1$ MPa

Figure 19 Calculated time histories of process temperature T during self-ignition of the stoichiometric H_2–air mixtures ($T_0 = T_a = 850$ K and $p_0 = 0.1$ MPa) with different propylene additives and different values of the heat loss coefficient α_S: *1* — without additives and $\alpha_S = 1.315$ W/K; *2* — with the addition of 2 %(vol.) C_3H_6 and $\alpha_S = 1.315$ W/K; and *3* — with the addition of 1 %(vol.) C_3H_6 and $\alpha_S = 4.544$ W/K

Figure 20 Calculated time histories of species volume fractions during self-ignition of the stoichiometric H_2–air mixtures ($T_0 = T_a = 850$ K and $p_0 = 0.1$ MPa) with different propylene additives and different values of the heat loss coefficient α_S: solid lines — addition of 2 %(vol.) C_3H_6 at $\alpha_S = 1.315$ W/K; dashed-dotted lines — addition of 1 %(vol.) C_3H_6 at $\alpha_S = 4.544$ W/K; *1* and *1′* — $[H_2]$; *2* — [H]; *2′* — [H] $\cdot 10^5$; *3* and *3′* — $[H_2O]$; *4* and*4′* — $[HO_2] \cdot 10^3$; and *5* and *5′* — $[C_3H_6] \cdot 10$

Table Captions

Table 1 Calculated values of the self-ignition induction period τ_i and adiabatic temperature T_{ad} for the stoichiometric H_2–air mixture at $p_0 = 0.1$ MPa and three values of the initial temperature T_0

Table 2 Calculated values of the self-ignition induction period τ_i for the stoichiometric ($[H_2]_0 = 29.6$ %(vol.)) and fuel-lean ($[H_2]_0 = 15$ %(vol.)) H_2–air mixtures without additives and with propylene additive 1 %(vol.) at $p_0 = 0.1$ MPa and $T_0 = 850$ and 1000 K

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