

Insights on the effect of ethanol on the formation of aromatics

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Introduction:

Transportation is the largest consumer of petroleum-derived fuels in the world and the main emitter of atmospheric pollutants in urban centers (>75%). Due to the growing energy demand, the severe air pollution issues in city centers, and the more restrictive environmental regulations to the road transport sector, there is an enormous need to develop and find alternative fuel sources and new technologies to reduce the vehicular emissions of air pollutants. Ethanol is a fuel produced mainly from crop materials, such as sugarcane and corn, which makes it an attractive substitute for gasoline for reducing dependence on fossil fuels and reducing CO₂ net emissions released into the atmosphere.

Ethanol, as other oxygenated biofuels, contains oxygen as an additional element in their molecular constitution. This feature distinguishes them from the hydrocarbons in conventional petroleum-based fuels, the combustion chemistry of which has long been studied. The presence of the oxygen atom in the oxygenated fuel molecules alters the electronic structure, and most of the C-H bond strengths for the oxygenated fuels are different from their values for structurally related hydrocarbon fuels. Many studies have reported on the effect that doping hydrocarbon fuels, such as ethylene, with ethanol can have on the distribution of small gas-phase species formed during combustion [1], but much less is known on the effect of the formation of large polycyclic aromatic compounds (PACs) that leads to incipient soot particles. A recent study on this topic [2] has revealed the importance of including the chemistry of oxygenated PACs in order to explain some experimental observations collected in flames.

In this work, we report an analysis of the effect that ethanol addition to an ethylene flame has on the formation and growth of polycyclic aromatic coimounds. Growth mechanisms are characterized in terms of kinetic pathways at different locations in the flame and their relative importance is assessed at different stage along the combustion process in the flame.

System and Method:

Premixed ethylene/air (pure) and ethylene/ethanol/air (doped) flames have been characterized experimentally by Salamanca et al. [3]. These flames are a great system to understand the effect of chemistry since the two flames present the same equivalence ratio 2.01 and carbon flow rates, with the doped ethanol equals to 30% of the total carbon flow rate. The temperature profiles were experimentally measured and reported.

The analysis of the small gas-phase chemistry was studied previously by Elvati et al., [2] using CHEMKIN-PRO [4], employing the D'Anna and Kent mechanisms [5] together with ethanol oxidation mechanism by Marinov [6].

In order to analyze the kinetic pathways of growth, following the atomistic evolution of the system, we employed a stochastic modeling code, SNapS2, to study the PACs growth history in both flames. The SNapS2 code utilizes kinetic Monte Carlo scheme coupled with generic reaction and chemical sites descriptions to generate time evolutions of aromatics as they travel in the gas-phase environment identified via CHEMKIN simulations. Considering thousands of trajectories, we can obtain a statistical representation of the system evolution. Additional details on SNapS2 code can be found in [7].

Results:

Using the SNapS2 code, we obtained the statistical representation on PACs time history in both flames with the molecular mass range between 100 u to 600 u, at various heights above the burner (HAB) ranging from 0 to 12 mm. Around 32,000 traces (single molecule time history) were simulated for both flames.

At a height just above the burner (within a HAB of 1 mm), the two flames show very different growth mechanisms. While the doped flame is mainly producing pure hydrocarbons, the pure flame produces a lot of oxygenated species due to a higher concentration of small oxidizing species such as O, OH, and O₂ compared with the doped flame. The simulated mass spectra in the range of 200 u to 600 u are shown in Fig. 1 for the two flames at a height of 0.5 mm from the burner.

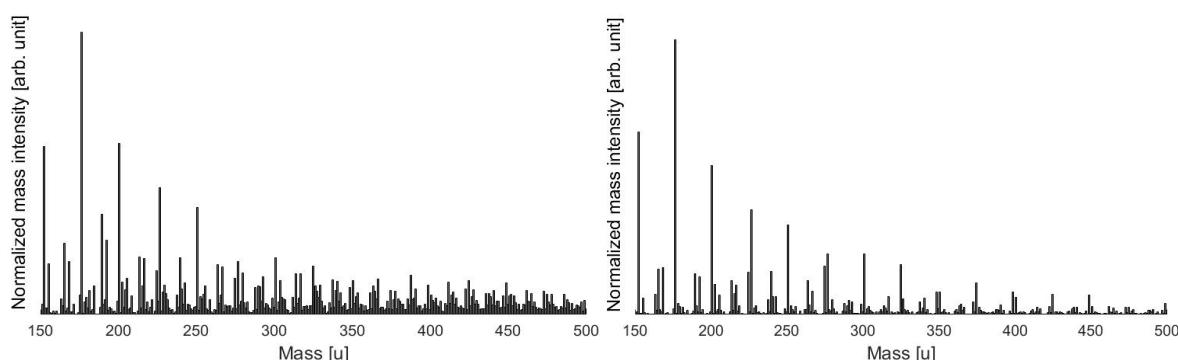


Fig. 1: Simulated mass spectra for pure (left) and doped (right) flames at a HAB of 0.5 mm. The intensities are normalized with respect to the highest peak in the graph.

From Fig. 1, the mass spectrum for the doped flame shows very sharp peaks corresponding to the pure hydrocarbon stabilomers [8] with different number of carbons. Meanwhile, the mass spectrum for the pure flame is spread over a wide mass range. Varieties of oxygenated species such as furans, ethers and phenols are filling the gaps between the pure hydrocarbons. This result indicates that adding ethanol to the ethylene fuel causes a removal of these various oxygenated molecules early in the flame, leaving the gaps on the mass spectrum. Examples of structures formed in a single trace early in both flames are shown below in Fig. 2 and 3 for the pure and doped flame respectively.

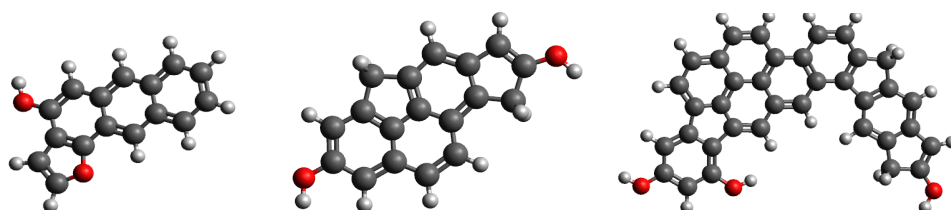


Fig. 2: Examples of compounds obtained using SNapS2 for the pure flame. Snapshots of the time-history of a single benzene molecule at a HAB of 0.1 mm (left), 0.3 mm (middle), and 0.5 mm (right).

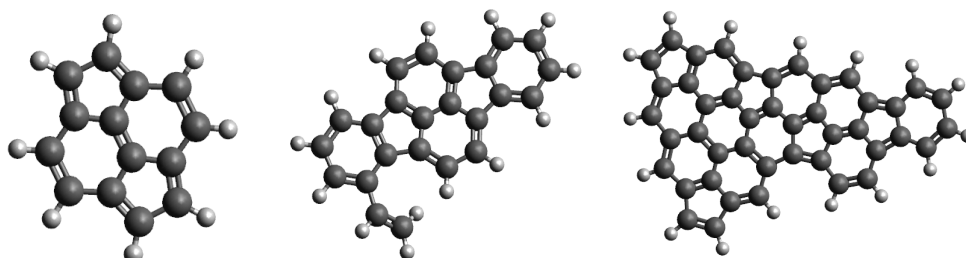


Fig. 3: Examples of structures obtained using the SNapS2 code for the doped flame. Snapshot of the time-history of a single benzene molecule at a HAB of 0.6 mm (left), 0.9 mm (middle), and 1.3 mm (right).

In the pure flame, some furans are observed at a very low HAB (Fig. 2, left), where both O and C_2H_2 have maximum concentrations. But a much larger number of phenols are formed meanwhile, attaching to the edges of large aromatic structures, and later evolving into ethers. In the doped flame, however, almost only pure hydrocarbons are formed with many 5-membered rings both on the edges and embedded. These PACs seem to have less aliphatic chains with rather condensed rings (Fig. 3, right) and thus low H/C ratio.

At a higher HAB (above 1 mm), the PACs growth in both flames is driven by the Hydrogen-Abstraction- C_2H_2 -Addition (HACA) mechanism [9-11] due to the rapid decrease of oxidizing species and relatively high H and C_2H_2 concentrations. Fig. 3 shows the simulated mass spectra at a HAB of 5 mm for both flames.

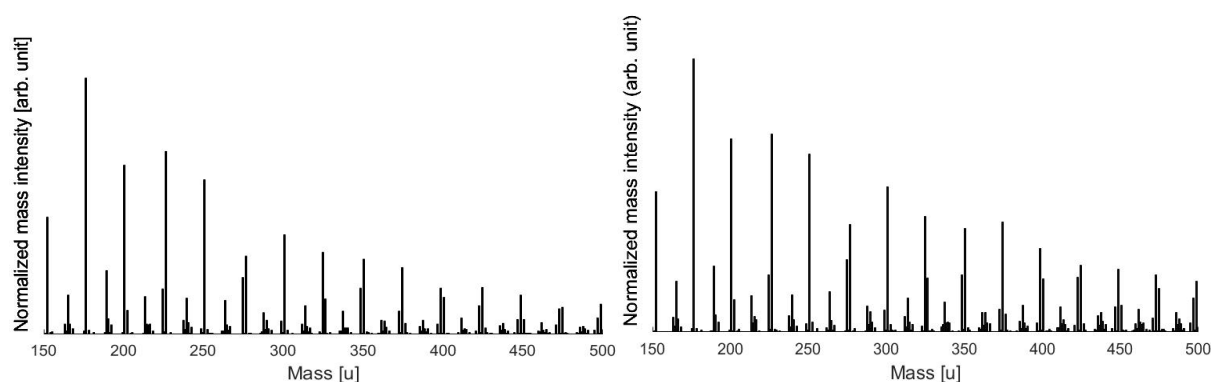


Fig. 3: Simulated mass spectra for pure (left) and doped (right) flames at a HAB of 5 mm. The intensities are normalized with respect to the highest peak in the graph.

Both flames show identical peak values indicating that the growth mechanisms are very similar, which HACA is responsible for the pure hydrocarbon growth in this region. However, compare with the pure flame, the mass spectrum of the doped flame shifts slightly to the right, showing a higher average mass at this height. Thus, it is of the interest to examine the chemical growth rate at different HAB of the two flames, as shown in Fig. 5, left.

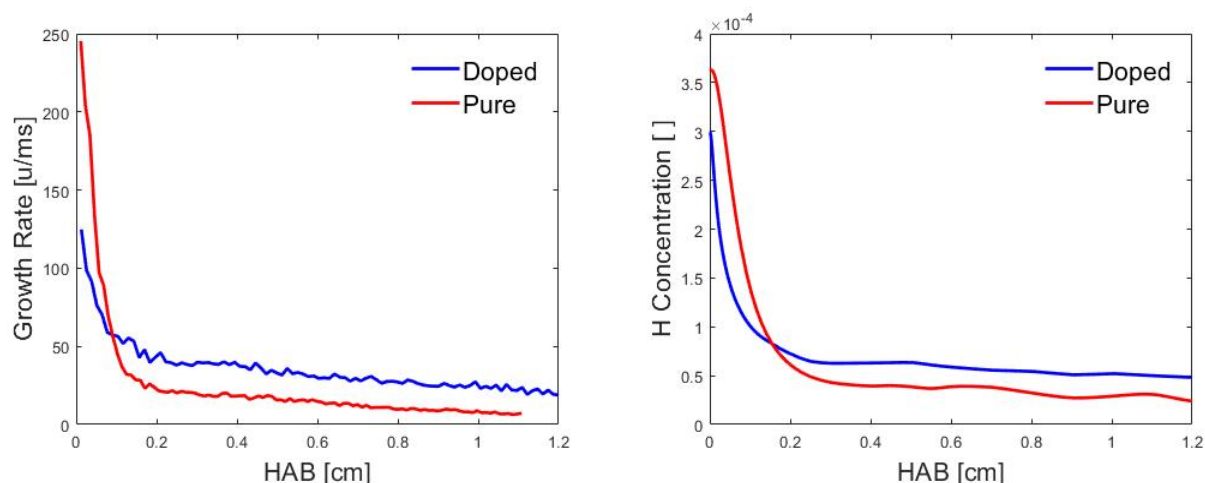


Fig. 5: Left: Chemical growth rate of PACs at different HAB in the doped (blue) and pure (red) flames, obtained using benzene as starting molecule for the SNapS code. Right: H concentration at different HAB in the doped (blue) and pure (red) flames.

The chemical growth rate of the pure flame is much faster at start, despite that the doped flame has higher C_2H_2 concentration than the pure flame. It rapidly decreases and gets slower compare with the doped flame at around 1 mm HAB. This trend corresponds to the H concentration profiles of the two flames (Fig. 5, right). The H radical are important for both HACA and many oxygen reactions, acting as an activation of aromatic edges for further reactions. Adding the fact that C_2H_2 concentration for the doped flame is all-time higher than the pure flame tells that, higher C_2H_2 concentration alone cannot drive the PACs growth. The H radical concentration plays the critical role in the growth rate of PACs. Furthermore, the much higher growth rate at the beginning of the pure flame is also contributed a lot by the oxygen chemistry, as we see in Fig. 2. The cumulative chemical growth shown in Fig. 6 is obtained by integrating over the growth rate in Fig. 5. While the cumulative chemical growth in the pure flame is larger than the doped flame for molecules under 1500 u, the doped flame surpasses the pure flame in cumulative chemical growth after that point. It should be noted that the physical growth starts to be relevant at high molecule masses [12-14] (above 1000-1100 u), thus the

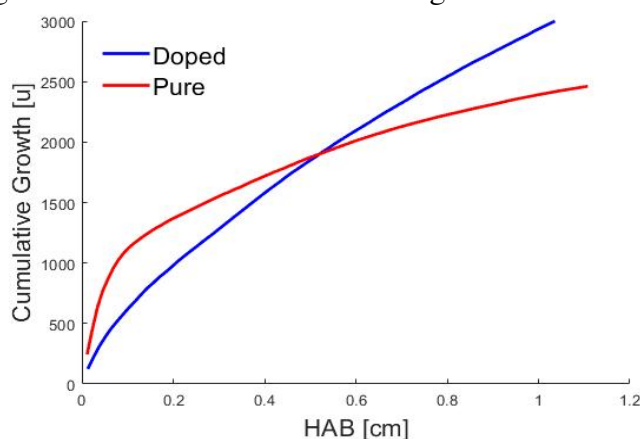


Fig. 6: Cumulative chemical growth of PACs at different HAB in the doped (blue) and pure (red) flames obtained integrating the growth rate.

curves above 1100 u cannot be approximated as the total molecule growth (chemical + physical). Nevertheless, for masses less than 1100 u, pure flame shows a higher tendency to soot compare with the doped flame, which matches the experimental observations [3]. But to explain the experimental observations for soot tendency above 1500 u in the figure, physical models should be incorporated into the chemical growth discussed above.

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