

# EFFECT OF C<sub>9</sub> ALKYL BENZENES ON PARTICLE FORMATION IN DIFFUSION FLAMES: AN EXPERIMENTAL STUDY

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## **Abstract**

In this work we have extended to C<sub>9</sub>H<sub>12</sub> isomers the study about the tendency of light alkylbenzenes to emit particulate matter. N-propylbenzene, iso-propylbenzene and mesitylene have been studied in atmospheric pressure, counter-flow diffusion flames of ethylene, whose fuel stream was doped with 10%, 20% and 30% of C<sub>9</sub>H<sub>12</sub> isomers. The detection of different types of combustion-formed nanoparticles has been performed with in-situ spectroscopy, namely laser UV-induced emission, by changing the detection wavelength from the UV to the visible. Laser induced incandescence has been also measured to detect soot particles. Experimental results have been compared to those obtained in an ethylene/toluene flame operated in the same operating conditions to understand the effect of the alkyl chain length and branching on particulate formation.

The experimental results showed that a branched alkyl chain in the fuel molecular structure enhances particles formation. In particular, in the pyrolytic zone of the flame, the additives with a single chain produced particulate in larger amount with respect to the oxidant side. Instead the presence of three single methyl groups attached to the aromatic ring stabilizes radicals during pyrolysis, making harder the pyrolytic degradation of the compounds. At the same time, radical stabilization allows these compounds to be more exposed to oxygenated radical attacks in the oxidative flame region, subtracting species to particulate formation, and slowing-down the soot formation pathways.

## **Introduction**

Alkylbenzenes, toluene being the most common example, represent a class of six-membered ring aromatic compounds that have a variety of alkyl groups attached. They are used primarily as solvents or as starting materials in the synthesis of other

chemicals and drugs, but they are also integral components of gasoline, distillate fuels and other petroleum products because of their anti-knock properties. Their resistance to low-temperature oxidation and auto-ignition is due to the inhibitory effect of the aromatic ring on chain radical reactions. At the same time, the aromatic ring in their structure enhances the formation of soot precursors such as Polycyclic Aromatic Hydrocarbons (PAHs) [1].

Studies on alkylbenzenes oxidation [2], self-ignition [3], pyrolysis [4], cracking [5], fill the scientific literature but few studies have been performed on their sooting tendency. The investigation of sooting propensity of alkylbenzenes starts in 80's with the works of Olson et al. [6]. More recently McEnally and Pfefferle [7, 8] studied sooting tendency of aromatic hydrocarbons in a coflowing methane/air flame doped with 5-400 ppm of the test hydrocarbons, and Yang et al. that made a study of jet fuel sooting tendency using the threshold sooting index (TSI) model [9]. Using an experimental system similar to that of McEnally & Pfefferle [7, 8], Witkowski et al. [10] evaluated the soot properties of real fuels and surrogate fuels, while Xuan and Blanquart [11] investigated through a numerical modeling study the sooting tendencies of some aromatic and aliphatic compounds. Finally Botero et al. [12] studied the sooting tendency of heptane-toluene diffusion flames.

This study is the continuation of our previous work [13] on the investigation of particulate emissions from four  $C_8H_{10}$  isomers. Now, we extend the investigation to three  $C_9H_{12}$  isomers. The purpose is to confirm modelling studies present in the scientific literature and to ideally integrate previous experimental works through the adoption of different investigation techniques and operating conditions.

### **Experimental methods**

The experimental equipment used in this study have been described in detail in [13, 14]. Counter-flow diffusion atmospheric flames were stabilized by feeding 25%vol ethylene-aromatic mixtures and 75%vol Ar as fuel stream, and 22%vol  $O_2$  and the remaining Ar as oxidizer stream. The oxidizer and fuel stream velocities were fixed at 16.1 and 13.2 cm/s at standard conditions, respectively.

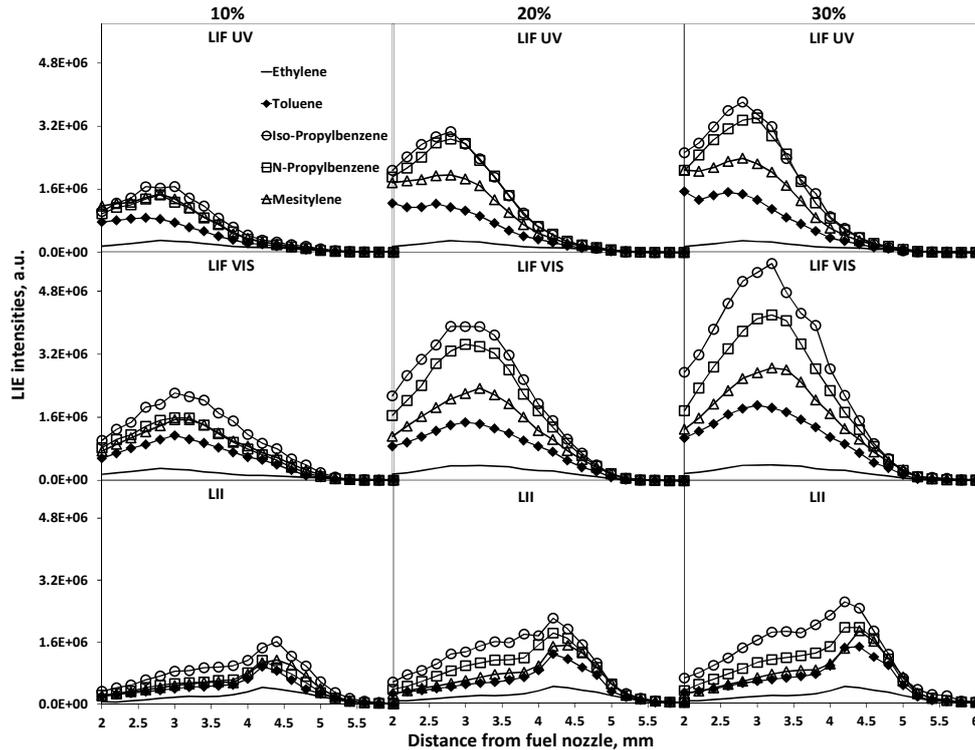
Three  $C_9H_{12}$  liquid isomers, n-propylbenzene, iso-propylbenzene and mesitylene, were selected as fuel additives. Toluene was used as reference mono-ring aromatic. The aromatic component amount was added as 10%, 20% and 30% of aromatic carbon of the total carbon fed to the flame in order to have alkylbenzene concentration up to 250,000 ppm in blend with ethylene, keeping constant the total carbon flow rate. In order to achieve these conditions, the argon flow rate in the fuel stream was adjusted to account for the different molecular weight of the additives. It results in an identical carbon flow rate as well as cold gas velocity, allowing a reliable comparison for the different additives used [14]. Fuel stream was preheated up to 150°C to allow aromatic fuels to completely evaporate before exiting the fuel nozzle.

Particulate matter formation was detected by spectral laser induced emission measurements in the 200-550 nm range, performed by using as excitation source

the fourth harmonic of a Nd:YAG laser at 266 nm. The experimental setup was the same as that used in previous works [13]. The simultaneous detection of UV-Laser Induced Fluorescence (LIF) and Laser Induced Incandescence (LII) allowed to track soot precursor nanoparticles and soot particles contemporarily. In particular, LIF signal in the UV was attributed to single high-molecular weight aromatic molecules with few condensed aromatic rings, whereas LIF in the visible was attributed to highly-packed clusters of aromatic hydrocarbons.

### Experimental results

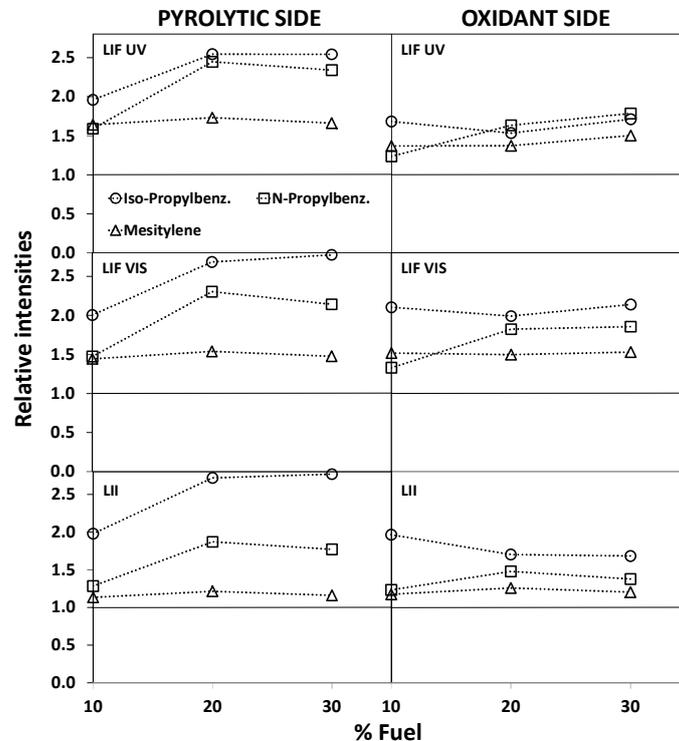
Emission signals were measured along the distance between the two jets, starting from the fuel nozzle.



**Figure 1.** Measured intensity of UV-LIF at 350 nm, Vis-LIF at 400 nm and LII at 550 nm for the pure ethylene flame and for flames with 10% (left), 20% (center) and 30% (right) of  $C_9H_{12}$  isomers.

Figure 1 reports LIF signals in the UV at 350 nm (UV-LIF) and in the visible at 400 nm (vis-LIF), and LII signals at 550 nm for ethylene flames blended with 10%, 20% and 30% of  $C_9H_{12}$ , respectively. As stated in our previous works [13, 14], adiabatic flame temperatures do not show significant variation by changing the

additive; hence the location of the stagnation plane remains almost unchanged in the four flames. Nevertheless, the addition of the aromatic fuels results in the enhancement of the fluorescence and incandescence intensities. Moreover, when the substituent percentage in the blends increases, the intensities of the fluorescence and the incandescence signals increase correspondingly.



**Figure 2.** Relative emissions with respect to the ethylene/*toluene* flame as a function of the percentage of aromatic added. Top to bottom: UV-LIF at 350 nm, vis-LIF at 400 nm and LII at 550 nm. Left (right) column reports relative intensity measured in the fuel (oxidant) side.

Figure 2 summarizes the effect of the addition of alkylated aromatic fuels on the formation of the particulate in fuel and oxidant sides of the flame. It shows the ratio between the maximum intensity of the fluorescence and incandescence signals found in ethylene/additive flames and those found in ethylene/*toluene* flame in the same conditions, as function of the amount of aromatic fuel substituted to ethylene. The addition of alkylated aromatic compounds enhances both fluorescence and incandescence signals and thus the formation of small nanoparticles as well as soot.

Also, the increase of the emission signals is found in both fuel (pyrolytic) and oxidant sides.

The largest effect in the production of particulate matter is due to iso-propylbenzene. In particular, in the fuel side (pyrolytic) the presence of long chains as for iso- and n-propylbenzene gives the highest increase of the LIF and LII signals. Also, the effect of the chain branching is more marked for LIF visible and incandescence signals.

In the oxidative zone of the flame, the three C<sub>9</sub> isomers behave similarly to the pyrolytic region even if the increase of the signals with respect to the reference flame is smaller. Furthermore, while in fuel side iso-propylbenzene shows a strong enhancement of particulate formation when its percentage of addition increases, in the oxidative side it shows a light decrease of relative LIE at increasing percentages in the blend.

### Conclusions

The effect of the chain length and methyl group position of alkylated aromatic hydrocarbons has been investigated experimentally in a counter-flow diffusion flame configuration. Iso-propylbenzene, n-propylbenzene and mesitylene have been chosen among C<sub>9</sub>H<sub>12</sub> isomers. A blend of ethylene and toluene has been used as reference fuel. Laser induced fluorescence and incandescence technique, previously validated [14], has been used to detect small nanoparticles and soot aggregates, respectively.

The two regions of the flame, a fuel pyrolytic region characterized by low temperatures and an oxidant region characterized by high temperatures, have been analyzed, and UV and visible fluorescence and incandescence signals have been detected in both regions.

The addition in blend with ethylene of toluene, iso-propylbenzene, n-propylbenzene and mesitylene has resulted in a great enhancement of particles production. In both flame regions, n-propylbenzene and mesitylene showed the same tendency to form particles when added in blend with ethylene as 10% of aromatic carbon, while for higher percentages n-propylbenzene contributed more strongly. Globally, iso-propylbenzene flame produced the highest LIE signals because the branching of its alkyl chain makes it more exposed to radical attacks. LIE intensities found in oxidative zone were lower than signals in pyrolytic side because of the higher temperature and the presence of oxygenated species that make the environment more reactive and contribute to the oxidation of compound fragments, arising a competition for particles formation pathways. Results showed that the longer and more branched is the side alkyl chain, the higher is particles formation enhancement.

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