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# Experimental Study of the Impact of Oxygenated Fuels on Pollutant Emissions in Flame Conditions

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## Abstract

Oxygenated biofuels work as a promising renewable alternative. Despite the fact that biofuels tend to decrease the soot emissions, they may lead to new emission problems such as the formation of aldehydes (notably formaldehyde and acetaldehyde). In this study, experimental work is carried out to analyze the chemical processes involved during combustion of the oxygenated biofuels. Atmospheric premixed laminar flames of a toluene reference fuel (iso-octane, n-heptane, toluene) mixed with two biofuels (ethanol and butanol) stabilized on a McKenna burner were investigated in fuel-rich flame conditions. Mole fractions of several saturated and unsaturated aliphatics, aldehydes, ketones and aromatic species were measured using gas chromatography in order to elucidate the chemical structure of the flames.

## Introduction

In order to reduce the fossil fuel dependency and the net CO<sub>2</sub> emissions of spark-ignition engines, bio-fuels, containing oxygen atoms, are being considered as a promising lever. This is why the percentage of ethanol in gasoline, up to 10% today, should continue to increase in the coming years. Although oxygenated fuels tend to reduce soot emissions, fundamentals concerning their chemical interaction with Polycyclic Aromatic Hydrocarbons (PAHs) and soot particles are still rudimentary. Moreover, the use of such alternative fuels gives rise to new pollutant issues. For example, they produce much larger amounts of formaldehyde and aldehyde as compared to standard fuels. As these molecules are highly toxic, they will be regulated in the future Euro 7 norm. The influence of the structure of the oxygenated fuels on the formation of these specific pollutants is also not well known.

A better understanding of the chemical processes related to the use of these new bio-fuels requires experimental measurements to establish a detailed database including aldehydes, PAHs and soot during the combustion of oxygenated fuels. The objective of this study is to establish an experimental detailed database to characterize the combustion chemistry of the *ternary* toluene reference fuel (TRF) blended with ethanol and iso-butanol, and the influence of these oxygenated biofuels on key chemical species involved in pollutant emissions. In the literature, there are some studies on the combustion chemistry of TRF [1–3] and a few ones with TRF/alcohol mixtures [4,5], but studies with quantitative analysis of chemical species under flame conditions remain very limited. Some preliminary results of our work are presented in this paper.

## Experimental methods

Fig. 1 presents a schematic diagram of the used experimental setup. It includes a flame burner, three Gas Chromatograph (GC) setups and a NO-LIF (Laser Induced Fluorescence) system. These setups are briefly described below.

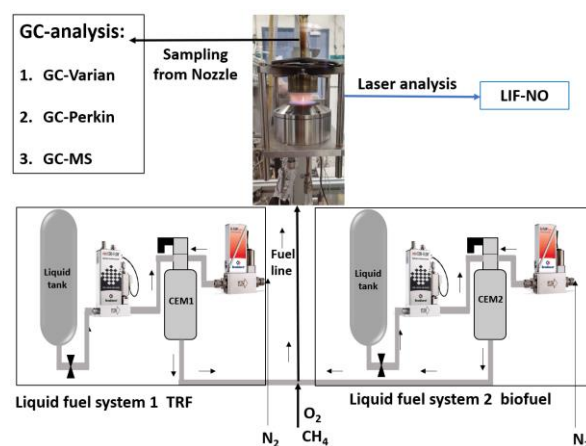


Fig. 1. Experimental setup including two liquid fuel systems, a burner, and analytical techniques.

## Atmospheric flame burner setup:

The used burner is a McKenna atmospheric flat laminar premixed flame burner. It consists of a central bronze porous plug (60 mm in diameter). The porous zone is surrounded by another co-annular porous used for the nitrogen shroud (27 L<sub>n</sub>/min), which protects the flame from air entrainment responsible for the formation of any peripheral diffusion flame and aerodynamic perturbations. The temperature of the burner is constantly maintained at 55°C using a cryostat. In order to stabilize fuel-rich flames, a stainless-steel disc, also known as the stagnation plate (6 cm in diameter and 3 cm thick) was surmounted at a

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distance of 21 mm with respect to the burner surface and is pierced at its center to provide access for the sampling quartz microprobe. An additional metallic grid was placed directly on the stagnation plate, to avoid peripheral flame ignition.

In this study, liquid TRF fuels were prepared using a system of three volumetric burettes and subsequently used in System 1 (Fig. 1). The composition of the mixture was based on the individual densities and the molar ratios of its three component fuels. Specifically, the mixture was formulated using a fixed molar ratio for each component: 0.447 for iso-octane, 0.423 for toluene, and 0.13 for n-heptane, with corresponding densities of 0.692 g/mL, 0.867 g/mL, and 0.684 g/mL, respectively. In contrast, System 2 (Fig. 1) was filled with one biofuel at a time (either ethanol or iso-butanol). The liquid flow rate of a TRF fuel was controlled using a Coriolis flow controller (Bronkhorst, error  $\pm 0.2\%$ ) followed by an evaporator/mixer, in which TRF is evaporated and mixed with  $N_2$ . The gaseous stream is then mixed with  $O_2$  and  $CH_4$  and fed to the burner. Flow rates of  $CH_4$  (Air Liquide, purity  $\geq 99.95\%$ ),  $O_2$  and  $N_2$  (Air Liquide, purity  $\geq 99.995\%$ ) were controlled using mass flow controllers (Bronkhorst, error  $\pm 0.5\%$ ). Flame conditions are listed in Table 1.

*Table 1: Flame conditions. TRF: ternary toluene reference fuel. TRF-E: TRF with ethanol. TRF-B: TRF with iso-butanol.*

Name	Flow rate (Ln/min)						$\Phi$
	$O_2$	$N_2$	$CH_4$	TRF	Biofuel	Total	
TRF	2.313	6.6	0.678	0.264	0.000	9.9	1.82
TRF-E	2.243	6.6	0.728	0.227	0.057	9.9	1.82
TRF-B	2.269	6.6	0.710	0.218	0.058	9.9	1.82

#### **Temperature measurements:**

NO-LIF (Laser Induced Fluorescence) thermometry was used to measure flame temperatures profiles. A small amount of NO (500 ppm) was substituted to the nitrogen diluent. This small quantity does not perturb the chemical structure or the temperature of the flame and is sufficient to provide a good signal-to-noise ratio. The laser (Quantel, TDL+ pumped with a seeded YAG Q-smart 850) was tuned over 225.65 – 225.73 nm to excite NO in the A-X(0,0) band. The laser energy was maintained at 100  $\mu$ J, which is within the linear LIF regime. The LIF signal was then collected in the complete A-X(0,2) band of NO using a spectrometer centered at 245 nm. Temperatures were determined by fitting synthetic LIF excitation spectra to the experimental spectra following a procedure previously detailed [6].

#### **Chemical species measurements:**

A quartz sampling microprobe (orifice  $\sim 180 \mu$ m) was used to collect the gaseous samples from each studied flame at different heights above the burner (HAB) in order to be able to identify and quantify the

chemical species produced during combustion processes by using three different gas chromatograph (GC) systems. So gaseous samples are directed to GCs through a transfer line that was heated at 130  $^\circ$ C to avoid condensation of the heavy products. The first GC system is a CP-3800 Varian, which is used to measure  $O_2$ ,  $N_2$ , CO, hydrocarbon species from  $C_1$  (methane) to  $C_7$  (toluene). In this system, the chemical species were analyzed using two columns (CP- $Al_2O_3/KCL$  50 m $\times$ 0.32 mm $\times$ 5  $\mu$ m and HPMOLSIV 30 m $\times$ 0.53 mm  $\times$ 50  $\mu$ m) and two detectors: the FID (flame ionization detector) and the TCD (thermal conductivity detector). The second GC is a PerkinElmer Clarus 580, used to measure and analyze small oxygenated  $C_1$ - $C_8$  species (alcohols, aldehydes, and ketones). This system can also detect  $CO_2$  and some hydrocarbon species that allows us to compare our results with GC Varian thereby reinforcing the confidence in our measurements. In GC-Perkin, the gaseous sample is analyzed with three different columns (HaysepQ 1/16" 2m $\times$ 1mm ID, MS5A 1/16 2m $\times$ 1mm ID, Rt-Q-Bond 30m $\times$ 0.25mm $\times$ 8 $\mu$ m), which are connected to TCD detector and FID detector coupled with a methanizer (nickel catalyst hydrogenating reactor). The third GC system (Agilent Technologies 5975C), which is equipped with MS with electron ionization at 70 eV, is used for the identification of chemical species by comparison of the obtained MS spectra with the NIST database. This GC-MS uses the same column as used in Perkin (RtQ-Bond 30m $\times$ 0.25mm $\times$ 8 $\mu$ m). Chemical species were identified by their individual retention times and MS spectra. The direct calibration has been done using commercial bottle cylinders when possible, otherwise calibration factors from the methanizer (Perkin) or effective carbon number approach (Varian) were used.

#### **Results and discussions**

Table 2 provides an overview of the detected species that were sampled from the centerline of the flame. Non-oxygenated and oxygenated species from  $C_0$  to  $C_8$  were identified. They are categorized based on their respective number of C-atoms. Oxygen ( $O_2$ ), hydrogen ( $H_2$ ), and nitrogen ( $N_2$ ) are denoted as  $C_0$ . The  $C_7$  species include n-heptane ( $C_7H_{16}$ ) and toluene ( $C_7H_8$ ), while the  $C_8$  species include iso-octane ( $C_8H_{18}$ ) and monoaromatics like styrene ( $C_8H_8$ ), ethylbenzene ( $C_8H_{10}$ ). Additionally, the study also encompasses oxygenated biofuel reactants such as ethanol ( $C_2H_5OH$ ) and iso-butanol ( $C_4H_9OH$ ). Furthermore, some of the major intermediates detected during the experiment include acetylene ( $C_2H_2$ ) and benzene ( $C_6H_6$ ), amongst others. Finally, the identified products include carbon dioxide ( $CO_2$ ), which is a significant contributor to the greenhouse effect, carbon monoxide (CO), which is a primary pollutant in engine exhaust, and hydrogen ( $H_2$ ). The species were identified based on their retention times in the chromatogram and were quantified according to their respective areas.

Table 2: Summary of the detected species.

<b>C<sub>0</sub> species</b>	O <sub>2</sub> , H <sub>2</sub> , N <sub>2</sub>
<b>C<sub>1</sub> species</b>	CO, CO <sub>2</sub> , CH <sub>4</sub>
<b>C<sub>2</sub> species</b>	C <sub>2</sub> H <sub>6</sub> (Ethane), C <sub>2</sub> H <sub>4</sub> (Ethylene), C <sub>2</sub> H <sub>2</sub> (Acetylene)
<b>C<sub>3</sub> species</b>	C <sub>3</sub> H <sub>8</sub> (Propane), C <sub>3</sub> H <sub>6</sub> (Propene), aC <sub>3</sub> H <sub>4</sub> (Allene), pC <sub>3</sub> H <sub>4</sub> (Propyne)
<b>C<sub>4</sub> species</b>	i-C <sub>4</sub> H <sub>8</sub> (iso-Butene), 1C <sub>4</sub> H <sub>8</sub> (1-Butene), 1,3C <sub>4</sub> H <sub>6</sub> (1,3-Butadiene), BC <sub>4</sub> H <sub>6</sub> (1-Butyne), i-C <sub>4</sub> H <sub>10</sub> (iso-Butane), C <sub>4</sub> H <sub>4</sub> (Vinylacetylene)
<b>C<sub>5</sub> species</b>	n-C <sub>5</sub> H <sub>12</sub> (n-Pentane), C <sub>5</sub> H <sub>10</sub> (1-Pentene, cis, trans-2-Pentene), ...
<b>C<sub>6</sub> species</b>	C <sub>6</sub> H <sub>6</sub> (Benzene), ...
<b>C<sub>7</sub> species</b>	C <sub>7</sub> H <sub>8</sub> (Toluene), C <sub>7</sub> H <sub>16</sub> (n-heptane)
<b>C<sub>8</sub> species</b>	C <sub>8</sub> H <sub>18</sub> (iso-octane), C <sub>8</sub> H <sub>8</sub> (styrene), C <sub>8</sub> H <sub>10</sub> (ethylbenzene), ...

<b>Oxygenated species</b>	C <sub>2</sub> H <sub>5</sub> OH (Ethanol), C <sub>4</sub> H <sub>9</sub> OH (Iso-butanol), CH <sub>2</sub> O (Formaldehyde), CH <sub>3</sub> OH (Methanol), CH <sub>3</sub> CHO (Acetaldehyde), C <sub>2</sub> H <sub>3</sub> CHO (Acrolein), C <sub>2</sub> H <sub>5</sub> CHO (Propanal), CH <sub>3</sub> COCH <sub>3</sub> (Acetone), ...
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#### TRF flame structure:

Fig. 2 presents the flame temperature and the mole fraction profiles as a function of the HAB of the main species including reactants (fuels, O<sub>2</sub>) and final products (CO, CO<sub>2</sub>, H<sub>2</sub>) for the reference TRF flame. As expected, the mole fractions of reactants decrease, while the mole fractions of products increase in the reaction zone (HAB=0-4 mm). Because of the fuel-rich conditions, CO and H<sub>2</sub> are predominant in the burnt gas. CO<sub>2</sub> is about 4 times lower than CO. In the burnt gases, the temperature reaches about 1850 K and then reduces when close to the stabilization plate.

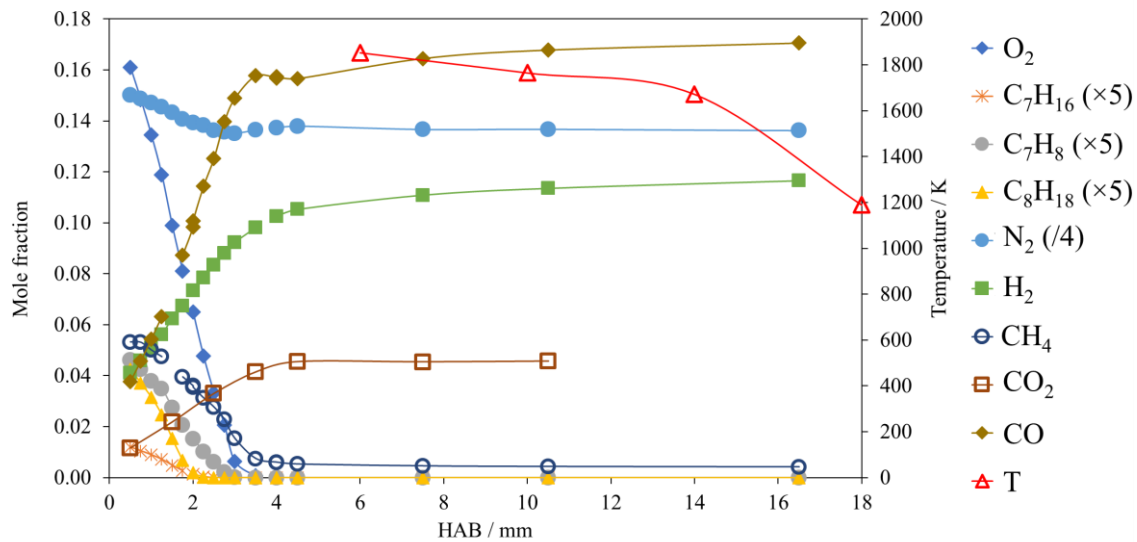


Fig. 2. TRF flame structure: mole fraction profiles of reactants (*n*-heptane C<sub>7</sub>H<sub>16</sub>, toluene C<sub>7</sub>H<sub>8</sub>, iso-octane C<sub>8</sub>H<sub>18</sub>, CH<sub>4</sub>, O<sub>2</sub>), diluent (N<sub>2</sub>), major products (H<sub>2</sub>, CO, CO<sub>2</sub>), and temperature points in the burned gas zone.

#### Influence of the addition of ethanol and iso-butanol on final products and flame temperature:

Fig. 3 illustrates the final CO and H<sub>2</sub> mole fraction profiles obtained in the three flames studied at different HABs ranging from 0.5 mm to 16.5 mm, along with the temperature profile for each flame at HAB = 6 mm. The results show that the addition of ethanol or iso-butanol to the TRF flame did not result in any significant effects on the mole fraction profiles for CO and H<sub>2</sub>. However,

a slight decrease in the mole fraction of CO, accounting for 11%, is observed at 16.5 mm in TRF-E flame. Similarly, the temperature profiles of the three flames exhibit a marginal difference. The temperature difference between TRF and TRF-E is only 33K, equivalent to 1.8%, and it is 54K, equivalent to 2.9%, for TRF and TRF-B. Nonetheless, these differences fall within the uncertainty range of the temperature measurement technique, which is ±100K.

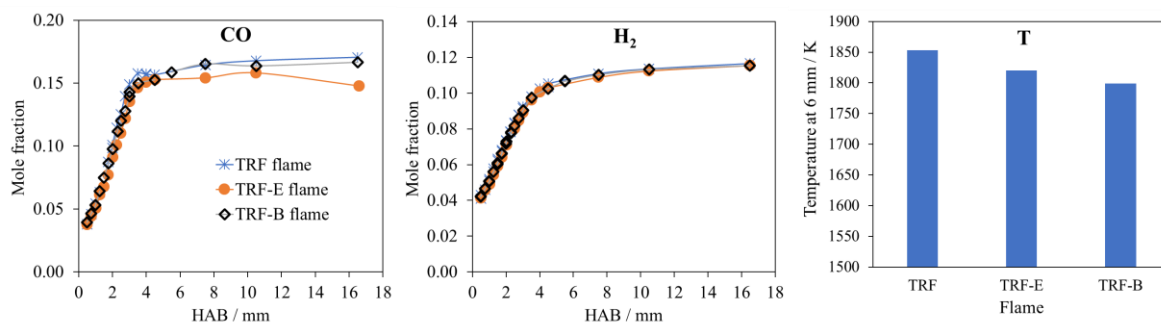


Fig. 3. CO and H<sub>2</sub> mole fraction profiles and temperature at 6mm. See flame names and conditions in Table 1.

#### ***Influence of the addition of ethanol and iso-butanol on (small) soot precursors and oxygenated species:***

Fig. 4 (left panel) presents some selected hydrocarbons, e.g. acetylene (C<sub>2</sub>H<sub>2</sub>), propene (C<sub>3</sub>H<sub>6</sub>), iso-butene (i-C<sub>4</sub>H<sub>8</sub>), benzene (C<sub>6</sub>H<sub>6</sub>) and styrene (C<sub>8</sub>H<sub>8</sub>). These species are known as soot precursors. For example, C<sub>2</sub>H<sub>2</sub> participates in the HACA mechanism of growing PAHs [7]. The intermediate species analysis of the three flames investigated in this study revealed C<sub>2</sub>H<sub>2</sub> as the most abundant species, with a concentration of ~16000 ppm. C<sub>3</sub>H<sub>6</sub> and i-C<sub>4</sub>H<sub>8</sub> are known to participate in the formation of the first aromatics. C<sub>6</sub>H<sub>6</sub> and C<sub>8</sub>H<sub>8</sub> are important mono aromatics involved in forming heavier aromatics [8]. To explain the influence of the addition of biofuels in the TRF flame, Fig. 5 shows some possible reaction pathways from fuels and their association with the formation of the aforementioned products.

The experimental mole fractions of acetylene (C<sub>2</sub>H<sub>2</sub>) exhibited similar behavior when the TRF flame was added with either ethanol or iso-butanol at an equivalence ratio of 1.82. One of the reaction pathways for propene (C<sub>3</sub>H<sub>6</sub>) production is through n-heptane (C<sub>7</sub>H<sub>16</sub>), as shown in Fig. 5. When n-heptane undergoes a H-abstraction reaction, a fuel radical is formed, which then decomposes through β-scission to produce propene. Iso-butene (i-C<sub>4</sub>H<sub>8</sub>) is primarily produced from iso-octane, through H-abstraction forming a tertiary fuel radical which then undergoes β-scission to produce iso-butene [9]. Styrene could be predominantly produced through an H-abstraction reaction from toluene by an X radical at the methyl group (lowest C-H bond dissociation energy [10]), forming a fuel radical that then undergoes a recombination reaction, while benzene could be produced through H ipso-addition. Upon the addition of either ethanol or iso-butanol, significant decreases in

mole fraction were observed for the aforementioned intermediate species. The mole fraction of C<sub>3</sub>H<sub>6</sub> decreased from 3371 ppm in TRF flame to 2535 ppm and 2323 ppm in iso-butanol and ethanol added flames, respectively. Also, concentration of i-C<sub>4</sub>H<sub>8</sub> decreases from 3165 ppm to 2394 ppm and 2122 ppm, respectively. The same trend has been shown with C<sub>6</sub>H<sub>6</sub> from 1094 ppm to 785 ppm and 835 ppm, and C<sub>8</sub>H<sub>8</sub> from 101 ppm to 66 ppm in the two biofuel added flames.

The right panel of Fig. 4 displays selected oxygenated hydrocarbons, including methanol (CH<sub>3</sub>OH), formaldehyde (CH<sub>2</sub>O), acetaldehyde (CH<sub>3</sub>CHO), acrolein (C<sub>2</sub>H<sub>3</sub>CHO), and propanal (C<sub>2</sub>H<sub>5</sub>CHO). Most of them are known to be highly toxic and produced in significant amounts in the flames under the studied conditions. Fig. 5 shows some possible reaction pathways from fuels and their association with the formation of these intermediates. One of possible formation paths of acetaldehyde is through the H-abstraction reaction at alpha position of ethanol (lowest C-H bond dissociation energy [11]) to form a fuel radical, followed by β-scission. This explains the clear increase in the mole fraction of acetaldehyde from 99 ppm in TRF flame to 413 ppm in TRF with added ethanol (Fig. 4). Similarly, the production of propanal from iso-butanol could occur via the H-abstraction reaction at the alpha position (lowest C-H bond dissociation energy [12]) to form a fuel radical, followed by the β-scission reaction and then tautomerization to form propanal. This clarifies the significant increase of propanal in Fig. 4 after adding iso-butanol to the TRF flame, from 13 ppm in TRF to 103 ppm in the iso-butanol added flame. However, the addition of ethanol or iso-butanol does not show significant influence on the formation of CH<sub>3</sub>OH, CH<sub>2</sub>O, and C<sub>2</sub>H<sub>3</sub>CHO.

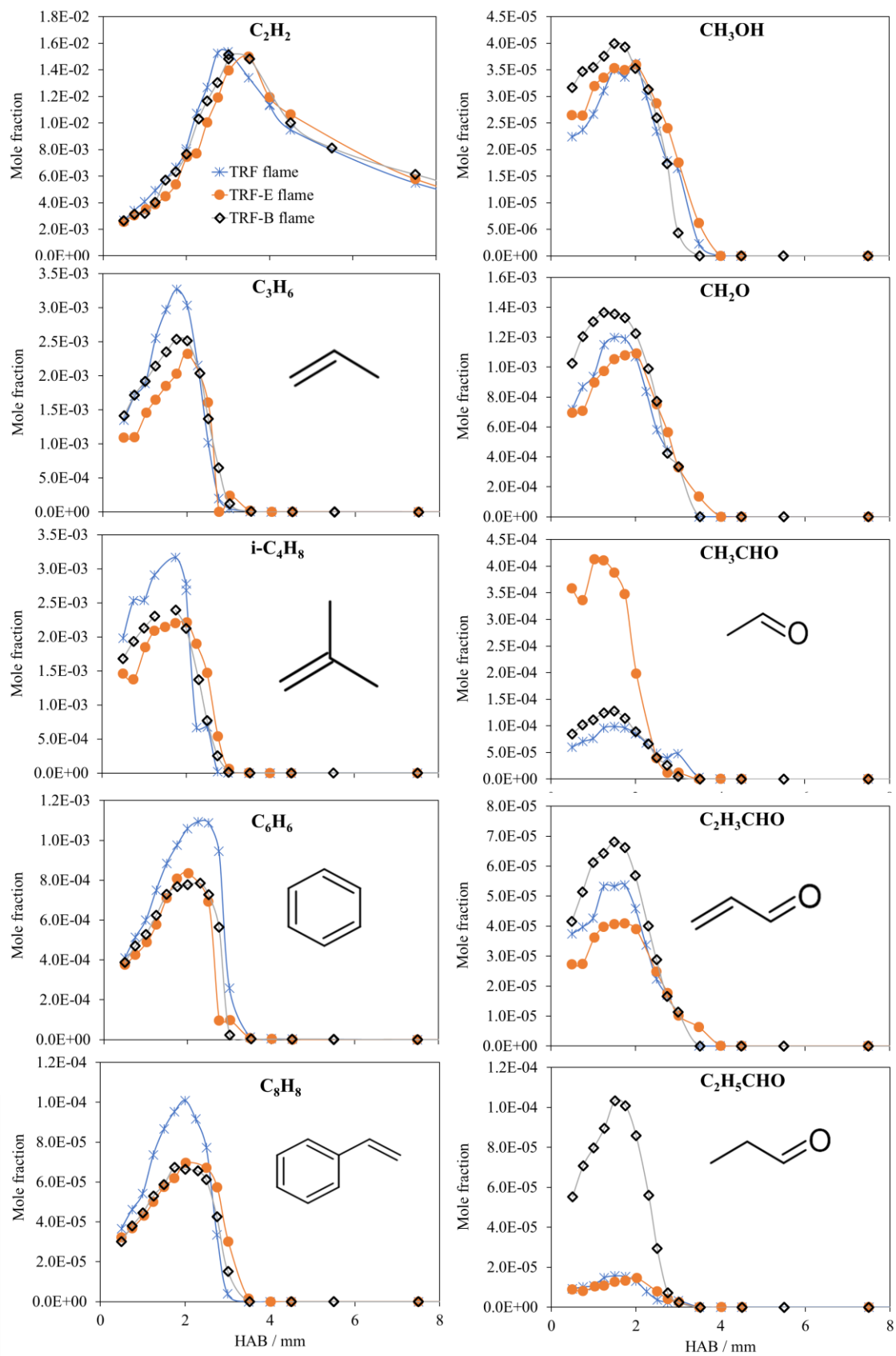


Fig. 4. Mole fraction profiles of selected soot precursors (left panel) and oxygenated intermediates (right panel) measured in the three flames.

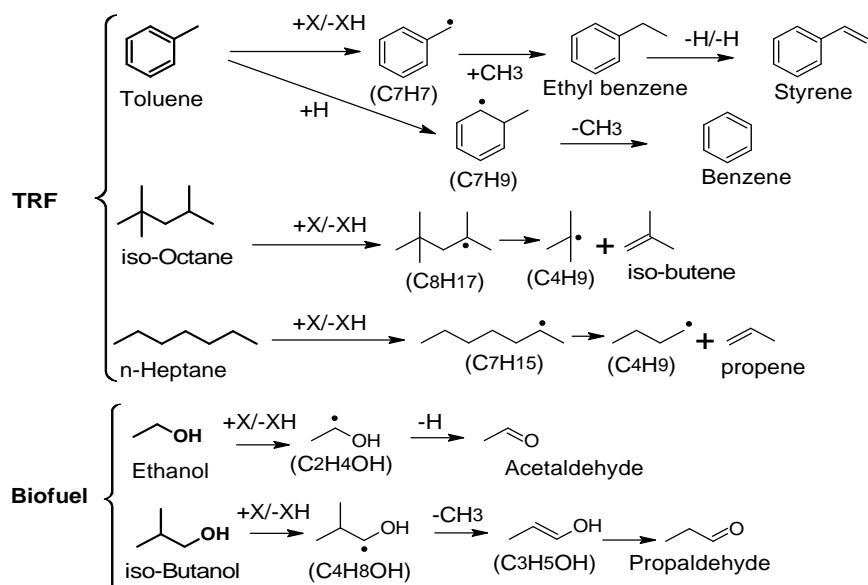


Fig. 5. Some possible reaction pathways from fuels to selected products

### Conclusion and perspectives

Based on the results of this study, it can be concluded that the addition of biofuels to atmospheric laminar premixed flames stabilized at the McKenna burner leads to significant changes in the mole fractions of certain species. Specifically, a decrease in the mole fractions of C<sub>3</sub>H<sub>6</sub>, i-C<sub>4</sub>H<sub>8</sub>, C<sub>6</sub>H<sub>6</sub>, and C<sub>8</sub>H<sub>8</sub> was observed, while no change was observed for C<sub>2</sub>H<sub>2</sub>. Additionally, an increase in the amounts of oxygenated species, particularly CH<sub>3</sub>CHO and C<sub>2</sub>H<sub>5</sub>CHO, was observed. However, the temperature of the flame was not significantly affected by the addition of biofuels. Further investigation is needed to explore the influence of biofuel addition on heavier species such as PAHs and soot.

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