

Laboratory studies of the combustion of terpenes biofuels and pollutants characterization.

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1 Introduction

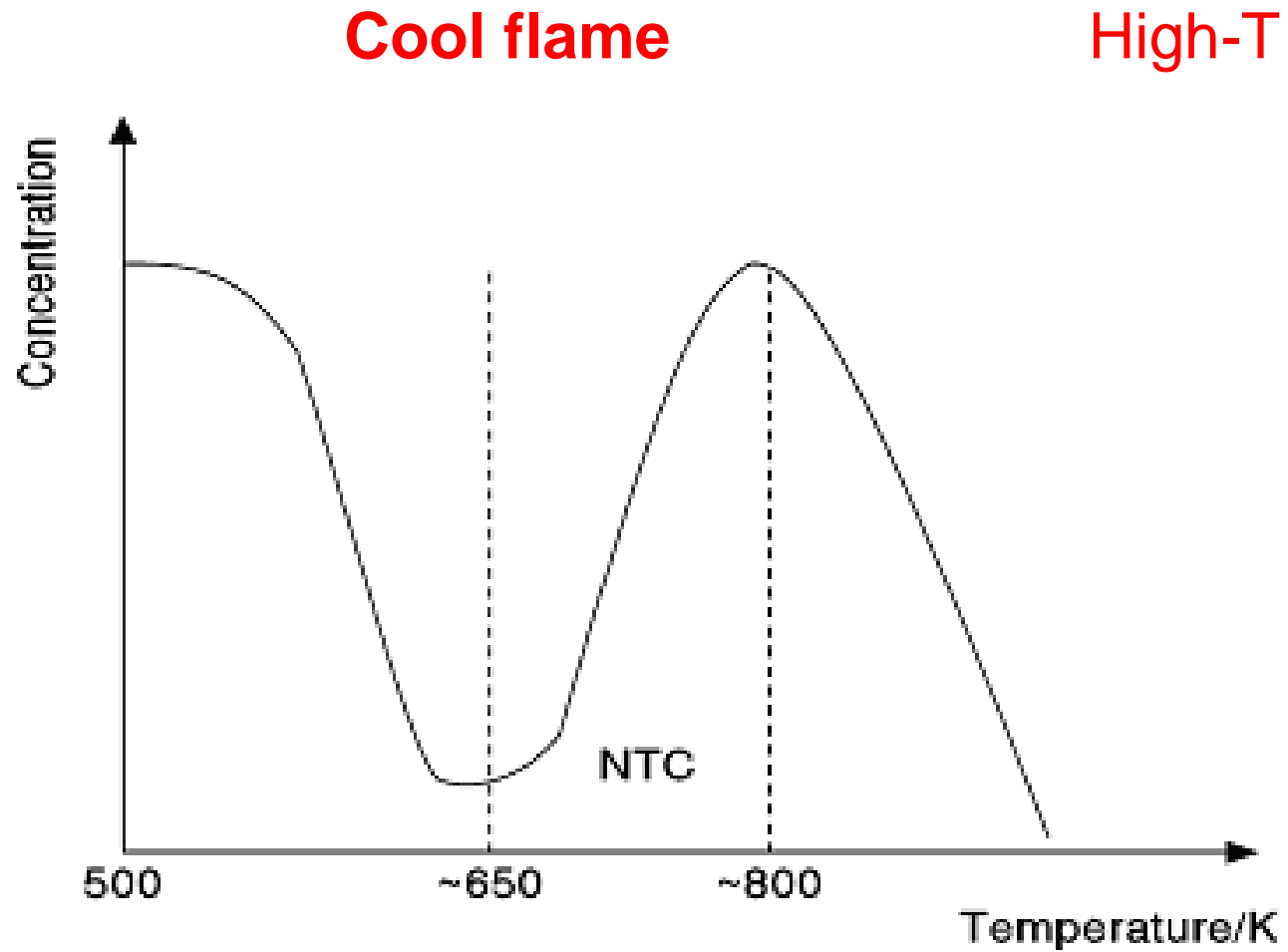
Terpenes are naturally emitted by vegetation. They represent an important fraction of volatile organic compounds (VOCs) present in the troposphere.

Because of their **high-energy-density**, they could potentially be used as **biojet fuels** for greener transportation. The introduction of terpenes as fuel would contribute inevitably to increased emissions into the troposphere via unburnt fuel emissions and evaporation during, e.g., refueling.

Although, the kinetics of oxidation of terpenes under simulated tropospheric conditions has been extensively studied, a good knowledge of the numerous oxidation processes involved has not been reached.

Regarding the kinetics of combustion of this class of compounds, even less is known since, to our knowledge, only flame speeds and impact on ignition have been studied.

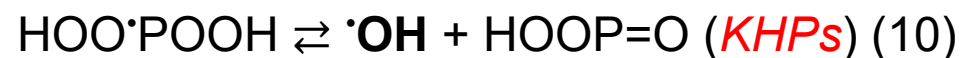
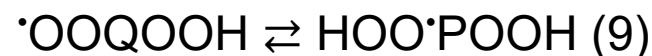
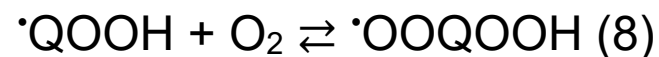
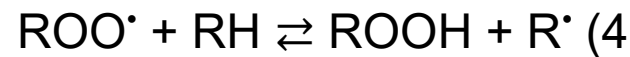
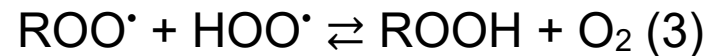
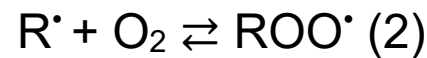
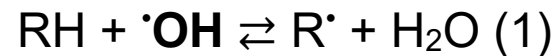
Combustion regimes

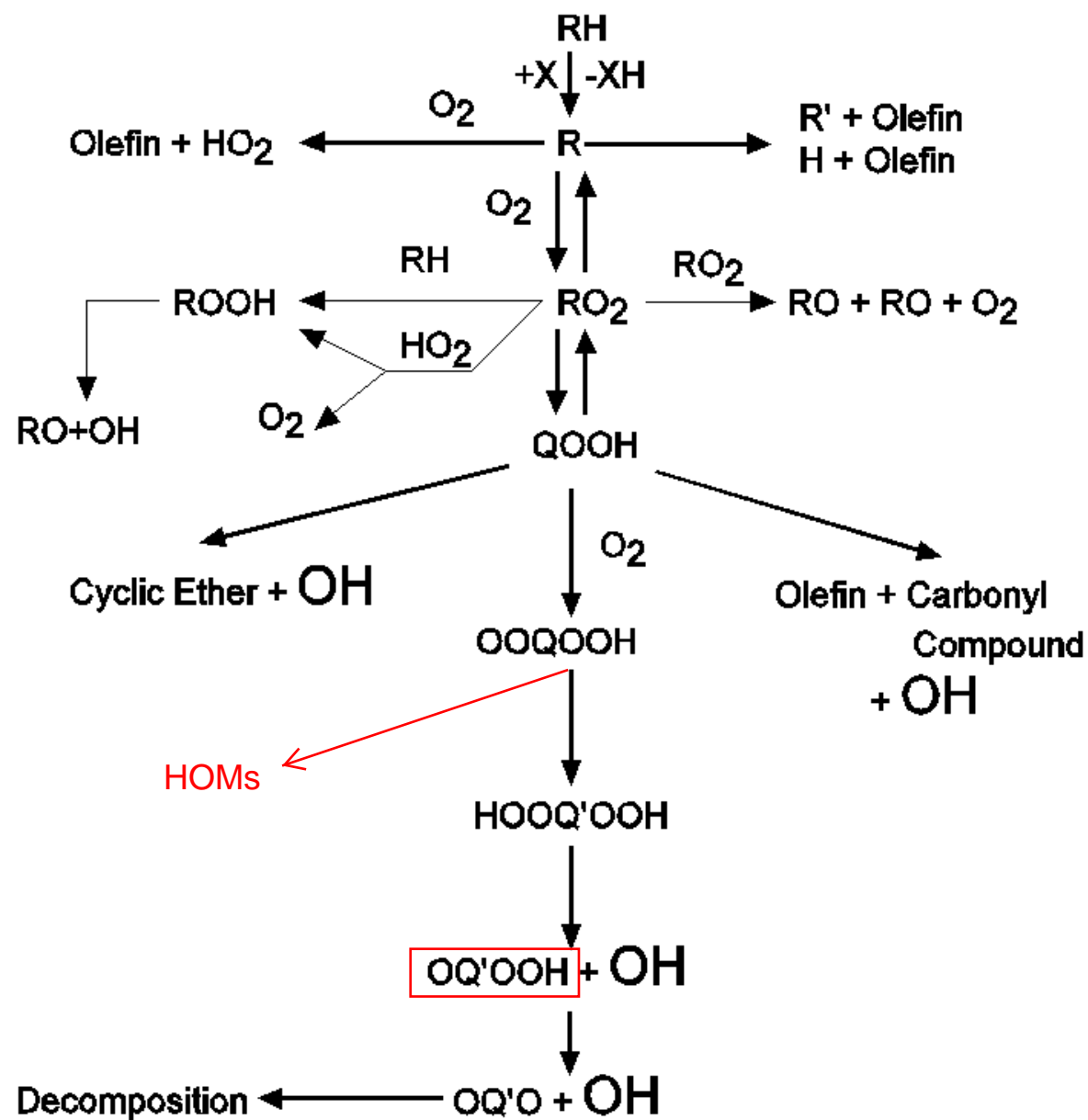


Fuel concentration vs. temperature

Combustion chemistry (simplified)

In combustion we consider that **autoxidation** of hydrocarbons (RH) produces oxygenated products such as ketohydroperoxides (*KHPs*) which lead to chain branching via decomposition:





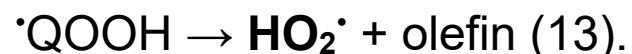
Besides, the production of **highly oxidized organic products** in cool flames of alkanes, cycloalkanes, alcohols, aldehydes, ethers, and esters has been reported in recent studies (Wang *Combust. Flame* **187** (2018) 199-216; Wang *PNAS* **114** (2017) 13102-13107; Belhadj *Combust. Flame* **222** (2020) 133-144).

This alternative oxidation pathway proceeds via an H-shift in the $\cdot\text{OOQOOH}$ intermediate involving a H-C group other than the H-C(OOH)- group responsible for the formation of KHPs.

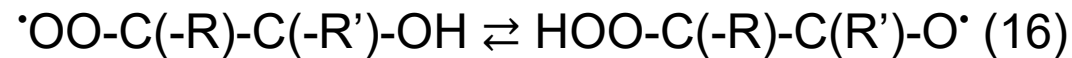
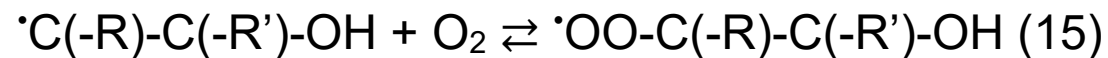
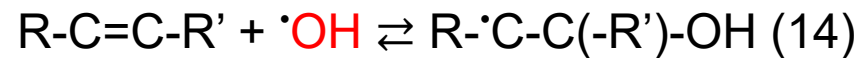
It opens **new oxidation pathways** including a third O_2 addition to $\text{HOOP}\cdot\text{OOH}$ yielding $\cdot\text{OOP}(\text{OOH})_2$.

Such sequence of H-shift and O_2 addition can repeat, yielding highly oxidized products.

Besides, $\cdot\text{QOOH}$ can decompose to yield radicals and stable products:



In the case of **unsaturated reactant**, the **Waddington** mechanism, which involves $\cdot\text{OH}$ addition to the C=C double bond followed by O_2 addition and H-shift from the $-\text{OH}$ group to the $-\text{OO}\cdot$ peroxy group, followed by decomposition, can occur:



Through this mechanism, the **OH** radical initially consumed is finally regenerated in Reaction (17).

Also, as demonstrated initially in the liquid phase, the **Korcek** mechanism, which transforms **γ -ketohydroperoxides** into a carboxylic acid and a ketone or an aldehyde, can occur.

The production of these chemicals via the Korcek mechanism has been suggested to happen under tropospheric conditions and has also been introduced in recently proposed combustion kinetic reaction mechanisms (Ranzi *Combust. Flame* **162** (2015) 1679-1691; Xie *Combust. Flame* **242** (2022) 112177).

Further evidence of the occurrence of that mechanism has been presented recently (Popolan-Vaida, *Angewandte Chemie-Int. Ed.* **61** (2022) 9168-9168).

Finally, the potential formation of **aromatic or polyunsaturated products** from the oxidation of terpenes or simple surrogates has not received much attention whereas aromatics are recognized to play a role in secondary organic aerosols formation (Li, *Chem* **8** (2022) 2688-2699).

This study aims to:

- better characterize the autoxidation products of limonene and a simple surrogate
- investigate the formation of aromatics/polyunsaturated products there.

To this end, we performed oxidation experiments in a JSR at 1 bar and oxidation products were characterized using a range of complementary analytical techniques.

2 Methods

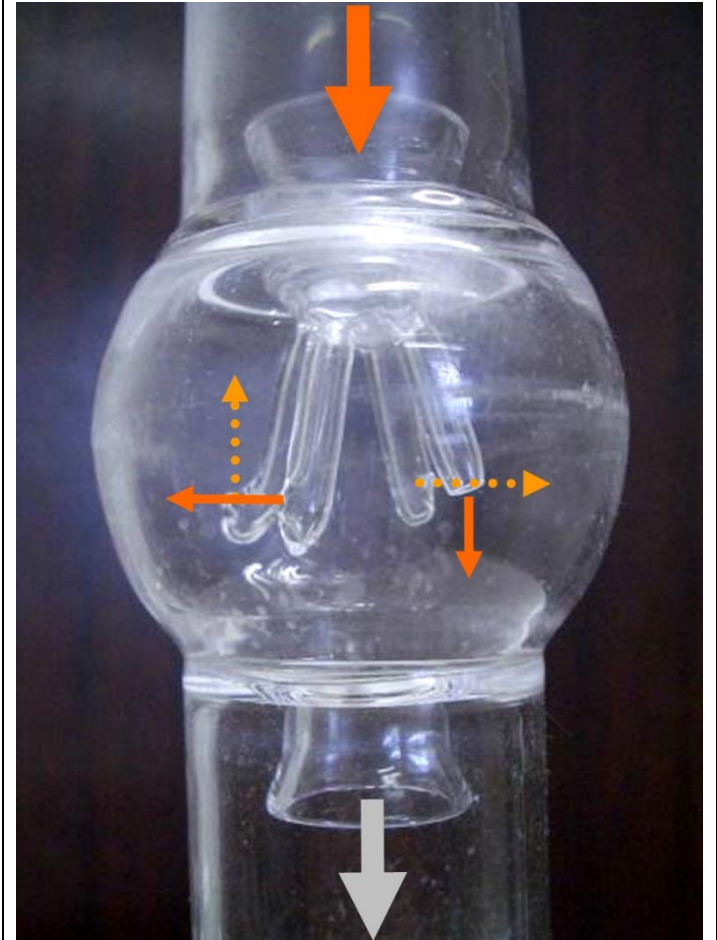
2.1 JSR Experiments

A fused silica JSR (42 mL) was used.

The fuels were pumped using a HPLC pump with an online degasser. The fuels were delivered to a vaporizer assembly fed with a flow of N_2 . Fuel- N_2 and O_2 - N_2 flowed separately to the JSR to avoid premature oxidation before reaching the reactor. Mass flow meters were used.

A thermocouple (0.1 mm Pt-Pt/Rh-10%) was moved along the vertical axis of the JSR to verify thermal homogeneity (gradients of < 1 K/cm).

We oxidized 1% of fuel at 1 bar, in excess of O_2 ($\varphi = 0.5$), at a residence time of 1.5 s, over the T-range 520-680 K.

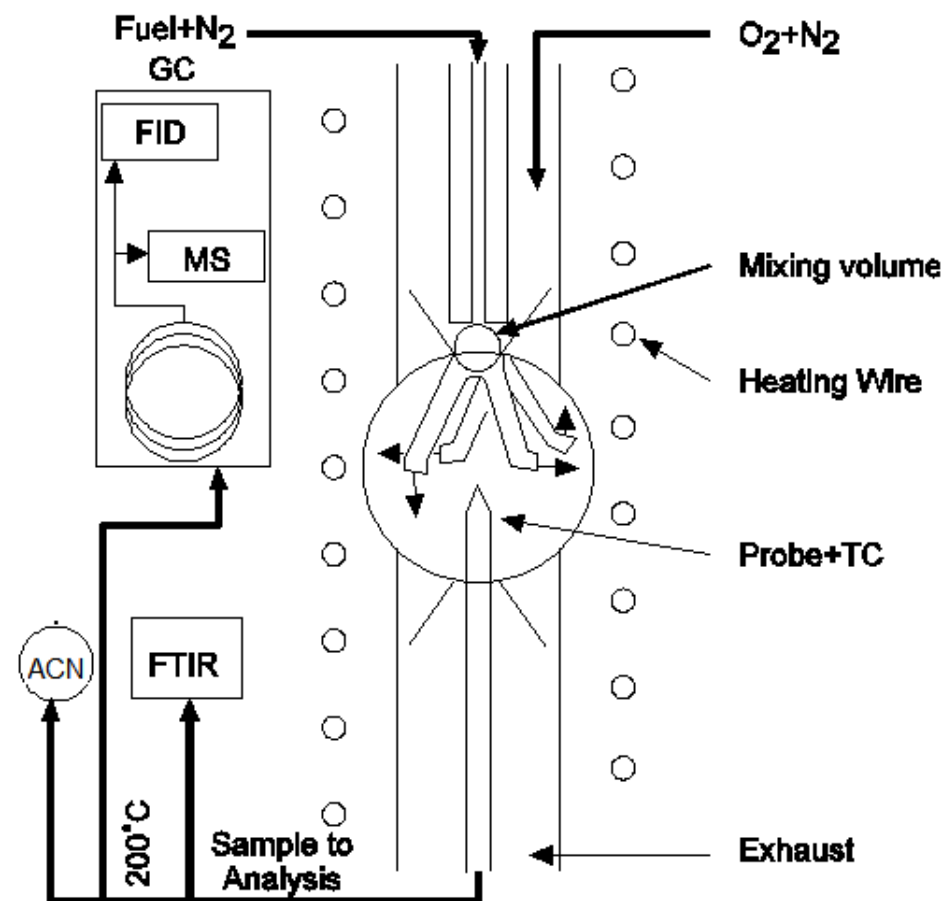


JSR Experimental Set-Up

Low-P **samples** taken by sonic probe sampling for

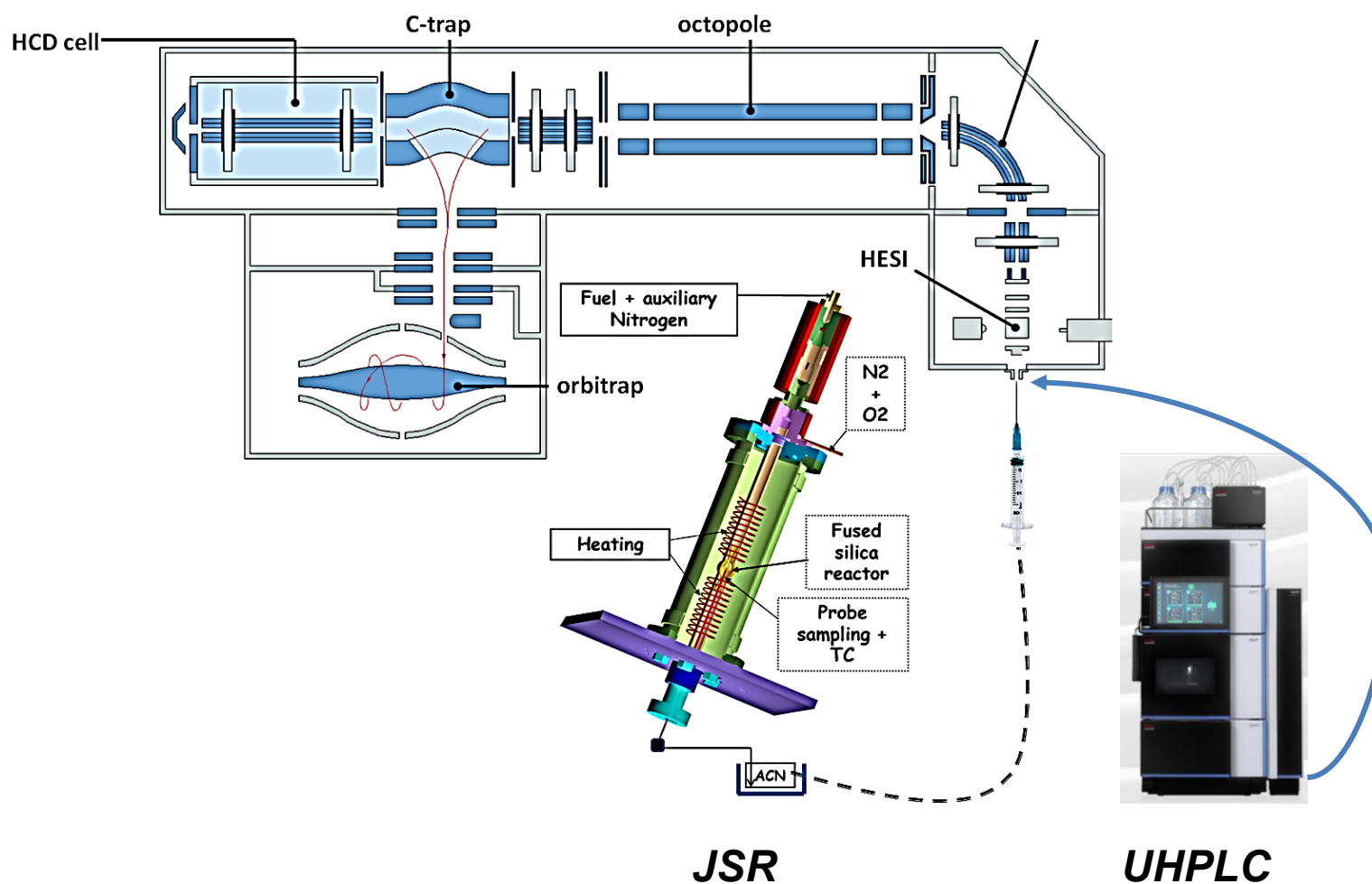
- Trapping in cool acetonitrile, **HPLC-HRMS**.

- on-line **FTIR** analyses



JSR/HRMS Experimental Set-Up

Orbitrap Q-Exactive

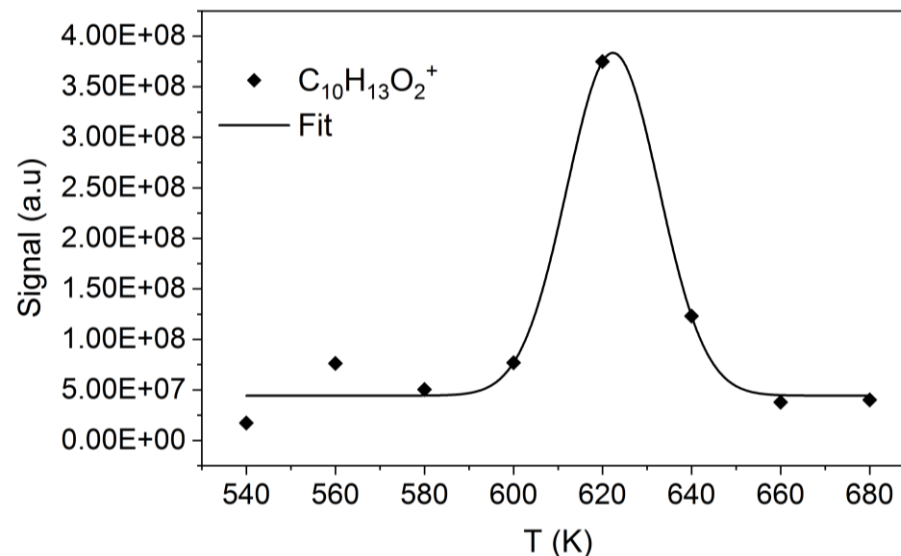
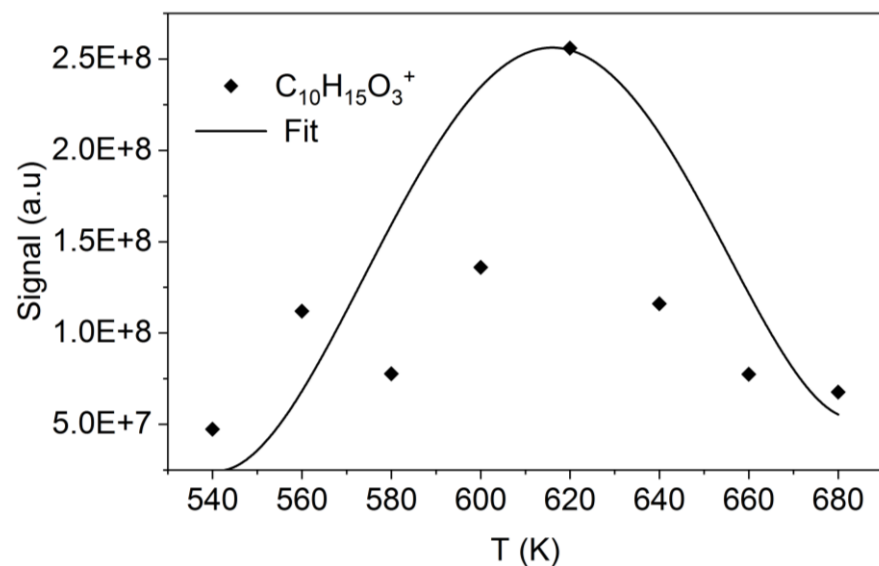


2.2 Chemical analyzes

- Low-temperature oxidation products were collected by bubbling gas samples for 60 min into 20 mL of UHPLC grade ≥ 99.9 acetonitrile (ACN) maintained at 273 K.
- We conducted flow injection analyses/heated electrospray ionization (FIA/HESI or APCI).
- Reverse-phase ultra-high-performance liquid chromatography (RP-UHPLC) analyses conducted using a C₁₈ analytical column. Atmospheric pressure chemical ionization (APCI) was used in positive and negative modes for the ionization of products.
- Determination of the chemical structure of oxidation products by MS/MS (HCD 10 eV).
- 2,4-Dinitrophenylhydrazine was used to assess the presence of carbonyl compounds.
- The fast OH/OD exchange was used to assess to the presence of a hydroxyl (-OH) or hydroperoxyl (-OOH) groups in oxidation products: 300 μ L of high-purity D₂O added to 1 mL of samples reacting for 20 min. Solution analyzed by FIA-HESI-HRMS and UHPLC-APCI-HRMS.

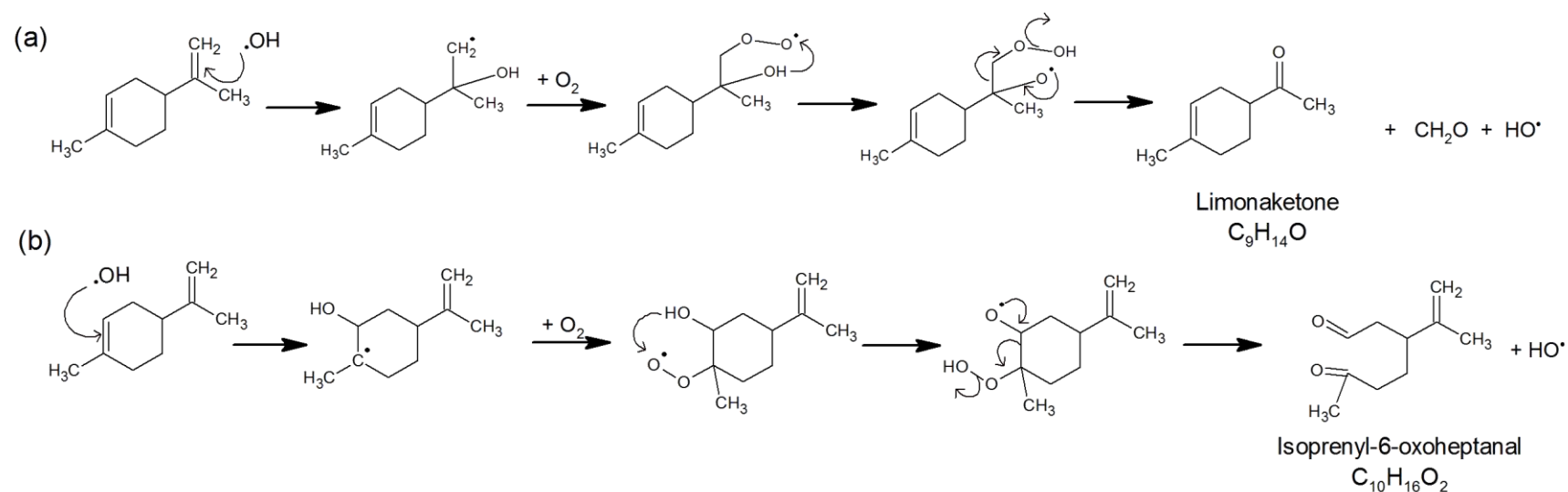
3 Results and Discussion

A broad range of oxidation products ranging from water to highly oxygenated products, containing five and more O-atoms, was detected: $C_7H_{10}O_{4,5}$, $C_8H_{12}O_{2,4}$, $C_8H_{14}O_{2,4}$, $C_9H_{12}O$, $C_9H_{14}O_{1,3-5}$, $C_{10}H_{12}O_2$, $C_{10}H_{14}O_{1-9}$, $C_{10}H_{16}O_{2-5}$, and $C_{10}H_{18}O_6$.



HRMS signal obtained for limonene products of oxidation. The data for KHPs and isomers ($C_{10}H_{14}O_3$) and diketones and isomers ($C_{10}H_{12}O_2$) were obtained via FIA and HESI (+), i.e., $C_{10}H_{15}O_3^+$ m/z 183.1015 and $C_{10}H_{13}O_2^+$ m/z 165.0910, respectively. (Dbouk et al., *J. Phys. Chem. A* **126** (2022), 9087–9096)

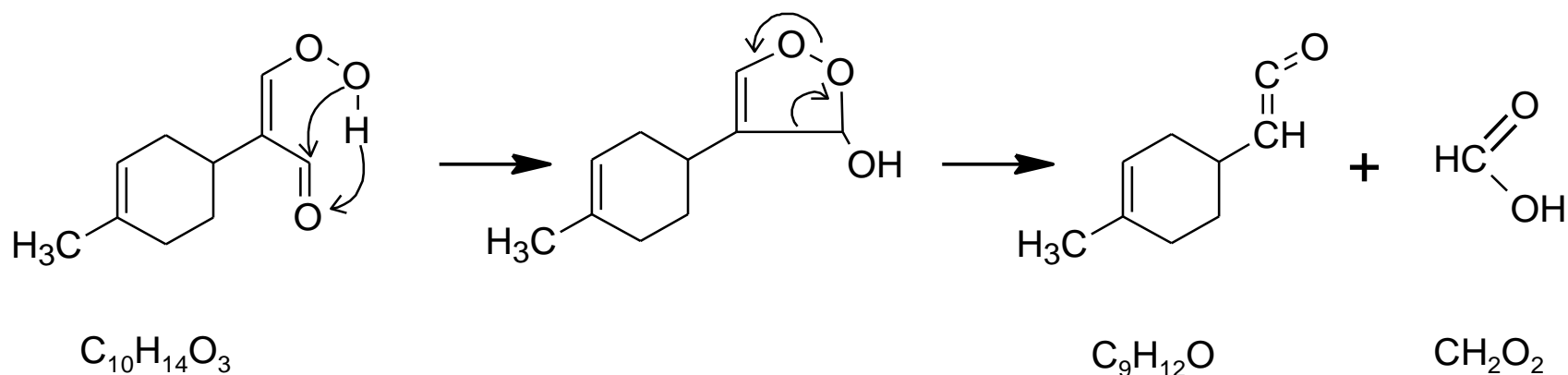
Carbonyl compounds from the **Waddington** mechanism on *exo*- and *endo*-double bonds (C=C) were observed as well as their products of further oxidation. The earlier reported (Witkowski et al. *Environ. Sci. Technol.* **52** (2018) 11583-11590) higher reactivity of the *endo* double bond vs the *exo* double bond seems to be confirmed here since higher ion signal was obtained for isoprenyl-6-oxoheptanal ($C_{10}H_{17}O_2^+$) than for limonaketone ($C_9H_{15}O^+$).



Oxidation of *exo*- (a) and *endo*- (b) cyclic C=C groups in limonene via the **Waddington mechanism**.

Products of the **Korcek** mechanism (carboxylic acids and carbonyls) were also detected. Among the 18 KHPs deriving from limonene oxidation, four isomers could decompose according to the Korcek mechanism but only one will likely form a cyclic organic peroxide intermediate between the carbonyl and OOH groups which yields carbonyl compound, $C_9H_{12}O$, and formic acid, CH_2O_2 by decomposition. Both products were detected in this study.

Based on the present identification of 1-methyl cyclohexene oxidation products, one can say that mechanism occurs also.

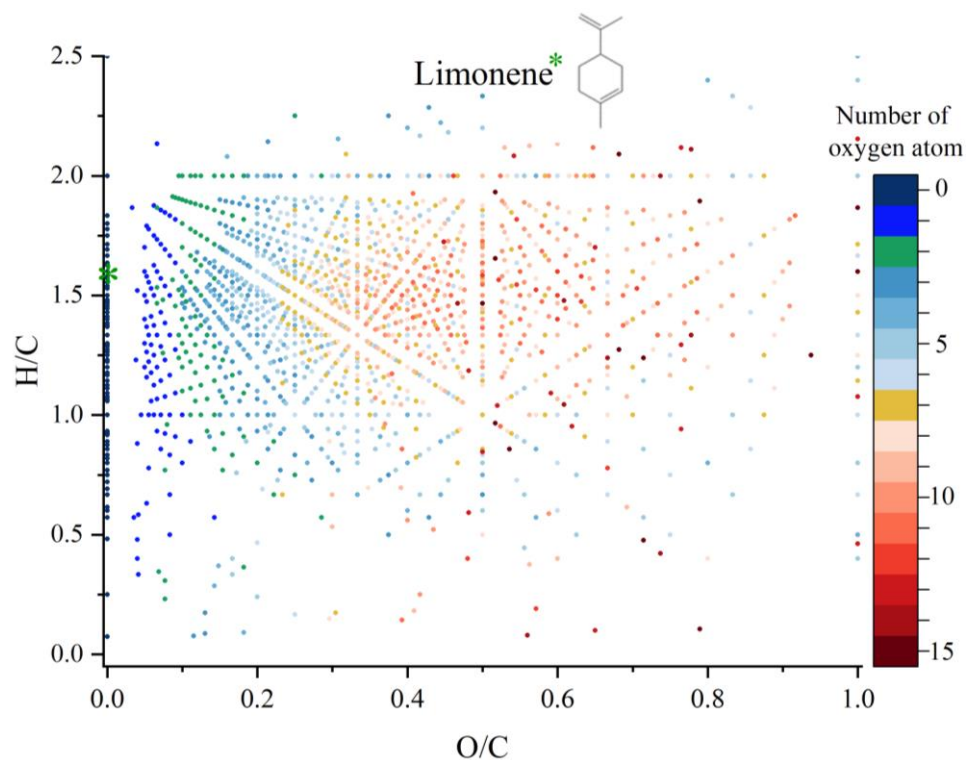


Korcek mechanism forming $C_9H_{12}O$ and CH_2O_2 .

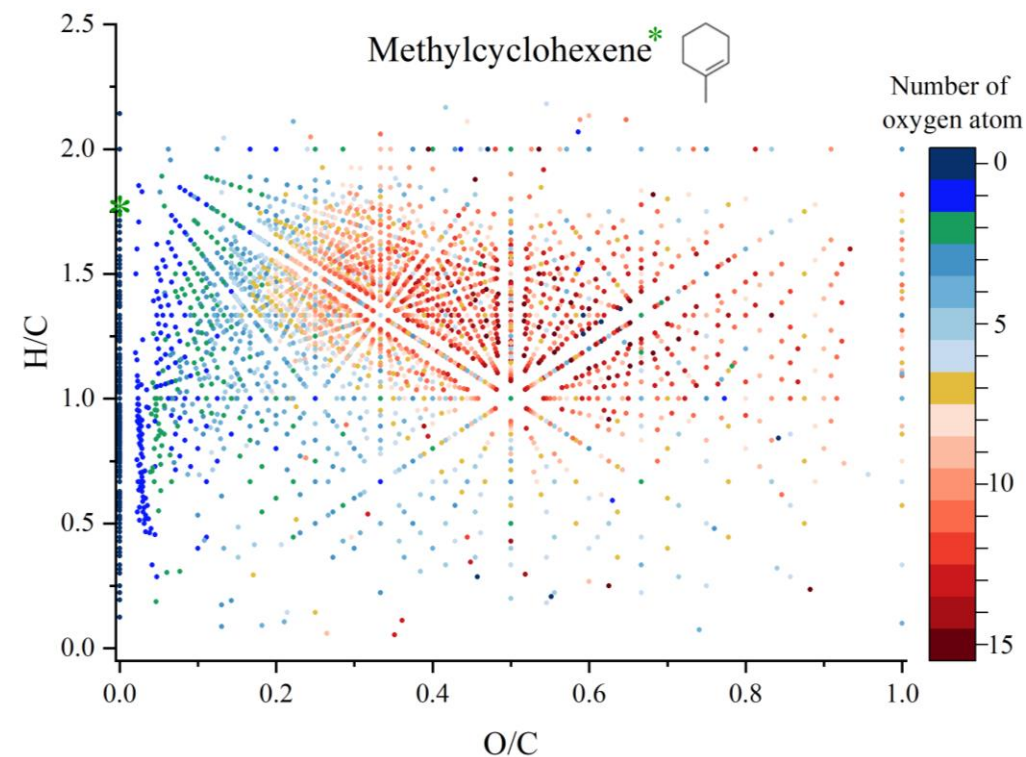
Formation of polyunsaturated and aromatic products:

We observed by GC-MS the formation of benzene, phenol, cresols, benzaldehyde, and toluene. Besides, vinylacetylene, 2-butene, 1,3-butadiene, cyclopentene, 1-methyl cyclopentene, 1-methyl-1,3-cyclopentadiene, 5,5-dimethyl-4,3-cyclopentadiene, and methyl-cyclohexadienes were also detected by GC-MS.

The **formation of C_nH_4 ($n = 4-6$), and C_nH_6 ($n = 6-9$)** isomers was observed for the two fuels considered, but **more importantly in case of 1-methylcyclohexene.**



Van Krevelen plot for **limonene** oxidation. APCI+/-, FIA-HRMS (sample taken at 640 K).

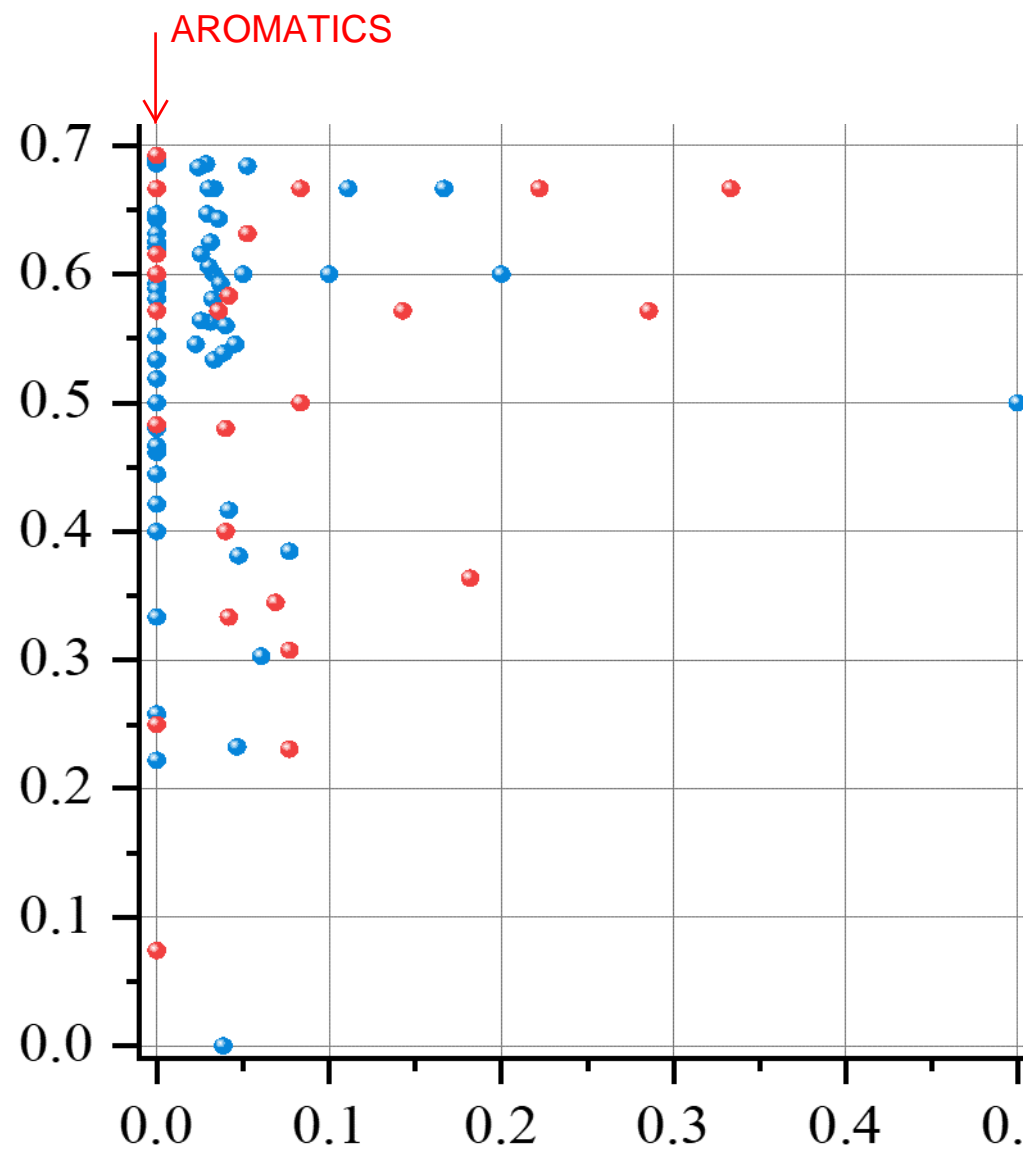


Van Krevelen plot for **1-methylcyclohexene** oxidation. APCI+/-, FIA-HRMS (sample taken at 640 K).

Van Krevelen plots based on HRMS data show the formation of aromatics and polyunsaturated products ($H/C < 0.7$ and $O/C = 0$) is **more important in the case of 1-methyl cyclohexene**.

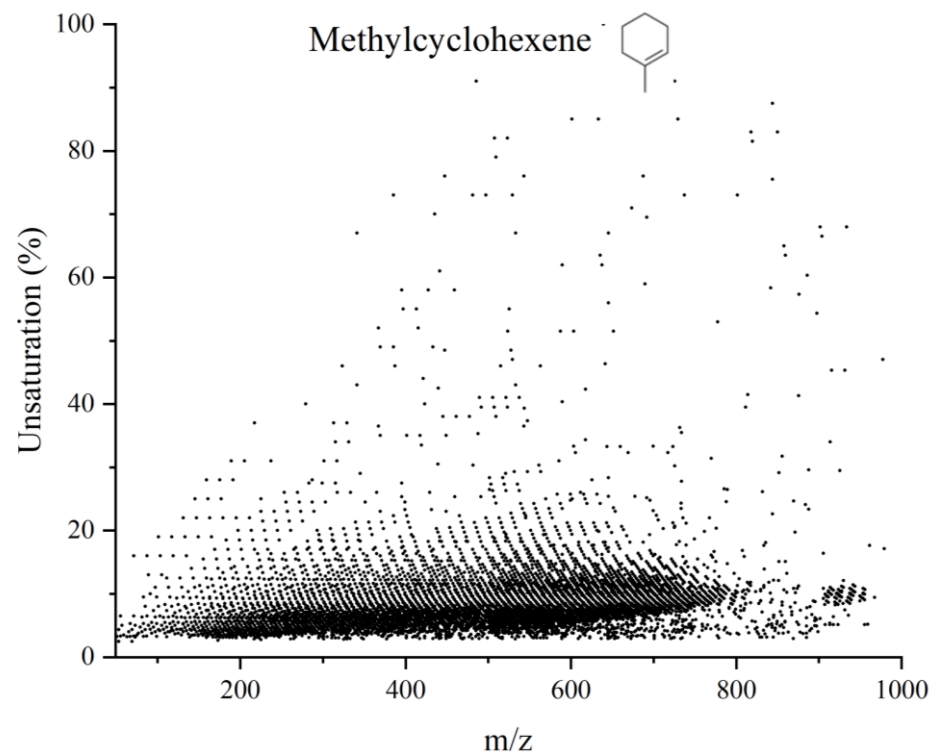
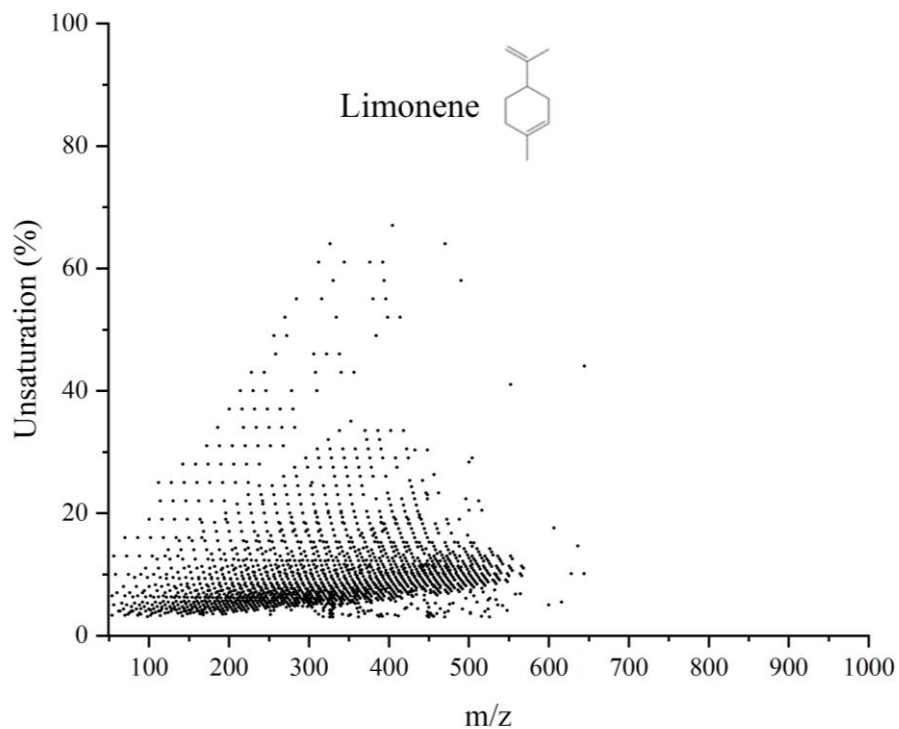
In the space $0 < O/C < 0.2$ and $H/C < 1$, we observed more products of oxidation and dehydrogenation from 1-methylcyclohexene.

For $H/C < 1$, the degree of oxidation of products is less than for $H/C > 1$.

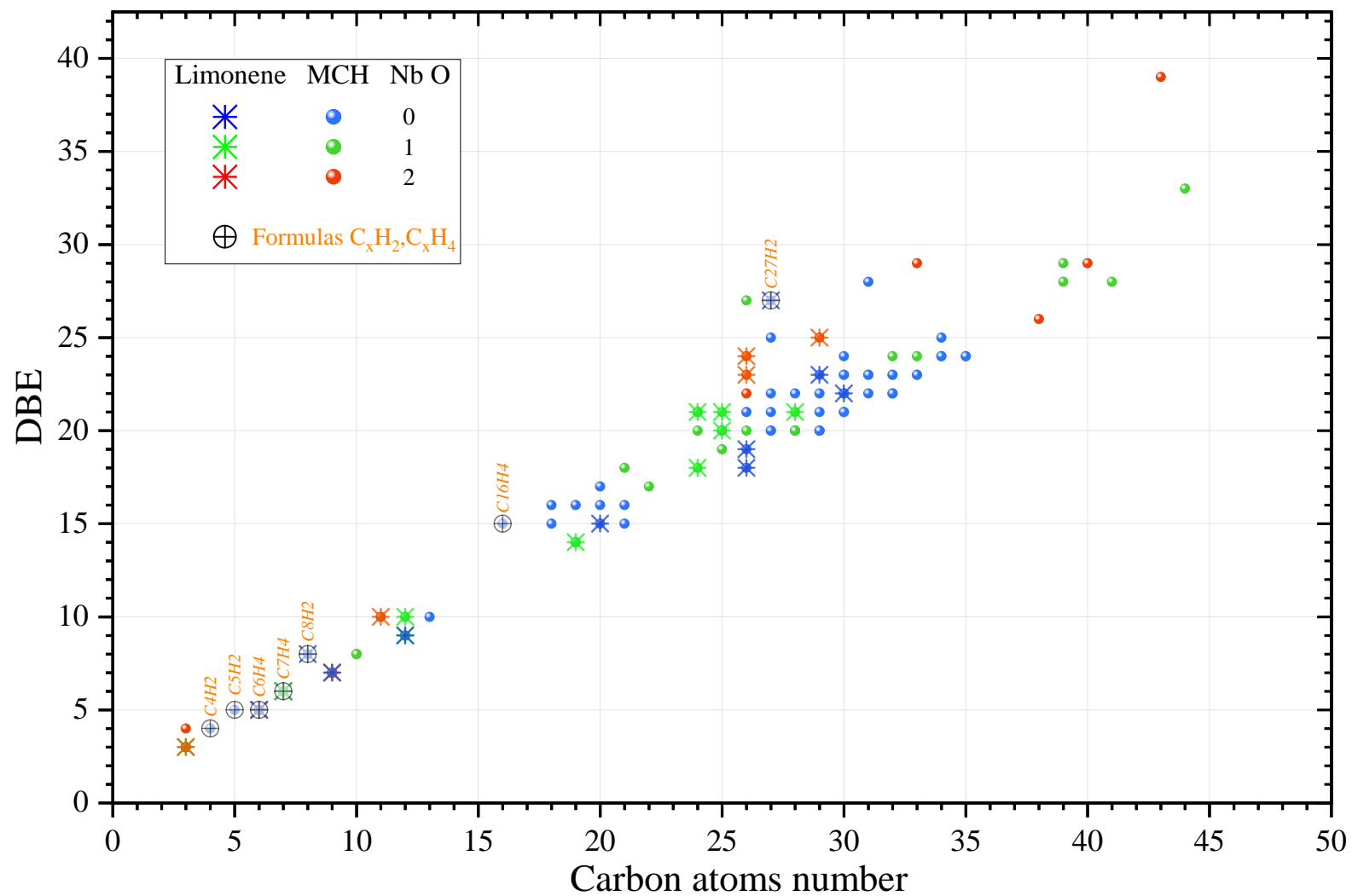


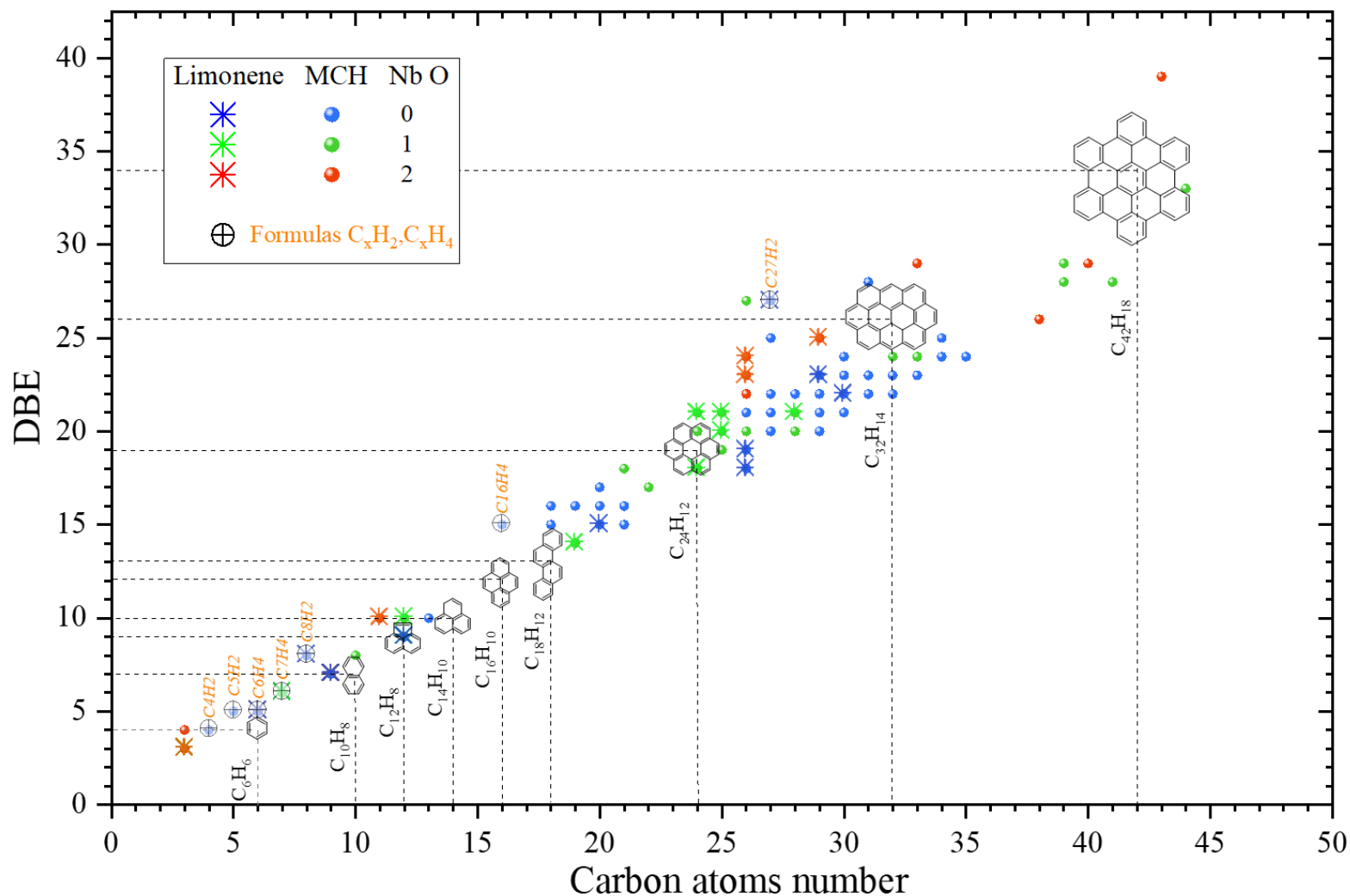
H/C vs. O/C for MeCHX and limonene; $C_xH_yO_{0-2}$ only

Plotting the percentage of unsaturation versus m/z in the products confirms **higher degrees of unsaturation in 1-methyl cyclohexene products**:



Variation of the degree of unsaturation $(3 \times C + 1) / (C - H/2 + 1)$ vs. m/z . APCI+/-, FIA-HRMS





Results obtained for the formation of aromatics and polyunsaturated products under CF conditions was not expected. It should be investigated under simulated atmospheric oxidation conditions since the oxidation of aromatics could play an important role in the formation of SOAs.

4 Conclusions

- A broad range of complex oxidation products formed during cool flame of terpenes or surrogates.
- Reaction pathways include autoxidation, the Korcek mechanism, the Waddington mechanism on *exo*- and *endo*-double bonds (C=C) and autoxidation of its products.
- The formation of aromatic and polyunsaturated products was observed during the autoxidation of the two fuels.
- The formation of aromatic and polyunsaturated oxidation products is more important in the case of 1-methylcyclohexene.
- Then a more appropriate surrogate needs to be proposed.
- We demonstrated the complexity of oxidation routes and products in the present chemical system. Our results are expected to help build detailed chemical kinetic reaction schemes for the oxidation of the terpene class of fuel.
- The oxidation products observed here will likely be released into the troposphere, potentially increasing the pool of VOCs which, in turn will contribute to particulates formation

5 Acknowledgments

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