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AN INNOVATIVE MICROFLUIDIC REACTOR FOR TESTING THE OXIDATION STABILITY OF FUELS: APPLICATION TO A SAF SURROGATE AND COMPARISON WITH THE PETROOXY TEST

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ABSTRACT

One potential solution to diminish the aviation carbon footprint is to blend Sustainable Aviation Fuel (SAF) into jet fuels. However, the thermal stability and oxidation stability of standard jet-fuels may be affected by the addition of SAF¹. In this context, we developed a Si-glass microfluidic reactor with a fluid supply made of inert polyether ether ketone (PEEK). The experimental rig PEEK-ACHU (Autoxidation μ Chip Heated Unit) was used to investigate the oxidation stability of a SAF surrogate and the results were compared to Induction Period (IP) measures, obtained in a standard PetroOxy device. A mixture of *n*-decane and iso-octane was used as the surrogate SAF². The thermal oxidation stability of the mixtures was measured in the microreactor, working at conditions up to 453 K and 30 bar, with a gas-liquid segmented flow that allows the liquid oxidation to occur in homogeneous, self-agitated liquid slugs. PEEK-ACHU enables residence times as long as 3.8 hours to be reached on a 4-inch diameter Si/glass wafer, visual access to the reactor, and a well-defined kinetic study of the liquid fuel autoxidation. The total hydroperoxide (ROOH) concentration was quantified at the exit of the microreactor using a specifically designed HPLC device with a post-column reactor³. For comparison, the same analysis was conducted on the SAF oxidized in the PetroOxy apparatus, with the same residence time. The results of this study show that the microfluidic apparatus is able to perform reliable autoxidation measurements and allows a better understanding of the kinetics. The self-stirring ensures a homogenous phase, and the visual access of the reactor is relevant for other applications, such as spectroscopic monitoring of deposit formation.

KEYWORDS: microfluidic, Sustainable Aviation Fuel (SAF), oxidation, High performance Liquid Chromatography (HPLC), hydroperoxide (ROOH).

INTRODUCTION

The environmental issues regarding the impact of the transportation sector on the emissions of CO₂ and their consequences lead to the establishment of rules and regulations to limit carbon footprints. For the aviation sector, the diminution of emissions remains a challenge because of the increase in worldwide air traffic which is predicted to be multiplied by 2 within 15 years, in a business as usual scenario⁴. Although the development of aircraft fueled with decarbonized jet fuel, such as hydrogen, is a promising solution, technical obstacles are delaying their deployment for at least 20 years⁵. For this reason, the most effective way of rapidly limiting the global carbon impact of the aviation sector is to develop Sustainable Aviation Fuel (SAF) as a drop-in fuel for current jet engines².

The composition of SAF varies according their feedstock and their production processes, which leads to different distributions of chemical compounds compared to traditional petroleum jet fuels. These changes affect their physical and chemical properties, either used as pure fuels or blended with traditional jet fuels, and can make it difficult to comply with standard norms dedicated to jet fuels, such as those defined by the ASTM. One of the specific features of jet fuels is that they are used both as an energy carrier and as a coolant, which subjects them to thermal and oxidative stress. The formulation of alternative fuels must therefore take this constraint into account, which also apply for storage⁶. Thermal stability refers to the tendency of fuels to degrade and generate soluble or insoluble oxidation by-products, depending on the temperature. There are several ASTM standards that determine the oxidation or storage stability of jet fuels, such as ASTM D3241⁷ relying on the Jet Fuel Thermal Oxidative Tester (JFTOT) procedure, ASTM D7739⁸ that use the Quartz Crystal Microbalance⁹ (QCM) and ASTM D7545¹⁰ based on the Rapid Small Scale Oxidation Test (RSSOT). The JFTOT and QCM methods measure the deposits induced by the autooxidation of fuels, which form at significant extent of reaction in the oxidation process. The PetroOxy apparatus, a RSSOT, is widely used for the kinetic study of jet fuels oxidation because it measures quantitative Induction Periods (IP) that characterize the oxidation phenomenon at lower extent of reaction, in principle before deposit formation⁶.

The PetroOxy is a gold-plated batch reactor, which uses a small quantity of liquid fuel (5 mL) and 7 bar of gas oxygen, at the beginning of the test, and monitors the total pressure in the cell as a function of time. The decrease of pressure corresponds to the consumption of oxygen in the liquid phase of the fuel. The fastest oxygen is consumed, the lowest the IP and therefore its oxidation stability. Since, this method usually does not yield any deposit formation, this reactor is practical to study the homogeneous liquid phase oxidation of petroleum or synthetic fuels. It requires a small quantity of fuel and, the IP measure is quantitative and repeatable in a short period of time.

However, even if the PetroOxy is increasingly used to study fuel autoxidation kinetics in the literature¹¹⁻¹⁸, it fundamentally remains a rapid test to compare the relative stability of different

traditional fuels. The opaque nature of PetroOxy, without optical access, makes it more difficult to study the oxidation stability of synthetic fuels. These fuels are usually made up of a mixture of a few compounds, and demixing or evaporation of only the lightest compound (changing the composition of the liquid fuel) can occur but is impossible to observe when the device is running at the set temperature under high-pressure conditions. In addition, although several studies have used the PetroOxy to carry out kinetic studies of the autoxidation of surrogate fuels, with or without simulations based on kinetic models, the reactor remains not well defined for kinetics. The heating time is a few minutes and the cooling time is several tens of minutes which allow the oxidation reaction to take place at different rates. The opaque, closed cell of the PetroOxy makes it difficult to make rigorous *in situ* analyses. The test cell is not stirred, which can induce concentration gradients or oxygen mass transfer limitations. Even if the quantity of fuel used is small, there are safety issues linked with high-temperature and oxygen rich conditions that restrain the maximum pressure in the cell (18 bar). The characteristic time of the IP can be several hours. Given the intrinsic leakage rate of the device, uncertainty increases for fuels that are more oxidatively stable, which is generally the case with SAF compared with fossil fuels⁵.

The goal of this study is to develop a new experimental rig to study the oxidation stability of fuels which is kinetically well-defined, with no concentration gradient or mass-transfer limitations, chemically inert and transparent for *in-situ* analyses, versatile for a large range of temperature, pressure, residence time, and safe, even beyond explosive limits. Microfluidics tools and theories are a solution of choice to achieve this goal. Thanks to this well-defined reactor, it will be possible to perform rigorous homogeneous kinetic simulations of fuel autoxidation with kinetic models to better understand this phenomenon. It will also be possible to rapidly and efficiently compare the reactivity of different fuels within tens of minutes.

BACKGROUND

Numerous studies have shown that it is possible to follow the kinetics of oxidation of liquid fuels with PetroOxy^{9,11,14,17,19}. These studies are based on experiments with varying degrees of characterization and kinetic analyses, ranging from global rate constants derived from experiments to simulations based on detailed kinetic models containing hundreds of reactions. One of the most comprehensive characterizations of the kinetics of formation of liquid and gaseous products in the literature, measured during the oxidation of *n*-dodecane in a PetroOxy, is the recent study by Aminane et al.¹². The wide range of quantitative chemical analyses enabled the authors to establish the different stages in the autoxidation mechanism and to propose rate constants of several reactions. This study allowed a better understanding of the oxidation mechanism before the formation of solid gums. Chatelain et al.¹⁵ or recently Le et al.¹⁹ used detailed chemical kinetic models to simulate IPs measured in PetroOxy and proposed different approaches for simulating this value that is fundamentally biphasic (the liquid phase oxidation rate is measured as a gas pressure drop) with a homogenous liquid reactor model. Chatelain et al.¹⁵ defined the IP as the simulation time needed to reach 5% of fuel conversion. Le et al.¹⁹ defined it as the time required in the simulation to reach the total ROOH concentration measured

experimentally at the IP. Auzani et al.²⁰ proposed a simplified python code to predict the pressure drop of the PetroOxy, trying to account for the liquid phase oxidation in the liquid with detailed kinetic simulations and the mass transfer of O₂ from and into the liquid.

The complexity of the simulation of the IP with detailed or semi-detailed kinetic models led to the search of more well-defined reactor for the validation of kinetic models. Alborzi et al.²¹ proposed to use a near isothermal tubular reactor to study the oxidation of n-paraffinic solvent used as a model aviation fuel and simulate their results with a reduced kinetic model. They used a 1 m long stainless-steel tube with a 0.65 cm inner diameter, for temperature ranging between 135 and 150°C, to follow the variation in dissolved O₂ concentration in the paraffinic fuel for residence times up to 20 minutes. However, this system cannot achieve characteristic residence times similar to those achieved with the PetroOxy and the fuel oxidation kinetics is difficult to follow because the reactor material is not chemically inert and the availability of dissolved oxygen can be the rate limiting step at early reaction extent.

One of the best solutions in the literature for studying hydrocarbon oxidation in a chemically inert material, at high temperature and high pressure, with transparent access throughout the reactor, is the use of Si-glass microreactors. Indeed, microfluidics makes it easy to use with less reactants and allow a modularity (versatility) of use. The micro scale enables a fine control of well-defined experimental conditions that remain safe beyond explosive limits, especially for the use of pure oxygen with organic compounds. The possibility of establishing a Taylor flow for a gas-liquid system is also a considerable advantage of these systems, which ensures oxygen saturation in the liquid slugs throughout the reactor. The market for ultra-small scale reactors, which employs microfluidic devices for the oxidation of organic compounds, is developing in parallel with the emergence of the microfluidics market, which is witnessing a growing interest since 2010²²⁻²⁵.

For example, Leclerc et al.²² performed a study of the gas-liquid oxidation of cyclohexane at high temperature (>473K) and pressure (up to 25 bar) in a microfluidic Silicon / glass reactor with a residence time in the reactor of 1 min. The consumption and the extent of the fuel oxidation is visible thanks to the transparent glass and the gas bubble consumption was monitored. The goal of the authors was to test such device for the intensification of the production of cyclohexanone and cyclohexanol in the cyclohexane autoxidation process. In 2014, Fräulin et al.²⁴ also used a microchip to study the liquid phase oxidation of cyclohexane, with dissolved oxygen, and were able to perform *in situ* analyses using Raman spectroscopy, recording simultaneously the concentrations of dissolved molecular oxygen, cyclohexane and of oxidation products. They achieved a residence time of 10 seconds at 503 K.

If the Si-glass microreactors of the literature used to study the autoxidation of hydrocarbons can withstand high temperatures and high pressures, achieving long residence times, typically of the order of magnitude of the IP in PetroOxy, remains a challenge never before met in the literature. In this work, we present a Si-glass microfluidic device able to operate at high pressure and

temperature, with a gas-liquid Taylor flow, and able to reach long residence time. The experimental rig PEEK-ACHU (Autoxidation μ Chip Heated Unit) also allows the oxidation of hydrocarbons with proportions of pure oxygen beyond the explosive limits. To develop this microfluidic pilot, several preliminary studies were carried out to predict as much as possible the hydrodynamics of the microreactor, given the physico-chemical properties of the hydrocarbon reactants. In this work, we do not focus on the work performed to design the microreactor but we present oxidation results and compare them with those obtained in a PetroOxy. Figure 1 gives an overview of the PEEK-ACHU rig.

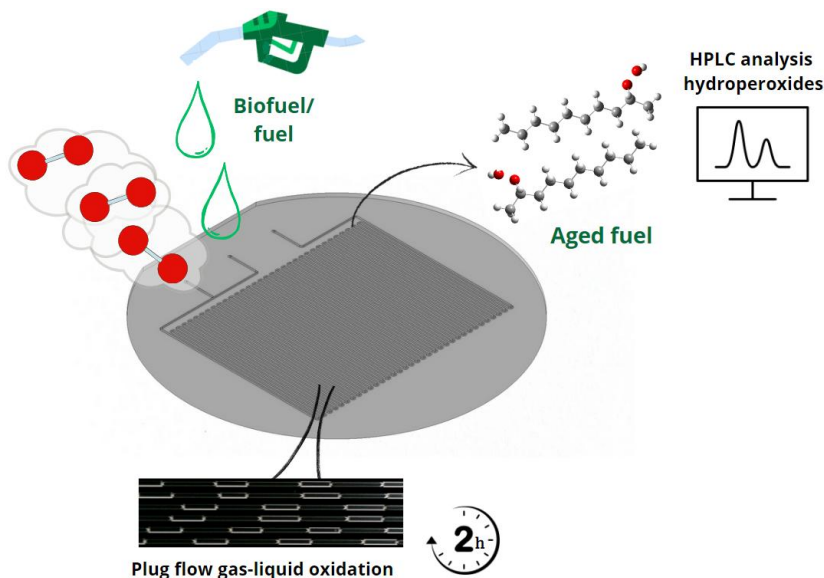


Figure 1: General overview of the Si-glass microreactor of PEEK-ACHU and the analyses of the oxidized fuel.

We first present the results of the oxidation of a single component surrogate fuel, *n*-decane, with the PEEK-ACHU rig. Oxidation is characterized by measuring the total hydroperoxide content in the oxidized liquid at the exit of the reactor. These results are compared to the one measured in the standard PetroOxy test. In the second part of the paper, we explore the oxidation kinetics of a surrogate SAF, which is defined as a blend of *n*-decane and isooctane, using the PEEK-ACHU and PetroOxy devices. Comparisons of thermal oxidation stability of *n*-decane and the SAF surrogate are discussed with both experiments.

EXPERIMENTAL

Methods:

1. Oxidation of fuel: experimental devices

The PetroOxy method

The PetroOxy from Anton Paar is a Rapid Small-Scale Oxidation Test (RSSOT) and is designed to determine the thermal oxidation stability of liquid fuels (gasoline, diesel, biodiesel/FAME and blends). The oxidation of the liquid is made in a 25 mL gold-plated cell, where 5 mL of fuel is introduced and pressurized with 7 bar of O₂. The gas pressure is monitored in the cell and the IP is defined as the time required to reach a 10% decrease of the maximum pressure in the cell. This test meets requirements for standardized norms ASTM D7525, D7545, EN 16091, IP 595 for liquid fuels.

The IP measurements in our PetroOxy have a reported uncertainty of around 10%¹⁹. At the end of the PetroOxy test, the total amount of hydroperoxide was systematically determined. It can be noted that the cell can take up to 20 min to cool down and it can impact the rates of formation or decomposition of oxidation products, especially for short IPs. In this work, we also measured the total hydroperoxide content of oxidized fuels as a function of time. For these experiments, the test was pre-set to a defined residence time and the apparatus stopped after this test duration and the liquid was withdrawn after the cool down of the cell.

PEEK-ACHU: a new gas-liquid oxidation microreactor

The microfluidic reactor and the whole experimental setup were designed to be able to reach long residence times. The different constraints regarding the oxidation process were taken into consideration in the design. The use of PEEK, an inert polymer, was chosen to prevent the catalysis of fragile compounds, such as ROOH, by metal or inox material. The process was dimensioned for extremely low flows, at high temperatures and pressures, and modular, i.e., easy to connect and disconnect from fluid supply system. This process also allows to reach conditions beyond the explosivity limits compared to macroscale processes.

The Si/glass is chemically inert and withstand high-pressure/high-temperature conditions. In the literature, this system was reported to reach 80 bar and 503 K²⁴. The serpentine shaped microchannel is 3.5 m long and was designed as a square cross-section channel and a simple T-junction was used to generate a Taylor flow²⁶ as described in Figure 2.

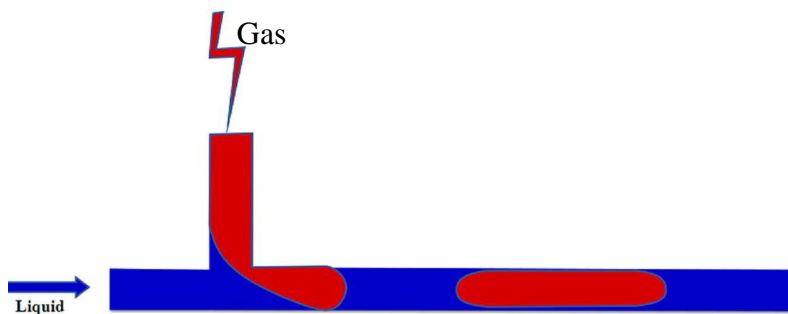


Figure 2: Gas-liquid Taylor flow formation (adapted from Zhang et al. 2021²⁷).

Taylor flow is a type of gas–liquid flow pattern. It consists of elongated gas bubbles with a length many times that of the channel width. The bubbles adopt a capsular shape and can fill the channel. This flow was chosen due to its ability to produce small perfectly agitated reactors of liquid surrounded by gas bubble ensuring a constant concentration of dissolved gas in the liquid phase.²⁸ The formation of Taylor flow and the serpentine shaped reactor induce a homogeneous recirculation in the liquid slug as shown in Figure 3^{29–31}.



Figure 3: Illustration of the recirculation inside the liquid slug in microfluidic reactor at Taylor flow (adaptation of Abadie et al. 2013²⁹).

The channel length was optimized to have the longest residence time in the microfluidic reactor. The microreactor was manufactured by the MIMENTO technology center of the FEMTO-ST laboratory (Besancon, France), and is shown in Figure 4, along with the experimental set-up.

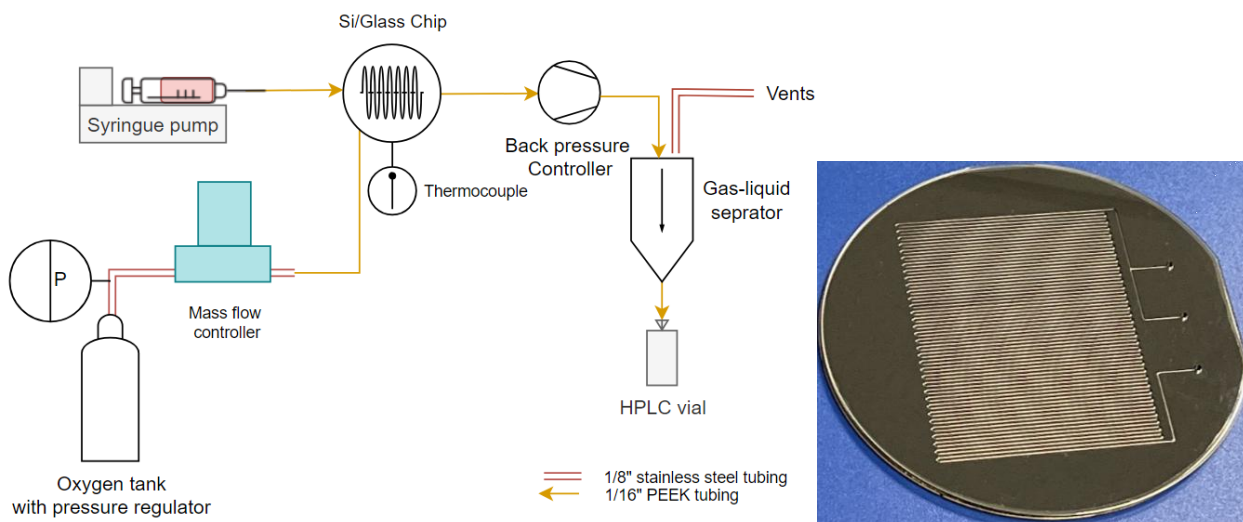


Figure 4: Experimental setup overview and photography of the microreactor 4-inches in Si/glass.

The liquid fuel is cooled down in the PEEK tubing at the exit of the reactor with an ice cooling system, so that the oxidation reactions are frozen, up to the gas-liquid separator. The temperatures, pressures and residence time ranges reached by the experimental set up are given in Table 1. The residence time is determined as the time of the fuel spent in the Taylor flow.

Table 1: Range of use of PEEK-ACHU rig

Residence time (min)	16-230
Temperature range (K)	298-458

Pressure range (bar)	1-40
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2. Hydroperoxide content

Following the concentration of hydroperoxides is a good indicator for the extent of the fuel autoxidation process since hydroperoxides are the primary oxygenated products formed following the simplified mechanism shown in Figure 5³².

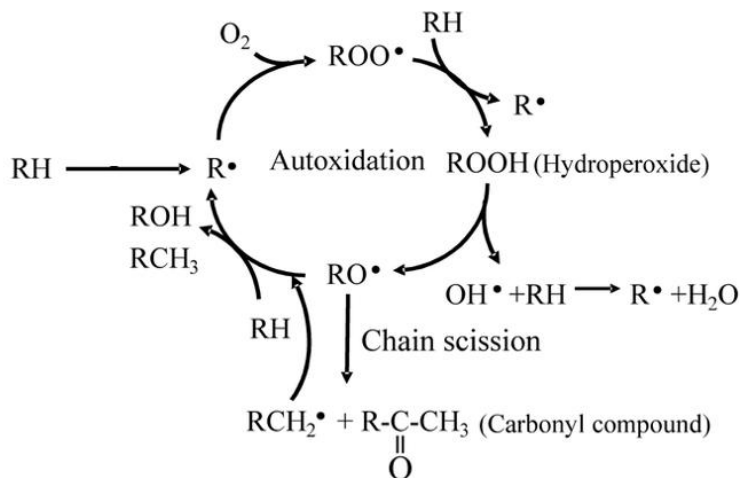


Figure 5: Autoxidation mechanism (adapted from Nakatani et al.³²).

The total hydroperoxide content was measured using a high-performance liquid chromatography (HPLC) device based on a separation column in the normal phase (silica) combined with a post-column reactor (P-cR). This system designed by our group in 2024³ was shown to be able to quantify hydroperoxides for concentrations ranging between $5 \cdot 10^{-7}$ and $1 \cdot 10^{-3}$ mol. L⁻¹. The HPLC- P-cR, schematically presented in Figure 6: Representation of the HPLC-P-cR to determine the ROOH content of each samples Figure 6, was used at a flow of 1 mL per minute of solvent (isooctane: absolute ethanol 95:5). 10 μ L of the sample of aged surrogate fuels and fuel blends was injected using an autosampler through the system. A selective iodometric reaction takes place in the reactive column that permit a precise quantification and a separation of the different hydroperoxides contained in the samples.

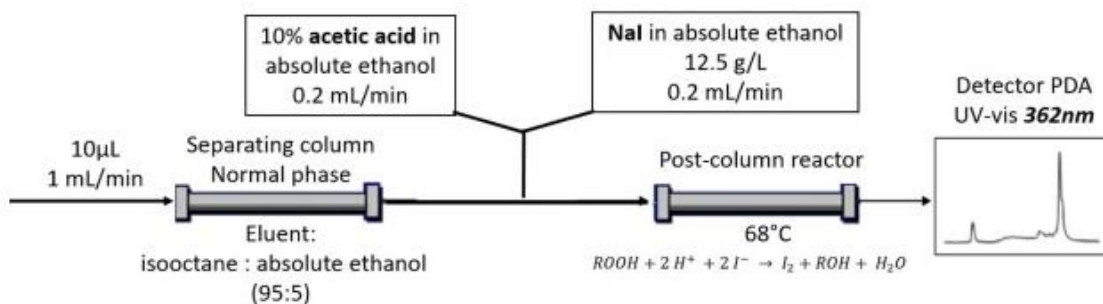


Figure 6: Representation of the HPLC-P-cR to determine the ROOH content of each samples

The final chromatogram combined with a calibration curve is used for the quantification of the hydroperoxide content of each sample.³ This method was found to be more efficient, and more reproducible than traditional hydroperoxide quantification methods.³

Materials

n-Decane was purchased from Acros Chemicals. Among reactants necessary for the iodometric titration of peroxides, absolute ethanol was purchased from VWR Chemicals, whereas sodium iodide (NaI) (> 99 %), acetic acid (≥ 99.8 %) and 2,2,4-trimethylpentane (isooctane; HPLC quality ≥ 99.5 %) were purchased from ThermoFisher Chemicals. A bottle of oxygen (purity 6.0) was obtained from Air Liquide.

The reference induction period (IP) measured with the PetroOxy device of *n*-decane used in this work at 413K and 7 bar of oxygen was 189 min.

The SAF surrogate was chosen as a blend of isooctane and *n*-decane at 50/50 %mol and 55/45 % weight as proposed by Mawid³³. The blend for SAF surrogate was made with a precision scale of Mettler Toledo with an accuracy of +/- 0.01mg. Table 1 summarizes surrogate data.

Table 2: Characteristics of the SAF used in this study.

298 K 1.01325 bar	
Isooctane (iC ₈)	50 %mol
<i>n</i> -decane (nC ₁₀)	50 %mol
Density (kg/m ³)	710.65
IP measured in PetroOxy (413K/7 bar O ₂)	286 min

The IP of the SAF is more than 100 minutes longer than the IP of *n*-decane. The addition of a branched alkane, isooctane, to *n*-decane is known to increase its oxidation stability. The observed increase under the conditions of Table 1 is significant.

RESULTS AND DISCUSSION

Validation of the PEEK-ACHU rig for gas-liquid fuel oxidation

As mentioned previously, it is important to establish a Taylor flow regime in the microreactor to ensure homogeneity and dissolved oxygen saturation of the liquid slugs. Problems of mass transfer limitation from gas to liquid and oxygen depletion in the liquid are thus avoided. Multiple experiments were conducted to map of the different flow regimes as a function of the gas and liquid volume flow rates. The map of flow regimes obtained is presented in Figure 7.

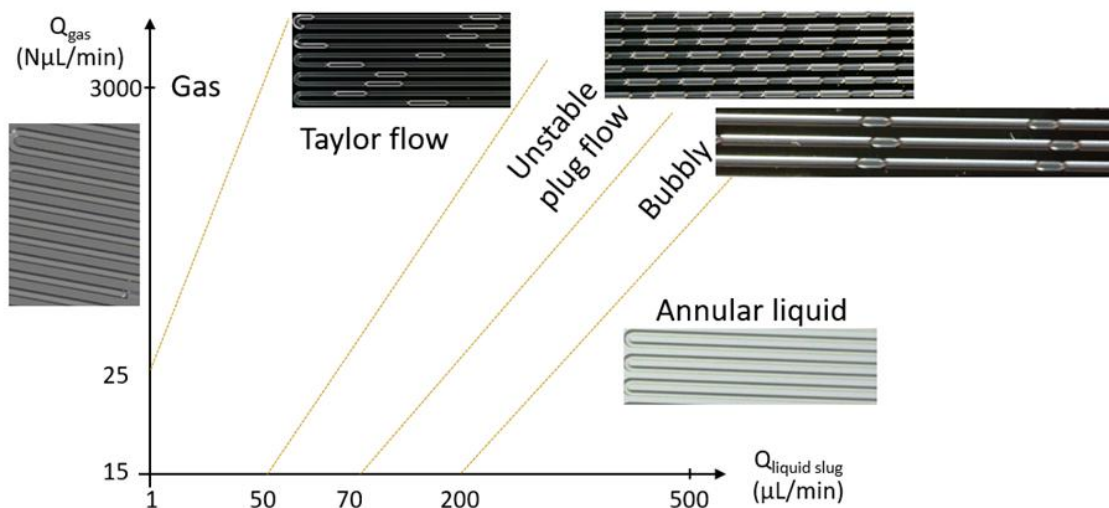


Figure 7: Gas-liquid flow regimes map in our microreactor at 413K and 20 bar.

In Figure 7, it can be seen that a stable Taylor flow regime can be established for a wide range of flow rates. The lowest gas and liquid flow rates, enabling a Taylor-type flow to be maintained, impose limits on the minimum residence time that can be achieved in the reactor. Using the rig configuration presented in the paper, the minimum time is 16 minutes and the maximum 230 minutes. The rigorous characterization of the microreactor was conducted as a function of temperature and pressure. Figure 8 gives an example of a Taylor flow during a fuel oxidation experiment conducted at 413 K and 20 bar.

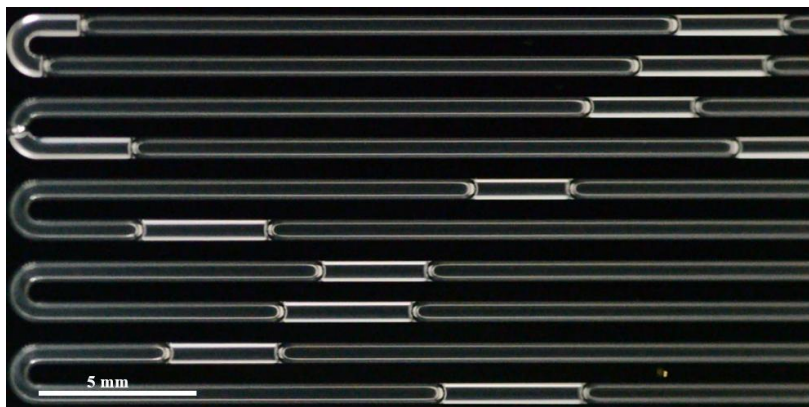
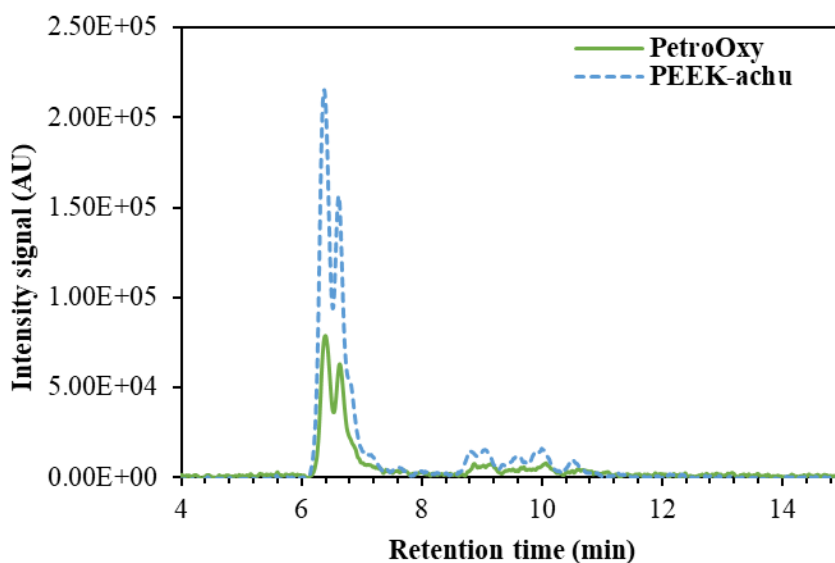


Figure 8: Photography of the gas-liquid *n*-decane autoxidation (residence time: 45 min | 20 bar | 413 K | O₂/C₁₀ volumic ratio: 3.02) in the microreactor. White slugs: liquid fuel; grey bubbles: oxygen.

All the autoxidation experiments were performed on microfluidic gas-liquid flows looking like Figure 8, with a Taylor flow based on a significant molar and volume excess of oxygen over fuel (a ratio of 3). The relative size of liquid slugs and gas bubbles ensure a permanent saturation of dissolved oxygen in the liquid slugs.

At the exit of the reactor, the oxidized liquid was collected in vials cooled by a cryostat operating at 263 K. The vials were then diluted in the HPLC eluent (isooctane: absolute ethanol 95:5) and analyzed in the HPLC-P-cR to probe the types and total quantity of hydroperoxides. Figure 9 presents a comparison between chromatograms of aged *n*-decane obtained in experiments performed in the PetroOxy and in PEEK-ACHU.

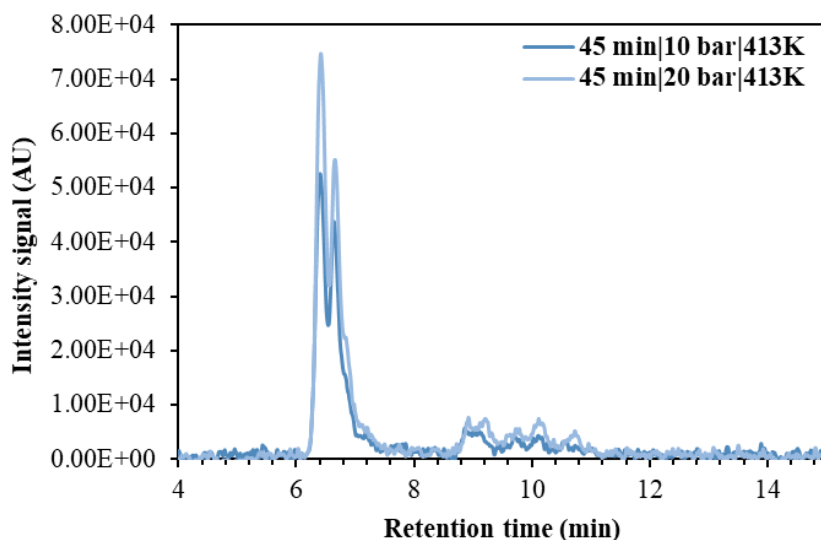


	[ROOH] (mol/L)	Deviation
Peekachu	7.07E-03	30%
PetroOxy	5.07E-03	

Figure 9: Chromatograms of hydroperoxides formed in *n*-decane ageing in the PetroOxy and in PEEK-ACHU (PetroOxy: 413 K, 7 bar initial O₂ pressure yielding P_{max} ≈ 10 bar, 45 min experiment | PEEK-ACHU: 413 K, 10 bar, 45 min residence time). The Table included in the Figure is the total concentration of hydroperoxides (ROOH) calculated from the chromatograms.

In Figure 9, the pressure in PEEK-ACHU was set to 10 bar to mimic the pressure inside the PetroOxy (P_{max}). Figure 9 shows that different types of ROOH are formed, those with a retention time of 7 minutes and those with a retention time around 10 minutes. The ROOH eluting at 7 min are decane hydroperoxides and the chromatogram show that two groups of molecules can be separated according to their polarity. Even more polar hydroperoxide elute around 10 minutes and we make the hypothesis that they are dihydroperoxides, hydroperoxide dimers or smaller molecular weight hydroperoxides. A clear difference (above the uncertainty limits) in the total [ROOH] concentration of 30% is observed between the two reactors, with experiments performed in PEEK-ACHU yielding more hydroperoxide than in the PetroOxy. This can be explained by the better oxygen mass transfer achieved in the microfluidic device and the self-agitation inside the liquid slugs. Indeed, the auto-agitation in this type of microfluidic systems is well established and allows a better gas-liquid surface contact and ensures a homogeneity in the liquid fuel slug during the oxidation process.

The apparatus is more functional at high pressure since the regulation of microfluidic parameter are more straightforward. The influence of pressure on the measured [ROOH] in oxidized *n*-decane was tested to check for possible oxygen mass-transfer limitations. To do so, experiments were conducted at different pressures (10 bar and 20 bar) for the same residence time in the microreactor with *n*-decane. Figure 10 gives the peroxide concentrations as a function of pressure, with the corresponding chromatograms.



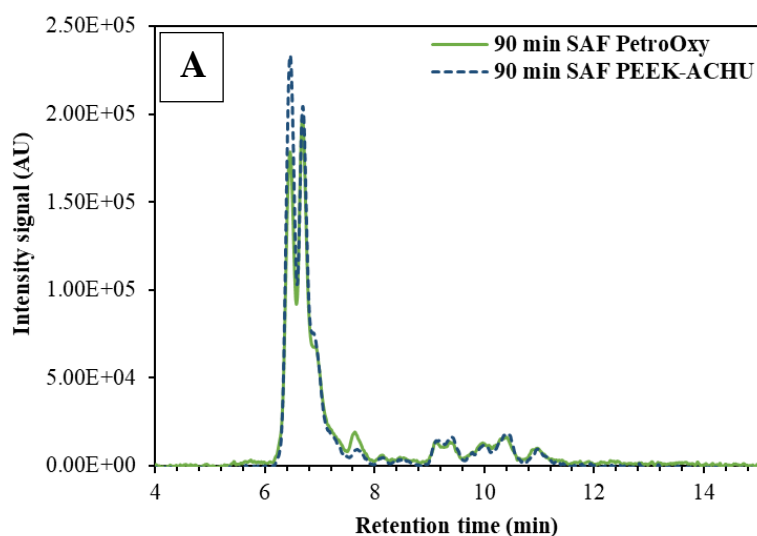
	[ROOH] (mol/L)	Deviation
45 min 20 bar	8.08E-03	13%
45 min 10 bar	7.07E-03	

Figure 10: Hydroperoxides chromatograms obtained for *n*-decane autoxidation at two different pressures (10 and 20 bar) in PEEK-ACHU; at 413 K temperature and 45 min residence time.

The two chromatograms presented in Figure 10 are very similar and the deviation between the hydroperoxides concentrations obtained at two pressures is 13%. Since this difference lies within the error of the method of analysis, it can be concluded that we are not in a regime limited by the mass transfer of oxygen in the liquid in the microreactor.

Comparison of the oxidation of the SAF surrogate in the PetroOxy and in PEEK-ACHU

The comparison of the total ROOH content after oxidation of the surrogate SAF in the two experimental devices was performed as a function of residence time. The chromatograms are presented in Figure 11.



	[ROOH] (mol/L)	Deviation
90min SAF Peekachu	7.37E-03	12%
90min SAF PetroOxy	6.51E-03	

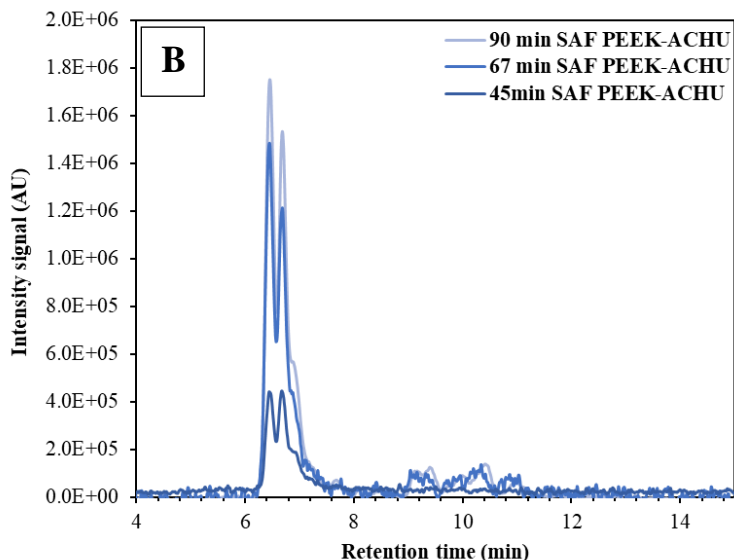


Figure 11: **A** panel: Comparison of the ROOH chromatograms of the SAF aged in the PetroOxy and PEEK-ACHU devices. (PetroOxy: 413 K, 7 bar initial O₂ pressure yielding P_{max} ≈ 10 bar, 90 min experiment | PEEK-ACHU: 413 K, 20 bar, 90 min residence time). The Table gives the total concentration of hydroperoxides (ROOH) calculated from the chromatograms. **B** panel: evolution of the hydroperoxides chromatograms as a function of residence time in PEKK-ACHU (same temperature and pressure as in the **A** panel).

Chromatograms in Figure 11 show the various types of hydroperoxides that are formed during the oxidation of the SAF surrogate. This can be observed by the number of peaks that are present. Each peak represents a different hydroperoxide, depending on its polarity. It can be observed in Figure 11 that the hydroperoxides that are formed with PEEK-ACHU and the PetroOxy have the same peaks and feature close area (12% deviation in the total amount of ROOH). The chromatograms in the right panel of Figure 11 demonstrate that peaks around 10 minutes of retention time appear only when the residence time is long enough (67 and 90 minutes) and are characteristic of secondary hydroperoxides.

The total ROOH content as a function of time is presented in Figure 12, for both experiments performed in the PetroOxy and PEEK-ACHU.

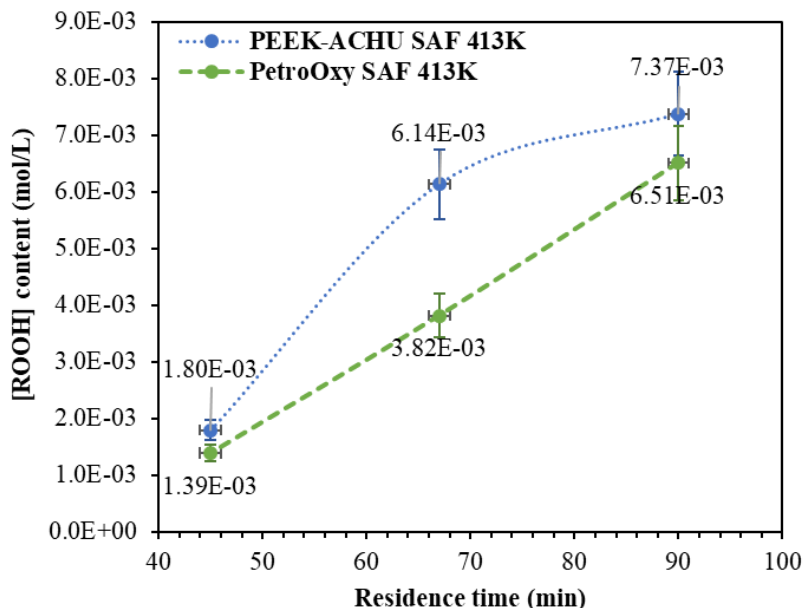


Figure 12: Comparison of total ROOH content at different residence times in PEEK-ACHU and PetroOxy (PetroOxy: 413 K, 7 bar initial O₂ pressure yielding P_{max} ≈ 10 bar, | PEEK-ACHU: 413 K, 20 bar).

Average deviation of 33% is observed between the [ROOH] content of the sample in PEEK-ACHU and the sample of PetroOxy, with systematic higher values in the fuel aged in the microreactor. From a practical point of view, the experiments performed in PEEK-ACHU are highly versatile, with changes of temperature, pressure and residence time without interruption of the experiments compared to PetroOxy measures that requires several manipulations and interruptions. A comparison between all the PetroOxy and PEEK-ACHU results (total [ROOH] content at the exit of the reactor) is presented in Figure 13.

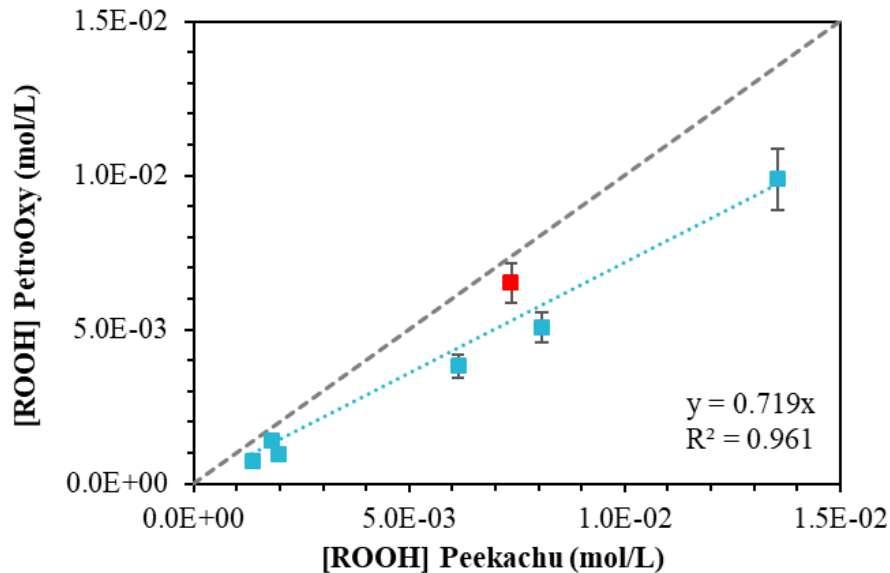


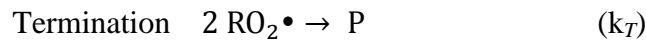
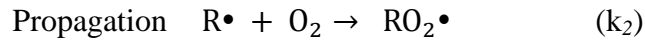
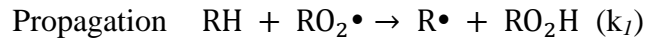
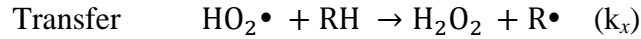
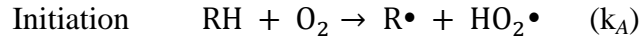
Figure 13: Parity curve of total [ROOH] from SAF and *n*-decane oxidized in PEEK-ACHU and the PetroOxy (413 K and 7 bar for PetroOxy and 20 bar for PEEK-ACHU). Blue symbols: residence times from 16 to 65 min; red symbol: 90 min residence time.

We can observe in Figure 13 that for low residence times (16-65 min), the correlation between the concentration of hydroperoxides from samples aged with PEEK-ACHU and the PetroOxy is almost linear. The data are all below the grey curve $y=x$, which reflects the fact that more hydroperoxide are formed in the microreactor, by about 30%. The red symbol of Figure 13 appears to be closer $x=y$ curve. It corresponds to the [ROOH] measured for 90 min of residence time in both reactors which is the longer time we measured in this study. For longer residence time, the uncertainties associated with the analysis of the samples oxidized in the PetroOxy may diminish or partially cancel.

Our reactor has been shown to be capable of oxidizing liquid fuels at least as effectively as the PetroOxy, but with more efficient O_2 mass transfer into the liquid, with no visible depletion of dissolved oxygen along the reactor, and in homogeneous controlled conditions for the liquid slugs. The PetroOxy is widely used as a certification test that provides a binary response (pass / fail) and its quantitative measurement enables it to compare the oxidation stabilities of different fuels and thus give reactivity rankings. In this work, we propose a way to quantitatively compare the reactivity of two different fuels with the new PEEK-ACHU device, by comparing the ROOH data of oxidation measured for *n*-decane and the SAF surrogate. To do this, we first established the rate laws in our microreactor for low extent of reaction.

Liquid fuel oxidation kinetics in PEEK-ACHU

From a detailed kinetic mechanism approach, we can trace the rate laws and validate these laws on the basis of experimental results. In particular, we can show the influence of oxygen and fuel concentration on the rate of formation of ROOH at low reaction extent, where the fuel oxidation mechanism may be approximated by the following primary mechanism (at the beginning of the autoxidation process):



where each elementary reaction of the above mechanism has a given rate constant k_i .

Applying the Quasi-Steady-State Approximation (QSSA) on the radicals of the reactions above, the well-known relation between the rate of initiation (r_A) and the rate of termination (r_T) is obtained:

$$r_A = r_T \quad (1)$$

with $r_A = k_A[\text{RH}][\text{O}_2]$ and $r_T = k_T[\text{RO}_2\cdot]^2$. Noting that the rate of formation of ROOH is $r_1 = k_1[\text{RH}][\text{RO}_2\cdot]$ in the first reaction of propagation, the rate of formation of ROOH can be rearranged as:

$$r_{\text{ROOH}} = k_1 \sqrt{\frac{k_A}{k_T}} [\text{RH}]^{3/2} [\text{O}_2]^{1/2} \quad (2)$$

This result shows that for low extent of reaction, when the decomposition of hydroperoxides is negligible, their rate of formation depends on the concentration of O_2 and a global rate constant involving the H-abstraction by $\text{RO}_2\cdot$ as well as initiation and termination. Within this approach, we conducted a kinetic study at low residence time for the SAF surrogate and *n*-decane fuels to validate these laws. Figure 14 presents the ROOH concentration as a function of residence time.

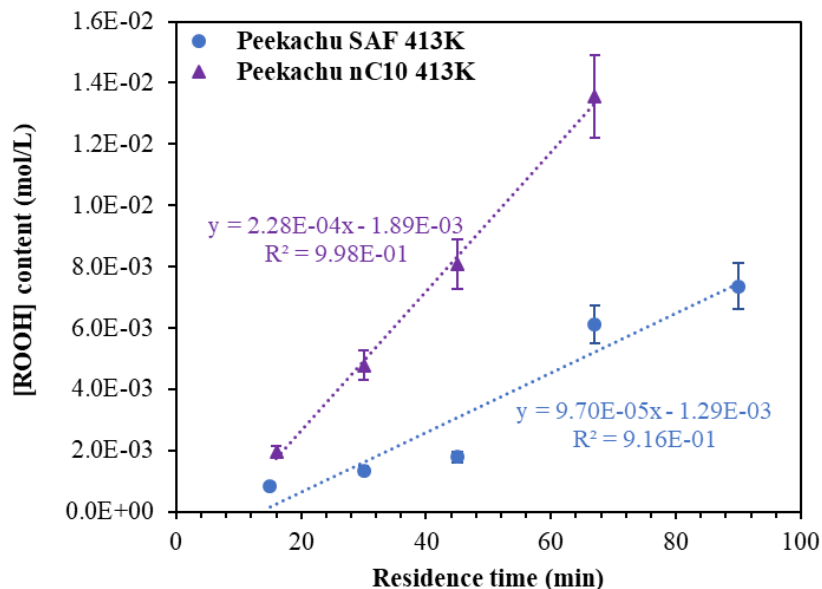


Figure 14: ROOH content of *n*-decane and SAF surrogate as a function of residence time (SAF blend (in blue)/ *n*-decane (in purple) | 413 K | 20 bar).

Figure 14 shows that a linear correlation is obtained for the building of hydroperoxide concentration as a function of time, as expected from the rate law given in equation 2 corresponding to a slow oxidation regime, with no self-acceleration phenomena induced by the decomposition of hydroperoxides. The slopes of the curves are very different, with a slope twice as steep for *n*-decane compared with the SAF surrogate, meaning the rate of formation of ROOH during the SAF oxidation is slower than for *n*-decane. This observation allows us to compare the oxidation stability of the two fuels and to conclude that the SAF is more oxidatively stable than *n*-decane. This conclusion is observed in the of PetroOxy tests, where *n*-decane has an IP of 189 minutes at 413K, while the SAF surrogate has an IP of 286 minutes. This first comparison of fuel stability is promising and need to be extended to other fuels. One of the very strong advantage of PEEK-ACHU for this comparison is that the residence time required to perform this comparison could be reduced to a handful of minutes, compared to hours in a PetroOxy and could be enforce by including variations in temperatures (instantaneous in the microreactor).

CONCLUSIONS

In this work, the validation of a gas-liquid microreactor for studying the kinetics of oxidation of fuels in the liquid phase is presented. The experimental set-up consists of a Si-glass reactor and PEEK fluid supply and recovery systems, both of which are chemically inert. The system developed makes it possible to reach temperatures of up to 458 K and pressures of 1 to 40 bar. Within the reactor, a Taylor-type flow alternating liquid fuel slugs and oxygen gas bubbles is ensured over all operating ranges. This type of flow maximizes oxygen mass transfer in homogeneous liquid slugs, which are self-stirred, thanks to the serpentine design of the microchannel, and isothermal. For the first time in the literature, residence times up to 230 minutes can be reached on a 4 inches diameter silicon wafer. The size ratio between the oxygen bubbles and the size of the liquid plugs is maximized to ensure a constant oxygen concentration throughout the reactor. In order to characterize the capabilities of this new experimental device for oxidizing liquid fuels, comparisons were made with model liquid fuels oxidized with PetroOxy. The basis for comparison is the total amount of hydroperoxide measured after each fuel oxidation in the two experimental set-ups. ROOH quantification was carried out using a method developed in our group using HPLC combined with a post-column reactor. The results showed that the new PEEK-ACHU rig is capable of oxidizing liquid fuels at least as effectively as the PetroOxy, but with more efficient O₂ mass transfer into the liquid, with no visible depletion of dissolved oxygen along the reactor, and in homogeneous controlled conditions for the liquid slugs. These advantages make it a well-defined reactor to study the chemical kinetics of liquid fuel oxidation. At low extent of reaction, we demonstrated that a fast comparison of the thermal oxidation stability of the SAF and *n*-decane fuels is possible and agree with the standardized results of IP in the PetroOxy.

The use of alternative fuel such as sustainable aviation fuel can challenge current standard norms and our new approach could be interesting to explore, even if more tests need to be done.

PEEK-ACHU was found to be a reproducible, versatile rig that allow a high range of use, this rig can be used as to study oxidation kinetics before the formation of solid, but can also be used to study the formation of gums and deposits thanks to its modularity and its transparent access to the reactor. This optical access is also an advantage to perform *in situ* analyses with, for example Raman spectroscopy.

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