

Oxidation of n-butane in a RF discharge at atmospheric pressure

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Abstract: The oxidation of n-butane in an atmospheric pressure RF helium oxygen discharge is studied. The results highlight a conversion towards CO, CO₂ and H₂O with no coating on the walls. The low admixture of O₂ leads to a shift towards CO over CO₂ production. Absolute densities measurements have been performed for both reactants and products.

Keywords: RF discharge, atmospheric pressure, VOC, n-butane, conversion

1. Introduction

Volatile organic compounds (VOCs) are present in our surrounding atmosphere, they result from human activities as well as from biological processes. In urban areas, the ones originating from human activities are often dominating compared to the natural ones. On one hand, those VOCs can present health and environmental issues depending on their identity and are the topic of research on air depollution. On the other hand, among those VOCs, alkanes constitute reactants to produce value added molecules for industry when involved in gas conversion processes.

The molecule n-butane has been chosen as an alkane example. N-butane with its longer chain compared to CH₄ more readily adsorbs on the walls, which would enhance the contribution of any surface processes. Moreover, it is a stable species that is difficult to convert and it is used therefore for a benchmarking.

In this work the oxidation of n-butane in an atmospheric pressure RF discharge is investigated by mass spectrometry. The densities of the different species involved are measured and the overall reaction leading to the conversion is analysed. The study has been performed for one gas mixture at different plasma powers and for different O₂ admixtures at fixed power. The densities can then be used as input parameters for a global chemical model.

The final aim of this study is the identification of the mechanisms involved in the oxidation of n-butane in an RF discharge to optimize the process according to the application targeted.

2. Experimental setup

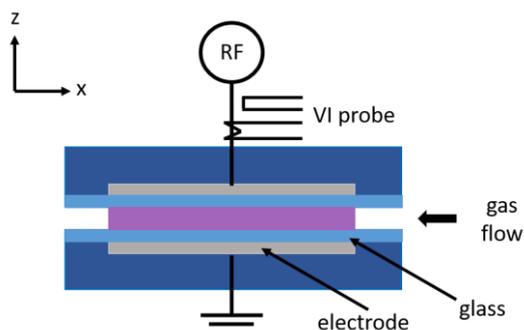


Fig. 1: Side view of the plasma chamber along the gas flow.

The plasma chamber used for this study has been described in [1] and will be shortly introduced here. It consists of two copper electrodes, isolated from the plasma by glass plates, and placed apart of each other by a gap of 1 mm. They are enclosed in a chamber with large windows to provide an optical access to the plasma. A cross section view of the plasma chamber can be seen figure 1. The system is operated at atmospheric pressure.

The gas flows through the chamber is composed of 250 sccm of helium admixed with 0.125 % of n-butane (C₄H₁₀) and variable admixtures of O₂. The reference O₂ admixture corresponds to the stoichiometric ratio considering a full conversion to CO₂, i.e. 0.8125 %. The chamber is powered by an RF signal at 13.56 MHz.

In this work the species are investigated with a molecular beam mass spectrometer (MBMS) dedicated to the study of neutral species. The mass spectrometer is a Hiden Analytical EPIC quadrupole system mounted on an atmospheric interface described in [2]. The species within the plasma are sampled in-situ through a fused silica capillary embedded in a macor block and connected to the interface at atmospheric pressure of the mass spectrometer. This sampler has already been introduced here [3]. The sampling system design and positioning on the side of the chamber are shown on figure 2. For this study the sampling is placed in the middle of the chamber along the x axis. Only stable species can be measured.

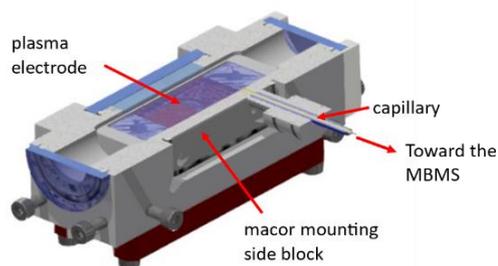


Fig. 2: In-situ sampling system connected to the chamber.

In order to achieve absolute densities for the different species, calibrations have been performed with comparable gas composition as being used in the experiments. The calibration gases are summarized table 1.

Table 1: species studied and the corresponding calibration gas used.

<i>Species studied</i>	<i>Calibration gas</i>
n-butane	n-butane
CO ₂	CO ₂
CO	N ₂
O ₂	O ₂
H ₂ O	Ne

3. n-butane conversion

The conversion efficiency is estimated from the n-butane depletion. The intensity of n-butane without plasma (S_i) is compared to the one when a discharge is ignited (S_f), following:

$$\alpha = \frac{S_i - S_f}{S_i}$$

Alike, the consumption of O₂ can be estimated.

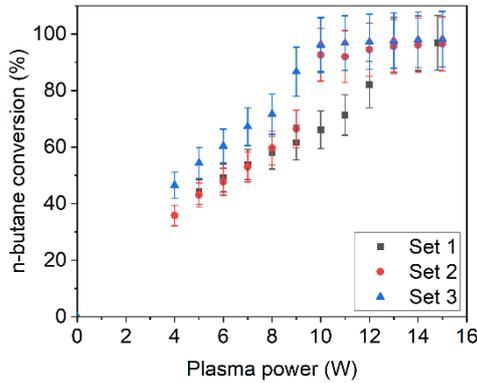
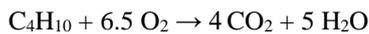


Fig. 3: N-butane conversion as function of the plasma power for 3 independent sets of measurements.

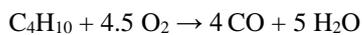
In figure 3, the n-butane conversion efficiency is plotted with increasing power for the reference O₂ admixture. The full conversion is reached at 11 ± 1 W. The measurements are consistent for the different sets performed on different days.

4. Mass balance

At first, O₂ has been introduced in stoichiometric concentration assuming a full oxidation of the n-butane towards CO₂, following:



Thus, leading to the 0.8125 % O₂ reference admixture for 0.125 % of n-butane. On the other hand, if we consider the conversion to CO, we obtain the reaction:



Corresponding to a 0.5625 % O₂ admixture.

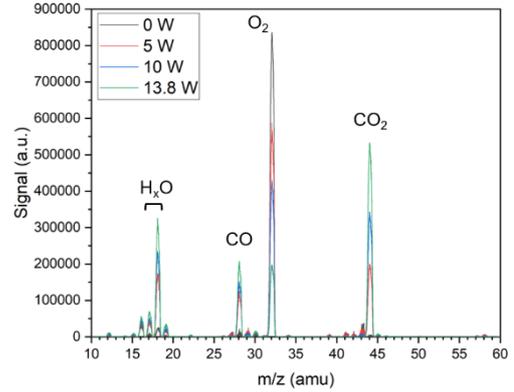


Fig. 4: Mass spectra, from which the cracking pattern of n-butane has been subtracted, obtained at different plasma powers.

The mass spectra show CO, CO₂ and H₂O as the reaction products from the conversion of n-butane and O₂. When admixing the reference ratio of O₂, no stable smaller hydrocarbons have been detected (figure 4). The overall reaction can then be summarized as:



With $\alpha_1, \alpha_2, \alpha_3$ the stoichiometric coefficients.

The complete conversion towards CO and CO₂ products has been confirmed via an analysis of the carbon and oxygen balances obtained when considering the densities estimated for each species (figure 5). The balances show a good agreement between consumption of the reactants and the generated products confirming that the overall reaction above is a good approximation. Nevertheless, the oxygen balance shows some discrepancy at high power from unity, as will be discussed below.

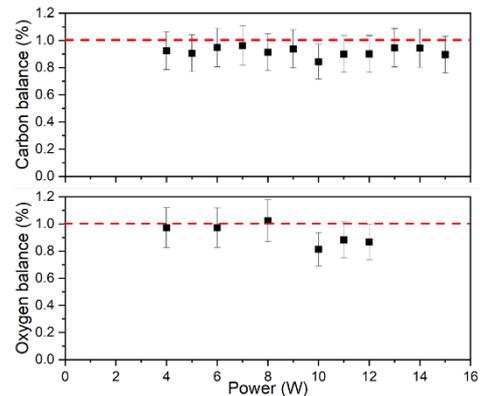


Fig. 5: Carbon and oxygen balances at different plasma powers, the red dashed line indicates the unity.

The carbon mass balance presents no loss of carbon indicating that no carbon is deposited on the walls. This is consistent with the observation that the glass plates after treatment seems to be as clean as before.

5. Densities measurements

The estimated densities of the species are shown figure 6 with increasing power. Those results show a higher production of CO_2 compared to CO with a maximum production of CO being 3 times lower than the maximum for CO_2 . The optimum in CO production coincides with the power threshold for which the full conversion of n-butane is reached. At higher powers the density of CO decreases showing a shift to CO_2 production. A decrease of H_2O is also observed at higher power, this should lead to an extra amount of hydrogen as H_2 . Nevertheless, this effect could not be quantified due to a lack of calibration gas for this mass

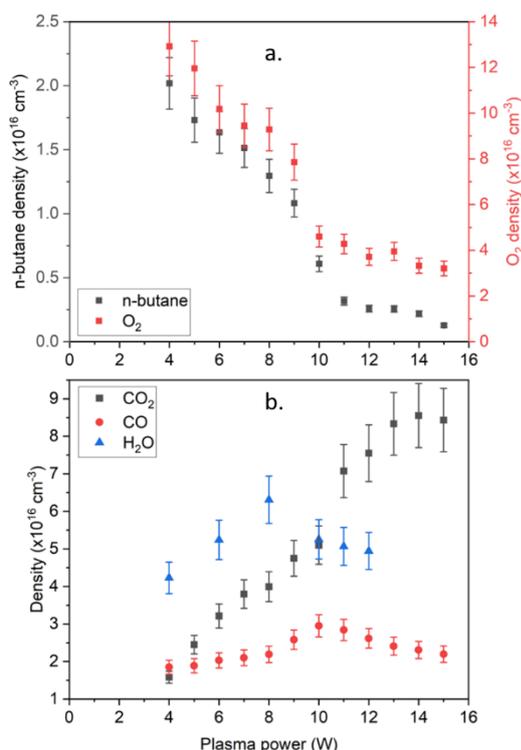


Fig. 6: Measured densities of the reactants (a.) and the products (b.) as function of the plasma powers.

It also appears that O_2 is not fully consumed at high powers. The stoichiometric admixture of O_2 used in this study was quantified assuming full conversion of n-butane to CO_2 . The presence of CO indicates an excess of oxygen. The remaining amount of O_2 at high powers result from the leftover of the conversion to CO , leading to $\frac{1}{2} \text{O}_2$ not consumed.

Regarding the deviation from unity observed in the oxygen balance above 10 W in figure 5, one could postulate an adsorption of oxygen at the walls because no other oxygen containing products have been identified.

6. Influence of the O_2 admixture

To better understand the influence of the O_2 flow rate has on the oxidation process of n-butane, the admixture of oxygen has been varied at a plasma power of 8 W and the

conversion rate of n-butane has been measured. The results are plotted in figure 7.

Surprisingly, the conversion of n-butane at 0 % O_2 admixture is already 60 %. This is attributed to the fragmentation of n-butane leading to smaller hydrocarbon chains, which eventually recombine and form longer hydrocarbon chains. Such longer chain products have been observed in a mass spectrum for a discharge of helium with only n-butane admixed (not shown here).

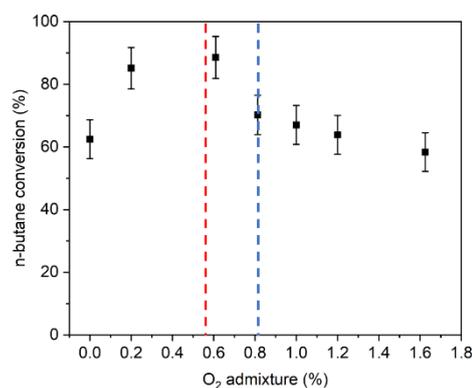


Fig. 7: n-butane conversion rate as function of the O_2 admixture at a constant 8 W plasma power. The red and blue dashed lines correspond to the stoichiometric ratio of O_2 for a full conversion to respectively CO and CO_2 .

Moreover, the conversion rate is at its maximum for an admixture of O_2 of 0.6 %, which could indicate a shift towards the production of CO . Indeed, when considering a full conversion to CO the stoichiometric ratio of O_2 is 0.5625 %.

It is also interesting to note that above the 0.8125 % reference admixture, the conversion rate decreases which could indicate a decrease of the plasma density due to the quenching by O_2 molecules.

7. Conclusion

This work describes the n-butane conversion in a RF atmospheric pressure plasma reactor through oxidation. The main products of the reaction have been identified and their densities measured. To complete the understanding of this process, a study of the influence of O_2 on the overall reaction would be necessary.

8. References

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