EXPERIMENTAL AND MODELING STUDY OF SURFACE REACTIONS OF PLASMA GENERATED ATOMIC OXYGEN WITH PHENOL SOLUTIONS

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The interaction of plasma generated atomic oxygen with phenol solution is studied experimentally using an atmospheric pressure plasma jet (COST-Jet). With varied gas admixtures of He/O_2 the amount of produced atomic oxygen leaving the plasma source and its recombination lifetime with O_2 are controlled at the same time. The use of different phenol concentrations allows a change of surface reaction probability to investigate the importance of surface reactions on liquid for atomic oxygen. A developed transport and reaction simulation of the experimental setup supports the findings and provides insight into the details of the reaction processes.

In recent decades plasma treated liquid became a relevant topic for various fields due to its high reactivity with biological substrates or organic compounds [1]. This increased reactivity is induced by reactive species like atomic oxygen or hydroxyl radicals. However, as the lifetime of atomic oxygen is short, knowledge about its reactions with dissolved species in aqueous solutions is limited. For example, it is not known whether the reactions occur dominantly at the liquid surface or in the liquid bulk. As the density of atomic oxygen leaving the COST-Jet is well known [2,3], this source suits well the investigations of ongoing oxygen reactions. Furthermore, it was proven in previous studies that phenol reacts directly with atomic oxygen without any intermediate reactions with or in water [4,5]. With phenol being a surfactant, a variation of phenol concentration between 0.1 and 25 mM changes the surface reaction probability of atomic oxygen with it. To reveal the reaction process, the consumption of phenol and the production of diols and triols are studied using mass spectrometry (MS) and high-performance liquid chromatography (HPLC).

To investigate the reaction rates at liquid surface or in its bulk and to support the experimental results, a 2D axisymmetric model has been developed in COMSOL Multiphysics without the necessity of simulating the plasma itself, as the densities of reacting species are well known from experiments [2,3]. A fluid dynamic simulation is performed to render the gas stream impinging on liquid surface and induced stirring of the liquid. After that, transport and reaction rate equations are solved for phenol, O, O_2 and O_3 species. Several values which are not reported in the literature, like the Henry's solubility law constant of atomic oxygen or surface reaction rate of atomic oxygen with phenol, were fitted and varied in this model. The implementation of surface coverage of surfactants and surface reactions on the liquid surface allow studying important reaction probabilities of atomic oxygen.

The results of the experimental and modeling studies show a good agreement (fig. 1). It is found that the reactions of atomic oxygen at the liquid surface are the key player of the degradation process of phenol molecules and therefore also for other surfactant molecules (fig. 2).

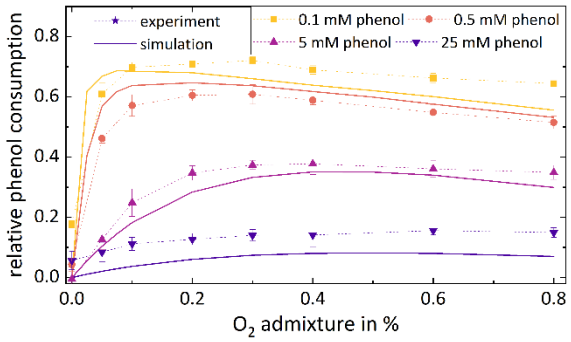

Fig. 1. Phenol consumption relative to initial phenol concentration varying between 0.1 and 25 mM for different O_2 admixtures. Comparison of experimental and modeling results.

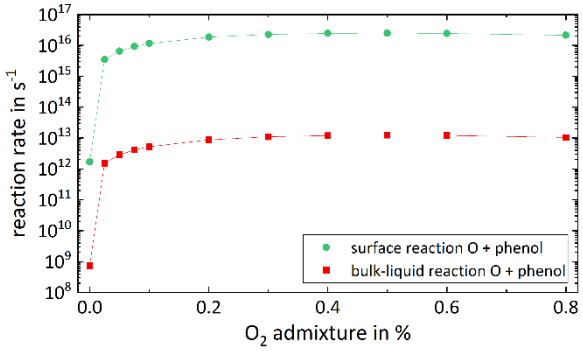

Fig. 2. Calculated reaction rates per second of atomic oxygen in 25 mM phenol solution at the liquid surface and in bulk-liquid depending on different O_2 admixtures in He/O_2 plasma.

The results of the simulation clearly show that most of the atomic oxygen reactions with phenol take place at the liquid surface, mainly due to the low value of Henry's solubility law constant of atomic oxygen and the surfactant character of phenol molecules. This study is relevant for atomic oxygen reactions with other species as well, for example the reaction with Cl^- anions in PBS or in saline solution to form ClO^-, because they are very probably also taking place dominantly at the surface of the liquid. The knowledge provided in this work has important implications for further development of plasma-liquid treatments involving atomic oxygen as reactant.

1. References

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