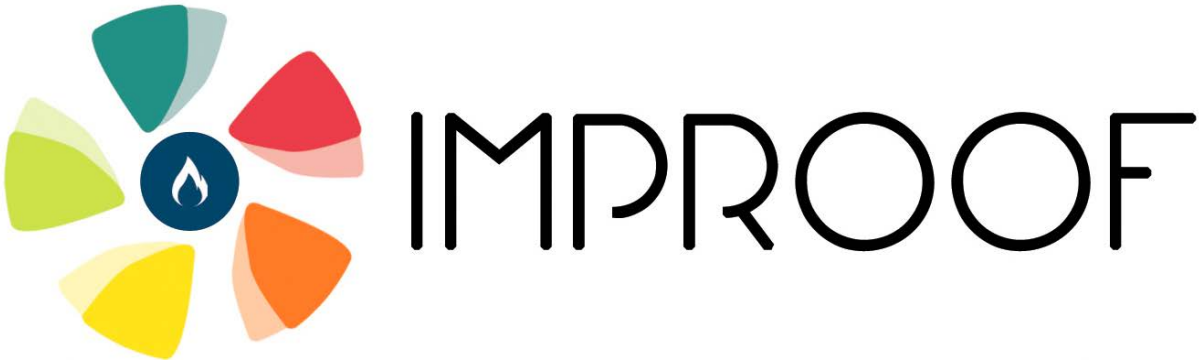

D1.3: Detailed and reduced kinetic mechanism and their validation

Contractual delivery date: M24
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EXECUTIVE SUMMARY

1.1 Description of the deliverable content and purpose

This deliverable describes the development of the detailed kinetic mechanism of bio-gas and bio-oil combustion, as potential candidate fuels for feeding the next generation steam cracking furnaces. Following that, the creation of a reduced kinetic mechanism is illustrated in detail, being a necessary input for the successive Computational Fluid Dynamic (CFD) simulations of the whole furnace.
Such deliverable is part of the Work Package (WP) 1 of the IMPROOF project, and has been carried out in the timeframe M3 – M24 (November 2016 – August 2018), within the Task T1.3: "Kinetic mechanism development/reduction". The obtained output is then mainly functional to the activity of WP2: "Innovative Furnace System developments and integration".
The first step of such process has been the development of a core mechanism of pyrolysis and oxidation of small hydrocarbon fuels, by exploiting the latest quantum chemistry calculations available in literature. Particular attention has been devoted to the oxycombustion conditions, which are of specific interest for the present project.
Following that, the kinetic modeling of several classes of compounds has been carried out. This last part has proceeded in parallel to the analysis of the composition of bio-gas and bio-oils mixtures, accomplished in the first 12 months of the project and described in D1.1: "Description of the mixture of bio-gas and bio-oil to be used in the modelling and experiments".

1.2 Brief description of the state of the art and the innovation breakthroughs

The kinetic modeling of the oxidation of natural gas, usually found in fossil reservoirs, has been widely studied for the latest 40 years [1-3]: more than 15 mechanisms describing the pyrolysis, partial oxidation and combustion of methane have been developed over time [3-9]; thus, the understanding of methane behavior in conventional conditions can be considered as mature.
On the other side, much less is known about the combustion of biogas and bio-oils. Although potentially carbon-neutral, their "organic" origin results in the presence of a variety of compounds within the feed, requiring a proper kinetic investigation, since they might result in unwanted, toxic byproducts downstream of the combustion process. Also, a comprehensive kinetic understanding of their oxidation in CO_2- and H_2O-diluted conditions has not been attained so far. These two topics, both cornerstones of the present project, are the foundation of the kinetic modeling work carried out in WP1 of the IMPROOF project, and described in the remainder of this deliverable.

5 CONCLUSIONS

The present deliverable has explained in detail the work carried out within the kinetic modeling part of WP1, i.e. the development of a detailed mechanism of biogas and bio oil combustion, its validation and its successive reduction to a skeletal level. Such work has laid its foundation on the consolidated methodology for modeling the pyrolysis and oxidation of hydrocarbons developed by Politecnico di Milano in the latest 40 years. As a matter of fact, the recent improvements in terms of theoretical methods for kinetic constant evaluation, and the increasing availability of computing power has allowed a major revision and consolidation of the mechanism, also extending its reliability to non-conventional conditions like oxyfuel ones, with the dilution of CO_2 and/or H_2O (of interest in this project).
Starting from this point, a novel mechanism for the oxy-combustion of biogas has been developed and validated, and a sub-model of NO_x formation has been obtained.
In parallel, after the identification of the major classes of bio-oil constituents, the kinetic model of alcohols, aldehydes and carboxylic acids has been developed. This has been possible also thanks to the experimental campaigns carried out at CNRS, which will be subject of a separate deliverable (D1.3, due by M36). They have served as a useful validation benchmark, in parallel to the data already available in literature.
Finally, the use of a reduction methodology has allowed to identify the key governing species and reactions, within the kinetic model, such that the resulting computing load of the downstream CFD simulations can be significantly reduced. Their validation of the major targets of the work, i.e. fuel reactivity, and formation of intermediate species and pollutants like NO have proved the effectiveness of this approach, thus paving the way to its systematic application for the forthcoming classes of compounds within the IMPROOF project.