ADVANCED PROCESSES FOR COMBUSTION OF NON-CONVENTIONAL FUELS FOR THE DECARBONIZATION OF THE ENERGY CARRIES

Maria Virginia Manna – Advisor: Prof. Antonio Cavaliere, Giancarlo Sorrentino

Curriculum: Ingegneria Chimica

The world energy demand is currently facing with the constraint to reduce the Green Houses Gases (GHG) emissions due to the global warming acceleration. The Paris Agreement adopted at the Conference of Parties 21 (COP21) establishes the goal to reduce the increase in the global average temperature to below 2°C and each signatory Nation proposes its Intended Nationally Determined Contribution (INDC). From the analysis modeled in the New Policies Scenario emerges that the energy demand is expected to grow by more than 25% to 2040, under current and planned policies.

A huge transformation is assaulting the electricity market because of the increasing demand brought by the digital economy, electrification in transportation and other technologies, leading to a peak in oil demand by 2030, which in turn, would have a relevant impact on carbon emission. In this context, whatever energy supply system have to face with the compulsory criteria defined by the World Energy Council, which delineate the so-called *Energy Trilemma*. Nowadays thanks to supportive government policies, the Renewable Energy Sources (RES) are emerging significantly, to the extent that they could provide almost two third of the global capacity additions to 2040. New issues arise from the share of Variable Renewable Energetic Sources (VRES, particularly solar and wind). In particular, renewables are dependent on the availability of the so-called *critical metals* needed in term of reserve and resource.

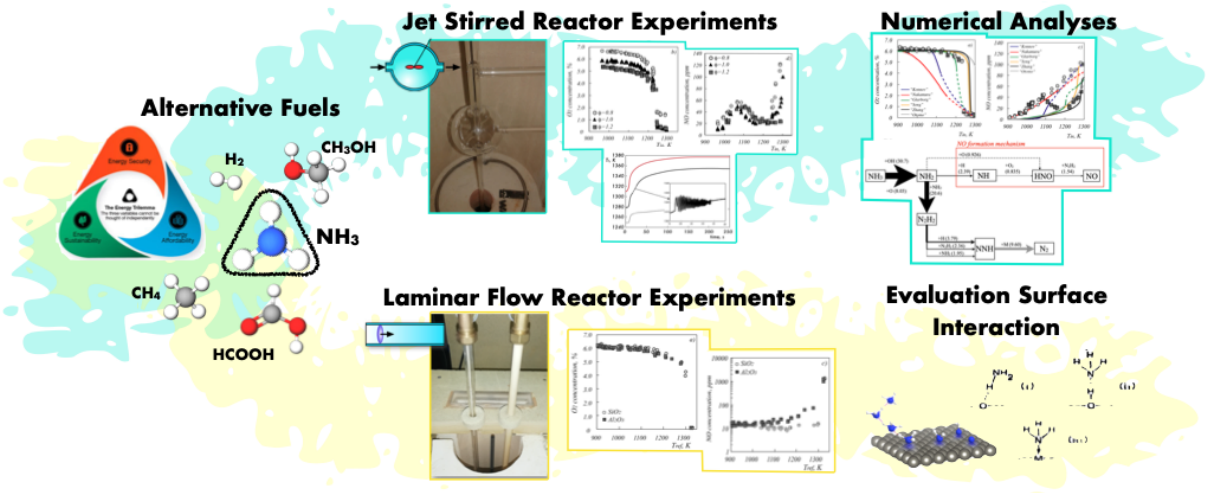
The integration of combustion processes in the energy mix can support the deployment of RES because it is the only process with the appropriate characteristics to fill the gap of the RES intermittency. The back-up potentials of combustion process are twice effective, as the surplus of renewables can be stored in molecules, which can be used as energy carries. The storage in a chemical form is more economical than the storage in batteries and, additionally, batteries have lower energy density and shorter discharge time than energy carriers.

Ammonia is considered an interesting candidate as energy vector and hydrogen carrier, because it can be easily cracked to produce hydrogen for use in fuel cells or other hydrogen applications and it has a high volumetric H_2 density if compared with other hydrogen carriers. Due to its several applications, consolidated infrastructures for ammonia transport and storage are available. The main drawbacks of a direct ammonia utilization in combustion systems come from its chemical properties as fuel (low calorific value, flame velocity, high ignition temperature, narrow flammability limits), that drastically undermine oxidation process stabilities, with loss of system efficiency. The common proposed strategies to overcome such limits rely on the use of fuel enhancers in traditional combustion systems (H_2 or hydrocarbon) or on the implementation of ammonia oxidation under non-conventional combustion modes. The operative conditions typical of MILD combustion envisage the use of mixtures highly diluted and pre-heated by an internal or external recirculation of mass and sensible enthalpy within the combustion system. Such operative conditions allow to control NOx emissions while ensuring the stability of the oxidation process, also for low calorific value fuels. The successful application of ammonia as an alternative fuel under diluted and pre-heated conditions requires a detailed understanding of its oxidation process, along with the development of an affordable detailed kinetic mechanism.

From the literature survey, it turns out that the available mechanisms have been developed staring from models used to describe the NOx formation and reduction in combustion processes. Therefore they have been validated against high-temperature and/or high-pressure data, for the most at fuel-rich conditions, that allow to minimize NOx emissions. However, disagreement exists in models predictions for relatively low-temperature and high diluted combustion conditions, relevant for MILD combustion. For these reasons, the comprehension of each aspect of ammonia combustion and the development of a reliable mechanism that can simulate experimental data are of

primary importance. To this aim, flow reactors are well-established configurations to study chemical reaction pathways in combustion.

Given this background, the objective of this PhD thesis is to investigate ammonia oxidation and decomposition in model reactors (Laminar Flow Reactors and Jet Stirred Flow Reactor), exploring the effect of the external system parameters (mixture composition, pre-heating temperature, dilution, residence time) on the oxidation regimes and on the stable species concentration profiles. The study focuses on low-intermediate temperature conditions of practical interest to diluted combustion applications.
Obtaining measurements is the primary objective of the present study, since they not only reveal peculiar behavior of ammonia oxidation, but also provide validation constraints for kinetic mechanism development. In fact, as further step, the performance of updated kinetic models in predicting the experimental data under the investigated conditions is tested. Numerical simulations and kinetic analyses are performed to identify the most important reactions and to suggest possible sources of disagreement between the model predictions and experimental data.



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