

tools and methodologies from the Information and Communication Technology (ICT) community to create and exploit valuable databases that will be utilized long after the completion of the Action. Nevertheless, the core of this Action remains in the development of oxidation kinetic mechanism for new classes of fuels having the potential to become SECs capable to sustainably meet the future energy demand. It addresses this task starting from the already relevant competences of involved research institutions and exploiting the capabilities of increasingly powerful diagnostics tools, in particular for their capabilities to identify and quantify pollutant emissions.

The success of this Action will be measured by the capacity of realizing a significant transfer of knowledge and competences toward their practical application. This transfer must necessarily be guided, through the definition of appropriate standard and tools, by the final users of the chemical and diagnostic tools that are the designers and the manufacturers of combustion systems and plants. The huge amount of experimental and numerical data cannot be efficiently transferred without resorting to advanced information and communication tools. A specific part of this Action is devoted to the analysis and definition of requisites, to the identification of available commercial tools and, in particular, to the realization of a cyber network among scientist and engineers interested to the study and application of SECs.

According to this methodology the SMARTCATS work programme is structured in five Working Groups (WG) whose main objectives and expected results are reported in the following.

#### *WG1. Smart Energy Carriers gas phase chemistry: from experiments to kinetic models*

The work in WG1 aims to improve the knowledge on detailed chemistry and thermochemistry for the combustion, pyrolysis, and oxidation of fuels, such as:

- Natural gas mixtures (compressed natural gas, liquefied natural gas, syngas natural gas, bio-methane),
- Simple molecules (large normal and iso-paraffins, alcohols, esters, saturated and unsaturated cyclic ethers (e.g. derivatives of furans)) which can be present in 1st and 2nd generation biofuels,
- More complex molecules, such as the polymers which can be obtained from wood as lignin, cellulose, and ligno-cellulose, and derived molecules, such as  $\gamma$ -valerolactone,
- Complex mixtures of molecules actually found in 1st and 2nd generation biofuels, such as fatty acid methyl esters (FAME), hydrotreated vegetal oils (HVO), or biomass to liquid fuels (BTL, obtained by gasification followed by Fischer-Tropsch synthesis), or in the proposed surrogates, i.e. mixture of simple molecules whose oxidation mimics that of the real fuel.

The oxidation chemistry of some of these biofuels, like FAME, has been already investigated but

for others the knowledge is only partial, as in the case of HVO and lignin. Chemical characterization is indeed a difficult task mainly in the case of biomass derived fuels. Lignin, as an example, is a complex racemic polymer, whose composition varies according to biomass source. The Action aims to fill the gap with the improvement of the existing detailed kinetic models as well as the development of new ones, thanks to the availability of new experimental data and the easier accessibility to quantum chemistry computation for thermodynamic and rate constant estimation. One of the main difficulties in all these cases is related to the large dimensions of the resulting detailed kinetic models, due to the high molecular weight of the species and the lack of symmetry, inherent in such molecules. A general approach will be to start from automatic generation and subsequently adopt proper simplifying rules, like chemical lumping, to control the total number of species, which could make the global scheme impossible to manage. Several software programs already exist in Europe for the automatic generation of mechanisms for components of HVO and FAME. Their possibilities need to be extended. Experimental investigations will be performed in well characterized laboratory combustion environments for ignition (shock tubes and rapid compression machines), flames (laminar premixed and diffusion), and pyrolysis/ oxidation (plug and stirred flow reactors). Experimental data at higher pressures are particularly needed, such as ignition delay times (at pressures > 40-50 atm) and flame speeds (at 20 atm or more). Also the effects of multicomponent mixture, and of diluents, especially CO<sub>2</sub> and H<sub>2</sub>O, and Exhaust Gas Recirculation will be considered.

These models require thermodynamic and kinetic parameters of included elementary reactions. The key strategy will be the establishment of close collaborations between experimentalist and theoreticians. Theoretical analysis will use modern quantum chemical methods (e.g. density functional theory or coupled cluster methods). Kinetic data are to be obtained from advanced statistical rate theories (e.g. Rice-Ramsperger-Kassel-Marcus theory and master equations). A particular effort will be devoted to use these theoretical methods to derive data for molecules of increasing size.

In addition to their comparison against a range of experimental studies, a critical part of the evaluation of chemical mechanisms for the prediction of combustion products is uncertainty analysis. This investigates the uncertainty in the model output given defined uncertainties in the model input parameters. These can include for example, reaction rate constants, as well as thermodynamic and transport properties of key species. If enough information is available about the model inputs, uncertainty analysis can be used to provide error bars on model predictions.

*WG2: Chemistry for control of by-products in Smart Energy Carrier conversion*