

# SMARTCATs STSM final report

Impact of the NO<sub>x</sub> addition on methane JSR oxidation, with different types of diagnostic techniques (GC, CRDS, IRTF)

## 1. Details of the STSM

**Reference number:** ECOST-STSM-CM1404-38317

### **Applicant details**

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### **Host institution**

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### **Working groups involved**

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

WG1: Smart energy carriers gas phase chemistry: from experiments to kinetic models

### **Type and length of stay**

STSM, from 11/09/2017 to 20/12/2017

## 2. Purpose of the STSM

The limited fossil fuel resource and its harmful effects on the climate have increased the interest for environmentally friendly fuels. Biomass looks like a promising fuel source due to its sustainability, security supply and low threat to the environment. Produced from the biomass anaerobic digestion procedure, the so-called “biogas”, consists mainly of methane and carbon dioxide with trace amounts of nitrogen and sulfur compounds. Biogas plays an important role as potential renewable gas-phase fuel. It can be used to the generation of electricity or heat and also as a fuel. The main nitrogen

compound present in biogas is ammonia, which could easily convert to NO with the presence of oxygen even at low temperatures.

In this context, the main objective of this research stay is to carry out a study of the effect of the NO<sub>x</sub> addition on the oxidation of methane, identifying and quantifying the species formed during the oxidation in a jet-stirred reactor. The experimental data obtained will be used for the validation of a detailed kinetic-chemical mechanism that can be used as a prediction tool to evaluate the behavior of methane under conditions different from those tested in this study and, therefore, help in the decision of engine design.

### **3. Description of work carried out during the STSM and the main results obtained**

During the STSM, the different oxidation experiments were carried out in a laboratory-scale spherical fused silica jet-stirred reactor, JSR (volume of 85 cm<sup>3</sup>). The reactant gases were premixed in a preheating zone before entering the reactor center through four nozzles which create high turbulence resulting in homogeneity in composition and temperature of the gas phase. The residence time inside the preheater was quite short with respect to the one in the reactor which was fixed at 1.5 s within all the experiments investigated. Both the reactor and the preheater were heated using Thermocoax resistances. The reactor temperature was measured by a type-K thermocouple located at the center of the reactor. The pressure in the reactor was controlled by a needle valve positioned downstream of the reactor and kept at 107 kPa. Argon, oxygen, NO, NO<sub>2</sub> and methane were provided by Messer (purities of 99.99%, respectively). The flow rates of the reactants were controlled by mass flow controllers. The uncertainty in the flow rate measurements is 0.5%. The gases leaving the reactor were analyzed on-line using two gas chromatographs (GCs), a NO<sub>x</sub> analyzer (Thermo Scientific Model 42i), a FTIR (Thermo Scientific Antaris) spectrometer and a cw-CRDS spectroscopy cell.

- The first GC equipped with a thermal conductivity detector was used to quantify O<sub>2</sub>. The second GC equipped with flame-ionization detector preceded by a methanizer and a Plot-Q capillary column was used to quantify CH<sub>4</sub>, CO, CO<sub>2</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>6</sub> and C<sub>2</sub>H<sub>2</sub>.
- The chemiluminescence NO<sub>x</sub> analyzer was adopted to measure NO and NO<sub>2</sub>.
- The FTIR spectrometer was used to detect the CH<sub>3</sub>NO<sub>2</sub> (if any) and HCN species.
- cw-CRDS infrared spectroscopy was used to detect H<sub>2</sub>O, CH<sub>2</sub>O and HONO (if any) species, the detailed description of this instrument is provided in [1].

Experiments for the oxidation of methane, and methane doped with NO and NO<sub>2</sub> were performed for different equivalence ratios, from fuel-lean ( $\phi=0.5$ ) to fuel-rich ( $\phi=2$ ) conditions over the 650-1200 K temperature range. The experimental conditions investigated in this study are presented in Table 1.

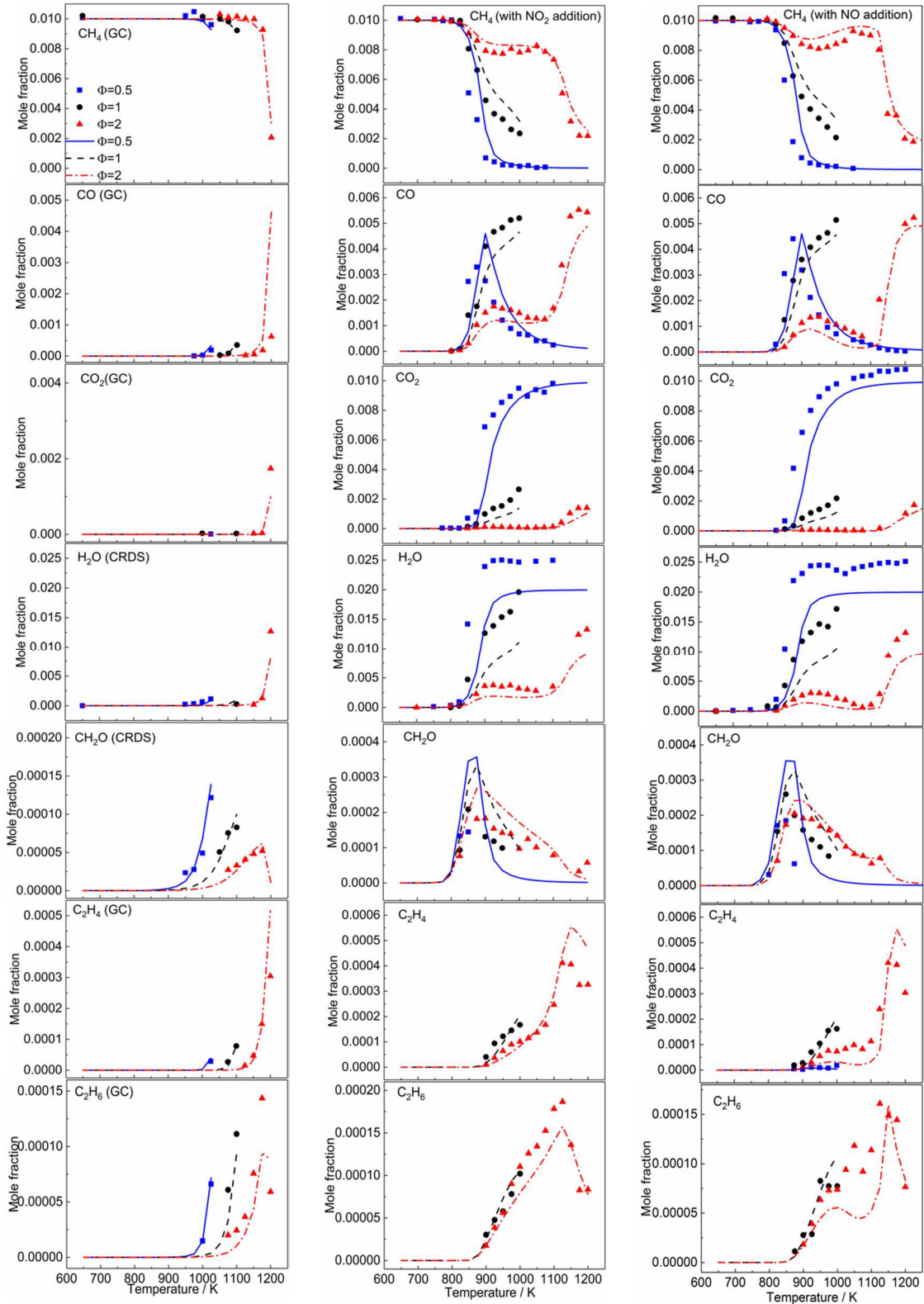
Numerical calculations were conducted with CHEMKIN-PRO software package [2]. Transient solver was applied in the simulation tasks with sufficient time allowed to reach the steady state solution. A detailed kinetic mechanism, derived from POLIMI kinetic framework, was used to interpret the experimental data.

**Table 1.** Experimental conditions (inlet composition volume basis; balanced Ar).

Exp.	$X_{CH_4}$	$X_{NO}$ ppm	$X_{NO_2}$ ppm	$X_{O_2}$	$\Phi$
1	0.01	-	-	0.04	0.5
2	0.01	-	-	0.02	1
3	0.01	-	-	0.01	2
4	0.01	500	-	0.04	0.5
5	0.01	500	-	0.02	1
6	0.01	500	-	0.01	2
7	0.01	100	-	0.02	1
8	0.01	-	400	0.04	0.5
9	0.01	-	400	0.02	1
10	0.01	-	400	0.01	2
11	0.01	-	100	0.02	1
12	0.01	1000	-	0.02	1

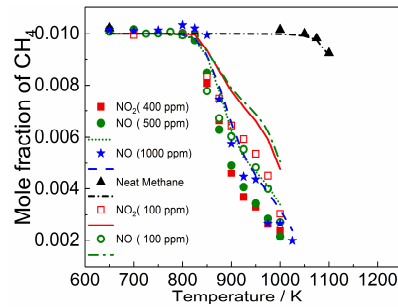
Figure 1 shows the evolution of major carbon compound species and water for the oxidation of methane (left), methane doped with NO (middle) and NO (right) for the three studied equivalence ratios ( $\phi=0.5, 1$  and  $2$ ). Dynamic behaviors (oscillations) occur under oxidizing and stoichiometric conditions when the temperature is above 1050 K and 1100 K, respectively. This is, too, an interesting topic of research in such systems, but beyond the goals of this specific study.

In general, there is a good agreement between experimental results and modeling calculations. In particular, the addition of  $NO_2$  or  $NO$  produces comparable results on the methane oxidation, anticipating the onset temperature for  $CH_4$  consumption to lower temperatures (825 K) regardless of the equivalence ratio.



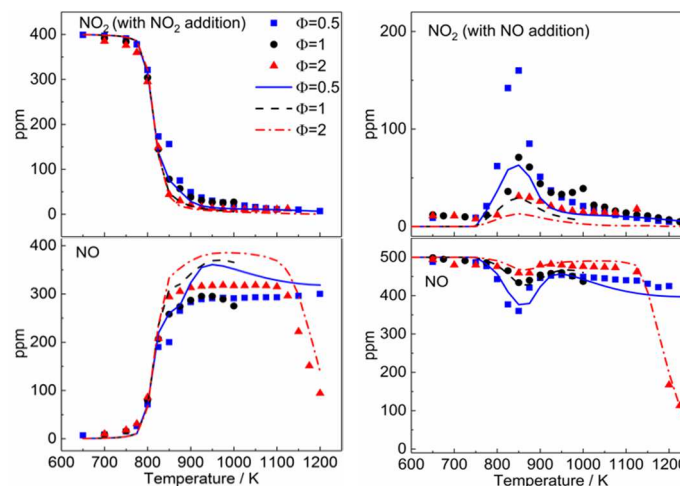
**Figure 1.** Species profiles comparison between experimental data and model predictions. The left column is for the oxidation of neat methane; the middle column is for the oxidation of methane doped with  $\text{NO}_2$  (400 ppm); the right column is for the oxidation of methane doped with  $\text{NO}$  (500 ppm). From now on, symbols represent experiments and lines denote simulations. Experiments and simulations are not presented for conditions where oscillations were observed.

In order to evaluate the effect of the amount of added  $\text{NO}_2$  and  $\text{NO}$  on the methane oxidation, three more sets of experiments with addition of 100 ppm  $\text{NO}_2$  or  $\text{NO}$  and addition of 1000 ppm  $\text{NO}$  (sets 7,11 and 12 in Table 1), respectively, were conducted. The experimental results are shown in Figure 2. It was found that the onset temperature for methane oxidation is independent of the added amount of  $\text{NO}_2$  and  $\text{NO}$ . Moreover, with the lower added amount of  $\text{NO}_2$  or  $\text{NO}$ , the methane conversion is slower. With 1000 ppm of added  $\text{NO}$ , methane conversion shows a trend similar to that with 500 ppm  $\text{NO}$  addition.



**Figure 2.** Mole fractions of methane for different amount of  $\text{NO}_2$  and  $\text{NO}$ .

Figure 3 shows the evolution of  $\text{NO}_2$  and  $\text{NO}$  profiles as a function of temperature for methane oxidation in presence of  $\text{NO}_2$  (left) and  $\text{NO}$  (right), respectively. When  $\text{NO}_2$  is added to the reactant mixture it converts to  $\text{NO}$ . The increase of the  $\text{NO}$  mole fraction is quite sharp over the range 800-900 K, and is independent of equivalence ratio. After that, it attains a “plateau”. Only under rich conditions the  $\text{NO}$  concentration drops from 300 to 100 ppm when the temperature increases from 1100 K to 1200 K, temperatures at which  $\text{HCN}$  has been detected by FTIR.



**Figure 3.** Experimental and modeling profiles for  $\text{NO}_2$  and  $\text{NO}$  during the oxidation of methane in presence of 400 ppm  $\text{NO}_2$  (left) and in presence of 500 ppm  $\text{NO}$  (right).

In the presence of  $\text{NO}$  (500 ppm), the mole fraction of  $\text{NO}_2$  peaks at 850 K, which corresponds to the maximum consumption of  $\text{NO}$  for all equivalence ratios. The amount of  $\text{NO}_2$  drops gradually as the

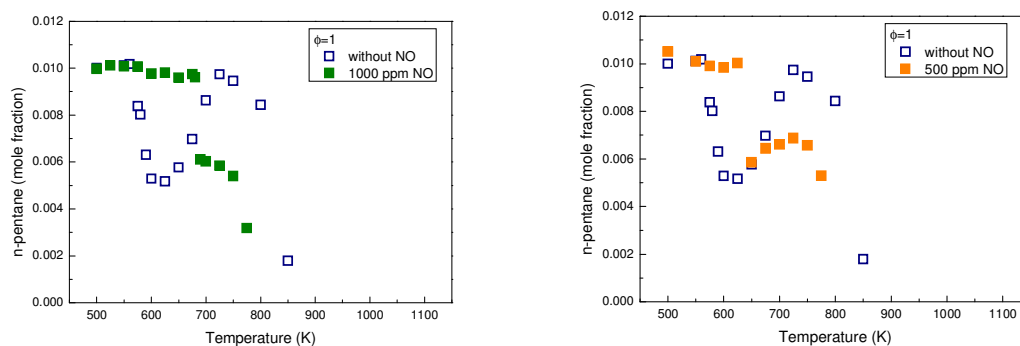
temperature is above 850 K, meanwhile, the mole fraction of NO increases to a stable value until the temperature is beyond 900 K.

### ADDITIONAL WORK: study of the effect of NO<sub>x</sub> addition in the oxidation of n-pentane

As the main purpose of the STSM was successfully completed, we started a new project but related to the previous one: the experimental jet-stirred oxidation of fuel components doped with NO<sub>x</sub>. In this case the fuel component selected was n-pentane because it is a component of gas-turbine and gasoline engine fuel blends and it is an intermediate species in the oxidation of higher hydrocarbons.

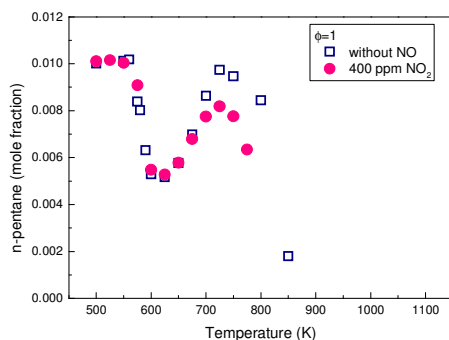
The experimental procedure is similar to that previously described in the case of methane. In this case, the residence time was kept constant at value of 2 s, the mole fraction of the fuel was 0.01 and only one equivalence ratio was analyzed  $\phi=1$ . Different amounts of NO were added to the reactant mixture, 1000 ppm and 500 ppm, and in the case of NO<sub>2</sub>, only 400 ppm.

Figure 4 shows the results obtained during the oxidation of n-pentane without NO and with different amounts of NO and stoichiometric conditions. In the low temperature range it can be observed the characteristic NTC region of n-pentane. However, when NO is added to the mixture, independently of the amount, the conversion of n-pentane shifts to higher temperatures, and this characteristic region almost disappears in the case of 1000 ppm of NO, and shyly appears but at higher temperatures in the case of 500 ppm of NO. As can be observed, NO inhibits the conversion of n-pentane.



**Figure 4.** Mole fraction of n-pentane obtained experimentally during its oxidation without NO (opened symbols) and with NO (filled symbols), for 1000 ppm of NO (left) and 500 ppm of NO (right) and stoichiometric conditions.

In the case of the addition of NO<sub>2</sub> (Figure 5), the trend in the n-pentane consumption is almost the same that in the absence of NO<sub>2</sub> at low temperatures, and the NTC region can also be observed, but as the temperature is increased, above 750 K, the n-pentane consumption seems to be promoted by the presence of NO<sub>2</sub>.



**Figure 5.** Mole fraction of n-pentane obtained experimentally during its oxidation without NO<sub>x</sub> (opened symbols) and with 400 ppm of NO<sub>2</sub> (filled symbols) and stoichiometric conditions.

#### 4. How the STSM has contributed to the action's aim

In relation to the SMARTCATs COST Action (CM1404), this STSM represents a collaboration between two different Working Group, WG1: Smart energy carriers gas phase chemistry: from experiments to kinetic models, and WG2: Chemistry for control of by-products in Smart Energy Carriers conversion. Moreover, the core of the Action is to improve the understanding of combustion kinetics and by-products formation, so the work carried out during this STSM with the study of the oxidation of methane and n-pentane, two fuel components, and the knowledge of the impact of NO<sub>x</sub> addition will contribute to define the strategies for a cleaner operation mode in engines and minimize their pollutant emissions, which clearly contributes to the Action's objectives.

#### 5. Future collaboration

This research collaboration has been a good opportunity to obtain interesting advances and results concerning the effect of NO<sub>x</sub> addition on the oxidation of methane and n-pentane. Our intention is to continue and deeply analyze the inhibiting or promoting effect of NO<sub>x</sub> in the oxidation of n-pentane, not only from an experimental point of view, also with the validation of a kinetic mechanism able to describe the trends experimentally observed.

At this point I would like to thank the host institution (research group of Frédérique Battin-Leclerc) for giving me the opportunity of working with them and for all the support during my stay in Nancy.

#### 6. Foreseen publications/articles resulting from the STSM

The main results obtained from the study of the impact of NO<sub>x</sub> addition on methane oxidation have been submitted to be considered in the 37<sup>th</sup> International Symposium on Combustion, which will be held in Dublin, Ireland next year.

## **7. Acknowledgements**

The authors acknowledge COST Action CM1404 (EU) for financial support. Ms. Marrodán acknowledges Aragon Government for the predoctoral grant awarded.

## **8. References**

- [1] C. Bahrini, O. Herbinet, P.-A. Glaude, C. Schoemaeker, C. Fittschen, F. Battin-Leclerc, *Chem. Phys. Lett.*, 534 (2012) 1-7.
- [2] CHEMKIN-PRO 15151, Reaction Design, San Diego, (2013).