



Project no.016937

Project acronym: BURNERCAT

Project title

Instrument: specific research project for SME / cooperative research

Thematic Priority: CRAFT

## **Final activity report**

Period covered: from 02/11/2005 to 31/01/2008

Date of preparation: 15/04/08

Start date of project: 02/11/2005

Duration: 27 months

Project coordinator name: Jean-Marc PIASCO

Project coordinator organisation name: Gaz de France

Revision [1]

## 1. PUBLISHABLE EXECUTIVE SUMMARY

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### 1.1. Contractors involved

|                       |  |
|-----------------------|--|
| <b>SMEs</b>           | SUNKISS,<br>SCHWANK,<br>NORTA,<br>TECNES,  |
| <b>RTD performers</b> | Politecnico di Torino (POLITO),<br>Laboratoire d'Application de la Catalyse à l'Environnement (LACE),<br>Gaz de France SA (GDF), |
| <b>End-user</b>       | Merloni TermoSanitari (MTS)  |

Co-ordinator: Gaz de France SA  
Contact: JM PIASCO

### 1.2. Project objectives

Due to the growing concern of the European Union regarding NO<sub>x</sub> emissions, greenhouse gas emissions (CO<sub>2</sub>, ...) and energy savings, household appliance manufacturers must develop technologies able to comply with existing and forthcoming regulations that will be more and more stringent. For domestic boilers, the burner is the critical component for such progress. However, optimization of the design of traditional burners has reached its limits in this field and induces technology suppliers of the sector to embark on the catalytic combustion track.

The BURNERCAT project aims to provide the SME partners of the consortium a cost-effective solution to manufacture efficient and reliable catalytic burners. A successful implementation of this innovative technology requires the necessary R&D investments. The main deliverable of the BURNERCAT project will be a catalytic burner for a domestic boiler application (average heat input 10 kW) with the following specifications:

- ultra-low NO<sub>x</sub> emissions ( < 20 mg / kWh),
- cost-effectiveness through optimized use of noble metals,
- fuel-flexibility (methane, LPG),
- high modulation properties leading to savings in terms of gas consumption and CO emissions through operating abilities in the lowest heating powers (below 3 kW).

### 1.3. Work performed

The technical specifications have been defined by the end-user, the boiler manufacturer Merloni TermoSanitari. The burner manufacturers, SUNKISS, SCHWANK and TECNES, have taken into account that specifications in their burner design and catalysts specifications. Two different technologies of supports of burners (ceramics and metallic) are taken in consideration in order to define the lowest cost system.

The technical objectives of the project will be achieved through innovative development on:

- the combustion support,
- the catalyst,
- the deposition methods.

Concerning the catalysts development, during the first year, the LACE has identified the best catalytic supports among various supports and determined the best nominal compositions of noble metals Pd, Pt and bimetallic Pd-Pt catalysts.

Moreover, various supports, both metallic and ceramic, were characterized as combustion supports by POLITO. The main goal of the characterization of new materials is to find some valid economic alternatives to the ACOTECH metallic supports used as reference.

As concerns the metallic fibres, they present very similar compositions, but different morphological structure; quality is not constant with the various batches provided. Identified supports seem a valid alternative to ACOTECH. NORTA strips are not suitable for this kind of application.

Then, LACE worked on the preparation of a second generation of Pd-Pt based catalyst by optimising parameters as the calcinations temperature and metal precursors. The most performing catalyst found was the one prepared with nitrates precursors of palladium and platinum calcined at an optimal temperature of 500°C. Thus, the catalyst used for deposition on supports is **Pd<sub>0,7</sub>-Pt<sub>0,3</sub>/Si-Al<sub>2</sub>O<sub>3</sub>**.

After LACE study, POLITO tried to prepare the optimised catalyst according to their preparation method: Solution Combustion Synthesis Technique (SC-ST). Both catalysts were, then characterised by POLITO and it was observed that they presented the same structure and catalytic activity.

After characterisation of the several supports, only four were considered as the promising ones:

- WORGAS fibre
- NEXTEL Fibre
- SCHWANK new generation
- SCHWANK ceramic
- BISCOTTO (could not be applied on the boiler test rig of GDF).

Catalyst deposition technique developed by POLITO based on a spray pyrolysis method was applied over the supports.

Each support was tested in order to determine the operating range as a function of the Blue Angel label and only three have been chosen for the catalytic tests:

- WORGAS fibre
- NEXTEL Fibre
- SCHWANK new generation

According to POLITO and GDF evaluation of catalytic performance of fresh and aged catalysed supports, SCHWANK tiles were chosen as the most appropriate. With SCHWANK catalytic tiles we reach 16 mg/kWh at 20kW and 10 mg/kWh at 10 kW.

SUNKISS was then responsible for the fabrication of a new burner prototype reaching the major requirements of all MTS partners. Then, burner modelling and its validation was performed by POLITO.

According to the cost-effectiveness evaluation performed by POLITO and SCHWANK, the cost of the burner is  $7,7 + 8 = 15,7\text{€}$  (catalysed tiles + burner casing), which is superior to the fixed price proposed in the beginning of the project. However, according SCHWANK, this price total can be enhanced by the optimisation of the deposition technique (recycle of the spray).

At last, it is presented the work published and presented in several meeting by the several partners of this project. It was also possible to submit some papers in congress and the publication of work in scientific magazines.

## 2. SECTION 1: PROJECT OBJECTIVES AND MAJOR ACHIEVEMENTS DURING THE REPORTING PERIOD

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### 2.1. General project objectives

#### 2.1.1. Objectives of the project

The objective of the project is two-folded:

- to obtain two different burners answering basically to the end-user specifications. The first burner will be ceramic supported, the second one metallic supported (each support has a different washcoating procedure),
- to assess, the cost-effectiveness of each burner. The consortium will analyze the cost-effectiveness regarding the environmental performances (pollutant emissions). If the most expensive solution is the less effective pollutant reduction one, this solution will be given up and the research effort will be put on the most effective solution.

During the second year, the research effort will be on prototype(s) improvements concerning:

- integration in the boiler,
- cost effectiveness of the burner,
- decrease of NOx emissions,

### 2.1.2. Work performed during the project

The technical specifications have been defined by the end-user, the boiler manufacturer Merloni TermoSanitari. The burner manufacturers, SUNKISS, SCHWANK and TECNES, have taken into account that specifications in their burner design and catalysts specifications. Two different technologies of supports of burners (ceramics and metallic) are taken in consideration in order to define the lowest cost system.

On the three points, innovative development have been performed:

- The combustion support,
- The catalyst,
- The deposition methods.

Concerning the catalysts development, during the first year, the LACE has identified the best catalytic supports among various supports and determined the best nominal compositions of noble metals Pd, Pt and bimetallic Pd-Pt catalysts. The main conclusions are the followings:

1. The best palladium precursor is  $\text{Pd}(\text{NO}_3)_2$ ,
2. For the palladium supported catalysts, the best supports are commercial  $\text{Al}_2\text{O}_3$  and Si stabilized  $\text{Al}_2\text{O}_3$  ( $\text{Si-Al}_2\text{O}_3$ ),
3. The best Pd loading on  $\text{Si-Al}_2\text{O}_3$  is comprised between 2wt.% and 3wt.%,
4. For the bimetallic Pd-Pt catalysts supported on  $\text{Al}_2\text{O}_3$  or  $\text{Si-Al}_2\text{O}_3$ , the best synthesis method is the successive impregnation one,
5. At last, the physical and chemical characterizations performed on fresh monometallic catalyst ( $\text{Pd/Si-Al}_2\text{O}_3$ ) synthesized by two different methods used by LACE and POLITO showed similar results.

Moreover, various combustion supports, both metallic and ceramic, were characterized as combustion supports by POLITO. The main goal of the characterization of new materials is to find some valid economic alternatives to the ACOTECH metallic supports used as reference.

The different tested supports are:

- Metallic fibres from ACOTECH,
- Metallic fibres from FIBERTECH (2 different versions),
- Metallic fibres from WORGAS,
- Metallic stripes from partner NORTA,
- Ceramic tiles from partner SCHWANK (2 different versions),
- Ceramic fibres from 3M NEXTEL.

As concerns the metallic fibres (ACOTECH, FIBERTECH, WORGAS), they present very similar compositions, but different morphological structure; FIBERTECH quality is not constant with the various batches provided. **WORGAS supports seem a valid alternative to ACOTECH.** NORTA strips are not suitable for this kind of application.

As concerns **the ceramic supports** (SCHWANK and 3M NEXTEL), they are very different but both **very interesting for the combustion of methane.**

Before the ageing procedure, the fresh combustion support tests are still in progress at Gaz de France. The Acotech metallic fibre has been tested. For the new supports, the first one tested was the Schwank ceramic tile and problem concerning the distribution grill has been solved.

For POLITO, the MERLONI boiler test rig was assessed in order to obtain a boiler suitable to the characteristics requested by the BURNERCAT project.

**Remark:** NORTA has worked on the deposition methods. Today, this point is unsuccessfully and further work is needed to study the feasibility of thermal plasma spray catalytic coating on ceramic support (see §3362)

During the second and last period of activity, LACE laboratory proceeded with their activities concerning the preparation of the 2<sup>nd</sup> generation catalysts. The goal of this work is to optimise the preparation procedure in order to obtain the best efficient catalyst. Parameters as calcination temperature and the effect of the metal precursor were optimised. At last it was studied the effect of the ageing process on the catalytic performance. Thus, according to the obtained results, it was possible to verify that the best

catalyst found was the catalyst prepared with nitrate precursors of Pd and Pt and that the optimal calcinations temperature is 500°C. Comparing both catalysts prepared using exactly the same procedure (Pd-Pt/Al<sub>2</sub>O<sub>3</sub> and Pd-Pt/Si-Al<sub>2</sub>O<sub>3</sub>), the Pd/Pt impregnated on alumina stabilised with Si catalyst shows superior catalytic performance.

Ageing process was also applied in order to study the catalyst stability and it was found almost the same results for both mentioned catalyst: no activity decrease was verified at low temperatures and PdO-Pd transition is almost cancelled.

After LACE study, POLITO tried to prepare the optimised catalyst according to their preparation method: Solution Combustion Synthesis Technique (SC-ST). Both catalysts were, then characterised by POLITO and it was observed that they presented the same structure and catalytic activity.

Before catalyst deposition, the different supports (metallic and ceramic) were characterised by POLITO.

- Metallic fibres from ACOTECH,
- Metallic fibres from FIBERTECH (2 different versions),
- Metallic fibres from WORGAS,
- Metallic stripes from partner NORTA,
- Ceramic tiles from partner SCHWANK (2 different versions),
- Ceramic fibres from 3M NEXTEL.

The catalyst deposition was essentially performed by POLITO. Finally, it was decided that only four supports were considered as the promising ones, in order to proceed with the manufacturing of catalysed burners prototype to be tested by GDF and also POLITO:

- WORGAS fibre
- NEXTEL Fibre
- SCHWANK new generation
- SCHWANK ceramic
- BISCOTTO (could not be applied on the boiler test rig of GDF).

According to the activities developed by GDF, concerning the WP4, besides the four supports mentioned above, it was also tested the ACOTHEC NIT 100 metallic as reference support. Each support was tested in order to determine the operating range as a function of the Blue Angel label. Thus, according to the obtained results, only three supports have been chosen for the catalytic tests:

- WORGAS fibre
- NEXTEL Fibre
- SCHWANK new generation

POLITO and GDF proceeded with their study in order to determine the catalytic performance of the catalysed burners. GDF continued in the same kind of tests while that POLITO proceeded to burners evaluation on a commercial MERLONI burner which was possible to quantify the CO and NO emissions as a function of air excess introduced and power output.

According to GDF results, WORGAS can reach lowers air ratios than the no-catalysed one, while that NEXTEL fibres present better results than the respective catalysed support; however, with SCHWANK new generation, the catalysed support is better especially for small thermal power. In what concerns POLITO results obtained by testing supports and catalysed supports on a commercial MERLONI burner, even if no major differences between catalytic and non-catalytic burners were verified, catalytic **SCHWANK** tiles and catalytic BISCOTTO were found as the most interesting burners tested. With SCHWANK catalytic tiles we reach 16 mg/kWh at 20kW and 10 mg/kWh at 10 kW instead of 51 and 32 mg/kWh, respectively, obtained with the commercial burner.

Then, the catalysed supports were submitted to an ageing process, in order to study their stability in function of time of working. After ageing, these catalysts were characterised leading to the conclusion that among the three studied substrates (SCHWANK new generation, NEXTEL fibre and WORGAS fibre), only WORGAS catalysed substrate (working in a mixed radiant/blue flame mode-phase1) stability is constant in function of time; working in radiant mode it was found SCHWANK substrates behaviour keeps stable and NEXTEL and WORGAS substrates presented a decrease of NOx emissions in function of time.

In what concerns the WP5, SUNKISS was responsible for the fabrication of a new burner prototype reaching the major requirements of all MTS partners. Then, burner modelling and its validation were performed by POLITO.

According to the cost-effectiveness WP6, the catalyst preparation is quite expensive due to the presence of precursors of palladium and platinum. The SCHWANK tile costs 1,80 €/tile. Considering the catalyst preparation and the tiles (including catalyst deposition) costs, the final price of the burner is about 15,7€ which is superior to the fixed price proposed in the beginning of the project. However, according SCHWANK, this price total can be improved by a deposition technique optimisation (recycle of the spray). At last, it is presented the work published and presented in several meeting by the several partners of this project.

Finally, due to the activities developed during this project it was possible to submit some papers in congress and the publication of work in scientific magazines (more details in D20).

### 3. SECTION 2: WORKPACKAGE PROGRESS

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In order to reach the technical objectives that have been defined, the workprogramme has been divided into 7 main tasks.

#### 3.1. WP 1: Technical specifications (*WP leader: MTS*)

The burner technical specifications have been defined by the end-user Merloni TermoSanitari boiler manufacturer. The others manufacturers as SUNKISS, SCHWANK and TECNES, have taken in account these specifications in their burner design and catalysts specifications. Two types of burners were taking in consideration: the metallic and ceramic one.

Thus, as defined in WP1, MTS defined the burners specifications:

1. **Burner drawing and dimension:** burner should be placed in a domestic boiler (ARISTON ACO-27). The maximum heat input power is 27 kW and the surface of the boiler is about 100mm x 190mm;
2. **Definition of the turn-down ratio of the burner in a specific boiler application and of the nominal heat input condition:** in order to produce DHW (domestic hot water) and CH (central heating), the ratio between the minimum heat input power and the maximum heat input power is 1 to 5 (the minimum heat input power is about 5,5 kW for a maximum heat input power of 27 kW);
3. **CE approval test:** tests will be accorded with standards UNI-EN 483:2002 and UNI-EN 677:2000 needed for the qualification of the burner;
4. **Burner target cost:** the ceramic burner cost is about 10 €.

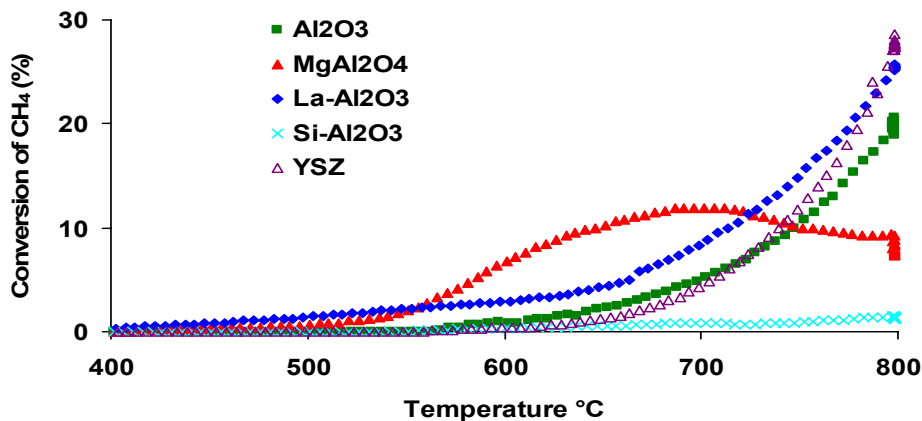
#### 3.2. WP 2: Catalysts development (*WP leader: LACE*)

In what concerns the catalyst development, LACE laboratory was the leader of **WP2**, which main objective is to find the best catalyst based on a selected Pd+Pt combination deposited on a thermally stabilised support via a selected method. Finally, the best catalyst studied by LACE Laboratory will be scale-up by POLITO for washcoated on either ceramic foam or on metallic gauze and tested in real conditions by the other partners of the project.

##### 3.2.1. Preparation of the actives phases- *first catalyst generation*

For the preparation of the active phases of the first generation catalysts, two catalysts supports have been used: a modified alumina (for its stability increase) and an yttria stabilized zirconia.

Palladium was deposited onto the five different supports by impregnation method using a Pd(NO<sub>3</sub>)<sub>2</sub> aqueous solution as metal precursor, in order to obtain 2wt% of metal loading.



**Figure 1: Conversion of methane (%) over several supports:**  
 $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (■), MgAl<sub>2</sub>O<sub>4</sub> (▲), La-Al<sub>2</sub>O<sub>3</sub> (◆), Si-Al<sub>2</sub>O<sub>3</sub> (×) and Y<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub> (△)

Among all the tested supports, two have been chosen: Al<sub>2</sub>O<sub>3</sub> and Si-Al<sub>2</sub>O<sub>3</sub> and the metal precursors were Pd(NO<sub>3</sub>)<sub>2</sub> and Pt(NH<sub>3</sub>)<sub>4</sub>(NO<sub>3</sub>)<sub>2</sub>.

These **bimetallic catalysts** have been synthesized following two different methods: a co-impregnation method and a successive one. These catalysts were characterized by X-Ray diffraction and by BET technique for specific areas measurements. After preparation and characterization of the catalysts, they were tested under the following conditions:

- The reaction temperature increases from 250°C to 800°C at 1°C/min,
- A plateau at 800°C was maintained for 1h,
- A cooling down to 250°C at 1°C/min was experienced,
- A second reaction temperature increase from 250°C to 800°C at 1°C/min identical to the first one.

According to these tests, it was possible to conclude that:

1. The best palladium precursor is Pd(NO<sub>3</sub>)<sub>2</sub>,
2. For the palladium supported catalysts, the best supports are commercial Al<sub>2</sub>O<sub>3</sub> and Si stabilized Al<sub>2</sub>O<sub>3</sub> (Si-Al<sub>2</sub>O<sub>3</sub>),
3. The best Pd loading on Si-Al<sub>2</sub>O<sub>3</sub> is comprised between 2wt.% and 3wt.%,
4. For the bimetallic Pd-Pt catalysts supported on Al<sub>2</sub>O<sub>3</sub> or Si-Al<sub>2</sub>O<sub>3</sub>, the best synthesis method is the successive impregnation one.

### 3.2.2. Preparation and optimisation of the second generation catalyst

The work performed during the second year was exclusively dedicated to the second-generation catalysts of Pt and Pt deposited on Al<sub>2</sub>O<sub>3</sub> and Si-stabilised Al<sub>2</sub>O<sub>3</sub> only.

The effect of platinum on palladium properties has been previously observed for Pd<sub>0.7</sub>Pt<sub>0.3</sub>/Al<sub>2</sub>O<sub>3</sub> and Pd<sub>0.7</sub>Pt<sub>0.3</sub>/Si-Al<sub>2</sub>O<sub>3</sub> and it was assumed to be due to a specific synergy between both metals. In order to enhance this kind of interaction a new catalyst stabilization procedure, calcinations process was performed at two different temperatures (500°C and 800°C). For this propose, 3 catalysts were prepared:

1. 2wt% Pd<sub>0.7</sub>Pt<sub>0.3</sub>/Si-Al<sub>2</sub>O<sub>3</sub> catalyst has been prepared from Pd(NO<sub>3</sub>)<sub>2</sub> and Pt(NO<sub>3</sub>)<sub>2</sub> impregnated on Si-Al<sub>2</sub>O<sub>3</sub> and calcined at 500°C;
2. 2wt% Pd<sub>0.7</sub>Pt<sub>0.3</sub>/Si-Al<sub>2</sub>O<sub>3</sub> prepared from Pd(NO<sub>3</sub>)<sub>2</sub> and Pt(NH<sub>3</sub>)<sub>4</sub>(NO<sub>3</sub>)<sub>2</sub> impregnated on Si-Al<sub>2</sub>O<sub>3</sub> and calcined at 800°C;
3. Pd<sub>0.7</sub>Pt<sub>0.3</sub>/Al<sub>2</sub>O<sub>3</sub> using the same procedure (Pd(NO<sub>3</sub>)<sub>2</sub> and Pt(NO<sub>3</sub>)<sub>2</sub> impregnated on Al<sub>2</sub>O<sub>3</sub>).

At last, it was performed the ageing tests, in order to evaluate its catalytic behaviour at high temperature levels ( $T=900^{\circ}\text{C}$ ,  $1000^{\circ}\text{C}$  and compared with  $800^{\circ}\text{C}$ ). These tests showed that  $2\text{wt.}\% \text{Pd}_{0.7}\text{Pt}_{0.3}/\text{Si-Al}_2\text{O}_3$  and  $2\text{wt.}\% \text{Pd}_{0.7}\text{Pt}_{0.3}/\text{Al}_2\text{O}_3$  catalysts (prepared with nitrate precursors and calcined at  $500^{\circ}\text{C}$ ) present the same behaviour: no limited loss of catalytic activity at low temperature, neither PdO-Pd transitions are observed.

POLITO laboratory after receiving the catalyst formulation from LACE was reviewed in order to further deposition over metallic and ceramic supports. As preliminary step, the catalyst in powder was synthesized by POLITO by using the same precursors proposed by LACE but using a different technique, the Solution Combustion Synthesis (SCS), which is much more feasible on an industrial point of view.

### 3.2.3. Conclusions

The catalytic tests led to the following conclusions:

- Catalysts preparation with nitrate precursors followed by calcination at  $500^{\circ}\text{C}$  lead to higher active catalysts.
- $2\text{wt.}\% \text{Pd}_{0.7}\text{Pt}_{0.3}/\text{Si-Al}_2\text{O}_3$  leads to superior catalytic performance than  $2\text{wt.}\% \text{Pd}_{0.7}\text{Pt}_{0.3}/\text{Al}_2\text{O}_3$  catalysts prepared from the procedure described above.
- According to the physical and chemical characterization demonstrated that the two catalytic powders obtained (obtained from first and second generation) by the two different techniques are exactly the same.

## 3.3. WP 3: Catalysts deposition methods (*WP leader: POLITO*)

### 3.3.1. Characterisation of the supports

According to the proposed activities by **WP3**, POLITO (as WP leader) started for **characterised by SEM/EDS**, 6 commercial supports:

- Metallic fibres from ACOTECH (used as reference support),
- Metallic fibres from FIBERTECH (2 different versions provided by partner TECNES),
- Metallic fibres from WORGAS (provided by partner TECNES),
- Metallic stripes from partner NORTA,
- Ceramic tiles from partner SCHWANK,
- Ceramic fibres from 3M (provided by partner TECNES).

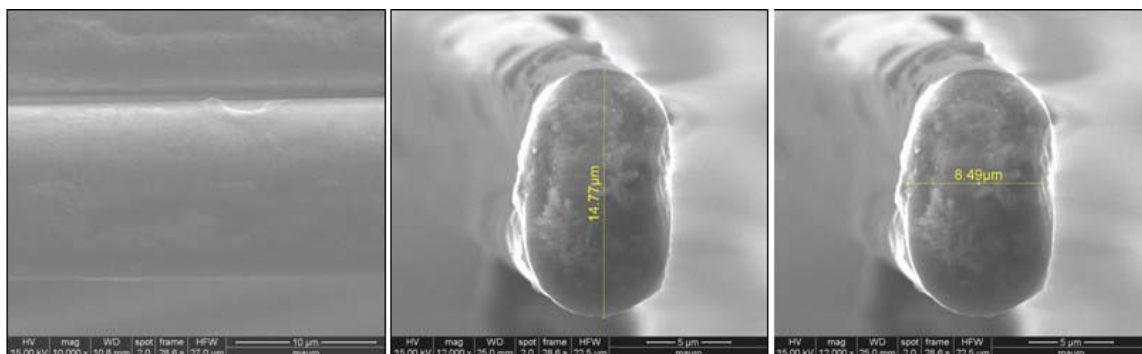


Figure 2: SEM micrographs of 3M NEXTEL ceramic support

From this characterisation, it was possible to verify that the metallic fibres (ACOTECH, FIBERTECH, WORGAS), present very similar compositions, but different morphological structure; FIBERTECH quality is not constant with the various batches provided. WORGAS supports seem a valid alternative to ACOTECH. NORTA strips are not suitable for this kind of application.

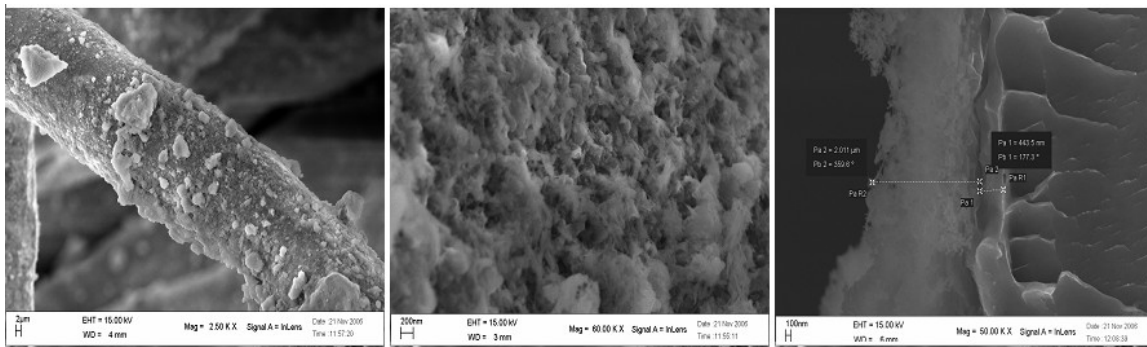
Ceramic supports (SCHWANK and 3M), they are very different but both very interesting for the combustion of methane.

### 3.3.2. Catalytic deposition method

Then, it was studied the **deposition method** over the support. Besides POLITO contribution, NORTA also applied its method of catalyst deposition on the support.

POLITO deposition method (called SCS-SP) is based on the pyrolysis of the proper catalyst precursor salts over a hot surface. The support had to be previously heated up to high temperature (400°C) and, immediately after extraction from the oven, impregnated by spraying with the catalyst precursor solution up to a catalyst load of about 2% in weight.

LACE catalyst was deposited by spray pyrolysis, on a FIBERTECH metallic support, in one shot over the fibres after the pre-oxidation treatment. SEM micrographs (Fig. 2) show a homogeneous layer covering the fibres; the thickness of the layer is approx 2 µm, absolutely comparable with the thickness of the perovskite-based catalysts.



**Figure 3: SEM micrographs of FIBERTECH new version support catalysed with LACE catalyst, included cross section.**

Based on the developed deposition methods by POLITO and the obtained results on the catalyst deposition on the various metallic and ceramic supports tested, all the partners together decided to select the following supports, as the most promising ones, to manufacture the burners prototype to be tested in WP4 by GDF and POLITO:

- Metallic fibres from WORGAS;
- Metallic tiles *BISCOTTO*;
- Ceramic fibres NEXTEL;
- Ceramic tiles SCHWANK.

POLITO prepared the final catalysed supports to be inserted in the frames, whereas TECNES assembled the two metallic burners and one ceramic (with NEXTEL support), both in the catalytic and no-catalytic versions, and SCHWANK assembled the other ceramic burner, both in the catalytic and no-catalytic version.

Beside POLITO, also NORTA and SCHWANK applied deposition methods: NORTA deposition method consists essentially on thermal spraying techniques whereas SCHWANK employs an automatic coating equipment for highly porous ceramic supports.

### 3.4. WP4: Catalysed combustion supports tests (*WP leader: Gaz de France*)

After preparation of catalysed supported, **catalytic combustion tests were performed over the catalysed and no-catalysed supports** in order to evaluate their performance and sulphur resistance. These were the objectives of **WP4** led by GDF.

### 3.4.1. Characterisation of supports

Firstly, GDF responsibility was to define a **protocol of characterisation and ageing procedure** for the burners supports that was after validated by all partners during the meeting at MTS (protocol defined in D7). Five **no-catalysed substrates** were characterised:

1. Metallic substrates:
  - ACOTECH NIT 100 which is used as the reference<sup>1</sup>,
  - Worgas fibre.
2. Ceramic substrates:
  - NEXTEL fibre,
  - SCHWANK cordierite,
  - SCHWANK new generation.

All these substrates were characterised according to the Blue Angel label:

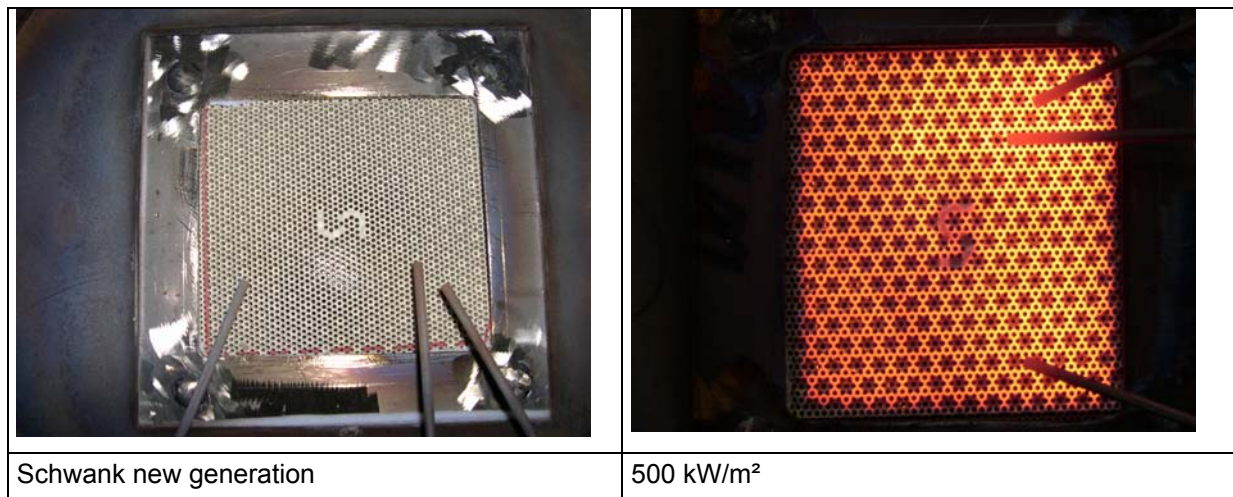
- CO < 60mg/kWh
- NOx < 70mg/kWh

This method allows the determination the operating range (input heat value and air ratio) that respects the Blue angel label. For all the tested substrates:

- at low air excess, the air ratio minimal value is given by the NOx level, *i.e.* below this value, NOx value is above the Blue Angel value,
- at high air excess, the air ratio maximal value is given by the CO level, *i.e.* above this value, CO value is above the Blue Angel value.

Thus, according to the obtained results, only three substrates have been chosen for the catalytic tests:

- WORGAS fibre (metallic substrate)
- NEXTEL fibre (ceramic substrate)
- SCHWANK new generation (ceramic substrate)



**Figure 4: SCHWANK new generation (ceramic tile)**

These substrates were catalysed by POLITO (D4) with the catalyst developed by LACE (D2). The chosen catalyst was 2% Pt<sub>0,3</sub>Pd<sub>0,7</sub>Si-Al<sub>2</sub>O<sub>3</sub>.

<sup>1</sup> This substrate presents very interesting performances but, because of its high cost, is not used in the project

### 3.4.2. Characterisation of catalysed supports

The **catalytic supports were also characterised** following the same protocol and then compared with the no-catalysed supports performance.

The main conclusions reached were:

- For the Worgas fibre, the catalysed substrate reaches lower air ratio i.e. 1,3 instead of 1.35 with the non-catalysed one. In high air ratio for the catalysed substrate reaches 1.5 and about 1.75 for the non-catalysed one.
- For the NEXTEL fibre, the non-catalysed substrate is better than the catalysed substrate for all the value of the air ratio.
- For the SCHWANK NewGeneration, the catalysed substrate is better than the non-catalysed substrate especially for the small thermal power (under 500 kW/m<sup>2</sup>). Air ratio reaches more than 1.8 for the catalysed substrate instead of 1.7 for the non-catalysed one.

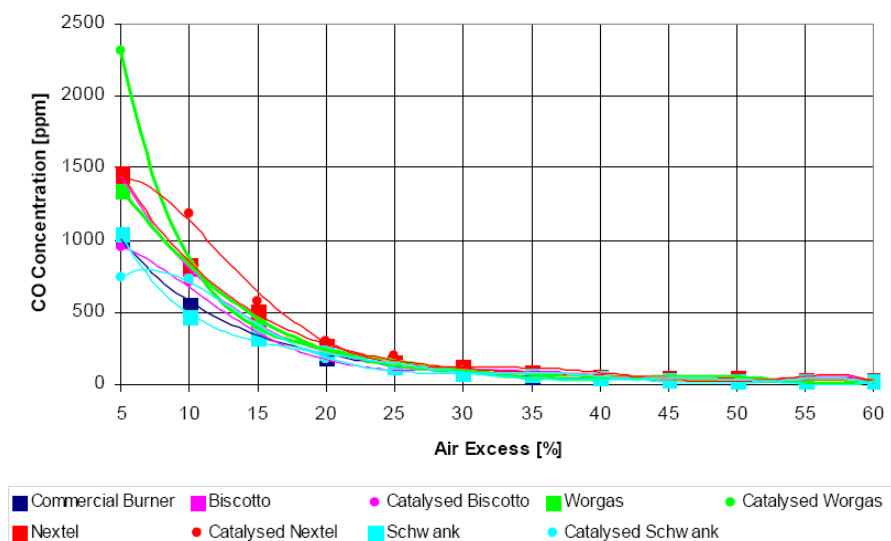
Also **POLITO** performed some tests with no-catalysed and catalysed metallic and ceramic supports (diameter 10 cm) to compare their performance respect to ACOTECH fibre mats, evaluated in previous EU projects.

These burner supports evaluation was performed on an ad-hoc domestic boiler test rig (max power ~ 50 kW) provided by GIANNONI FRANCE in previous EU projects.

In the second year the same kind of tests were developed on a new boiler test rig that was provided by partner MERLONI TERMOSANITARI in order to better assess a boiler suitable to the characteristics requested by the BURNERCAT project. The boiler, ACO 27 MFFI, was settled-up with all the necessary accessories in order to carry on safe combustion tests. The boiler hosts a rectangular shape burner deck with dimensions of approx 19x10 cm<sup>2</sup>.

Comparing all the tested burners shows that:

- Catalytic SCHWANK tiles and catalytic BISCOTTO are the most interesting burners tested, with emissions lower than the commercial MERLONI burner, **especially related to the NO emission.**
- The difference between catalytic and no-catalytic SCHWANK tiles is very subtle (non-catalytic SCHWANK better than commercial burner), whereas the difference between catalytic and non-catalytic BISCOTTO is much more consistent (non catalytic BISCOTTO worse than commercial (burner)).
- The heat exchange efficiency improved by the presence of the catalyst is practically evident on all burners.



**Figure 5: Comparison of CO emission among all burners at low and high air excess at 20 kW**

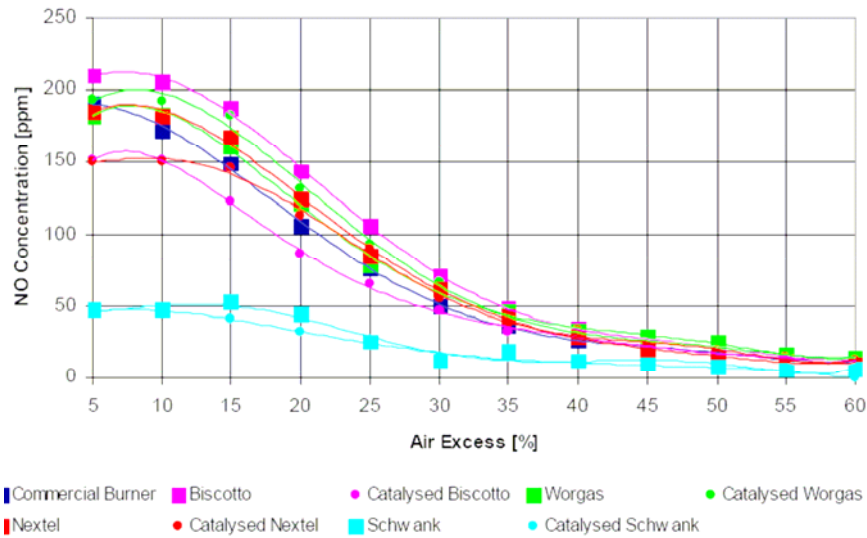


Figure 6: Comparison of NO emission among all burners at 20kW

Table 1: NOx emissions of commercial and SCHWANK catalysed burners

| Power output (kW)        |        | 10   |     | 20   |     |
|--------------------------|--------|------|-----|------|-----|
| Air excess               |        | 1,05 | 1,2 | 1,05 | 1,2 |
| Commercial burner        | ppm    | 90   | 70  | 180  | 110 |
|                          | mg/kWh | 47   | 32  | 94   | 51  |
| Catalysed SCHWANK burner | ppm    | 30   | 20  | 50   | 30  |
|                          | mg/kWh | 16   | 10  | 26   | 16  |

### 3.4.3. Ageing tests

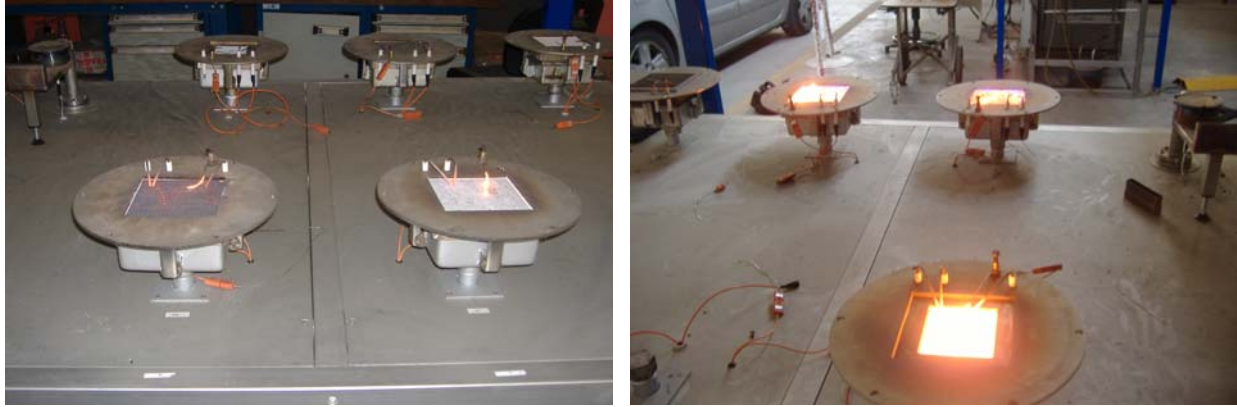
After studying the effect of fresh catalyst deposition over the supports in the methane oxidation reaction (following the blue angel parameters), **ageing procedures** will be applied to these catalysts in order to study the catalysed supports stability (D10).

The endurance cycle is based on the tests carried out during the preceding European projects (in particular Himocat and Lifeburn), which give scenarios of ageing of boilers taking into account the various operating modes (heating and Domestic Hot Water - DHW).

The estimated daily consumption in heating mode is 45 kWh and the time of cumulated drawing up is 60 minutes. The heating mode is carried out with a power of 10 kW and the DHW mode with the maximum power *i.e.* 27 kW.

The surface of the boiler burner is equal to  $S = 0,19 \times 0,1 = 0,019m^2$ , leading to an input heat value of 526 kW/m<sup>2</sup> for 10 kW and 1421 kW/m<sup>2</sup> for 27 kW.

At 526 kW/m<sup>2</sup>, the burner is supposed to be in radiant mode; at 1421 kW/m<sup>2</sup>, it is in blue flame mode. To consume 45 kWh of daily heating, it is necessary that the burner works 4,5 hours per day in radiant mode. More details about the ageing process can be found in D10.



Endurance bench "off"

Endurance bench "on"

**Figure 7: Bench of endurance**

The **NO<sub>x</sub>** and **CO** measurement is periodically done (once a week) in order to evaluate the catalyst deactivation during the ageing process.

This measurement is carried out by the means of a sample bell put above the substrate connected to the analysers (Chemiluminescence's and IR analysers, respectively for NO<sub>x</sub> and CO).

After the 3-month ageing period, corresponding to 12 months of use, the substrates have to be once again characterized on the tube hearth in order to evaluate their modifications.

These tests have been carried out with natural gas and, once again, the studied substrates were: SCHWANK new generation, NEXTEL fibre and WORGAS fibre

The test was divided in two phases:

- Phase 1: thermal surface power: 596 kW/m<sup>2</sup>, air ratio n = 1,2
- Phase 2: thermal surface power: 600 kW/m<sup>2</sup>, air ratio n = 1,1

Phase 1 lasts an equivalent functioning of about 6 months for Worgas and NEXTEL fibres and 4 months for SCHWANK's tile.

But, only the SCHWANK's tile worked in radiant mode, the two others worked in mixed radiant/ blue flame for WORGAS fibre and in blue flame for NEXTEL fibre.

The results showed that there was a small evolution in NO<sub>x</sub> emissions for SCHWANK and NEXTEL substrates; for WORGAS substrate NO<sub>x</sub> emission kept stable. CO emission was not detected.

Then, the regulation of the burners was changed in order to obtain radiant mode. This phase 2 lasts an equivalent functioning of about 8 months for WORGAS fibre and SCHWANK's tile and 4 months for NEXTEL fibre (trouble with the flame detection). The results showed that there is no evolution in NO<sub>x</sub> emissions for SCHWANK substrate and a little decrease for NEXTEL and WORGAS substrates. Here a little of CO appears due to the fact that the air ratio is lower.

Finally, the ageing process performed on the burners corresponded to one year of continuous working. The evolution of the NO<sub>x</sub> and CO is not significant.

Next, these substrates will be characterized in order to see if their behaviour has changed. Then, the same characterisation procedure used with no-catalysed and catalysed substrates, were also used for the aged burners. From these tests was verified that the performances of the aged catalysed substrates are, on the whole, better than the performances of the catalysed substrates, except for WORGAS.

- For the WORGAS fibre, the catalysed substrate reaches lower air ratio i.e. 1,3 instead of 1.35 with the aged catalysed one. In high air ratio for the catalysed substrate reaches 1.5 and about 1.75 for the aged catalysed one.
- For the NEXTEL fibre, the aged catalysed substrate is better than the catalysed substrate especially at high air ratio (1.75 instead of 1.65).

- For the SCHWANK NewGeneration, the aged catalysed substrate is better than the catalysed substrate especially for the small thermal power (under 500 kW/m<sup>2</sup>, air ratio reaches more than 1.85 for the aged catalysed substrate instead of 1.8 for the catalysed one. From 750 kW/m<sup>2</sup> and at low air ratio, the aged catalysed support is better and reaches 1.35 instead of 1.40.

#### 3.4.4. Conclusions

Among the three studied substrates, **SCHWANK** and NEXTEL provide the best results concerning the combustion area according to the Blue Angel label.

### 3.5. WP 5: Burner design, manufacturing and industrial validation (WP leader: SUNKISS)

#### 3.5.1. Fabrication of prototypes of burner

From the results resumed above, it was then go ahead with burner design, manufacturing and industrial validation, **WP5**, which leader is SUNKISS. This workpackage task is to design of the **catalytic burner by using the catalyzed supports prototyped** in the workpackage 3. Then a modelling of the burner will be made in order to describe the behaviour of the burner at different regimes. SUNKISS was the one responsible for its fabrication. (D13). After fabrication of the burner, it was verified that it obeys the MTS requirements, in what concerns the dimensions (the prototype fits in the size of the original burner), the position of fan, etc. No excessive noise was verified aiming a possible domestic application. No problems were detected in what concerns the gas flow or the pressure drop, but it seems that the temperature is too high to be fit into the original boiler (a thermic improvement should be carried out in the next prototype).

Thus, in conclusion, the result of this first prototype seems to be conclusive. Indeed the major requirements from MTS were reached. Of course ameliorations, ideas and experiences from end-users and partners should be integrated in the second version of prototype. To be completed this burner should be integrated in the original ARISTON ACO boiler. Moreover long-term tests on bench should be done to conclude that the prototype is fine.

#### 3.5.2. Burner modelling

Then, POLITO proceed with the **burner modelling and its validation**. The objective of this part of work is to realize a mathematical model able to simulate the real system "burner" in every working condition, as a meaning of the combustion regimes into the burner. Starting from the experimental data taken during the tests, it was necessary to make a linearization of those, to remove points out of range, just to have a good approximation of the real phenomenon. In this way, a database containing two parameters, air excess and power demand, was realized. The databased, implemented into the model, allows the estimation of four parameters, the CO concentration [ppm], the NO concentration [ppm], the N<sub>2</sub>O concentration [ppm] and the CO<sub>2</sub> concentration [%], for each catalytic or non-catalytic burner. The mathematical model was coded with the Simulink® software of MATLAB®. It was then verified that using the linearized data based, the model is able to predict the emission levels of each burner, as a certain value of power output and air excess. In Deliverable D15 the results from the model are reported in terms of CO and NO emission, in comparison with the experimental data. It is possible to notice how the data evaluated by the model are practically the same obtained by the experimental campaign. Thus, the model can be considered validated.

### 3.6. WP 6 : Exploitation & Dissemination activities (WP leader : Gaz de France)

In **WP6**, which main objective is to is to perform **an economic feasibility** all along the project to make sure that the developed catalytic burner will be indeed marketable by the SME proposals.

### 3.6.1. Economic feasibility study

For the determination of the cost-effectiveness of the burner, particular attention will be paid at each stage of the project:

- the catalyst development (content of precious metal)
- the development of combustion supports
- the design & prototyping of the catalytic burners

The following table resumes the costs estimation at lab scale of the necessary catalyst to be deposited onto SCHWANK tiles, performed by LACE:

**Table 2: Costs estimation at lab scale of the necessary catalyst to be deposited on SCHWANK tiles.**

| Precursors                                       | Costs [€] | Box of | Unit price | Costs [€]            |
|--|-----------|--------|------------|----------------------|
| Al <sub>2</sub> O <sub>3</sub> oxide             | 35,9 €    | 500 g  | 0,0718 €/g | 0,718 €              |
| PdNO <sub>3</sub> solution                       | 369 €     | 50 ml  | 7,38 €/ml  | 19,68 €              |
| PtNO <sub>3</sub> solution                       | 600 €     | 25 g   | 24 €/g     | 2,56 €               |
| Si(OC <sub>2</sub> H <sub>5</sub> ) <sub>4</sub> | 20 €      | 500 ml | 0,04 €/ml  | 0,533333 €           |
| Glycine  | 30 €      | 50 g   | 0,6 €/g    | 2,2 €                |
| Ethanol  | 30,6 €    | 2,5 l  | 12,24 €/l  | 1,632 €              |
|  |           |        |            | <b>Total 27,32 €</b> |

For the burner (2 tiles) the price of the catalysts preparation is 4.1€. This price was calculated considering that for each tile it is necessary 1,5g of catalyst (for a lab scale 10g of catalyst preparation costs 27,32€).

In what concerns the cost effectiveness estimated by SCHWANK, in an industrial point of view (see D16), the cost of the support should cost environ **€ 1.80/tile**.

Thus, the final cost of the catalysed support is:

| <b>Total Costs</b>             |             |
|--------------------------------|-------------|
| Catalyst solution preparation= | 4,1€        |
| Tile and catalyst deposition = | 3.6€        |
| <b>TOTAL</b>                   | <b>7,7€</b> |

Thus, a conclusion, in the beginning of the project, the cost of the new burner should not exceed 10€. (2 € for the tiles and 8 for the casing of the burner).

In this case, we reach about 15.7€ (7.7€ for the tiles and 8 for the casing of the burner). So we can consider that today, this burner is too expensive.

Nevertheless, improvements can be reached, by using an encapsulated coating plant and recycling the spray that can induce to a significantly reduced of 2-4€ per plate.

### 3.6.2. Dissemination activities

The results of the project are not patentable.

The aim of this task is to disseminate the scientific and industrial results. Various dissemination channels will be used such as publications, articles, and participation to conferences, workshops and exhibition like:

- Meetings / congresses: Conference abstracts will help disseminate results among the scientists, and in industry (Events on Combustion and the Environment, International Congress on Catalysis, Combustion Symposium, Surface Treatment Show, ATG congress ... ).
- Technical magazines (Laser, Laser Focus World)
- Associations (S.I.T.S., Surface Treatment Inter Professional Union, in Paris)

During the project the list of the publication and articles written for the two years of project are presented below:

First year activity dissemination

**LACE**

- Poster presentation

Authors: Taralunga M.; Kaddouri A.; Garbowski E.; Gelin P.

Title : Combustion catalytique du méthane sur des catalyseurs à base de palladium : rôle du support sur la stabilité de PdO et la résistance du catalyseur aux poisons soufrés.

3rd meeting GFZ-GECat-DivCat (39th meeting of the GECat-DivCat, Groupe d'Etude en Catalyse, Division Catalyse de la Société Française de Chimie).

29 May -1 June 2007 - La Grande Motte (France)

- Oral communication

Authors: Taralunga M.; Kaddouri A.; Gelin P.; Garbowski E.

Title: Catalytic combustion of CH<sub>4</sub> over palladium based catalysts. Role of the support on PdO stability and resistance to sulphur poisoning.

8th European Congress on Catalysis (EuropaCat VIII)

26-31 August 2007, Turku (Finland)

Second year activity dissemination

**POLITO**

- Poster presentation

Third European Combustion Meeting ECM2007, Chania, Creete (Greece) 13-17/04/07:

Palmisano P., Tortone G., Specchia S., Saracco G., Specchia V., "Combustion of natural gas on premixed catalysed metal fibre burners aged and poisoned by S-compounds"

Electronic proceeding, ref. 13.7

Future programme

After the end of the project (i.e. 31/01/2008) the following publications will be done:

**POLITO/LACE**

Publication of a paper in collaboration with POLITO concerning the properties of the bimetallic Pd-Pt/Si-Al<sub>2</sub>O<sub>3</sub> catalyst (second generation catalyst).

**POLITO/TECNES**

Manuscript on behaviour of metallic catalysed BISCOTTO burner compared to its non-catalytic counterpart;

**POLITO/SCHWANK**

Manuscript on behaviour of ceramic catalysed SCHWANK burner compared to its non-catalytic counterpart.

The publications above mentioned will be submitted to the following scientific international peer-reviewed journals:

- Catalysis Today
- Industrial and Engineering Chemistry Research
- Applied Catalysis B: Environmental

**LACE**

1) One oral communication in an international congress in Seoul Korea 13-18 July 2008

on the influence of the preparation method, catalyst precursors and activation process for Pd-Pt/Al<sub>2</sub>O<sub>3</sub> catalysts used in the catalytic combustion of CH<sub>4</sub>

3) Publication of an article to be written concerning the study of Pd/La stabilised-Al<sub>2</sub>O<sub>3</sub>.

4) Publication of an article to be written concerning the comparative properties of Pd catalyst deposited on various support.

**GDF**

A poster about the activities of the project will be proposed to the IGRC in Paris in October 2008

**SUNKISS**

*Articles will be published in trade magazine.* They will include the explanation of the European project and the funding. They could be published in specialized magazine technical application like 'L'usine Nouvelle' or 'Powder Coating'.

Those articles will be writing by the SUNKISS person in charge of the Burnercat project and SUNKISS engineer.

*Meetings and congress*

The application for the burner could be extend to the industrial perspective by example in the powder coating.

By example at the SITS 2008 (an exhibition at Paris from March 31st to April 4th) SUNKISS can design a presentation to promote the Burner in different application.

Workshop, conferences and exhibitions

Different meetings with end-users and customers could be organizing by SUNKISS to promote the burner.

But the major way to develop the burner is to meet distributor of boiler (MTS but also others) for the can put burner into the new boiler generation.

### **3.7. WP 7 : Project management (WP leader : Gaz de France)**

See section 3

### 3.8. List of Deliverables

All the deliverables were sent to the EU.

| Deliverable No | Output from Work Package | Deliverable title  | Responsible | Nature | Dissemination level |
|----------------|--------------------------|--|-------------|--------|---------------------|
| D1             | WP1                      | Report on technical specifications related to catalytic burner                                 | MTS         | R      | PP                  |
| D2 a/b         | WP2                      | Reports on 1 <sup>st</sup> (D2.a) and 2 <sup>nd</sup> (D2.b) generation catalyst (formulation) | LACE        | R      | CO                  |
| D2             | WP2                      | 1 <sup>st</sup> and 2 <sup>nd</sup> generation catalyst (formulation)                          | LACE        | R      | CO                  |
| D3             | WP3                      | Report on the tested material supports   | POLITO      | R      | RE                  |
| D4             | WP3                      | Report on the developed deposition methods   | POLITO      | R      | CO                  |
| D5             | WP3                      | Prototype of catalyzed metallic support  | NORTA       | P      | CO                  |
| D6             | WP3                      | Prototype of catalyzed ceramic support   | SCHWANK     | P      | CO                  |
| D7             | WP4                      | Protocol of the characterization & ageing procedure  | GDF         | R      | PP                  |
| D8             | WP4                      | Report on the characterization of non-catalyzed combustion supports                            | GDF         | R      | CO                  |
| D9             | WP4                      | Report on the characterization of catalyzed combustion supports                                | GDF         | R      | CO                  |
| D10            | WP4                      | Report on the ageing of catalyzed combustion supports  | GDF         | R      | CO                  |
| D11            | WP4                      | Report on the characterization of aged catalyzed combustion supports                           | GDF         | R      | CO                  |
| D12            | WP4                      | Report on deeper analyze of the various aged catalytic supports                                | POLITO      | R      | CO                  |
| D13            | WP5                      | Burner prototype (1 <sup>st</sup> generation)  | SUNKISS     | P      | RE                  |
| D14            | WP5                      | Report on burner modeling  | POLITO      | R      | RE                  |
| D15            | WP5                      | Report on the burner validation  | POLITO      | R      | PU                  |
| D16            | WP6                      | Report on the cost-effectiveness of the developed burner                                       | SCHWANK     | R      | PU                  |
| D17            | WP6                      | Publication on the developed catalysts   | LACE        | R      | PU                  |
| D18            | WP6                      | Publication on the deposition methods  | POLITO      | R      | PU                  |
| D19            | WP6                      | Plan for using and disseminating knowledge (1 <sup>st</sup> version)                           | SUNKISS     | R      | CO                  |
| D20            | WP6                      | Plan for using and disseminating knowledge (definitive version)                                | SUNKISS     | R      | CO                  |

## **4. SECTION 3 – CONSORTIUM MANAGEMENT**

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### **4.1. Consortium management tasks**

#### **4.1.1. First year**

GDF finalized the drafting of the consortium agreement and carried out the payment of the first payment to the partners (40% of the total amount).

It organized the kick of meeting (18/11/05) in its buildings in Saint Denis (France), wrote and sent the minute to the EU.

GDF organized also the second meeting at MTS in Osimo (Italy) wrote and sent the minute.

The third progress meeting took place in Lyon, hosted by LACE, on the 24/11/2006.

The minute was written by the partners and sent to the EU in December.

GDF carried out a request for amendment to the Burnercat contract for LACE at the E.C. for the taking into account of the costs of the personnel of LACE.

GDF asked for a postpone for the release of the documents (management report and periodic report) until the 31/01/2007.

#### **4.1.2. Second and last period**

GDF has asked and obtain a three months extension of the project. So the project ends on 31 January 2008 instead of 31 October 2007.

The reasons were:

- some substrates weren't available before may 2007
- new catalysts to tests,
- ageing procedure

GDF organized a meeting with POLITO and NORTA in NORTA's (Kaunas, Lituany) in February 2007 to define new catalysts to test.

GDF carried out the payment of the second payment to the partners (20% of the total amount).

As the project lasted three more months, GDF organized one more formal meeting. So, three meetings were organized:

- 16/03/07 in POLITO's –Turin - Italy,
- 28/09/07 in Schwank's – Cologne - Deutschland,
- final meeting 18/01/08 in GDF's –Paris - France

GDF wrote the minutes of these three meetings and sent them to the E.U.

GDF asked for a postpone for the final reports dissemination (management report and periodic report) until the 30/04/2008.

### **4.2. Project timetable, including an update**

As the project lasts three more months, a new time table has been defined as follow.

