Recent advances in multifunctional monolithic reactors for green mobility and clean energy fuels

A.G. Konstandopoulos[1,2], Dimitrios Zarvalis[1], Suzanna Lorentzou[1] and George Karagiannakis[1]

[1] Aerosol & Particle Technology Laboratory, CERTH/CPERI, P.O. Box 361, Thermi, Thessaloniki 57001, Greece

[2] Department of Chemical Engineering, Aristotle University, P.O. Box 1517, 54006, Thessaloniki, Greece

Introduction

Nowadays, combustion generated pollution and green house gas emissions causing climate change are attracting significant research efforts since they constitute major threats to the modern society. In this paper a research approach focused on achieving ground breaking advances in the area of Green Mobility and Clean Energy Production is presented. This research approach is based on the development of multifunctional ceramic monolithic reactors able to (a) eliminate particulate and gaseous emissions from the exhaust of combustion engines (b) enable the production of Carbon-Neutral Fuels using renewable raw materials, namely solar energy, water and captured Carbon Dioxide (CO_2) from combustion processes. The overall research approach is based on material science, engineering and simulation technology that the authors have developed in the area of Diesel Emission Control Reactors, further extended and cross-fertilized in the area of Solar Thermochemical Reactors. The latter is an emerging discipline of high importance for sustainable development, as it has the potential to produce on a large scale, pure renewable Hydrogen (H_2) from the thermochemical splitting of water. In the present paper we review recent progress in those fields.

Multifunctional reactors

A “multifunctional reactor” is a reaction device in which performance is synergetically enhanced by means of integrating more than one functions. The geometric layout is frequently structured as a monolithic ceramic reactor. The multifunctionality can occur over different spatial levels e.g. at the catalyst particle, in the interphase layer or at the reactor scale. One or more catalytic functions, for example transport functions & mechanisms, may be involved. The main advantages of such structures include:

- The large surface/volume ratio which contributes to compactness and material savings
- The low pressure drop compared to alternatives
- They can be easily functionalized/coated
- They can combine more than one function (e.g. separation/reaction)

The key features of these reactors have been firstly employed in the Diesel emission control area and secondly in the area of solar thermochemical H_2 and CO production.

Diesel engine emission control

The well-known Catalyzed Diesel Particulate Filter (CDPF) is in most cases a wall-flow monolithic reactor which utilizes a number of functions (Konstandopoulos et al., 2000). Its primary goal is nanoparticle separation. The filtration function of the DPF results into the accumulation of particulate matter (PM) inside the DPF. The time-scale of this process is in the order of hours to days. The CDPF could also be used as a reactor for the oxidation of the accumulated soot particles and gaseous emissions such as CO and HCs. It could also serve for NOx reduction purposes. The above phenomena are characterized by a time-scale in the order of minutes. Finally, the operation of the CDPF results also in trapping of ash particles produced by engine oil consumption and engine wear (time-scale in the order of months to years).

Modern Diesel engine exhaust emission control systems consist of multiple components such as the CDPF, the Diesel Oxidation Catalysts (DOCs) and DeNOx devices (usually Selective Catalysts Reduction systems and/or NOx traps). For the safe and efficient operation of this assembly of components, usually complex management and control systems are required adding significant development time and manufacturing/operation cost. Recent technological

trends call for integration of as many functions as possible into a single component, thus moving from “multi-brick” to “one-brick” solutions. The integration of many catalytic functions on a single substrate typically comes with a penalty on system’s performance with respect to pressure drop and catalytic activity, the latter due to inhibition phenomena. Nevertheless, there are research and technical efforts that enable the manufacture of multifunctional reactors without the adverse results mentioned above. These efforts were based on:

- Advanced simulation activities for the optimisation of the system design
- Fast and accurate performance assessment based on side-stream reactor technologies
- Novel catalyst synthesis and coating technologies

A conceptual framework for multi-scale/multi-temporal physico-chemical phenomena in Diesel emission control is required for the optimisation of the system performance based on simulation models. Advanced mathematical models have been developed at the filter wall scale (Konstandopoulos et al., 2002), the single channel level, the device level (multi-channel coupled with CFD and heat transfer, Konstandopoulos et al., 2003) and system level (many devices accounting for engine-out conditions (Konstandopoulos et al., 2003). Advanced simulation tools enabled optimisation of system’s operation at all scales and facilitated the realization of advanced system designs exploiting heat recovery by the implementation of heat exchange between the outlet and the inlet flow paths of the filter.

A significant part of the progress on multifunctional reactors has been based on benefits derived from side-stream reactor technologies (Konstandopoulos et al., 2006) able for fast technology screening (simultaneous evaluation of many samples) and identification of the necessary for the effective modelling physicochemical parameters under representative, real-life experimental conditions.

Conventionally, the catalyst synthesis and coating techniques consist of the preparation of the catalyst powder in slurry or a solution of the precursor materials and the subsequent impregnation of the ceramic substrate in the slurry or the solution, followed by drying and firing (wet chemistry techniques). Alternative methods have been exploited using the precursor materials either in the solid phase (sintering or combustion of metal/oxides powders) or in the liquid phase using solutions of metal salts followed by either combustion of gels (Liquid Phase Self-propagating High-temperature Synthesis LPSHS) or pyrolysis of droplets (Aerosol Spray Pyrolysis, ASP). The latter is able for simultaneous catalyst synthesis and deposition on a porous substrate in one step (Karadimitra et al., 2004). The aerosol based catalyst synthesis (ABS) and coating technologies have the advantages of the precise control of the catalyst particle composition and of the quantity deposited, as well as its spatial deposition profile along the porous filter wall. With this mechanism catalyst deposition can be tuned for maximisation of the catalyst activity e.g. in the case of soot oxidation catalysts the catalyst deposition pattern can maximize the contact of the soot particles with the pre-deposited catalyst sites, during filter operation. In addition, ABS technologies can be easily combined with conventional wet-chemistry techniques for the inclusion of additional catalytic functionalities (e.g. noble metals for enhancement of gas oxidation activity).

Based on the above developments full-scale emission control prototypes (Multi-Functional Reactors, MFRs) were realized combining: filtration, internal heat recovery, soot and gas oxidation functions (Figure 1). Due to the internal heat recovery capability, the developed MFR demonstrated faster thermal response and more even in-filter temperature distributions during regeneration conditions compared to a standard filter designs. The employed catalyst synthesis and application technology consisting of a combination of aerosol based and wet chemistry techniques enabled the increase in the soot oxidation activity and filtration efficiency with respect to a reference state-of-the-art catalysed filter (SA DPF) without any adverse effects on the filter pressure drop. Moreover, the MFR demonstrated significant HC/CO oxidation activity while minimizing the NO_2 emissions. Aging procedures applied on MFR prototypes did not result in losses in their catalytic activity and filtration efficiency. When compared to the SA DPF, the MFR indicated that significant economy can be achieved with respect to the fuel consumption related to filter operation (up to 45.2 % during NEDC driving conditions, Zarvalis et al., 2011, Figure 1). This gain comes from the fact that the developed catalyzed filter can be sufficiently regenerated at lower temperatures (e.g. 550 ^{o}C) than the SA DPF. Besides the fuel consumption gain, it is anticipated that additional advantages maybe realized such as less engine wear due to in cylinder oil-dilution during fuel post injection as well as enabling filter regeneration at lower engine load conditions.

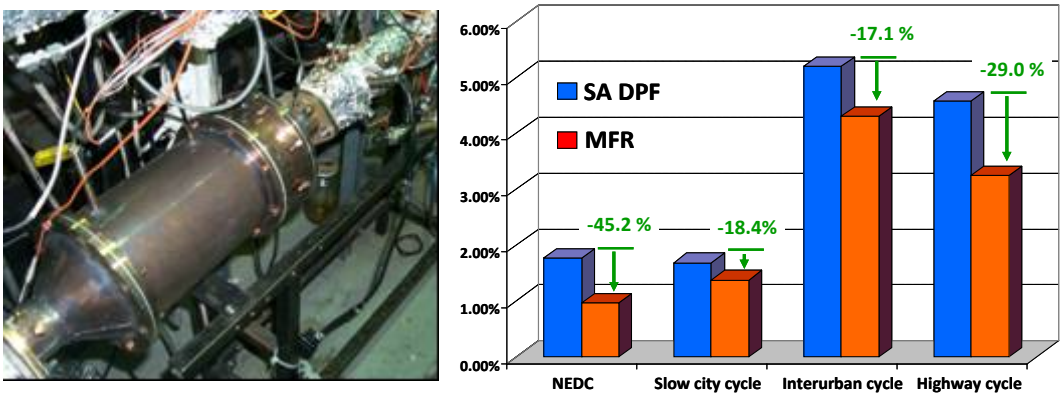

Figure 1.Left: the MFR prototype installed on engine bench. Right: Comparison of fuel penalty associated with the operation of the developed MFR and a state-of-the-art catalyzed DPF under different driving conditions.

In Figure 2, more details for the regeneration events during the NEDC and the Highway driving cycle are presented indicatively.

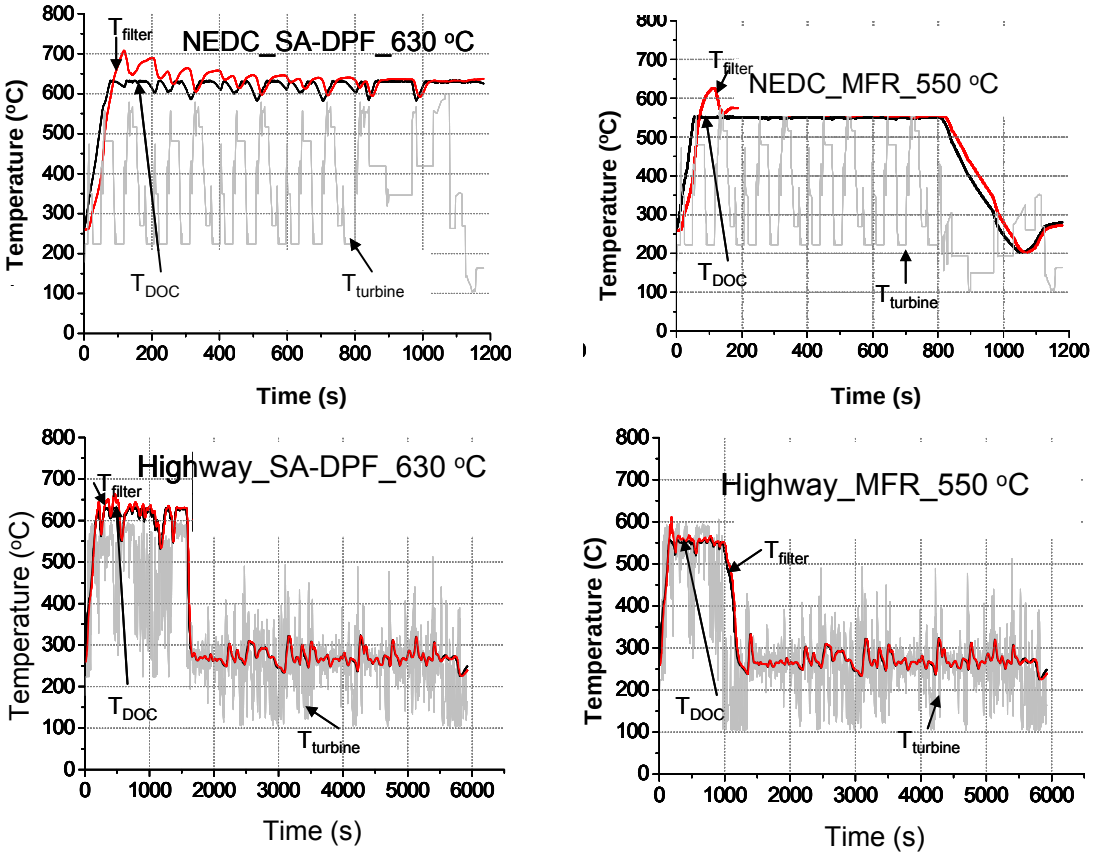

Figure 2. Regenration events during NEDC (top) and Highway cycle (down) conditions for the SA DPF (left) and the MFR (right).

The regeneration temperature was set at 630 °C and the regeneration soot mass limit was set to 7 g/L for the SA DPF. On the contrary, for the MFR the same targets were set to 550 °C and 5 g/L respectively to avoid any possible excessive exotherms due to the advanced catalyst and the heat recovery function. During the NEDC, the MFR regeneration temperature remains above or equal to the target temperature during the entire regeneration event. This is not the case for the SA DPF, where in many parts of the cycle the filter temperature does not reach the target. The regeneration takes only 800 s in the MFR case while an entire cycle (1200 s) is

needed in the SA DPF case. Remarkably, in the MFR case the temperature after turbine is higher than the target (550 ^{o}C) in a large part of the cycle during highway conditions. This means that no extra fuel is needed for the regeneration of the MFR. On the contrary the target temperature for regeneration is not reached for a significant part of the highway cycle for the SA DPF. While MFR needs only ~ 1000 s for regeneration, the SA DPF needs ~ 1600 s for regeneration. These outcomes, despite the lower safety limits set for the MFR, translate in significant fuel economies: 45.2 and 29.0 % decrease for NEDC and Highway cycle conditions respectively. It is important to notice that during highway conditions the MFR operation brings a ~ 1.3 % decrease in the total vehicle consumption.

Clean energy fuels

It is over a decade now that the reduction of CO_2 emissions became as much (if not more) important as the reduction of "traditional" pollutants like PM, CO, HCs and NOx. In response to the need for lower CO_2 emissions from Internal Combustion Engine (ICE) powered vehicles, two technological pathways are possible: to increase the vehicle efficiency (lower fuel consumption) or lower the carbon content of the fuel. Biofuels offer an option for low carbon fuels production but impose several problems, with the most important one being the competition to food production. Solar hydrogen from water thermochemical splitting is itself a totally renewable fuel and if combined with CO can produce clean energy fuels. Nevertheless, very high temperatures are required to directly dissociate water into hydrogen and oxygen. Because of thermodynamic restrictions, sufficient yields in the direct thermal splitting of water can only be achieved at temperatures above 2000 ^{o}C. Temperatures that high impose extraordinary demands on materials and reactor design and cannot be considered practical for real-life applications. In the past, numerous thermochemical cycles, for hydrogen production through water splitting have been studied but none has yet matured to production. An interesting concept is that of oxide-based thermochemical cycles, during which, a simple oxide (like iron, zinc or cerium oxide) or a mixed oxide (such as a ferrite) cycles between a lower and a higher valence state, participating in an oxidation-reduction process which produces H_2 and O_2 in separate steps. This concept has been proven experimentally for pairs of oxides of multivalent metals or metal/metal oxide systems (Schunk et al., 2008). Water splitting is taking place at temperatures ~700°C but material regeneration (i.e. reduction) takes place at much higher temperatures (> 1200°C). Solar reactors reported in the literature are based on particles fed into rotating cavity reactors, concepts that are complicated and costly to operate.

In contrast to bed type reactors, the HYDROSOL process (proposed by the EC co-funded project Hydrosol, 2002-2004) involves a multichannel ceramic honeycomb reactor which acts as a solar heat absorber as well as a gas reactor. The solar heat energy is needed as the thermochemical process involves an endothermic reaction that requires a significant energy input. The coated reactor is heated by concentrated solar radiation using a set of heliostats (mirrors) that concentrate the solar energy into a certain area and lead to an increase of the reactor temperature. Using concentrating solar power (CSP) plants it is possible to achieve temperatures in excess of 1200°C through proper sizing and control of the heliostat field (field of sun-tracking mirrors). The reactor is coated with active mixed iron oxides (redox-materials), with a high activity in water splitting reaction to make the process operate at feasible temperatures.

In the first step of water-splitting the activated redox reagent (usually the reduced state of a metal oxide) is oxidized by taking oxygen from water and producing hydrogen, according to reaction (1).

$MO_{x-1} + H_2O(g) \rightarrow MO_{ox} + H_2$ (1. exothermic)

During the second step the oxidized state of the reagent is reduced, to be used again (re-generation), delivering some of the oxygen of its lattice according to reaction (5):

$MO_{ox} \rightarrow MO_{x-1} + ½O_2$ (2. endothermic)

The advantage is the production of pure hydrogen and the removal of oxygen in separate steps, avoiding the need for high-temperature separation and the chance of explosive mixtures formation. The active redox material in fact is capable of water-splitting and regeneration, so that complete operation (water-splitting and redox material regeneration) is achieved in a closed solar reactor. The reactor's operating temperature can be cycled between the higher and the lower level by diversion in the number of mirrors focused onto the reactor's aperture.

A 100 kW solar reactor for continuous solar hydrogen production was installed in the Plataforma Solar de Almería, Spain on March 31st, 2008. This was the first ever, closed solar-only, thermochemical reactor for hydrogen production (HYDROSOL II, 2004-2008, Figure 3). Significant concentrations of hydrogen have been produced with a conversion of steam of up to 30% during operation of the plant for a high number of consecutive cycles of constant and continuous H_2 production. The HYDROSOL team is now working to scale up the technology and build a 1 MW hydrogen-producing plant, in a project known as HYDROSOL 3D. This project concerns the design of the whole plant including the solar hydrogen reactor and all necessary upstream and downstream units needed for reactants feeding and products separation and storage.

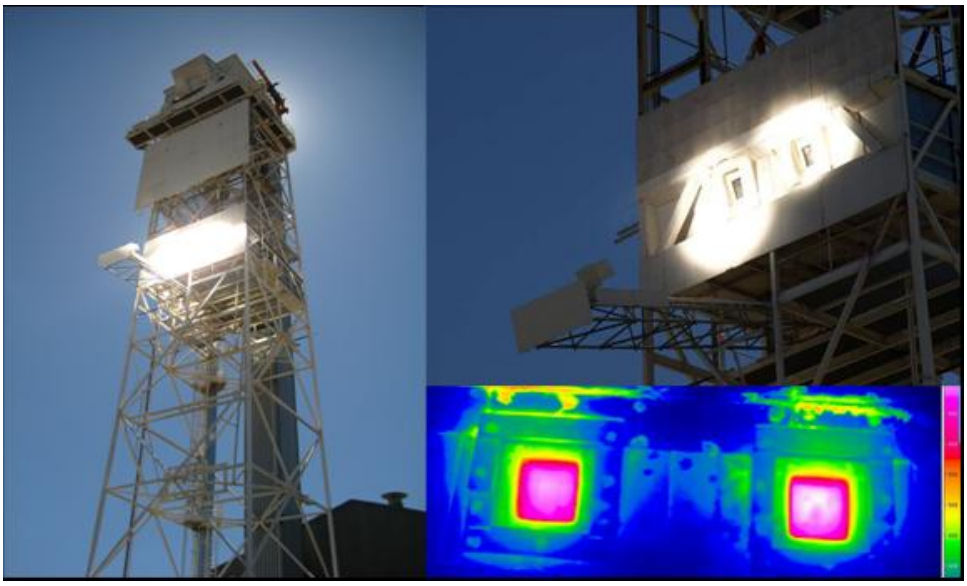

Figure 3. 100kW solar H_2 production pilot plat in Plataforma Solar de Almeria

Recently, the authors have successfully modified the HYDROSOL technology and managed to produce carbon monoxide by carbon dioxide (CO_2) splitting (Zygogianni et al., 2011). The operation of the CO_2 splitting reactor can be "combined" with the operation of the HYDROSOL reactor and the produced carbon monoxide and hydrogen, can be used to produce synthetic fuels by established chemical processes like the well-known Sabatier and Fischer-Tropsch processes to produce methane/methanol and liquid hydrocarbon fuels respectively (Figure 4). In addition to solar fuels, the solar "synthesis gas" can be used to synthesize "solar plastics".

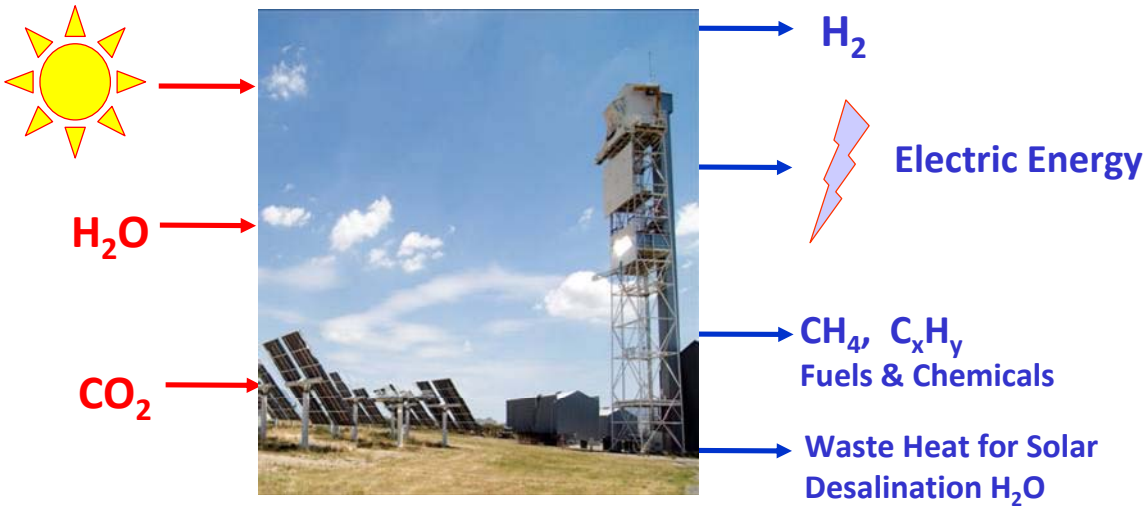

Figure 4. The concept of carbon neutral solar fuel plant

Summary

Multifunctional reactors based on advanced catalyst synthesis and coating techniques as well as on advanced simulation and performance assessment techniques are able to move forward the Diesel engine emission control area towards low-cost, more efficient and more compact systems. The same technologies can be applied in diverse fields such as the Clean Energy fuels production. The HYDROSOL process is such a successful example combining two novel concepts: nanoparticle materials with very high water-splitting activity and regenerability (synthesized by novel routes such as aerosol processes, combustion techniques and reactions under controlled oxygen pressure) and their incorporation as coatings on special refractory ceramic monolithic reactors whose geometry resembles the geometry of familiar automotive applications. The same concept proved to be applicable for CO_2 splitting as well. Consequently, the proposed technology can be considered as a reliable path towards sustainable Clean Energy fuels production from just solar energy, captured CO_2 and water.

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