

NEW CERAMIC TECHNOLOGY FOR CATALYSIS AND THE REDUCTION OF EMISSIONS AND PARTICULATE POLLUTANTS INTO THE ATMOSPHERE

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Abstract

Internal combustion engines have been causing a lot of pollution, as in their combustion process produce harmful gases such as CO, hydrocarbons, NO_x and particulate matter.

Environmental requirements on polluting aspects of the transport sector and in motor vehicles especially, and the demand for sustainable technology for the planet, lead to the need to improve the devices for depuration of gaseous and particulate matter emissions.

On the other hand, we can not forget the costs of implementing these systems in the automotive sector in a scenario of economic crisis, with increasing offer and declining demand.

In this context, we have been working on a project called MEDEA, which aims to achieve a new technology that combines the following parameters: simplicity; reduced cost of implementation; reduced emissions (able to meet Euro 6 regulations and reduce CO₂ emissions to 130 g/km); and durability.

In this paper we present the development and results of the first phase of this project carried out on behalf of the Chair SEAT.

Keywords: *Ceramic foam; Emissions; Gases; Particulate matter; Motor vehicles.*

1. Introduction

Internal combustion engines have been causing a lot of pollution, as in the combustion process produces harmful gases such as carbon monoxide (CO), hydrocarbons (HC), oxides of nitrogen (NO_x) and particulate matter (MP) as well as carbon dioxide (CO₂), gas largely responsible for the greenhouse effect. CO is odorless, colorless and very toxic. CO has a lifetime in the atmosphere of 1 to 2 months and CO₂ has a lifetime of 50 - 200 years, but CO is oxidized to CO₂ thus prolonging its stay in the atmosphere. Something similar happens with methane (Faust, 2009).

As for the hydrocarbons emitted, the most common is methane. It has not negative consequences on human health, but contributes to the greenhouse effect. However, there are other hydrocarbons that being in high concentrations can impair human health, especially cardio-respiratory tract, and become cancerous. Nitrogen oxides (NO_x) in the presence of hydrocarbons contribute to the formation of ozone in the troposphere and serve as a catalyst for the formation of photochemical smog and acid rain. Nitrous oxide (NO) is a major cause of global warming with a half-life of 170 years, then followed by ammonia and nitrate ion (Faust, 2009).

Particulate matter, also known as soot, is formed by particles of size < 3μm that enter the airways and into the bloodstream causing major health problems and can become cancerous.

Directive 70/220/EEC (EEC, 1970) has been the basis of the standards applied in the European Union for reducing emissions from internal combustion engines. Each Directive approved by the Council establishes some pollutant emission limit values that must be taken into account by the automakers. Table 1 shows the limit values regulated through Euro 1 until Euro 5 and 6 standards. The Euro 5 has a

date of application with a range from 9/2009 - 12/2010, while the Euro 6 has an open date from 01/2011, so it can be implemented and enforced by different countries of the European Union.

Table 1. Regulated emissions in the European Union (mg/km) (MMA, 2006)

		CO	HC	HC+NO _x	NO _x	PM
Diesel						
1991-1995	Euro 1	2720	-	970	-	140
1996-2000	Euro 2	1000	-	700	-	80
2001-2004	Euro 3	640	-	560	500	50
2005-8/2008	Euro 4	500	-	300	250	25
9/2009-12/2010	Euro 5	500	-	230	180	5
01/2011-	Euro 6	500	-	170	80	5
Gasoline						
1991-1995	Euro 1	2720	-	970	-	-
1996-2000	Euro 2	2200	-	500	-	-
2001-2004	Euro 3	2300	200	-	150	-
2005-8/2008	Euro 4	1000	100	-	80	-
9/2009-12/2010	Euro 5	1000	100	-	60	5
01/2011-	Euro 6	1000	100	-	60	5

(*) Note: Exemption, until September 1, 2012, for special heavy-duty M1 Diesel vehicles: Vehicles with a mass greater than 2000 kg that are designed to carry seven or more passengers, special, or to carry wheelchairs. These vehicles follow the rules for N1 vehicles.

Environmental requirements on pollution aspects of the transport sector and especially in motor vehicles, the recent impact on the climate change phenomenon and ultimately demand for sustainable technology for the world, lead to the need to improve the elements of cleaning of exhaust gases and particulate matter. On the other hand, we can not ignore the costs of implementing these systems in the automobile sector in a context of economic crisis, increased supply and reduced demand.

In January 2008, the Spanish government, in order to encourage the purchase of vehicles with fewer polluting emissions, decreed that new cars should have a tax rebate as follows:

- Vehicles emitting less than 120 g/km CO₂: Exempt.
- Vehicles emitting from 121 - 160 g/km CO₂: 4.75%.
- Vehicles emitting from 161 - 200 g/km CO₂: 9.75%.
- Vehicles emitting more than 201 g/km CO₂: 14.75%.

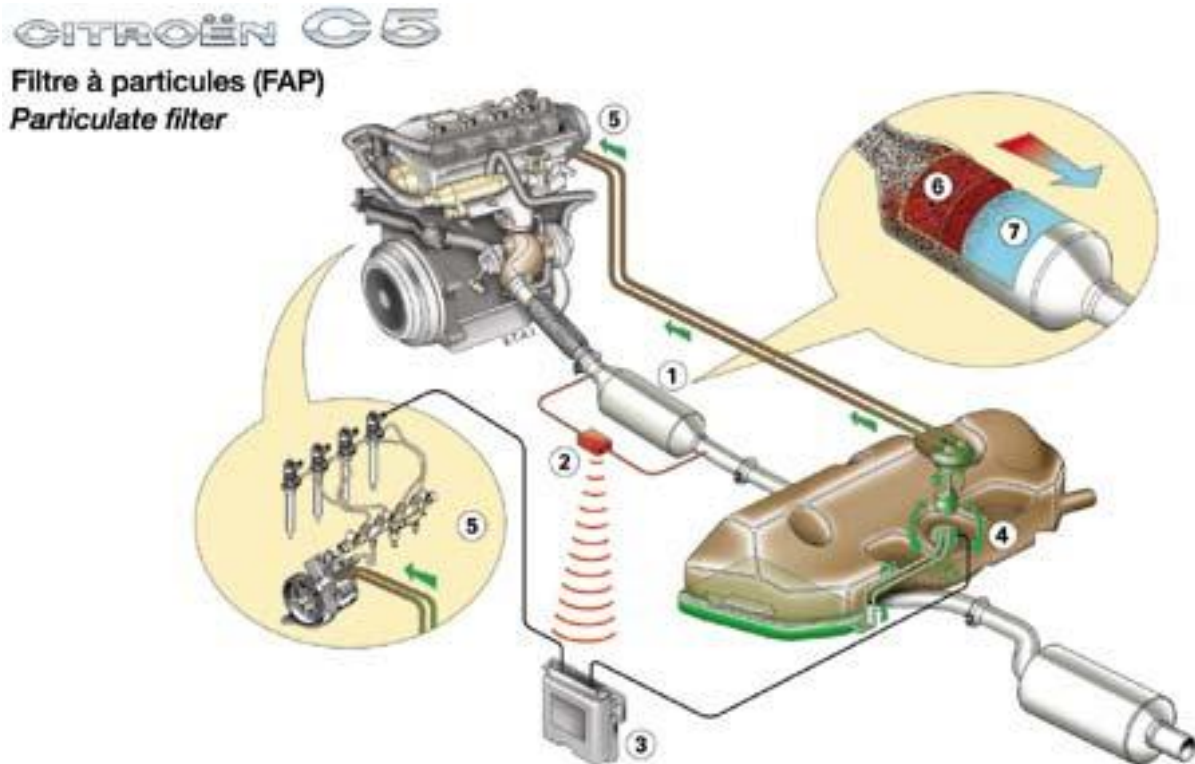
It is in this context that this work is presented. It is the result of a project called MEDEA, made for SEAT. Here are the results of the first phase of this project (Cusidó, Cremades & Ramirez, 2009).

2. Objective

The MEDEA project aims to implement a new technology for reducing CO₂ emissions, particulate matter and other contaminants from exhaust gases, both to comply with Euro 5 and 6 and to the exemption from registration tax. This technology should be simple, economical, and effective, as an alternative to existing systems.

There is already a technology that uses ceramic elements (usually, cordierite) doped with platinum to reduce significantly the emissions of CO and NO_x, which is completed with the addition of particulate filters, also with acceptable results. An example of this technology is the system implemented in the Citroën C5 (Figure 1).

Figure 1. Particulate filter of the Citroën C5 (PSA, 2008)



1. Particulate filter assembly and pre-catalyst
2. Temperature and pressure sensors
3. ECU unit of the engine
4. Additive injection to the fuel into the main tank, if necessary
5. Specific information sent to the injector head when post-combustion is needed
6. Pre-catalyst
7. Particulate filter

What is proposed here is to simplify both systems into one, with the aim to achieve two objectives:

- I. Improve yields in a single system.
- II. Reduce development costs.

It is therefore proposed to use a new sponge and refractory ceramic material based on alumina (Al_2O_3) and rutile (TiO_2) doped with self-developed catalysts based on insoluble salts of vanadium, rhodium and palladium, without ruling out the presence of minority platinum salts. An advantage of using alumina as the base material is that it itself also acts as a catalyst, an aspect that the conventionally employed cordierite has not. The characteristics of amorphous percolation as well as the microporous nature of the product, would lead to a much higher specific surface area of contact of the gases with catalysts and particulate filter, too. It would therefore be a brand new technology that could provide higher yields at lower cost.

3. Existing systems to reduce emissions from combustion engines

For reducing gaseous pollutants emissions several techniques are being used, among which we quote (Twigg, 2007): common rail, injection of air into the exhaust, exhaust gas recirculation, catalytic converters and particulate filters. Some of them are specific to Diesel engines.

3.1. Common rail

The modern system of direct injection used in Diesel engines is a variant of direct injection in gasoline engines. It has a high pressure feed (1000 bar) of fuel by a common duct ("common rail") to individual solenoid valves, as opposed to the low pressure fuel pump powered by a pump with high-pressure fuel injectors, controlled by the cams of the camshaft. One of the main features of the current Diesel common

rail systems are the piezo injectors to give more precise for the fuel feed and achieving pressures up to 1700 bar (Lai & Dingle, 2005).

The solenoid or piezoelectric valves allow good control over injection timing and quantity. Furthermore, the increased pressure provides better fuel atomization. Engines with "common rail" do not require warm up time and produce less noise and emissions compared with the older engines. In the old Diesel engines, a distributor of injection pump type is regulated by the engine, providing fuel bursts through the injectors and spraying fuel in the engine combustion chamber. As the fuel is at low pressure and the control of fuel delivery can not be precise, the spray is relatively coarse and the combustion process is relatively inefficient.

3.2. Air injection in the exhaust

This is a post-combustion device, which introduces a certain amount of air into the exhaust manifold in order to complete combustion of the exhaust gases from the cylinder, before going outside. The oxygen entered in this way combines readily with hydrocarbons coming out of the cylinder at high temperatures, completing combustion, and together with the carbon monoxide convert it into carbon dioxide. The injection is made near the exhaust valves, in order to exploit the maximum temperatures in these areas, using a pump.

3.3. Exhaust gas recirculation

Also called EGR, its fundamental purpose is the reduction of NO_x emitted during engine operation. This is accomplished by returning a small proportion (5 - 15%) of the exhaust gases to the intake manifold, to be introduced into the chamber combustion along with fresh ones. The resulting mixture is lean, which implies a significant decrease in the rate of combustion, reducing the temperature and pressure limits. And so, it reduces the rate of emission of NO_x, since they are only generated at high temperatures and pressures.

A limitation that arises is that the reduction of reactive components in the combustion chamber leads to an increase of soot. The amount of EGR also affects the ignition period. If the speed of the recirculation of exhaust gases is large enough to lower the partial load, the ignition delay is so large that the diffusive component of combustion decreases as the ignition does not occur until a large percentage of the air/fuel mixture has been reached.

3.4. Catalytic converters

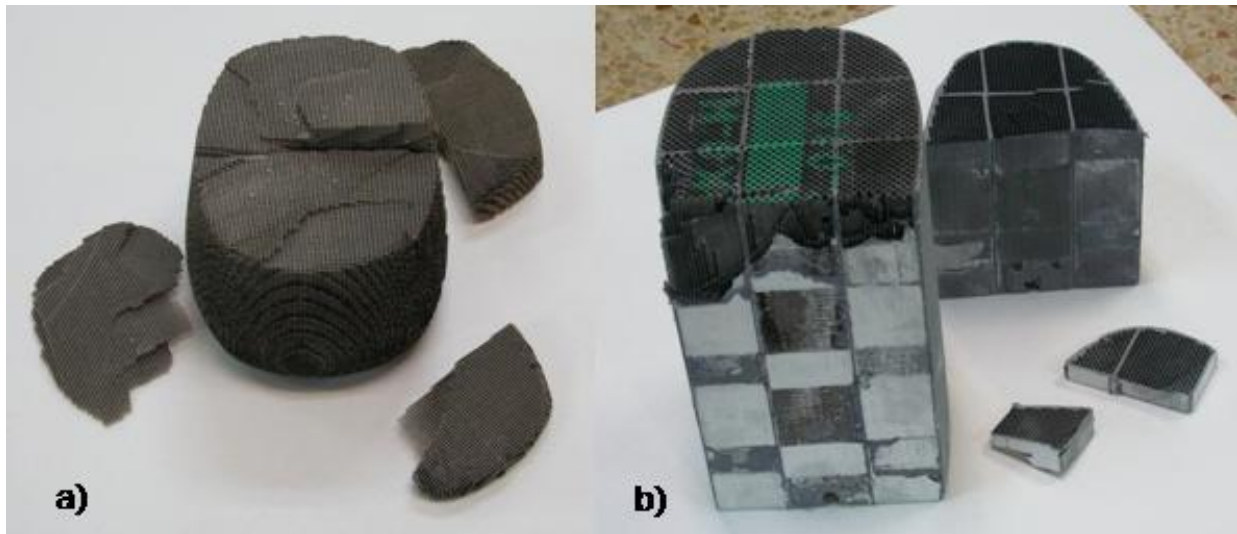
These devices convert HC, CO and NO_x present in exhaust gases in inactive compounds. The catalyst is a product that can cause a chemical change without actually participate in global action, but only in the intermediate stages, having the different gas molecules can contact more easily to form new compounds. The catalysts are arranged as liner in the expansion box of the exhaust system, where the gases are exposed to the catalytic action of the coating. Generally, there are two types of catalysts: one for NO_x and one for CO and HC. Under the catalytic action, NO_x are decomposed into oxygen and nitrogen; HC are converted into CO₂ and H₂O, and CO is converted to CO₂.

To ensure the catalytic action and complete combustion, it is necessary to ensure the presence of sufficient oxygen. To this, the catalytic converter system is often combined with an air injection system in the exhaust. In some cases it is usual to combine the gas recirculation system with the catalytic converter, where the former is responsible for the reduction of NO_x, while the other does the same for HC and CO. For this reason, there is a single catalyst instead of two (Alonso, 1997).

The catalyst consists of a structure or ceramic monolith in the form of honeycomb, so that there is a greater area of contact between the gas and the catalytic material which is coated. This material usually consists of precious metals like platinum and palladium that allow the function of oxidation, and rhodium which is involved in the reduction, speeding up the chemical reaction. On its outside the catalyst has a stainless steel container and is fitted with a metal screen cover, antithermic, made of stainless steel, which protects the bottom of vehicle from the high temperatures reached (Heck & Farrauto, 2001).

The catalysts in the market tend to have some scaffolds with the shape of square matrix made of cordierite (Figure 2a) or silicon carbide (SiC) (Figure 2b). To make them, it is used a mold with a grid through which the material is passed by extrusion.

Figure 2. Catalyst made of: a) cordierite y b) silicon carbide



3.5. Particulate filter

It consists of a device structure similar to honeycomb, with sealed and open holes, through which exhaust gases are forced to pass. Thus, the gases move freely and particulate matter is retained, forming a layer that with increasing temperature in the range of 350 - 650 °C, it will burn. This way, the filter is cleaned and the particulate matter is removed. The particulate filter is usually made of ceramic (cordierite, silicon carbide, aluminum titanate).

The process of regeneration of the particulate filter requires a control and monitoring system. This system records the state of the filter, such as the saturation level, the regeneration strategy to use, and monitoring of the filter itself. In addition, these systems may be involved in the fuel injection, air intake system and dosage of additives (Bosch, 2005).

4. New scaffold for the catalyst/particulate filter proposed

Under the framework of the MEDEA project, we conducted several laboratory tests to get a new catalyst scaffold using the technique of "replicated ceramic" from a base matrix. This technique consists of immersing the base material in a ceramic suspension, drain, dry and cook to a temperature such that the base material disappears, but the ceramic material does not, which "replicates" the lattice structure of the base material.

In our case, the base material is polyurethane foam. We used two different density foams: one of large pore and another of fine pore (Figure 3). On the other hand, we prepared different formulations of ceramic slurries in which the polyurethane foams were dipped.

After draining the excess fluid from the ceramic suspension, the slurry impregnated foams were dried in an oven and then cooked in an electric furnace to a temperature of 1200 °C for 1 hour, according to a ramp with a total duration of 14 hours . Examples of end products can be seen in Figure 4.

After obtaining the scaffold, it has to be sealed to prevent that combustion gases be evacuated by the side walls. To this, an outer coating has been tested based on refractory mortar, similar to that used in conventional catalyst systems (Figure 5).

Figure 3. Polyurethane foams of two different densities



Figure 4. Catalyst scaffolds with thick and fine pores obtained in laboratory



Figure 5. Thick-pore catalyst scaffold with and without outer coating, obtained in laboratory



The new product has certain advantages over cordierite or SiC catalyst scaffolds:

- For manufacturing, no need to use extrusion of ceramic paste, which is a technique much more expensive than the ceramic replica technique tested here.
- The product has irregularities in the free channels that leads to increase the gas-solid contact, which can improve the overall performance of the catalyst with a similar pressure drop for the removal of particles and gas pollutants.

- Ceramic materials used for the synthesis of scaffold are themselves active as catalysts for oxidation reactions, but it is possible to add active elements to enhance the catalytic oxidation or reduction.
- This scaffold has a much lower density than the conventional one, which means less weight of catalyst unit.
- The technology is easily scalable to industrial level.

5. Approach to industrial production of the catalyst/particulate filter

Here, we describe about what would be the industrial process to follow to scale up the technology from the laboratory experiments.

First, polyurethane foams are supplied in flat form of $2 \times 1 \text{ m}^2$ and 10 cm thick. This material exists in different forms and manufacturers; it is often used in air filters in industrial facilities, air conditioning, etc.

The base material should be previously dipped in a 5% solution of sodium salt, sodium aluminate and a organic layering product for providing some ionic charge to the material surface. After 5 minutes, it should be removed and dried at 100 °C for 12-24 hours. At industrial level, the process can benefit from the exchange of heat from furnace gases.

On the other hand, ceramic slurries are prepared by a ratio of about 35-40% water per dry matter. The mixture is placed in a conventional ball mill to homogenize and deflocculate the paste. After measuring the viscosity and thixotropy, it is moved to stirred tank to keep its rheological properties, and then poured into stainless steel ponds.

The polyurethane products are immersed in the ponds, provided in the bottom of a gentle agitation system that prevents the precipitation of the slurry. Polyurethane plates remain submerged in the slurry for a few minutes, then are raised above the pond and submerged again, repeating this step at least three times. The resulting slurry can be reused. Once the parts are drained by gravity and forced ventilation, they should be dried at high temperatures, i.e. above 100 °C and for a period exceeding 12 hours.

Next, we proceed to a second primer with a low viscosity slurry and high thixotropy for incorporating catalytic metal oxides. Remember that while the ceramic material already contains catalytic metals such as aluminum and titanium, its composition can be completed with buffer solutions of palladium oxide, rhodium, zirconium, tungsten, etc., to complete the oxidizing/reducing catalysis processes over gases from combustion engines.

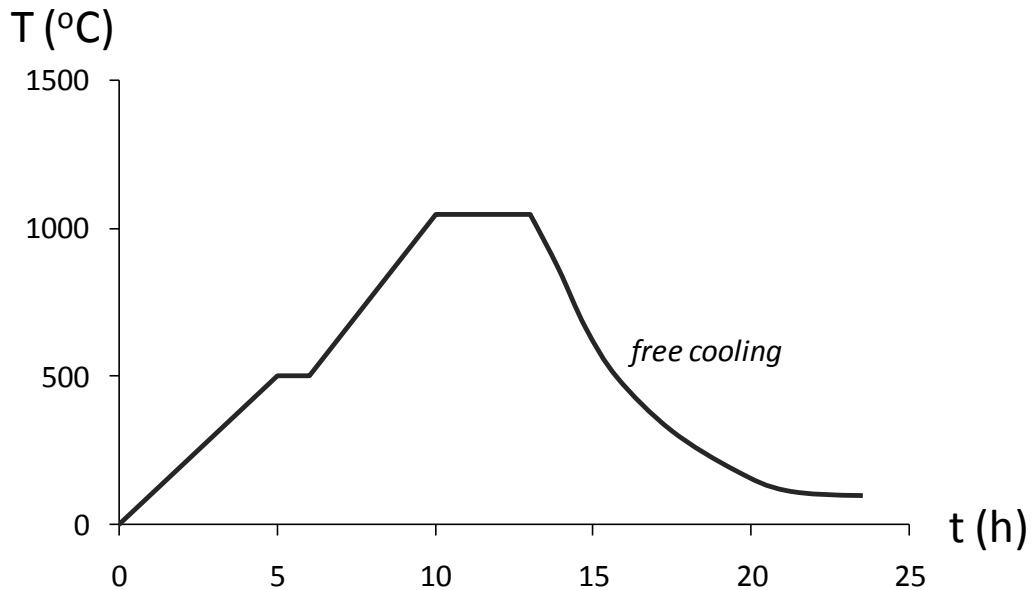
After priming, plates gain important weight each (\square 100 kg, at least five times the initial weight of polyurethane).

We note that at the actual stage of the research, we do not know if the second primer should be carried out with the green product (before cooking) or after the first sintering process. In any case, a second firing (double firing) would take place at low temperature (1000 °C) to prevent embedding catalytic oxides in the aluminum titanate substrate.

In the MEDEA project, we put special emphasis on finding low-cost industrial processes. Knowing that the process of ceramization can represent 40% of the cost of production, the proposal is limited to the field of a medium thermal process, i.e. for not overcoming the barrier of 1300 °C which is the case of furnaces for sanitary ceramics (porcelain, stoneware, etc.). They are intermittent furnaces easily available, which will not result in high costs of implementation. We should note that furnaces able to operate at higher temperatures (1800 °C), as in the case of opting for silicon carbide ceramics, could invalidate the proposal because of its high investment and operation costs.

Our proposal assumes that the production would take in a pre-existing sanitary-ceramic sector company for diversifying its usual production. The firing curve is shown in Figure 6, which has been proven by laboratory tests. On an industrial scale there may be some changes. Regarding the first part of it, it should be mentioned that occurs a destruction pyrolysis of polyurethane, therefore some caution should be taken in this first phase (5 hours) up to reach 500 °C and a plateau of 1 hour at this temperature. For the rest of the schedule, we do not foresee major difficulties to reach the maximum temperature other than those typical of a conventional heat treatment.

Figure 6. Rough ceramic sintering curve



A second sintering process would take place at temperatures around 1000 °C, in order that the catalytic metal oxide adhere to the surface of the ceramic matrix. This will ensure their presence at the surface of the ceramic body and thus to effectively perform the required chemical reactions.

The plates, once the firing process, are cut into parallelepiped of 30 x 10 x 9 cm³. We do not consider necessary to make a water-cooled cut, as it is a low density ceramic material.

It is well known that the ceramic is a hard and brittle material at a time. To maintain a spongy structure in mechanical and thermal conditions particularly harsh (vibration and high temperatures), it is necessary to protect the ceramic piece by cementing its sides. The refractory cement can be applied by "spray". Then, the product should be heated to 250 °C for optimum results. It should be taken special care in that drying does not lead to the separation of the filter surface from the ceramic layer in contact. Therefore, the refractory cement should be applied in diluted form and initially dried in ambient air before putting it into the oven at 250 °C.

6. Final remarks

In the industrial production of catalyst/filter body presented, the most important aspect to consider from the environmental point of view, is the formation of atmospheric pollutants during the early stages of the cooking process from the burning of polyurethane foam. However, emissions from the pyrolysis of polyurethane during the sintering process can comply with current legislation without major technical difficulties.

Assuming that the plant is included as a production line in a sanitary-ceramic industry that already exists, we estimate that the investment required would be about 500000 € for an annual production of 10000 units. In such an investment it is not counted the cost of sintering furnaces, as they are considered as existing in the ceramic industry (they would be the most expensive items by far). The estimated cost of each filter/catalyst unit would be at least about 50 €, taking into account all operating costs (raw materials, energy, labor, depreciation and indirect costs). To this, it must be added the cost of housing and assembling the unit (for reference, currently the price of a full conventional catalyst is around 1000 €).

This hypothesis would make it more viable an introduction of the product in the market and reduce risks. If the production were successful, of course, then the creation of an industry connected to manufacturers of metal parts for exhaust systems could be considered.

In the current state of the MEDEA project, the first phase has been completed. Experimentation is needed to perform a full-scale prototype for carrying out street and road tests (100000 or 200000 km). To continue the project, we are waiting to get the necessary funding.

7. Acknowledgements

The authors thank Claudia Ramírez for their help in preparing the MEDEA project report and the Chair SEAT for funding the first phase of the project.

8. References

- Alonso J.M. (1997). Técnicas del Automóvil: Motores. Madrid: Ed. Paraninfo.
- Bosch, R. (2005). Diesel Engine Management. NJ: Ed. Wiley.
- CEE (1970). Directiva 70/220/CEE del Consejo, de 20 de marzo de 1970, relativa a la aproximación de las legislaciones de los Estados Miembros en materia de medidas que deben adoptarse contra la contaminación del aire causada por los gases procedentes de los motores de explosión con los que están equipados los vehículos a motor. URL: http://eurlex.europa.eu/smartapi/cgi/sga_doc?smartapi!celexapi!prod!CELEXnumdoc&lg=ES&numdoc=31970L0220&model=guichett. Acceso octubre 2008.
- Cusidó, J.A., Cremades, L.V., & Ramírez, C.P. (2009). Desarrollo de tecnología cerámica para la catálisis y la disminución de la emisión de gases y partículas contaminantes a la atmósfera integrado en un único elemento. Proyecto MEDEA. Primera fase. Informe final. Barcelona: Ref. MEDEA_0912_0.
- Faust, D.R. (2009). Global Warming: Greenhouse Gases and the Ozone Layer. The Rosen Publishing Group, Inc.
- Heck, R.M., & Farrauto, R.J. (2001). Automobile exhaust catalysts. Applied Catalysis A: General, 221 (1), 443-457.
- Lai, M.D., & Dingle, P.J. (2005). Diesel Common Rail and Advanced Fuel Injection Systems. SAE International.
- MMA (2006). Energía, Transporte y Medio Ambiente. Ministerio de Medio Ambiente y Medio Rural Marino de España, Sección Estadística. URL: http://www.mma.es/secciones/info_estadistica_ambiental/estadisticas_info/memorias/2006/pdf/IV_4_ANEXO.pdf. Acceso noviembre 2008.
- PSA (2008). El sistema de filtro de partículas Citröen: para una mejor protección del medio ambiente. URL: <http://www.automotriz.net/tecnica/filtro-particulas-citroen.html>. Acceso Octubre 2008.
- Twigg, M.V. (2007). Progress an future challenges in controlling automotive exhaust gas emissions. Applied Catalysis B: Environmental, 70 (1-4), 2-15.

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