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Catalytic combustion: from reaction mechanism to commercial applications

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Abstract

The present commercial applications of catalytic combustion are briefly reviewed. Difficulties still hinder the commercial development of this type of combustion as an NO_x control technique. The problems are addressed by both academia and industry. The relevant activities of Gaz de France and GASTEC, both involved in several projects supported by the European Union, are described.

Keywords: Catalytic combustion; Commercial application; NO_x reduction

1. Introduction

The number of R&D projects on catalytic combustion in all industrialised countries has probably never been as high as now, spurred by the fact that catalytic combustion is one of the most promising technique to achieve the clean combustion of fuels [1]. Actually, catalytic combustion has already gone beyond the 'promising' status with a number of commercial applications that take advantage of some of its other interesting characteristics. The range of applications is wide, from industrial radiant heaters to household devices such as curling irons. However, progress remains to be accomplished before catalytic combustion becomes a widespread industrial technique to minimise the production of NO_x.

Catalytic combustion is the reaction of complete oxidation of a fuel (H_2, CH_4, LPG, Diesel fuel, etc.), carried out with the purpose of producing valuable heat in a controlled fashion, i.e., without flame or hot spots and at a controlled surface temperature. However, the complete oxidation of a chemical species, such as a pollutant, accomplished with the main objective of converting it into an innocuous product, should not be called a catalytic combustion process. Otherwise, confusion develops between catalytic combustion for heat production, which belongs to the category of clean processes, and pollution abatement processes whose objective is not primarily to produce heat but to annihilate a pollutant. Catalytic combustion is a clean process because the absence of flames and hot spots precludes NO_x formation and because the catalyst oxidises CO easily.

Catalytic combustors were first described by Pfefferle in the '70s [2,3], although catalytic

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total oxidation reactions have been studied since 1817 [4,5]. Beside the NO_x advantage, catalytic combustion has other benefits which will become apparent as we go through its present commercial applications. It must be kept in mind though that, at this moment, the fraction of fuels burned catalytically is insignificant compared to that burned conventionally.

2. Present commercial applications of catalytic combustion

2.1. Radiant heaters

Radiant heaters appear to be the main present commercial application of catalytic combustion. There are tens of manufacturers in the world. Most of the heaters are used in home appliances which burn LPG or kerosene type fuels. Radiant heaters insure flexibility (outdoor use possible) and safety of operation, especially in terms of low CO levels in the combustion effluents.

A few manufacturers offer industrial radiant heaters that burn natural gas. The power is usually limited to 60 kW/m^2. Radiant heaters can be used in explosive atmospheres. This is an essential point in paint drying applications. The phenomenon is not quite understood. This is an area where more experimental data are necessary in order to obtain a better view of the intricate hetero–homogeneous phenomena which characterise catalytic combustion.

Catalytic radiant heaters, because of their wide emissivity spectrum, may have a higher heating efficiency than electric radiant heaters for some applications such as plastic thermoforming [6].

2.2. Household appliances

Curling irons featuring catalytic combustion have been around for a few years now, especially for the benefit of travellers who do not have to worry any longer about differences in voltages and plugs. They usually work with a small cartridge of a butane fuel. On a small scale, their design takes into account all the features of a catalytic combustor. They show how heat production and dissipation can be matched and adjusted to yield the desired temperature of 55°C with a fuel whose adiabatic flame temperature is above 2000°C.

2.3. Sensors

Catalytic combustion devices are widely used as a convenient means of detecting flammable gases in air [7]. The concentration of the gas of interest is measured through the heat liberated during its combustion. In the most common design, the catalytically active sensing element forms one of the arms of a Wheatstone bridge. If a flammable gas is present, it will burn on the sensing element and raise its resistance, setting the bridge out of balance and causing the emission of a warning signal. Platinum is usually the catalyst chosen as it is less sensitive to poisons than palladium.

2.4. Domestic burners

The little blue flame associated with domestic burners in kitchen appliances is the symbol of natural gas for the public. The burner manufacturers may, therefore, hesitate to offer flameless catalytic burners, regardless of other considerations. In some instances however, the technical advantage of catalytic burners may be so high that the marketing considerations may be overcome. An example is offered by the French company Application des Gaz which has recently introduced a LPG stove for outdoor use on the market. The catalytic burner is not sensitive to wind, in contrast to conventional burners for which flame stability and efficiency in an outdoor environment is a problem. In Germany, Buderus has shown a prototype burner that runs on natural gas and aims at the zero emission level of NO_x and CO. The burner operation is microprocessor controlled [8].

2.5. *Furnace burners*

Several manufacturers (Viessmann in Germany, Frisquet in France, etc.) are now offering natural gas furnaces that feature surface assisted combustion. The heat transfer from the burner to the fluid to be heated is largely by radiation rather than by convection. These furnaces offer high efficiency as well as low NO_x emission.

2.6. *Fluidised beds*

Fluidised beds are known to have unique heat transfer characteristics and they should, therefore, represent an excellent system to carry out catalytic combustions. In Russia, there is an industrial reactor of that type where otherwise non-flammable solvents are oxidised into CO_2 and H_2O [9,10]. A fluidised bed prototype has been built in the Netherlands to produce hot water, as described later in this paper.

2.7. *Chemical reactor heaters*

Endothermic reactions such as steam reforming are usually carried out in long narrow tubes filled with catalysts and externally heated by flames. The heat could be provided more uniformly and more accurately at the necessary level by a combustion catalyst surrounding the tube in a uniform manner and in close contact with it. A commercial reactor exists in Russia, based on this concept [10].

3. Problems that remain to be solved in catalytic combustion

A catalytic combustor can function in a stable mode only if it is associated with an adequate heat exchanger or absorber. After fuel ignition, autothermal stable steady state operation is reached when the rates of heat dissipation and heat production become equal [11,12]. The problems that must be solved when designing a catalytic combustor associate therefore catalysis for heat production and heat transfer for heat dissipation. Kolaczkowski [13] has recently reviewed the problems specifically associated with gas turbines and radiant heaters, with this consideration in mind. However, research can address separately specific questions such as the search for high temperature catalytic materials, which will be our concern here. As in other area of catalysis, progress is accomplished by carrying out both basic and applied research.

3.1. *Basic research*

Uncertainties remain concerning the mechanism of the catalytic combustion of hydrocarbons and particularly methane. The reaction belongs to the class of hetero/homogeneous reactions [14], reviewed recently on the occasion of the intense activity on the oxidative coupling of methane [15]. The weak reactivity of methane sets it apart from the other hydrocarbons. Its very low sticking coefficient on surfaces render less effective many of the surface observation techniques which are adequate to follow the surface oxidation of higher hydrocarbons such as butanes. The nature of the active oxygen species, O_2^-, O^{2-} or O^-, which may originate directly from molecular oxygen or from an oxide or an oxidised metal surface, remains the subject of controversy. Other questions relate to the nature of the surface and radical intermediate involved and to the importance of the OH species [16].

A rather unusual behaviour was observed concerning the Pt and Pd catalysts, which are the catalysts mainly used so far in catalytic combustion: the activity increases with time on stream, up to a 100 fold if the activity is defined per unit area of metal catalyst [17–22]. It is established that reconstruction of the catalyst surface occurs during that period but the origin of the increase in activity is still debated. More active catalysts could be designed if the phenomenon could be clarified.

Observations on the sensitivity of combustion catalysts to poisons such as sulphur are not always in line [23]. Pt appears to be less sensitive than Pd. More information is needed on the mechanism of action of the potential poisons. For safety reasons, the gas companies add odoriferous sulphur compounds at some point in their distribution grid.

Finally, there is a need for an improved description of the mechanism of action of catalysts and 'catalytically inactive' surfaces at high temperatures, above 800 up to 1400°C. In the higher temperature range, the combustion of natural gas occurs essentially in the gas phase. Nevertheless, for gas turbine applications, the beneficial effect in the combustion chamber of a relatively low porosity, low activity hexaaluminate catalyst, stable at very high temperatures, has been demonstrated [24]. However, combustion experts question the presence of catalytic effects at such high temperatures and consider as well other approaches to prevent hot spots and NO_x formation [25]. There is an obvious need for joint forces of combustion experts and catalysis researchers to clarify matters in this area where surface, boundary layer and gas phase phenomena are intimately connected.

3.2. Applied research

There is a need for better catalysts at both ends of the temperature range covered by catalytic combustion.

Catalysts that will permit combustion to be initiated at lower temperatures at laboratory conditions (low gas velocity), will permit the ignition temperature at the high flow rates and pressure encountered in a gas turbine, for example, to be lowered as well. This improvement in catalyst performance will translate into lower NO_x emission for the turbine by diminishing the amount of gas to be burned in the preheater which is often used to raise the gas temperature at the outlet of the compressor ahead of the combustion chamber of the turbine [24].

Better light-off catalysts will render catalytic combustion more attractive but, at this moment, the elaboration of hydrothermally stable catalytic materials appears more urgent as it will condition the appearance of catalytic combustion as a feasible technology for large market applications such as gas turbines and high power radiant heaters. Aluminates, perovskites and hexaaluminates are good candidates [26–36].

4. GASTEC and Gaz de France's experience in catalytic combustion

GASTEC and Gaz de France formally joined their efforts for the development of catalytic combustion for the first time in 1985. GASTEC was then known as VEG-GASINSTITUUT.

4.1. 1985–1988 programme

4.1.1. Gaz de France

The activity at GDF was directed towards two applications: the flat radiant heater and the hot air generator. At that time, the main incentive was to improve the quality and the variety of natural gas combustion equipments and processes.

A collaboration was initiated with ACIR, a French manufacturer of industrial radiant heaters. These heaters are used essentially for paint drying. Tests were carried out to determine the influence of various parameters such as the fuel air ratio and the load of precious metals on the fibre support. The information obtained led to improved understanding of operation and better performances, particularly in terms of catalyst load and durability.

The work on the hot air generator was more ambitious. The objective was to prove the concept by demonstrating the operation of a 100 kW prototype. In order to design the prototype properly, intrinsic kinetic data, free of external diffusion limitations, were obtained in a spinning basket reactor. The hot air generator prototype was constructed and operated for more than a year. It was a fixed bed reactor and, retrospectively, one may say that it was not the best choice to manage the heat generated properly. No set of operating conditions could be found that would lead to constant operation, without rapid catalyst deactivation.

For both applications, there was a need for catalysts more stable at elevated temperature and more resistant to high water vapour concentration than the alumina supported Pt and Pd catalysts, commercially available. The search for novel catalyst formulations was subcontracted to the Institut de Recherches sur la Catalyse (IRC) in Villeurbanne. Dr. Michel Primet was the principal investigator in this sub-project.

Catalyst deactivation may originate from modifications of the active precious metal particles or of the support. The influence of various additives (Sr, La, Ba, etc.) on the thermal stability of γ-alumina was investigated in an accelerated ageing test. Similar studies were performed on alumina fibres, often used as catalyst support in radiant heaters. Lanthanum and silicon proved to be the most beneficial additives [37,38].

The activity of several noble catalysts, Pt, Pd, Rh and Ir, as function of time on stream was examined and correlated with physical and chemical modifications of the particles. Epitaxial growth of the platinum particles with the support habit was discovered to parallel the increase in catalytic activity with time on stream despite the fact that the metal particles sintered noticeably: after 10 h on stream at 600°C, the average size of the particles was 6–12 nm compared to 1–2 nm for the fresh catalyst [39].

Precious metal particles were supported on the stabilised aluminas. The increased thermal stability of the support did not prevent sintering of the metal particles. It was concluded that noble metals can be used only if the catalyst temperature remains below 700°C, i.e., in applications where low and moderate heat flux are sought. Actually, this domain of applications corresponds to the major segment of the combustion market.

For industrial applications, higher heat flux are often sought and more stable catalysts must be found. Oxides of transition metals (Cu, Co, Mn and Cr) supported on various common supports such as γ-alumina were screened. CuO/γ-alumina was found fairly active, being able to start converting methane at 300°C [32,36,40]. At high temperatures, above 1000°C, however, the catalysts were found to deactivate rapidly, due to the disappearance of the surface active cations by migration into the alumina lattice with the formation of an internal metal aluminate. The idea was then explored to use as support the alumina 'saturated' with the transition metal corresponding to the transition metal oxide used as the active phase. It partially prevented deactivation but better catalysts were finally obtained with $MgAl_2O_4$ and $ZnAl_2O_4$ as support for the copper oxide [29,31]. After ageing at 1000°C, 90% of the copper was still present at the surface of the $ZnAl_2O_4$ spinel. The absence of migration of Cu in the lattice of the support is explained by the fact that the vacant sites of the alumina lattice are now occupied by Zn ions which cannot be displaced by copper, in view of the stronger affinity of the alumina vacant sites for Zn ions.

Slow technical progress and the absence of a sufficient market for catalytic combustion devices resulted in the termination of activity in 1988 at GDF. In 1992, the activity was resumed with the involvement in a four year R&D project supported by the European Community.

4.1.2. GASTEC

The activities in catalytic combustion started at GASTEC in 1985 in the joint project with GDF. This was done in close cooperation with the universities of Utrecht and Twente. The main objective of the program was to build up experience and knowledge on this new combustion technology. The activities were directed towards various applications based on the following concepts and catalysts:

Concepts:

- catalytic fluidised bed reactor.
- catalytic sintered metal reactor.
- catalytic membrane reactor.
- catalytic fixed bed reactor.

Catalyst development:

- improvement of the thermal resistance of commercially available support materials.
- development of a new generation of catalysts based on cheaper transition metals: Cu based catalysts, Mn based catalysts, Ag/Mn based catalysts as an alternative to precious metals.
- development of new coating techniques on metal substrates with different geometries.

Kinetic data and mechanistic studies:

- Catalysts based on precious and transition metals were extensively tested to obtain reliable kinetic data to be used in the various concepts.

Applications:

Several of these concepts and developments were combined and tested for two applications:

- the fixed bed catalytic combustor for hot air production, under the responsibility of Gaz de France (see Section 4.1.1).
- the fluidised bed catalytic combustor for hot water production, under the responsibility of GASTEC. Five partners, GASTEC, TNO, Engelhard, the University of Utrecht (Geus) and the University of Twente (van Swaaij), were involved.

The copper/lanthanum stabilised alumina catalyst that was used in the prototype bed was developed by the University of Utrecht [31] and produced by Engelhard in sufficient quantity for testing. Models able to predict the behaviour of the fluidised bed were developed and validated by the University of Twente. A 150 kW fluidised bed combustor was constructed and operated at TNO to prove the concept. GASTEC managed the project. The fluidised bed operated for several months in the temperature range of 600–700°C. Nearly no deactivation of the catalyst was observed. The average level of the NO_x emitted was less than 1 mg/Nm^3.

Despite these technical achievements, the project was terminated in 1988 for the following reasons:

- fluidised bed combustion is a complicated technique in comparison to conventional combustion.
- conventional systems could meet the NO_x legal specifications at that time.
- the price per kW was too high in comparison with conventional systems.
- combustor manufacturers were not interested in an unproven technology as the National Government had no plans, then, to lower the NO_x specifications.

4.2. Present activities

The essential of the activities of GASTEC and GDF in catalytic combustion is presently carried out in the frame of an R&D project supported by the European Union (EU) and entitled "Catalytic Combustion System Concepts for Pollutant Suppression in Industrial Gas Turbines, Reformers and Radiant Heaters".

GASTEC is coordinator of the project which is part of the EU Brite EuRam Programme.

The project gathers 7 industrial companies and 4 universities or research institutes, located in five different countries of the European Community.

- GASTEC NV, the Dutch natural gas R&D institute, coordinator of the project, the University of Utrecht and N.V. Nederlandse Gasunie, the main natural gas transporter, in the Netherlands.
- Degussa AG, a company whose main business is the production of chemicals and the applications of precious metals and Krebsöge Sinterholding Gmbh, a supplier of sintered metal products, in Germany.
- Rolls–Royce Industrial and Marine Gas Turbines, AEA Technology, Harwell, a research institute in the energy field and the University of Bath, in the UK.
- Bettini SpA, a ceramic producer, in Italy.
- Gaz de France, the state gas transporter and distributor and a CNRS/University unit, in Villeurbanne, the Laboratoire d'Application de la Chimie à l'Environnement (LACE, recently created with IRC staff members), in France.

The aim of this four year project, which started in November 1992, is to search novel natural gas catalytic combustion concepts which will permit ultra low pollutant emissions to be achieved. These concepts will be utilised for the design of:

- high pressure ratio, high efficiency industrial gas turbines.
- heating devices for the tubular reactors of steam reformers.
- high power radiant heaters.

The major programme tasks are the following:

- determination of the combustion activity of existing and novel catalysts.
- identification of the best methods for depositing catalysts on refractory carriers.
- definition of the best geometries for catalyst supports.
- evaluation of performance sensitivity to the various qualities of natural gas.
- determination of the behaviour and ageing characteristics of the catalytic systems at high temperatures and pressures.
- computer modelling of the catalytic combustion devices and validation by experimental data.
- determination of the extent of homogeneous combustion reactions in the systems.
- design and manufacture of housings for catalyst elements for experimental testing.
- experimental evaluation of natural gas fuelled catalytic combustion devices in test facilities.

In addition to their involvement in this Brite EuRam project, GASTEC and Gaz de France are pursuing other research projects in catalytic combustion.

Gaz de France has an ambitious programme on catalytic and surface assisted combustion, targeting several applications of direct interest to the gas equipment manufacturers and customers. It is also supporting some basic research on the ignition phenomenon (University of Paris, Che).

GASTEC has also a large programme, supported by a variety of sources:

◆ R&D projects supported by the Dutch energy distribution companies:

· Fundamental research based on new catalyst formulations, high temperature materials and coating techniques for future applications. This work is carried out in close cooperation with the University of Utrecht.

· Proof of concept of catalytic combustion in a membrane reactor. The principle is to control the reaction rate by diffusion limitation inside a membrane. The membrane is developed in cooperation with the University of Twente.

· Proof of concept of a cooking device based on catalytic combustion. The aim of the project is to show that a closed cooking device with a high efficiency and nearly no NO_x production can be developed.

· Fundamental research in the area of the catalytic partial oxidation of methane to produce hydrogen. This research, in which a few of the basic principles of catalytic combustion are used, is partly undertaken by the Universities of Utrecht and Twente.

The basic knowledge obtained from this work resulted in several spin-off projects. The two main ones, also supported by the Dutch Energy Distribution Companies in combination with the National Government (NOVEM), focus on the catalytic treatment of exhaust gases produced by natural gas engines (NO_x reduction, CH_4 oxidation).

◆ R&D projects supported by the Dutch energy distribution companies and the European Union:

· Catalytic combustion in a sintered metal (high thermal conductivity) reactor with integrated heat exchanger. The aim of the project is to design, construct and test a sintered metal reactor using the catalytic combustion of methane and to develop a mathematical model that will predict the heat conductivity of sintered metals from their basic properties. This project, sponsored by the European Union in the frame of its Joule Programme, involves as partners the University of Stuttgart (Germany), the manufacturer of sintered metal parts Krebsöge

Sintermetalholding Gmbh (Germany), the Politechnica University of Bucharest (Romania) and, as coordinator, GASTEC (the Netherlands).

· Novel compact steam reformer for fuel cells, with heat generated by catalytic combustion, supplemented by induction heating. One of the aims of the project is to reach an ultra low NO_x level by catalytic combustion. This project is also sponsored by the European Union in the frame of its Brite EuRam Programme (# BRE2-CT94-0588) and involves 8 partners, located in five different countries of the European Union:

- GASTEC NV, the Dutch natural gas R&D institute, coordinator of the project.
- EA Technology, a British company involved in R&D for the electricity utilities.
- AEA Technology, a British research institute, working for this project in the field of catalysis.
- BCN, a Dutch company whose main business is the introduction of fuel cells into the market.
- Degussa AG, a German company whose main business is the production of chemicals and the application of precious metals.
- IST, a Portuguese university having a recognised expertise in fluid mechanics, combustion, heat transfer and pollutant formation.
- Powergen, a UK company whose main business is the generation of electricity.
- TGI, a Spanish company whose field of activities lies in the development and marketing of new technology.

5. Prospects for new commercial applications

In recent years, the spectacular growth of natural gas for power generation and the associated new requirements in turbine performances, has given catalytic combustion an exposure that it never had before.

Several turbine manufacturers consider catalytic combustion as the best technology to include in a turbine to ensure low NO_x emissions and stable operation. Two groups have disclosed their activity in that direction. Catalytica, working in collaboration with General Electric and Tanaka KK, has reported obtaining not more than a few ppm of NO_x, CO and unburned hydrocarbons in a multi stage catalytic reactor, operated at flow and pressure conditions typical of heavy frame industrial gas turbines [41]. The temperature of the catalyst is self regulating and multipoint injection of fuel is not mandatory. In cooperation with Catalysts and Chemicals and Kobe Steel, Osaka Gas has applied the high temperature catalytic materials developed at the University of Kyushu by Arai [42] in prototype turbines.

Less spectacular but possibly closer to commercialisation is the introduction of surface stabilised combustion techniques likely to become a determining factor for innovation and a commercial argument for the furnace manufacturers in future years. For these manufacturers, catalytic combustion offers the prospect of ultra low NO_x emission levels, higher efficiency and combustion stability. However, they do not wish to hear that catalyst life, at this moment, does not compare to the furnace average life of ten years or more. If catalysis is to conquer the huge combustion market, it will have to measure up to new challenges.

A good picture of the state of the art in catalytic combustion will develop on the occasion of the third International Workshop on Catalytic Combustion, to be organised in September 1996 in the Netherlands by GASTEC and GDF. The first workshop was organised in 1992 by SRI International in the United States. The second one was organised in 1994 in Japan by the Research Association for Catalytic Combustion of the Catalysis Society of Japan. The worldwide interest in catalytic combustion is clearly evident.

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