

CHAPTER II BACKGROUND AND LITERATURE SURVEY

2.1 Conventional Gas Turbine Emissions

In the commercialized gas turbine engine, the mechanical power, which may be transformed into electricity by means of an alternator, was generated by the expansion of hot combustion gas in the turbine. However, the combustion gas temperature was risen above the maximum allowance for turbine elements. Therefore, the addition of extra air between the combustion chamber and the turbine is required (Thevenin, 2002), as shown in Figure 2.1.

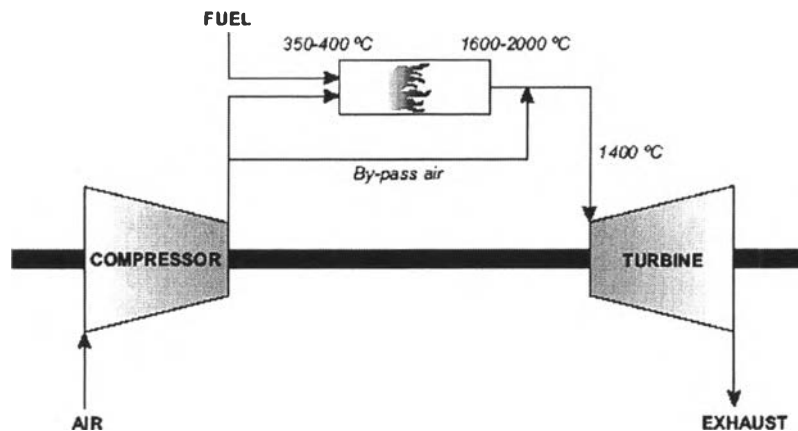


Figure 2.1 Conventional flame combustor in an open-cycle gas turbine (Thevenin, 2002).

The emissions from gas turbines combustion have been divided into two different types. The first one is formed due to incomplete oxidation of fuel, e.g. carbon monoxide, unburned hydrocarbon, while the second one is directly formed during the combustion process, e.g. nitrogen oxide, carbon dioxide, as discussed below:

2.1.1 Carbon Monoxide (CO)

Carbon monoxide is well known as a very highly toxic gas. Even in low amounts, CO may affect human beings by lowering the uptake of oxygen in the blood. Lefebvre (1983) has listed the causes for CO formation in gas turbines as:

- a) Inadequate burning rate in the primary zone due to high air/fuel ratio and/or insufficient residence time,
- b) Inadequate mixing of the fuel and the air, which produces fuel-rich regions as well as fuel-lean regions, yielding inadequate burning rates, and
- c) Quenching of the post-flame products by entrainment with the liner wall-cooling air (bypassing air).

2.1.2 Unburned Hydrocarbons (UHCs)

Unburned hydrocarbons may survive from the combustion zone and emit with the flue gas. These UHCs are well known in their high global warming potential. For the example, methane, which is a major constituent of natural gas, has more global warming potential than CO₂ by a factor of 21 in 100 years, as shown in Table 2.1 (IEA Greenhouse Gas R&D Program, 1998).

The main cause of UHC emission is due to the inadequate combustion in the combustion chamber.

Table 2.1 Comparison of methane global warming potential

	Global Warming Potential and Timescale		
	20 Years	100 Years	500 Years
CO ₂	1	1	1
CH ₄	56	21	6.5

2.1.3 Nitrogen Oxide (NO_x)

Nitrogen oxide consists of typically 95% NO and 5% NO₂. It has a high global warming potential as much as a toxicity to human beings even if it is in low concentrations (Pitchon and Fritz, 1997). Furthermore, NO_x is invoked in the acidification of water and soils as it is transformed into nitric acid.

The main culprit for NO_x emission in gas turbine engines is mostly from the reaction between oxygen and nitrogen in air stream at a highly sufficient temperature, which is called “Thermal NO_x ”. The thermal NO_x will be formed in a large volume at 1500°C , as shown in Figure 2.2.

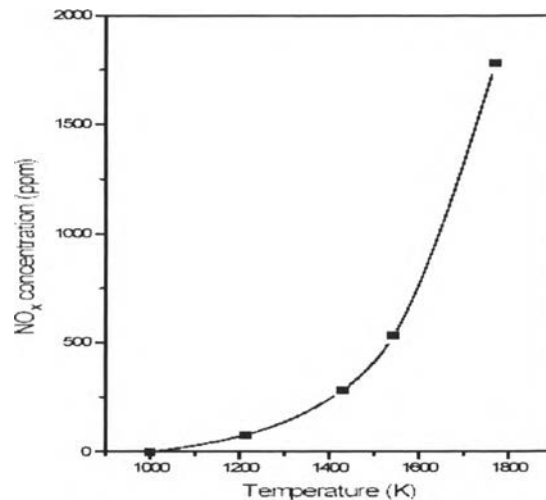


Figure 2.2 Dependence of thermal NO_x equilibrium concentration on temperature (Thevenin, 2002).

2.1.4 Carbon Dioxide (CO_2)

Carbon dioxide is one of the main products from complete combustion of hydrocarbon fuels. This emission is not considered as a pollutant because it is very hard to avoid producing it from the combustion, even if there is an increasing concern about the presence of carbon dioxide in the atmosphere. Its emission may be subject to governmental regulation.

2.1.5 Soot

Soot is a particulate emission from combustion of hydrocarbon fuels. These particles easily enter the lungs of humans and can cause cancer and other damages. Moreover, these particles also deposit at the wall of gas turbine. When such deposits break loose due to vibrations etc., the major damage may be made to the delicate turbine blades. Fortunately, this particulate emission can be avoided by using natural gas instead.

Nowadays, the increasing concern for environmental protection entails more stringent regulations with respect to the above-mentioned pollutants. This requires the development and implementation of a new technology, which can operate at the lowest possible cost without affecting the gas turbine efficiency.

2.2 Low-NO_x Technologies

Several technologies have been or are being developed to reduce the emissions from gas turbine system. Most of studies have paid attention to NO_x reduction since NO_x has a high global warming potential and toxicity to human beings.

The existing method for NO_x control in gas turbine system can be divided into two major categories: primary control technologies (the attempts to avoid the formation of pollutants) and secondary control technologies (the attempts to remove the pollutants from exhaust).

2.2.1 Primary Control Technologies (Vatcha, 1997 and Thevenin, 2002)

2.2.1.1 *Water Stream Injection (WSI)*

This technology is based on the decrease of combustion temperature by injecting water or steam into the combustion zone. Although thermal NO_x is reduced due to the moderate combustion temperature, the emission of CO and UHCs tends to be increased because of incomplete combustion at the quenching spot. The capital cost of WSI technology is moderate, but the operating cost is high due to the requirement on injection of very highly pure water.

2.2.1.2 *Dry Low NO_x Technique (DLN)*

DLN technology needs a specially designed or modified burner, which closely controls air/fuel ratio and other process variables in order to promote the primary zone of lean or rich combustion significantly lowering combustion temperature. However, in the case of rich-burn process, the formation of smoke and soot appears to be a major issue, whereas lean-burn operation entails strong flame instabilities when the power is reduced. The capital cost of DLN technology is ranged from moderate to high, and the operating cost is low.

2.2.1.3 Catalytic Combustion (CC)

The catalytic combustion is a lean-premixed combustion, in which the combustor is stabilized by a catalyst, as shown in Figure 2.3. Fuels-air premixture was burnt, subsequently lowering combustion temperature (typically below 1400°C). This technique can significantly reduce the formation of thermal NO_x from combustion chamber, while keeping the CO and UHC emissions at low level due to the heterogeneous combustion over the catalyst. Moreover, catalytic combustion enables high combustion stability, meanwhile reducing the level of acoustic noise and vibrations. The capital cost of catalytic combustion is quite low since the major re-designing of combustor is not required (the catalysts can be integrated directly to the existing combustion chamber).

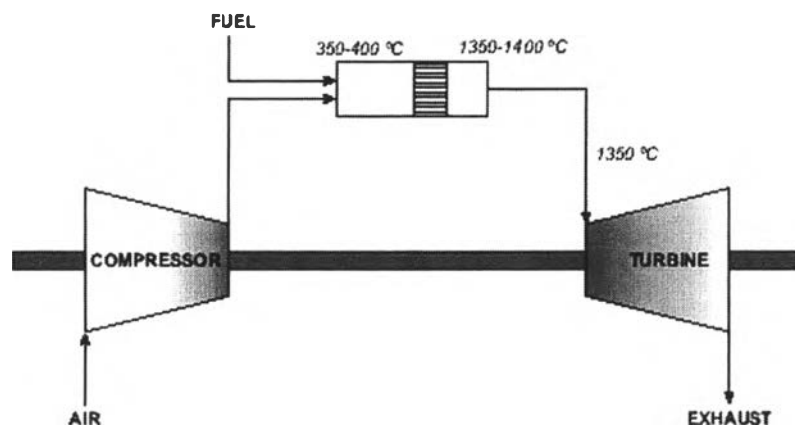


Figure 2.3 Open-cycle gas turbine equipped with a catalytic combustor (Thevenin, 2002).

2.2.2 Secondary Control Technologies (Vatcha, 1997 and Thevenin, 2002)

2.2.2.1 Selective Non-catalytic Reduction (SNCR)

In SNCR system, a reducing agent, typically urea or ammonia is injected into the flue gas in order to react with NO_x to form water and molecular nitrogen within an appropriate temperature window. The capital and operating cost of SNCR is very high due to the high consumption of ammonia.

2.2.2.2 Selective Catalytic Reduction (SCR)

The SCR technology consists of injecting ammonia into the exhaust from gas turbine and passing it through a catalyst bed where the NO_x and

ammonia react to form nitrogen and water vapor. Although the amount of ammonia consumption was reduced three or four times, the capital and operating cost are still high when compared to the primary control technology.

2.2.2.3 Nitrogen Oxide Decomposition

This is an adsorption process that takes place in two major steps. First, the NO and CO (if present) are oxidized over a catalyst to form NO₂ and CO₂, respectively. While NO₂ is adsorbed onto the KCO₃ surface to form potassium nitrate (KNO₂) and nitrates (KNO₃), CO₂ is the exhaust. In a second step, dilute hydrogen is streamed over the surface of adsorbents in order to decompose nitrate species into molecular nitrogen and water.

When considering the above-mentioned technologies for NO_x reduction, only three technologies can reach as low as 10 ppm NO_x concentration: selective catalytic reduction (5-9 ppm), nitrogen oxide decomposition (<2ppm) and catalytic combustion (<3 ppm). Among these technologies, catalytic combustion appears to be the most attractive simplicity and low cost (Dalla Betta, 1997). A comparison between the actual costs of catalytic combustion and other technologies have been published by United State Environmental Protection Agency, as shown in Figure 2.4

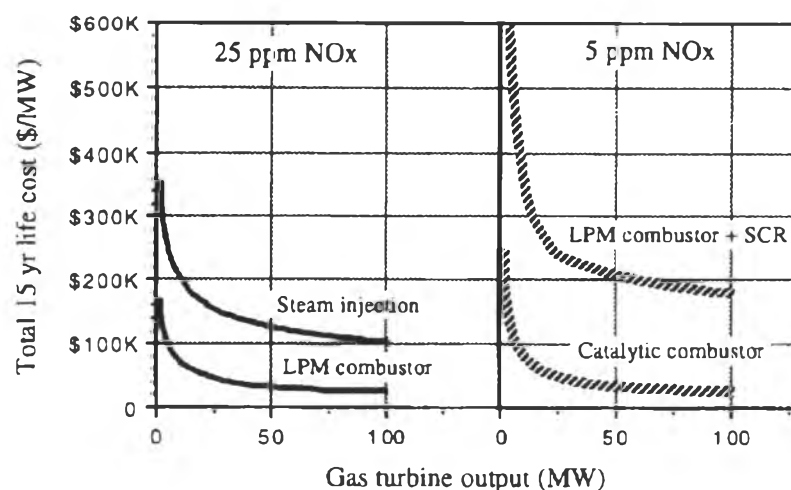


Figure 2.4 Cost comparison of several NO_x control technologies for emission level of 25 and 5 ppm (Dalla Betta, 1997).

2.3 Catalytically Stabilized Combustion (Thevenin, 2002)

Catalytic combustion can be broadly divided into two categories, depending on the catalytic reaction temperature.

2.3.1 Low Temperature Catalytic Combustion (LTCC)

LTCC is used in the temperature range of 300-500°C, aiming to eliminate an abate trace of volatile organic chemicals (VOC's), residual hydrocarbons or other organic compounds in purge-gas or tail-gas stream in chemical and petrochemical processes. Concentrations as low as hundreds of ppm as well as up to 4-6% can be burnt with 99% efficiency.

A typical operation is started by preheating vent or exhaust gases from processes in a heat exchanger. After that, the hot gases are passed over a combustion catalyst in order to burn out the trace of containing hydrocarbons. The clean air exhaust gas is vented out.

Since the combustion is an exothermic, therefore, the heat generated during the process can be fully recovered as a thermal utility source. Some examples of the LTCC integrated with electric power generation system are shown in Figures 2.5 and 2.6.

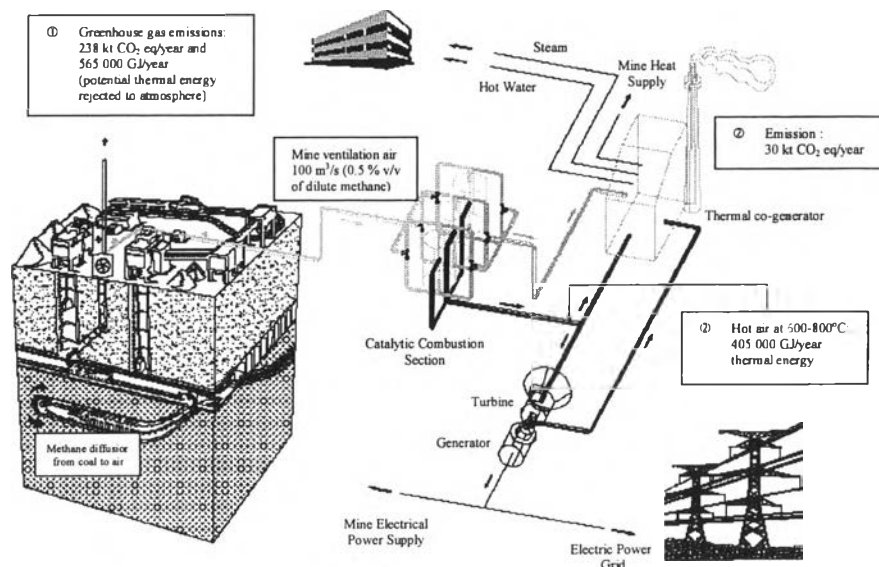


Figure 2.5 The integrated LTCC with electric power plant for the disposal of coal mine ventilation (Sapoundjiew, 1999).

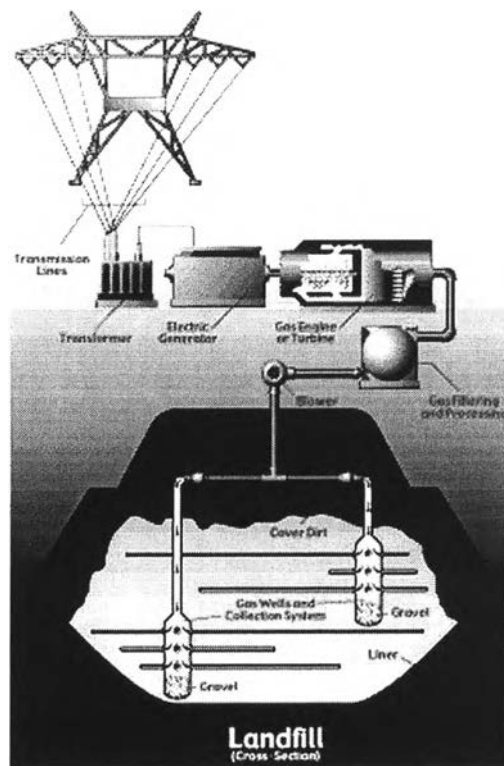


Figure 2.6 The integrated LTCC with electric power plant for the disposal of landfill ventilation (Snapping Shoals EMC, 2001).

Such catalyst systems are nowadays used very commonly to clean effluents from processes for spray painting sheds particularly for automobiles, organic chemical manufacture, natural gas vehicles, etc.

2.3.2 High Temperature Catalytic Combustion (HTCC)

HTCC is used at the temperatures above 500°C. Mostly, HTCC refers to the application in gas turbine combustors. Nevertheless, other applications such as radiant heaters, (compact) reformers and domestic boilers may be included.

For HTCC, the mixture between air and fuel is heterogeneously combusted over a catalyst mainly to produce heat either for direct use or for transformation to electricity or mechanical work, for example in a gas turbine.

The heterogeneous combustion on catalytic surface proceeds with lower activation energy than the homogeneous gas-phase combustion. Hence, complete combustion can be achieved at a much lower temperature than what is possible for homogeneous burning.

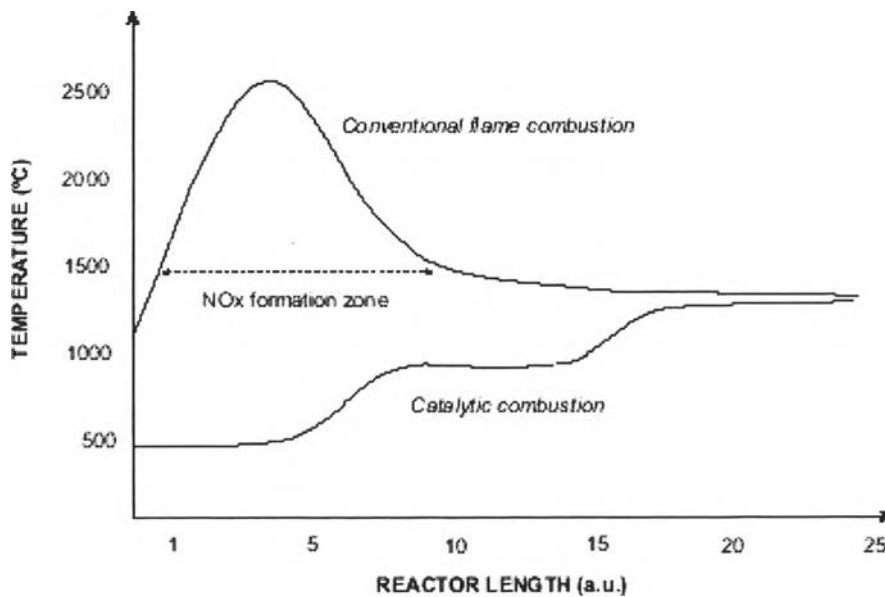


Figure 2.7 Comparison of the temperature profiles of flame combustion and catalytic combustion system (Thevenin, 2002).

Therefore, thermal NO_x , which is the main culprit of emissions from gas turbine system, is reduced by two orders of magnitude, as compared to conventional burners.

Although NO_x formation in HTCC can be reduced, the process still generates the same amount of heat utility as occurred in conventional combustion with outlet temperatures of about 1100-1400°C. No catalytic material has been found to withstand the severe operating condition of such a system. Therefore, the original design concepts, where complete combustion occurs within a catalyst-coated, honeycomb monolith, had to be discarded (Griffin *et al.*, 1995). Different alternative designs were also developed in order to cope with the lack of high temperature resistant materials.

2.4 Catalytic Combustor Designs

The main purpose of these different designs is to limit the operating temperature of the catalyst segment. As previously reported, no single material is available to achieve the gas turbine requirement due to thermal sintering and degradation of the catalyst at high required outlet temperature. Therefore, multistage catalytic combustor systems were developed.

2.4.1 Fully Catalytic Combustion Chamber

This is the first system approached by Osaka Gas Company in Japan (Sadamori *et al.*, 1995 and Sadamosi, 1999). They have designed the combustion chamber with multiple monolithic catalysts. In this design, different materials are used to fulfill different functions within the catalysts.

A palladium catalyst is used as a primary catalyst in order to ignite the catalytic combustion reaction and to raise the temperature, according to their higher combustion activity. After passing through this section, the temperature of stream will be high enough to maintain ignition and complete the combustion in the subsequent less active metal-oxide catalysts. These catalysts are Mn-substituted hexaaluminates.

The advantage of this type of combustor is its simplicity as no secondary fuel or air has to be mixed and no flame has to be anchored. However, the very high temperatures in the final segments as well as the difficulty of controlling the heat releases in the first segments (Ersson, 2003); and, the lower throughput of the system (Sadamori *et al.*, 1999) probably made this design far away from the installation into most of conventional gas turbine applications.

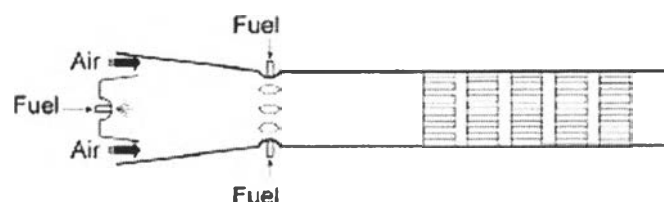


Figure 2.8 The scheme of fully catalytic combustion chamber (Thevenin, 2002).

The new attractive configuration of catalytic combustors is a hybrid and a partially catalytic combustor design. These designs are based on the system that combines a low temperature catalyst section and a high temperature post-catalyst homogeneous reaction section. This system was set up in order to avoid the deactivation of catalysts at high operating temperatures, giving flexibility in the choice of catalytic materials and also providing higher throughputs and high combustor outlet temperatures (Papadias, 2001).

The major obligations of each zone in this catalytic combustion chamber are (Beebe *et al.*, 2000);

- Heterogeneous catalytic combustion zone, which is the zone used to generate high enough outlet gas temperature in order to initiate gas phase homogeneous combustion just downstream of the catalyst exit and stabilize this homogeneous combustion of ultra lean mixtures.

- Homogeneous post-catalyst combustion zone, which is formed to rise up the outlet temperature, and also completes the combustion of the fuel and any remaining carbon monoxide (CO) and unburned hydrocarbons (UHCs) in order to achieve an ultra-low emission. Since fuel and air are mixed in a very lean ratio, so, the maximum temperature reached in this zone can be ensured to be below the thermal NO_x formation temperature.

Based on these concepts, such designs are often referred as a catalytic stabilized combustion.

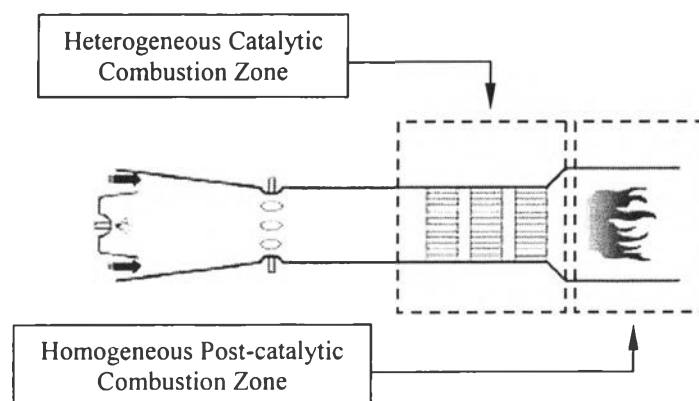


Figure 2.9 The basic scheme of partially catalytic combustor design.

2.4.2 Hybrid Combustion Chamber with Secondary Fuel

In this design, which has been developed by Toshiba in the collaboration with Tokyo Electric Power Company (Ozawa *et al.*, 1999), only part of the fuel is converted heterogeneously on the catalyst and maintained at the temperature below 1000°C. Another part of fuel was bypassed to mix with the downstream gas from the catalyst segment to attain the final combustion temperature. Therefore, the function of catalyst is to be a source of additional pre-heat to support the lean homogeneous downstream combustion.

The major challenges of this combustor system lie in obtaining a good mixing of the fuel at the catalyst exit. A complete mixing is crucial in order to avoid local temperature peaks and hence formation of high NO_x concentrations (Papadias, 2001).

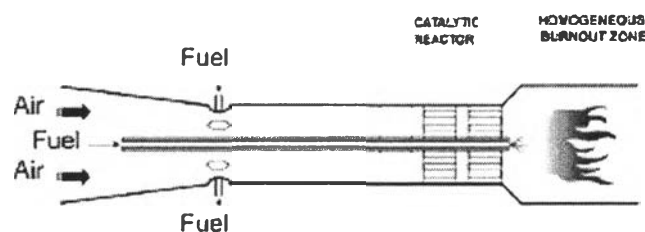


Figure 2.10 The scheme of hybrid combustion chamber with secondary fuel (Thevenin, 2002).

2.4.3 Hybrid Combustion Chamber with Secondary Air

This design has recently been proposed by Lyubovsky *et al.* (2002) based on fuel-rich combustion. They perform the partial oxidation of fuel-rich mixture over a first catalytic segment, so that the temperature increase is within the limits of what the catalyst may endure. After fuel partially combust within catalytic section, secondary air is mixed in a homogeneous combustion zone in order to achieve a complete combustion, which has low emission and rise the outlet temperature to reach the desired final temperature.

The catalyst, in this case, is used to perform a partial oxidation of the fuel, which will both preheat the gas and upgrade the fuel by producing more hydrogen and other easily combustible compounds (Ersson, 2003).

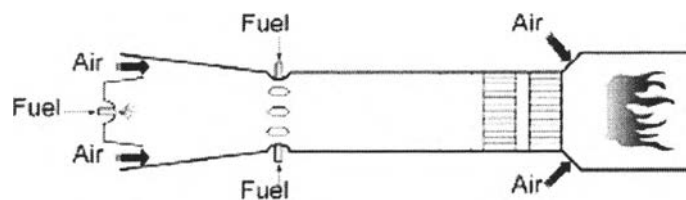


Figure 2.11 The scheme of hybrid combustion chamber with secondary air (Thevenin, 2002).

2.4.4 Partially Catalytic Combustion Chamber with Semi-active Catalyst

This design is based on the same principle as the first two cases described above. Such companies, e.g. Hitachi in Japan, Catalytica Energy Systems, have proposed this concept by localising a different catalysts in a small part of combustor, different catalysts for different zones, and keeping a low adiabatic temperature rise in order to prevent catalyst sintering and degradation (Dalla Betta *et al.*, 1993). Only part of fuel is combusted on catalytic surface and also further homogeneously combusted just downstream of the catalyst section.

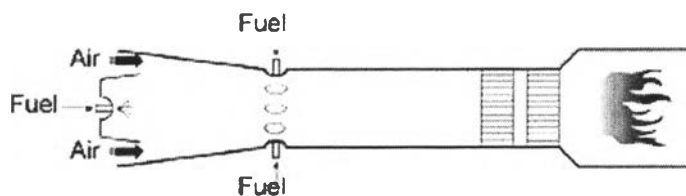


Figure 2.12 The scheme of partially catalytic combustion chamber with semi-active catalyst (Thevenin, 2002).

Such a design has a number of advantages; first, it will be no need for a secondary mixing zone after the last catalytic segment. That means it can be retrofitted to the existed gas turbines (both anular- and can-type combustors), without the need for a major redesign. Moreover, the reacted gas in the passive channels of monolithic catalyst can exchange some heat energy with the active channels and thereby limit the temperature of the catalyst (Ersson, 2003).

Although this design for catalytic combustor has been shown to be beneficial, the commercialization of such design is still restrained by the following factors (Etemad *et al.*, 1999 and Carroni *et al.*, 2002);

a) Fuel/air preheating required for sustaining catalytic activity given at compressor discharge temperatures (a preburner unit is generally required, which results in the NO_x emission no longer significantly below requirement and uneven velocity at the catalyst inlet),

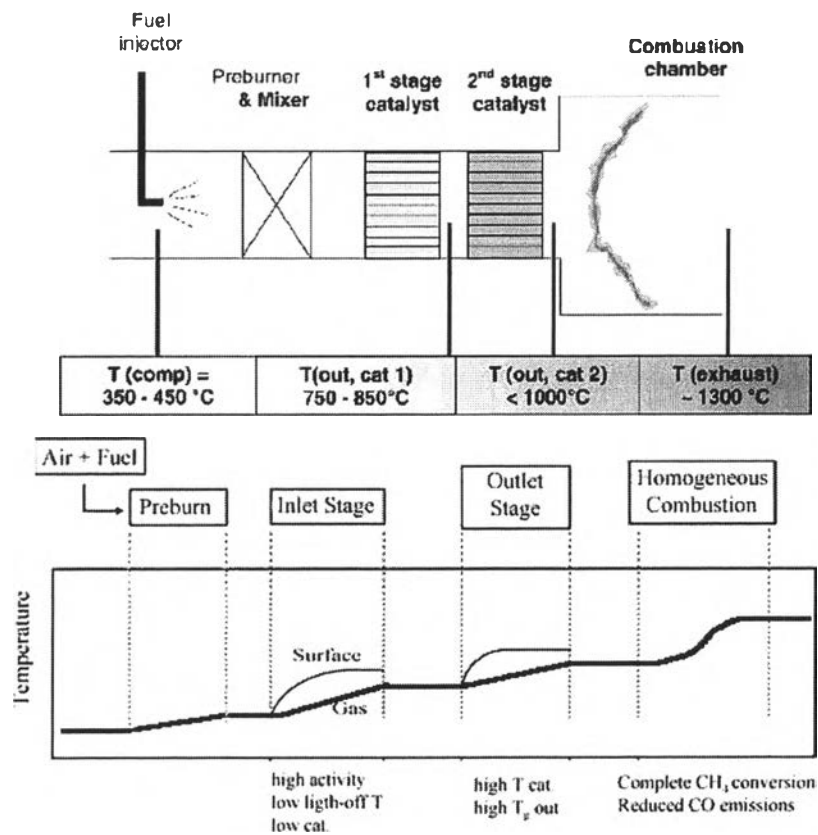


Figure 2.13 Basic scheme and the temperature profile of catalytic combustor integrated with preburner (modified from Carroni, 2002).

b) Turndown limits due to a relatively narrow operating band between minimum required inlet temperature (surface kinetics limited) and maximum survivable catalyst temperature,

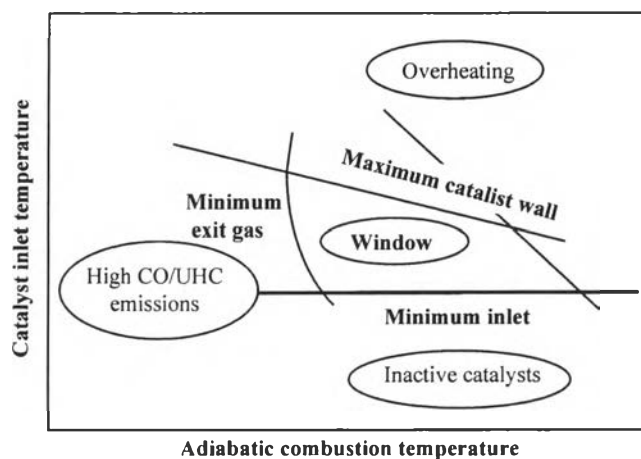


Figure 2.14 Operating window in catalytic combustor (Forzatti, 2000).

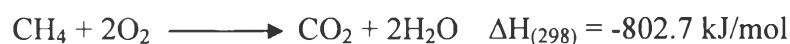
c) Uniform fuel/air mixture required to avoid catalyst substrate meltdown as a result of localized rich zone operation, and

d) High pressure drop associated with conventional catalytic combustion systems because a long monolith is required to convert all of the fuel/air mixture to products.

2.5 Methane Catalytic Combustion

The catalytic combustion or complete catalytic oxidation of methane has been extensively studied as an alternative to conventional thermal combustion in decade since methane is the major constituent in natural gas (Anderson *et al.*, 1961; Trimm, 1983; Baldwin and Burch, 1990 and Farrauto *et al.*, 1992). This method was shown to be effective in producing energy in a gas turbine combustor as well as reducing emission (Gélin and Primet, 2002).

Catalytic combustion involves multi-steps on catalytic surface. The combustion mechanism of methane may be represented by the equation:



This is a gross simplification, since the actual reaction mechanism involves many reactions. The possible reaction mechanism for methane catalytic oxidation was proposed by Lee and Trimm (1995) illustrated in Figure 2.15.

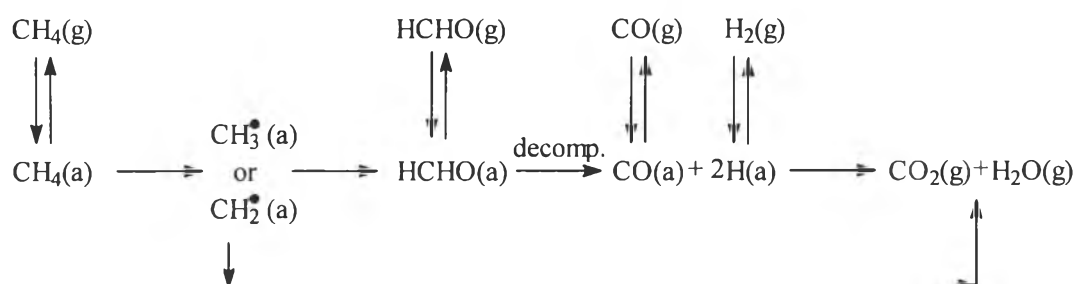


Figure 2.15 A possible mechanism for methane catalytic oxidation: (a) adsorbed, and (g) gas phase.

It is generally known that the activity of catalytic combustion is followed the temperature dependence shown in Figure 2.16 (Eguchi and Arai, 1996). In the low temperature region, the surface reaction over a catalyst enhances the conversion exponentially with a rise in temperature. In medium temperature region, however, the increase in catalytic activity is suppressed on the account of mass-transfer limited. At high temperatures, the conversion rises up very sharply and the gas phase radical combustion proceeds concurrently with the surface reaction. The sharp rise in conversion is the characteristic of the gas phase homogeneous reaction.

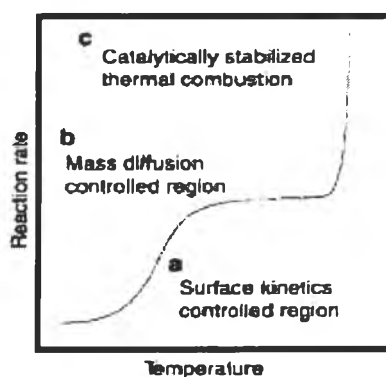


Figure 2.16 Temperature dependence of overall reaction rate in catalytic combustion.

Therefore, the conversion-temperature curve from the experiments will follow this trend and also represent in the “S” curve.

2.6 Methane Combustion Catalysts

There is very challenging for researcher to find a suitable material for using in catalytic combustion since the operating condition can be varied during operation. The best catalyst should remain high sufficient activity under all of these conditions, and its activity should be recovered when the severe conditions departed.

For a straggly combustor, three different temperature zones with different demands on the catalyst materials can be determined;

a) The low-temperature catalyst, which is the first section, that confronts with the compressed stream. This catalyst segment is expected to ignite the fuel at the compressor outlet temperature (usually 350-550°C, depending on the gas turbine). Therefore, this catalyst has to be highly active and moderately tolerate to the compressed stream conditions from the compressor. The materials mostly used for this segment are noble metals, such as Pd and Pt, which are also employed in this study.

b) The mid-temperature catalyst, which is the secondary catalyst used for further ignition the hot gas, and stabilization of the lean premixed aims to lower the combustion temperature. This catalyst segment has to be active in the temperature range between 500 and 1000°C, depending on the inlet temperature. Therefore, the high temperature resistant materials are desired and implied to the use of hexaaluminate materials.

c) The high-temperature catalyst, which is the last section for catalytically combusting the fuel, is used to increase the flue gas temperature and completely combust it before sending to turbine. Therefore, the catalyst has to be extremely stable at the severe condition. However, a high catalytic activity and a large surface area are rapidly lost at this severe condition, and the overall reaction rate will be mass-transfer limited.

For a fully catalytic design, all of these catalytic segments have to be presented in the combustion chamber, while only first two segments are required in the hybrid and partially catalytic combustion design.

Catalysts which are able to perform combustion may be divided into two groups: noble metals for which the reaction may start at the ambient temperature, and

transition metal oxides (such as hexaaluminates and perovskites), which have more high temperature resistance, but are usually also less efficient (Muller *et al.*, 1996; Widjaja *et al.*, 1999 and Sekizawa, 2000). Some catalysts have been tested for the methane combustion activity, as shown in Table 2.2.

Table 2.2 Methane oxidation rate on various metals and oxides at 400°C, 1 atm, and with the feed composition of 2% methane in air (Vatcha, 1997 and Betta, 1997)

Catalyst	Surface area (m ² /g at ~100°C)	Specific Rate	
		× 10 ⁻⁷ mol·m ⁻² ·s ⁻¹	× 10 ⁻⁷ mol·g ⁻¹ ·s ⁻¹
Pd/Al ₂ O ₃	2	140	300
Pt/Al ₂ O ₃	1	50	50
Co ₃ O ₄	3	4.4	13
La _{0.5} Sr _{0.5} CoO ₃	6	1.2	7
Cu/La//Al ₂ O ₃	80	0.09	7
Sr _{0.8} La _{0.2} MnAl ₁₁ O ₁₉	70	0.045	3
LaCoO ₃	3	0.36	1

Palladium (Pd) supported alumina was reported to be the most active species in the ignition and stabilization of methane combustion (Anderson *et al.*, 1961; Griffin and Weisenstein, 1995), when operated under oxidizing atmosphere (Briot and Primet, 1991). It was found that the oxide form of Pd (PdO) had more activity to oxidize methane than the metallic form (Pd). The results were confirmed by Robeiro *et al.* (1994) that the Pd sites on catalyst had very low or no activity. Moreover, the results also showed that only clusters of PdO were active while some dispersed forms were not.

Two different forms of PdO were suggested to have a higher combustion activity when compared with its dispersed form. The thin layer of PdO covered on metallic Pd core was observed to be the active layer for methane combustion by Oh *et al.* (1991), while the PdO dispersed on metallic Pd cluster was suggested by

Datye *et al.* (2000), as shown in Figure 2.17. On the other hand, the dispersed form of PdO on Al_2O_3 was also reported to have a low combustion activity as well.

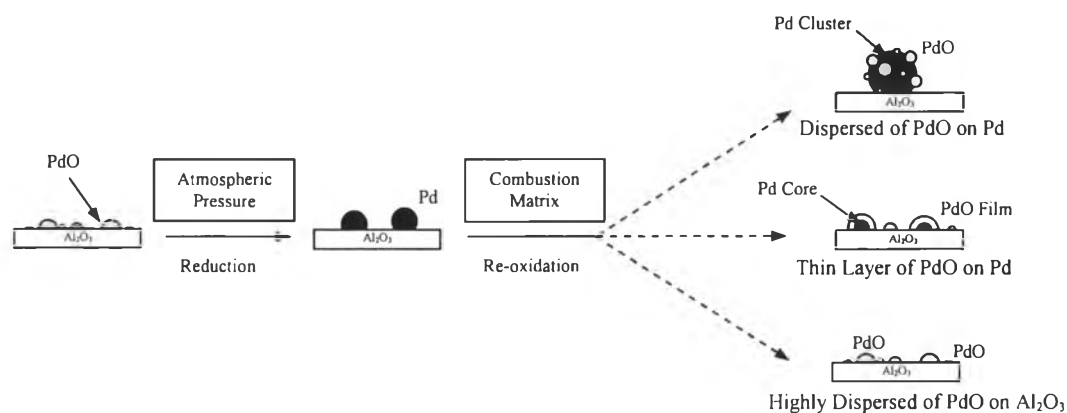


Figure 2.17 Possible models of palladium and palladium oxide on Al_2O_3 .

The main disadvantage of using Pd is its activity was easily deteriorated with small amount of sulfur in fuel, such as natural gas (Hoyos *et al.*, 1993).

Since platinum (Pt), rhodium (Rh) and ruthenium (Ru) are well known on their susceptibility sulfur tolerance. The additions of these compounds into Pd based catalyst were also investigated. It was found that, the addition of Ru and Rh can enhance the sulfur tolerance of Pd based catalyst (Ryu *et al.*, 1999) while the addition of Pt can also enhance both catalytic activity and sulfur tolerance (Narui *et al.*, 1999; Sadamori, 1999; and Ersson, 2003).

Another disadvantage of using Pd to catalytically combust methane gas has been found within a temperature range of 500 to 1000°C. Farrauto *et al.* (1992) found that PdO supported on alumina rapidly lost oxygen at about 800°C. When the similar temperature cycle was made in CH_4/air mixture, the methane oxidation activity above the PdO decomposition temperature was found to be the same as that of the bare alumina support (Salomonsson *et al.*, 1995). This result was insisted that metallic Pd was inactive. Therefore, the decomposition of PdO during combustion becomes an important drawback for using Pd supported catalyst in a sufficient high temperature (above 800°C) and also for using this material in the uneven operating conditions, which is the combustion in gas turbine.

Increasing the PdO dissociation temperature by strengthening the Pd-O bond through metal support interaction has also been applied to prevent loss of activity at high temperatures (Farrauto, 1995), but resulted in lower combustion activities in the lower temperature region. Enhanced metal-support interactions have been achieved by incorporation of additives.

The first way is by adding some metals into a solid support, such as Mn, Ni or some rare earth elements. For example, Sekizawa *et al.* (1996) found that the Mn-promoted supports gave a higher temperature resistance since the activity dropping at 800°C was not observed. However, the activity seemed to be lower than unpromoted catalysts at low temperatures. On the other hand, Ni-promoted- Al_2O_3 support was found to exhibit an overall increase in activity as well as to eliminate the drastic drop at high temperatures (Sekizawa *et al.*, 1996). Other types of modified alumina, e.g. Ba, La, Ce or Mg promoted- Al_2O_3 , were observed to improve the catalytic activity at high temperatures, and the significantly improved catalysts were found (Arai, 1991; Widjaja *et al.*, 1999 and Yang *et al.*, 2002). Some of these elements, e.g. La, has more advantage since they can retard the transformation of alumina phase that results in the surface area and activity depressing.

The uses of other supports were investigated for their effect on the thermal stability. For example, SiO_2 synthesized by sol-gel method was found to importantly enhance thermal stability of supported Pd (Lopez *et al.*, 1992). SiC (Méthivier *et al.*, 1998) and Si_3N_4 (Méthivier *et al.*, 1999) represented interesting support material giving the greater resistance to thermal sintering. TiO_2 and CeO_2 were thus shown to induce a sharp increase in the temperature of PdO decomposition (ca. 130°C) with respect to Al_2O_3 . These were concluded to increase the temperature domain for which PdO was stable, compared to Al_2O_3 or ZrO_2 (Gélin and Primet, 2002). Perovskites and hexaaluminates were also included in this area.

Another attractive way to improve the thermal stability is by using the Pd based bimetallic system. Addition of rare earth oxides has also been found useful for the stabilization of PdO against decomposition. For example, Kennelly *et al.* (1993) has presented examples in which the addition of La, Ce or Pr to PdO/ Al_2O_3 resulted in increases of the decomposition temperature. In the recent year, Kennelly *et al.* (1999) has patented the use of some rare earth elements (Ce, La, Nd and Sm) in Pd-

based binary oxide system. The claims were Nd and La can increase the onset decomposition temperature of PdO, when used in the active ingredients. Ozawa *et al.* (2003) found some afterwards encouraging result that both La (from La_2O_3) and Nd (from Nd_2O_3) has a high potential to prevent the transformation of PdO to Pd as well as prevent the reduction of active sites, by distraction the growth of PdO particles, in the reaction.

Nowadays, multi-metals catalysts were frequently used in many kinds of industry. They normally have the advantage over monometallic catalysts of being more selective, and having more lifetime and broader range of operating condition under which the catalyst can be used. For example, Ledwich and Su (2001) have investigated the use of precious metals (Pt, Pd and Rh) in the six different ingredients. But, the results have not been published since the conventional methodologies were used, and many parameters, e.g. catalyst types, space velocity, pressure, temperature, were concerned.

In order to use these catalysts in the real gas turbine application, their catalytic activity has to be investigated under the real or simulated operating conditions of commercialized gas turbine. Kikuchi *et al.* (2003) has performed some experiments under the simulated conditions and found that Pd/SnO₂/ceramic honeycomb monolith, that has a very good activity for abating methane in exhaust stream, can convert only 20% of methane when used as a low-temperature catalyst in gas turbine operating conditions. However, the complete combustion of methane to carbon dioxide was still observed. Therefore, this is still an ongoing challenge to test the other catalysts under the real or simulated conditions.

The method of catalyst preparation is also a very important influence on the activity of catalyst. Several studies have reported that catalysts pretreated under reducing conditions had a higher steady state activity than those pretreated under oxidizing atmospheres (Baldwin and Burch, 1990; Lee and Trimm, 1995 and Müller *et al.*, 1997).

Due to the cost of noble metals, it is important to know how much loading of catalyst on the support gives the highest activity. Lee and Trimm (1995) have reported on the effects of noble metal loading for Pt and Pd catalysts. Below 1.4 wt% Pt loading, the oxidation rate was nearly constant whereas at above 1.4 wt%, the rate increased with Pt loading up to about 5 wt%, and decreased as the loading was increased above 10 wt%. Sekizawa (2000) also studied the effect of metal loading on Pd catalyst, and reported that the highest activity for methane oxidation was 8.7 wt% loaded when using $\text{Pd}(\text{CH}_3\text{COO})_2$ as a precursor. Most of studies were performed with a fine powder of Pd supported alumina; however, the effects of metal loading need to be investigated under the real used situation, which is Pd supported on γ -alumina washcoated monolith.

2.7 Combinatorial Approach

The Combinatorial approach aims at the discovery and study of new materials that combines high-speed chemical synthesis, high-throughput screening and high-capacity information processing to create, analyze and interpret large numbers of new and diverse material composition (McFarland and Weinberg, 1999).

Holzwarth *et al.* (2001) suggested that this combinatorial approach might be viewed as two complementary methodologies: primary and secondary screening.

Primary screening deals with the systematic exploration of combination of elements, for the preparation of multicomponent materials, in order to discover the new lead formula. Typical screening techniques for primary screening are scanning mass spectroscopy and infrared thermography, but can be gas chromatography and selective gas sensor in many cases.

Secondary screening targets the optimization of already-existing formula from primary screening. The main characteristic of this screening is the association of high throughput preparation and evaluation of materials under the conditions that are as realistic as possible. This screening can be achieved by employing continuous flow parallel microreactor with identification of reaction products.

2.8 High Throughput Screening

High throughput methodologies become more and more attractive way for screening catalyst formulations nowadays since they can remove the bottleneck of conventional approach. The allowance for testing a large number of catalysts at the same time also had been developed. The first generation of high throughput has launched in pharmaceutical field, and has been extended to optimization of material in early part of the 20th century (Senken, 2001).

Many different types of reactor can be applied for catalyst testing, and it is primary importance to select the proper reactor configuration to obtain the required information. Several overviews of test reactors and recommendations for a proper reactor selection in the laboratory as well as in an industrial application have been published (Pérez-Ramírez *et al.*, 2000).

The advantage and drawbacks of frequently used laboratory reactor types were reported by Kapteijn and Moulijn (1996), as shown in Table 2.3.

Table 2.3 Summary of relative reactor ratings (Kapteijn and Moulijn, 1996)

Aspect	Reactor Type						
	PFR		CSTR			Batch	
	Differential Fixed bed	Integral Fixed bed	Riser	External recirculation	Internal fluid recirculation	Spinning Catalyst basket	Internal fluid recirculation
1.Ease of use	H	H	H	M-H	M	L-M	M
2.Ease of construction	H	H	L	M	M	L-M	M
3.Cost	L	L	H	L-M	M-H	M-H	M
4.Sampling and analysis ease	M	H	L	H	H	H	M
5.Approach ideal type	H	H	M	H	M-H	L-M	H
6.Fluid-catalyst contact	H	H	M	H	M-H	L-M	H
7.Isothermicity	H	M-H	H	M-H	H	M	H
8.Temperature measurement	H	H	H	H	M-H	L	H
9.Kinetics	H	H	M	M	M-H	L-M	M
10.Deactivation noticed	H	H	L	M	M	M	L
11.Gas-liquid-solid use	L-M	M-H	L	M-H	M-H	M	H

(L: Low; M: Medium; H: High)

Based on these guidelines and on general requirements for catalyst testing, the fixed-bed reactor is applied in the multi-flow channel technology.

The basic principle of eight-flow reactor used in this work was modified and further developed from the system designed by Pérez-Ramírez *et al.* (2000) as shown in Figure 2.18. Three difference sections can be distinguished: gas mixing section, reactor section and analysis section.

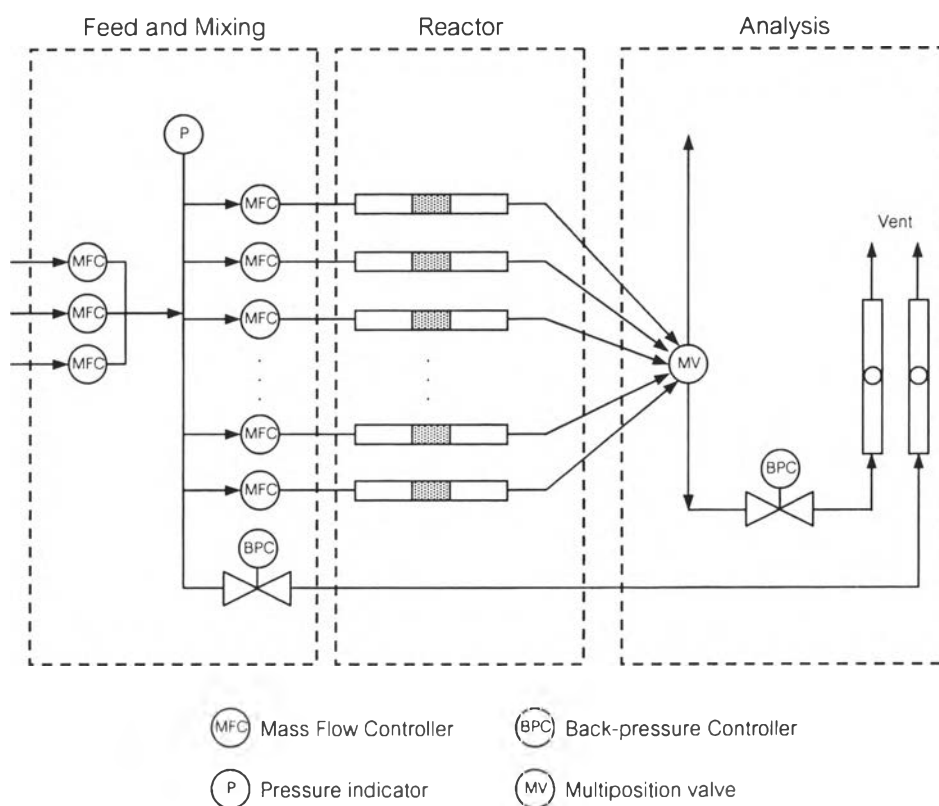


Figure 2.18 Basic schematic flow-sheet of the multi-flow reactor system for fast catalyst screening and kinetics studies (modified from Pérez-Ramírez *et al.*, 2000).

The concept of multi-flow system has been successfully applied in catalyst testing and kinetic studies. Some studies and developments with six-flow reactor were summarized by Pérez-Ramírez *et al.* (2000) as listed in the Table 4.

Table 2.4 Utilization of the six-flow technology in catalyst development: screening and kinetic studies (Pérez-Ramírez *et al.*, 2000)

Process	Catalytic System	Product Analysis
CO oxidation	Cu/Cr/activated carbon	} GC NO _x -analyzer
NO _x reduction with CO	Cu/Cr/activated carbon	
	Cu/Cr/ γ -Al ₂ O ₃	
Water shift reaction	Cu/Cr/activated carbon	
NO _x reduction with ammonia	Cu/Cr/activated carbon	} MS
	Mn oxides/activated carbon	
	Mn oxides/ γ -Al ₂ O ₃	
	Modified activated carbon Mn ₂ O ₃ -WO ₃ / γ -Al ₂ O ₃	
Soot oxidation	Ag/Mn/ZrO ₂	} NDRI HC-analyzer
	Cu-V/ Al ₂ O ₃	
	Cu/K/Mo/(Cl)/ ZrO ₂	
	Cu/K/Mo/(Cl)/ TiO ₂	
	Cu/ZrO ₂	
	Mo/ ZrO ₂	
	V/ ZrO ₂	
	Cs ₂ MoO ₄ -V ₂ O ₅	
	CsVO ₃ -MoO ₃	
	Cs ₂ SO ₄ -V ₂ O ₅	
Chlorofluorocarbon (CFC) hydrogenolysis	[Rh, Ru, Re, Pt, Pd, Ir]/ activated carbon	} GC NO _x -analyzer
	Pd/ activated carbon	
	Pd-zeoliteY	
	Pd-mordenite	
N ₂ O decomposition	Calcined hydrotalcites (Co, Pd, La, Rh)	} GC NO _x -analyzer
	[Fe, Co, Rh, Rd]-ZSM-5	
NO _x reduction with hydrocarbon	Pt/Al ₂ O ₃ Pt-ZSM-5	
Fischer-Tropsch synthesis	Co-zeoliteY Co/SiO ₂	} GC

GC: Gas Chromatography; NO_x: Nitrogen Oxides; MS: Mass Spectrometer; HC: Hydrocarbon
NDIR: Non-Dispersive InfraRed.

2.9 Reactor Types

A number of reactor types for catalytic combustion exist. These include the honeycomb monolith reactor, packed bed reactors, fluidized bed reactors, and membrane reactors (Ledwith and Su, 2001).

The frequently used is honeycomb monolith type since its outstanding characteristic of very low pressure drop at elevated mass throughput (which is necessary for high space velocities), high geometrical area (also asset where diffusion is limiting), and mechanical strength (Climino *et al.*, 2001; Heck *et al.*, 2001). Monoliths consist of structure of parallel channels with wall coated by a porous support with catalytically active particle (see Figure 2.19). The disadvantage of this type of reactor is that it is essentially an adiabatic reactor, so, control of temperature is difficult.

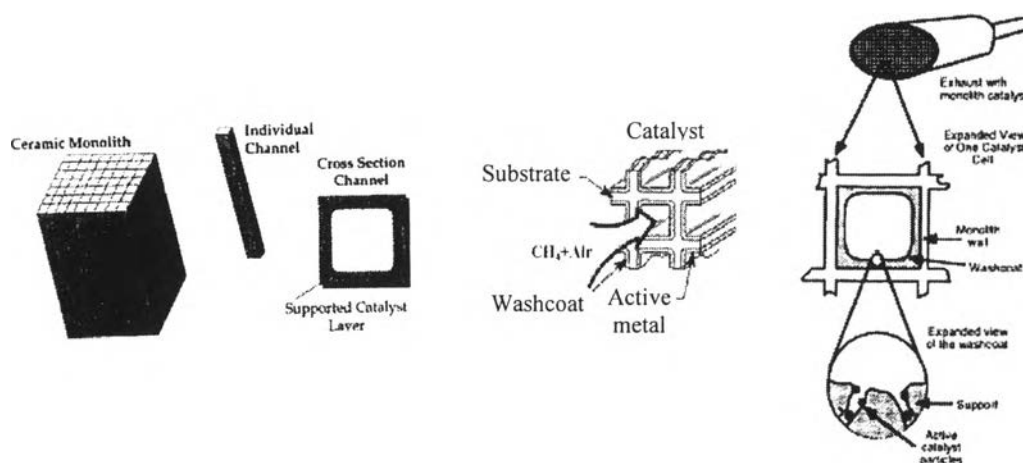


Figure 2.19 Illustration of monolith reactor (Geus and Giez-en, 1999; Ledwith and Su, 2001).

Fluidized bed reactors have a very good heat transfer properties, however, they are not suitable for small installations (Ledwith and Su, 2001). The large pressure drop over the reactor is a large disadvantage, especially when dealing with high flow rate. In the classic packed bed reactor, as compared fluidized bed reactors, the pressure drop for large flow rate is also a disadvantage.

Membrane reactors have been investigated by Neomangus *et al.* (2000) for using in a catalytic system. However, the maximum specific heat power generated may be too low, and it is not proven to be able to be used economically in this application.

In this study, palladium, platinum and lanthanum were employed as the active elements to perform the catalysts in various compositions in the low-temperature section of a hybrid designed combustor. Gamma-alumina washcoated monoliths were employed as catalyst support. The effects of calcination step, loading amount and using all elements in mono-, bi-, and tri-element were also investigated with a multi-flow reactor developed from high-throughput screening concepts, aiming to identify the lead formulations of methane combustion catalysts.