

**POROUS CERAMIC/ZEOLITE IN ENGINE EXHAUST
TREATMENT**

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ABSTRACT

Stricter regulations enforcement by many countries has led to utilization of catalytic converters to treat exhaust emission. Commercial catalytic converters use honeycomb monolith structure with uniform-sized and parallel channels. However, ceramic open cell foam has received particular attention and has been proposed as an alternative structure as a substrate in catalytic converters. This porous ceramic/zeolite combines interconnecting channels to promote radial mixing and enhance turbulence together with zeolite; microporous solid known as molecular sieve with the ability to absorb molecules based on size exclusion process. Most current research is focused on the synthesized zeolite and its coating on the surface of ceramic foam. This project focuses on developing and testing porous ceramic/zeolite to treat emissions from petrol engines. It involves of three major tasks: preparation and characterization of alumina and natural zeolite (clinoptilolite) in producing porous ceramic/zeolite filter. Second and third task involve experimental and numerical work in determining pressure drop characteristics and its effects on engine performance for cars and motorcycles application. Under task 1, sample preparation of alumina and zeolite are using two methods: casting and polymeric sponge. The purpose is to determine appropriate alumina loading and sintering profile of the sample. The sintered porous ceramic bodies are characterized by their physical and mechanical properties i.e. flexural strength, hardness, porosity and density. The samples which can meet requirement in engine exhaust system are selected to be tested further. Under task 2, determination of pressure drop characteristics using blower facility is conducted for different configurations of filters for motorcycles and cars application. It uses digital pressure manometer to measure pressure drop, pitot probe to determine air flow rate and K-type thermocouple for air temperature. In numerical analysis, it uses Computational Fluid Dynamics (CFD) to predict the pressure drop and to conduct laboratory studies for validation and actual application test of several configurations. Task 3 includes engine performance test which involves several parameters i.e. power, torque, engine speed, exhaust temperature and filter temperature conducted

using a chassis dynamometer under several different configurations of porous ceramic/zeolite filter. These tests are performed on both motorcycle and car. In all performance tests, gas analyzer is used to determine emissions of hydrocarbon (HC) and carbon monoxide (CO) before and after installation of filter in the system. Results presented here are focused on system performance of the porous ceramic/zeolite filter ability to reduce emissions without affecting engine performance. In terms as emission, it is observed that reduction of emission typically ranged from 25 % to 60 % without affecting power and torque of the engine. Based on the results obtained, porous ceramic/zeolite has indicated its advantages by reducing emissions from gasoline engines without affecting overall engine performance.

ABSTRAK

Penguatkuasaan peraturan lebih ketat yang dikenakan oleh kebanyakan negara untuk mengawal pencemaran yang berpunca dari asap ekzos kenderaan telah menyebabkan peningkatan penggunaan penukar bermangkin. Penukar bermangkin komersil ini kebanyakannya mempunyai struktur monolit sarang lebah dengan saluran yang selari dan bersaiz seragam. Bagaimanapun, sejak kebelakangan ini, penggunaan busa sel terbuka seramik telah menerima perhatian khusus dan telah dicadangkan sebagai satu struktur alternatif substrat dalam penukar bermangkin. Seramik/zeolite berliang ini menggabungkan saluran berstruktur kompleks untuk menggalakkan pencampuran dan peningkatan aliran gelora di dalam substrat. Apabila digabungkan struktur berliang ini dengan molekul zeolite, proses penapisan molekul gas akan berlaku mengikut saiz yang tertentu. Disebabkan faktor ini, kebanyakan penyelidikan terkini lebih terarah kepada sintesis zeolite yang disadur pada permukaan busa seramik. Namun begitu, projek ini lebih memberi fokus pada kaedah penghasilan seramik/zeolite berliang yang sesuai untuk merawat pencemaran dari enjin petrol. Ia melibatkan tiga tugas utama: persediaan dan pencirian alumina dan zeolite semulajadi (clinoptilolite) dalam menghasilkan penapis seramik/zeolite berliang. Tugas kedua adalah ujian penapis pada kenderaan untuk menentukan kesannya pada prestasi enjin kereta dan motosikal. Tugas ketiga melibatkan simulasi kejatuhan tekanan dan penentuan ciri-ciri kejatuhan tekanan. Dalam penyediaan sampel alumina dan zeolite, ia menggunakan dua kaedah iaitu tuangan dan polimerik span. Tujuannya ialah untuk menentukan kandungan alumina yang bersesuaian dan profil persinteran sampel. Persinteran badan seramik berliang ini dihasilkan dan diuji ciri-ciri fizikal dan mekanikal seperti kekuatan lenturan, kekerasan, keliangan dan ketumpatan. Sampel yang telah mengikut keperluan dalam sistem ekzos enjin dipilih untuk diuji selanjutnya. Di bawah tugas 2, penentuan ciri-ciri kejatuhan tekanan menggunakan eksperimen dijalankan untuk konfigurasi penapis

berlainan bagi motosikal dan kereta. Manometer tekanan digital untuk mengukur kejatuhan tekanan, tiub pitot untuk menentukan kadar aliran udara dan tolok pengukur suhu jenis K untuk suhu udara turut digunakan. Dalam analisis berangka, Computational Fluid Dynamics (CFD) digunakan untuk meramalkan kejatuhan tekanan manakala eksperimen digunakan untuk pengesahan dan hasil ujian aplikasi sebenar dari beberapa konfigurasi. Tugasan 3 termasuk ujian prestasi enjin yang melibatkan beberapa parameter seperti kuasa, tork, kelajuan enjin, suhu ekzos dan suhu penapis menggunakan dinamometer rangka di bawah beberapa konfigurasi berlainan untuk penapis seramik/zeolite berliang. Ujian ini dilaksanakan pada motosikal dan kereta yang menggunakan petrol. Dalam semua ujian prestasi, penganalisis gas digunakan untuk menentukan penyebaran dari hidrokarbon (HC) dan karbon monoksida (CO) sebelum dan selepas pemasangan penapis pada sistem. Keputusan yang ditunjukkan lebih terarah pada prestasi sistem penapis seramik/zeolite berliang untuk mengurangkan pencemaran tanpa memberi kesan pada prestasi enjin. Kajian ini mendapati bahawa berlaku kesan pengurangan pencemaran dari 25% hingga 60%. Berdasarkan keputusan yang diperolehi, seramik/zeolite berliang ini telah menunjukkan kelebihan dengan mengurangkan pencemaran dari enjin gasolin tanpa memberi kesan kepada prestasi keseluruhan enjin.

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CHAPTER 1

INTRODUCTION

1.1 Introduction

Incessant increase of vehicles all over the world has contributed to the serious issues due the emitted exhaust gases from the engines. Most countries have adopted continuous stringent emission regulation and enforcing the use of catalytic converter. Since then, exhaust after treatment technology has evolved and becomes one of the effective method in pollutant abatement. In the catalytic converter, platinum, palladium and rhodium have been widely used as catalysts in lowering the activation energy of chemical reaction without changing its characteristic while maintaining the performance of vehicle.

Catalytic converter is a device used to reduce the toxicity of emission from an internal combustion chamber. The involvement of ceramics in the automobile industry is far ranging. A typical unit consists of either a ceramic honeycomb monolithic structure or ceramic beads coated with precious metals. Catalysts for combustion application may be supported on a variety of materials, e.g. pellets, honeycomb monoliths, parallel plates, fibre pads and sintered metals.

Monolithic honeycomb carriers have found a large application field in the environmental area, because of their pressure drop. They did not manage, however, to penetrate the industrial production owing to some limitations such as the poor heat

transfer and lack of radial mixing. In the last few years monolithic ceramic or metal foam came increasingly in attention as a new type of low-pressure drop carries. Based on the very particular structure and morphology of foams there is much hope regarding a better tradeoff between the low-pressure drops, characteristic of honeycomb carries.

The converter in the exhaust system produces pressure drop that has an immediate and counteractive effect on engine performance and fuel economy. This pressure change is related to the frictional loss across the honeycomb matrix, created by the cell wall thickness and cell pitch. Reducing the pressure drop is a function of increasing the open frontal area and creating larger cells, which the thinner wall configurations. The high filtration efficiencies of wall-flow filters are obtained at the expense of a relatively high pressure drop, which increases with the filter soot load. Under steady-state engine conditions the pressure drop build up in a wall-flow monolith depends on the loading of the soot.

Ceramics can be considered as inorganic, nonmetallic materials and can be crystalline or amorphous (glassy). Ceramic compounds are formed between metallic and nonmetallic element such as aluminum and oxygen (alumina- Al_2O_3), calcium and oxygen (calcia- CaO), and silicon and nitrogen (silicon nitride- Si_3N_4). Porous ceramics are brittle materials with closed, fully open, or partially interconnected porosity. It's application is widely accepted in many fields including catalysis, filtration, impact absorbing structures, high specific strength materials, biomechanical implants and high efficiency combustion burners.

Zeolites are the aluminosilicate members of the family of microporous solids known as molecular sieves which refers to the ability to selectively absorb molecules based primarily on a size exclusion process. Zeolites represent a commercially important branch of advanced ceramic catalytic materials. Widely used as ion-exchange beds in water purification, molecule separation, catalysts and known for its potential in separation of specific gases. More than 150 zeolites have been synthesized and 48 naturally occurring zeolites are known. Clinoptilolite is one of the naturally occurring zeolite used in this study.

1.2 Objective

The objective of this research is to develop a porous ceramic/zeolite filter for the treatment of exhaust gases (particularly hydrocarbon and carbon monoxide) from a gasoline engine.

1.3 Scope

- (a) Develop, characterize and testing the physical properties of various different composition of the filter.
- (b) Determination of pressure drop characteristics of various configurations using blower facilities.
- (c) Application and testing of the filter on vehicles (car and motorcycle).
- (d) Measuring the emission and engine performance data from the tested vehicles.
- (e) Simulations of pressure drop prediction using Computational Fluid Dynamics (CFD).

1.4 Problem statement

Engine exhaust treatment requires a catalytic converter to reduce the harmful emissions from the gasoline and diesel engines. Two commercial types of the catalyst supports are ceramic honeycomb monolith and metallic foil (Bode, 2002). Alternative structures have also being proposed by the researchers including 'Microlith' and porous ceramic/ceramic foam (Bardhan, 1997). Zeolite had also being used as a hydrocarbon trap to enhance the performance of the catalytic converters including the synthetic zeolite (ZSM-5, Y-type, beta zeolite) and natural zeolite (Bode, 2002). Researchers had already fabricated ceramic foam coated with zeolite without the addition of binder materials. Another work was on the usage of zeolite impregnated with the catalyst and incorporated on the ceramic honeycomb. It

was tested on the diesel exhaust system and shows the reduction efficiency between 30-90% (Majewski & Khair, 2006).

However, most of the research focused on the synthesized zeolite and the effects of the zeolite coating on the substrate surface during the investigation of the performance for the ceramic filter. Therefore, this research will focus on the application of natural zeolite into the alumina substrate with the addition of organic binder and pore former to produce porous ceramic.

In order to be used in the exhaust system, several requirements need to be fulfilled by porous ceramic filter i.e i) low pressure drop ii) low light off temperature iii) high conversion efficiency. Pressure drop is strongly related to the porosity of the filter. A range of 76-86% porosity with pore size between 40 μm to 100 μm has been successfully obtained by the used of yeast as a pore former from previous research in the production of silicon carbide/natural zeolite porous ceramic (Patcas *et al.*, 2007).

Two essential criteria in the development of emission filter for automotive application are pressure loss and conversion efficiency. Pressure loss is a critical high back pressure which will reduce the engine performance while conversion efficiency is related to the surface area for reaction to occur. On the other hand, higher surface area increases pressure due to friction. Therefore, both criteria need to be balanced to fulfill its function as an exhaust gas filtration mechanism with affecting engine performance. Previous experiments conducted revealed that the develop porous ceramic/zeolite filter has an acceptable pressure drop characteristic but the work is costly, time consuming and limited to few configurations only. Thus, the current study aims to obtain the pressure drop characteristic and associated parameters of the filter with various configurations through CFD prediction, with validation from experimental work.

1.5 Rationale of study

This research is expected to contribute in the application of alternative substrate structure i.e. ceramic foam. It focuses on the preparation of the porous ceramic/zeolite filter with the various porosities to be tested on the stationary gasoline engine. It also looks into the potential of natural zeolite mixed with the

alumina and it is expected to improve the performance of the exhaust filter especially in treating hydrocarbon and carbon monoxide. The performance of the porous ceramic filter is tested on the stationary gasoline engine in the exhaust system. Experimental parameters including the measurement of the pressure drop, temperature and exhaust gas concentration at the inlet and outlet of the porous ceramic filter. This ceramic filter is expected to produce very economical yet capable to maintain the pressure drop in emission system which improved engine performance especially for torque and brake power. Porous ceramic/zeolite filter could hopefully reduce the air pollutant problem of automotive industry in Malaysia.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

This chapter presents the theoretical background and previous research related to porous ceramics and its application on the exhaust system. It discusses on the material development using ceramics with porous structure, vital parameters in automotive application and its related application on car and motorcycles. In addition, application of numerical analysis in this area is also presented.

2.2 Material development

Ceramics are classified as inorganic and nonmetallic materials that are essential to our daily lifestyle. In general, the properties of most ceramics are hard, wear-resistant, brittle, refractory, thermal insulators, electrical insulators, nonmagnetic, oxidation resistant, prone to thermal shock and chemically stable. Ceramic materials can be subdivided into traditional and advanced ceramics. Traditional ceramics include clay-base materials such as brick, tile, sanitary ware, dinnerware, clay pipe, and electrical porcelain (Inderscience, 2008). Advanced materials technology is often cited as an enabling technology, enabling engineers to design and build advanced systems for applications in fields such as aerospace, automotive, and electronics.

Depending on their method of formation, ceramics can be dense or lightweight. Typically, they will demonstrate excellent strength and hardness properties. However, they are often brittle in nature.

Alumina is the most cost effective and widely used material in the family of engineering ceramics, offering excellent electrical insulation properties together with high hardness and good wear resistance but relatively low strength and fracture toughness. Alumina has a high melting point, high hardness and high mechanical strength. Due to the relatively large coefficient of thermal expansion, thermal shock resistance is reduced. Alumina is an electrically insulating material, with a high electrical resistivity, increasing with purity. Good chemical stability of alumina, leads to a high corrosion resistance. It is insoluble in water and only slightly soluble in strong acid and alkaline solution (Inderscience, 2008 and Ganesh *et al.*, 2001). With an excellent combination of properties and an attractive price, it is no surprise that fine grain technical grade alumina has a very wide range of applications.

Alumina is the most common commercial material for an emission control catalyst washcoat; because of their excellent thermal stability and wide range of chemical, physical and catalytic properties (Ganesh *et al.*, 2001). It is characterized as catalytic materials, by very high purity. Alumina or aluminum oxide (Al_2O_3) family consist more than a dozen well-characterized amorphous or crystalline structures, which vary over wide range of surface area, pore size, distribution size and surface acidity. The structures and properties of alumina depend on its preparation, purity and thermal treatment history. Alumina has played a critical role in the development of durable high-temperature catalytic converters for emission control of automobiles (Ganesh *et al.*, 2001). Alumina also reactive with sulfur compounds, which has to be addressed during development of diesel catalysts (Inderscience, 2008).

The word "zeolite" was first used by Swedish mineralogist Axel Cronstedt that discovered zeolite in 1956 (Schilling *et al.*, 1983). In recent years, zeolites have been increasingly used for diesel emission control, both as catalysts and absorbers (hydrocarbon traps in diesel oxidation catalysts). There are two types of zeolite; natural and synthesis zeolite. Zeolites occur naturally as minerals and are extensively mined in many parts of the world (Inderscience, 2008). They are structurally unique in having cavities or pores with molecular sieve (Orton, 2007) as part of their crystalline structure. In the natural zeolite structure, the net negative

charge within the symmetrical voids hold the cations for the Cation Exchange Capacity (CEC). Ion exchangeable ions, such as potassium, calcium, magnesium and sodium, the major cations, are held electronically within the open structure (pore space); up to 38% void space.

Commercially available natural zeolites are usually of the clinoptilolite (clino) variety which is known chemically as hydrated sodium calcium aluminosilicates. Clino's unique crystalline structure and extraordinary properties are presented in Figure 2.1, regardless of the particle size (Orton, 2007).

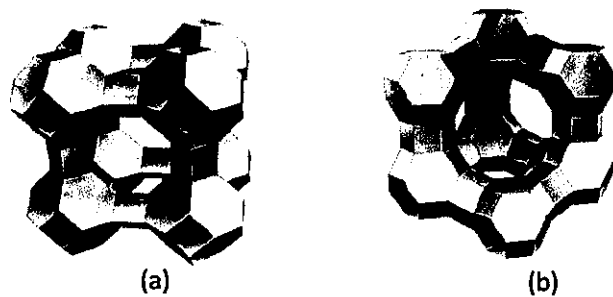


Figure 2.1: Zeolite molecular sieve (a) type A and (b) type X (Inderscience, 2008)

2.3 Porous body

Pores are a typical micro structural feature of ceramic materials. Their origins can differ widely. They can result from incomplete sintering process when firing temperature is too low or the firing time is too short. Pores can also occur when gas develops in a body which is already dense. Degassing pores are the result of incorrect processing. High-temperature stresses also lead to diffusion processes, which in turn promote the formation of creep pores. Closed and open pores are an important feature of ceramic materials (Washington Education, 2007).

They exert a strong influence on chemical resistance, strength, thermal conductivity, modulus of elasticity, and thermal shock characteristics. In characterizing a ceramic, it is important to determine not only its total porosity, but also the pore types, pore shapes, pore sizes and pore size distribution that are present. As the closed pore structure, this is a material in which the pathways or channels are

blocked and do not provide the fluid a continuous and interconnected network of channels to connect one surface of the material to an opposing surface. An open pore structure denotes a material that permits a fluid to move from one surface to an opposing surface in the material through a convoluted pathway of interconnecting networked channels. Soil moisture ceramics are an example of an open pore structured material (Grenn *et al.*, 1989).

The interest of porous ceramic has increased currently with new processes and new applications. Porous ceramic has traditionally been used for thermal insulation purposes and as building materials. Porous ceramics are produced within a wide range of porosities and pore sizes depending on the application intended. Some of the applications of porous ceramics are column work, moisture retention curves, solution extraction or tension measurement, pore water interface, filter or drains and aerators. In two steps sintering the sample is first heated at a higher temperature, where the pores between the aggregate and agglomerates are eliminated and a fast grain growth is observed, then cooled at a lower temperature with longer dwelling time until it is fully dense without further grain growth (Accuratus Corporation, 2007). In Figure 2.2, it shows the effect of fraction porosity on the value of modulus of rupture.

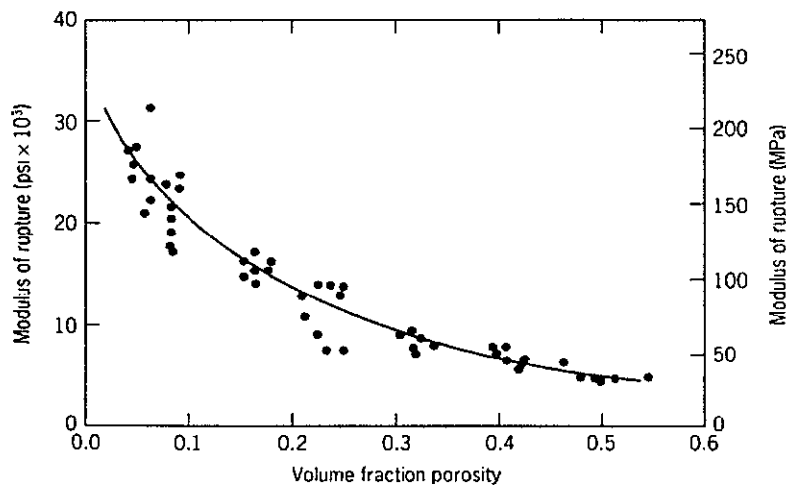


Figure 2.2: Effect of fraction porosity on the value of modulus of rupture (Accuratus Corporation, 2007)

Since the porosity of a ceramic is highly correlated with its mechanical properties, reducing the number of defects in a ceramic is a common way of increasing its strength. The most common way of lowering a ceramic's porosity is sintering. During sintering a ceramic material is heated in a furnace or oven where it is exposed to high temperatures. These temperatures depend on the material; they will always be below the melting point of the ceramic. During the sintering process pores in the ceramic will close up as seen in the Figure 2.3.

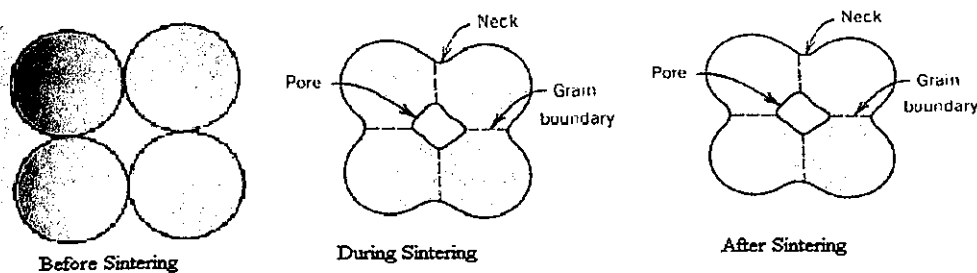


Figure 2.3: Sintering effects on porosity (Accuratus Corporation, 2007)

2.4 Catalytic Converter

Catalysis plays a prominent role in our society. The majority of all chemicals and fuels produced in the chemical industry have been in contact with one or more catalysts. Catalysis becomes also progressively more important in environmental pollution control. The three-way catalyst effectively reduces pollution from car engines. Catalytic processes to clean industrial exhaust gases are currently developed and installed. In short, catalysis is vitally important for our economies now and it will be even more important in the future (Majewski & Khair, 2006)(Hayes & Kolaczowski, 1997).

A modern catalytic converter, based on platinum group metals deposited on a ceramic honeycomb base or monolith, was patented in 1965. However the industrial used of catalysts was then dominated by catalysts deposited on pellet or bead support (Bode, 2002). In pellet beds, attrition is a problem (Bode, 2002) (Bartholomew &

Farrauto, 2006) as a result of pellet motion during use and pressure drop is higher compared to honeycomb structures.

A ceramic honeycomb substrate has been an integral part of automotive emission technology for the past 20 years. The honeycomb substrate gets its name from the array of parallel channels or cell that creates the look of a honeycomb. The converter in the exhaust system produces pressure drop that has an immediate and counteractive effect on engine performance and fuel economy (Bode, 2002).

Catalyst substrates coated with the active catalyst washcoat are packed in steel housing to form catalytic converter as shown in Figure 2.4 (Majewski and Khair, 2006). Catalytic converters are used for the control of carbon monoxide (CO), hydrocarbon (HC), and NO_x emission from vehicles that run on unleaded fuel (Hayes & Kolaczowski, 1997).

A catalytic converter is a unique emission-control device. It is designed for the sole purpose of decreasing exhaust emissions level. The catalysts use a monolithic construction that thinly coated by certain "precious metal" such as platinum, palladium, and rhodium. The two main types of catalytic converters: oxidation catalysts (or two-way catalysts) and three-way catalysts (Hollembek, 2006).

There are two-way converters: monolith and palletized. Both perform the same function; the difference is in its design. The monolith design uses a honeycomb of small ceramic passageways coated with a thin layer of platinum and palladium as catalysts. Palletized converters use a bed of aluminum oxide pellets coated with platinum and palladium (Hollembek, 2006).

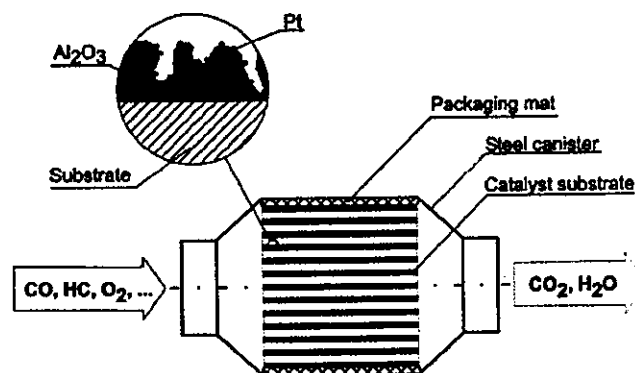


Figure 2.4: Schematic of catalytic converter (Majewski & Khair, 2006)

2.4.1 Physical properties of catalyst

Surface area, pore size, pore distribution, and pore volume are among the most fundamentally important properties of a catalyst (Bartholomew and Farrauto, 2006). The geometrical surface area (GSA) of the catalytic converter substrate is determined by cell density, cell shape and converter volume (Majewski & Khair, 2006) (Hayes & Kolaczkowski, 1997)(Bode, 2002)(Bartholomew and Farrauto, 2006) (Hans Bode, 1997). The size and number of pores determine the internal area. It is usually advantageous to have high surface area (high density of small pore size) to maximize the dispersion of catalytic component (Bartholomew and Farrauto, 2006) (Keane, 2003) (Bartholomew & Farrauto, 2006)(Patcas *et al.*, 2007). Thus, pore structure and surface area must be optimized to provide maximum utilization of active catalytic sites for given feedstock (Bartholomew and Farrauto, 2006).

Pore distribution is an important characteristic of porous catalysts where pores of diameter in excess 50 nm are considered macropores, those less than 2nm are term micropores and pores of intermediate size are donates mesopores (Hayes & Kolaczkowski, 1997)(Keane, 2003). The pore size distribution is an important factor in controlling diffusion of reactants within catalyst pore network. It is an essential characteristic property of catalyst. Pore distribution varies considerably for different catalysts and supports (Bartholomew and Farrauto, 2006).

2.4.2 Ceramic substrate

The ceramic systems consist of a ceramic substrate, an intumescent mat and a metallic outer shell. The mat is used to provide sufficient radial pressure on the substrate to compensate for the increased gap due to shell expansion and preserve substrate integrity against engine and chassis vibration. If high temperatures are applied to the converter, the expansion of the outer shell is higher than the thermal expansion of the ceramic substrate. Depending on the material, at mat temperature above 750°C, the mat reduces its canning pressure due to the material specific behavior. This associated with a decrease of the pre-stress on the ceramic substrate. The geometrical surface area (GSA) of the catalytic converter substrate is determined by the cell density, cell shape and converter volume (Hans Bode, 1997).

The interest in porous ceramics has increased concurrently with new processes and new applications. Porous ceramics have traditionally been used for thermal insulation purposes and as building materials. At present, applications such as filters, catalyst supports and membranes are rapidly growing in the global markets especially in environmental aspects. Porous ceramics are produced within a wide range of porosities and pore sizes depending on the application. Ceramic applications in catalysis are divided into two categories: (1) direct use as catalysts and (2) use as support materials (substrates) to anchor and disperse a variety of active metals.

2.4.3 Honeycomb monolith

Monoliths are structures that contain various types of interconnected or separated channels (straight, wavy or crimped) in a single block of material (e.g. honeycombs, foams or interconnected fibres) as in Figure 2.5. The channels of the most common honeycomb monoliths normally have circular, square or triangular cross-sections.

In the case of the square-channel monolith, the monolith geometry is fully defined by two parameters: channel size (d_h) and either wall thickness (w) or cell density (n), which is defined by as number of cell per square inch (psi). Among these parameters, channel size and shape affect the pressure drop across the channel and the hydrodynamics of the fluid phases (Hans Bode, 1997).



Figure 2.5: Ceramic monolith in variety of shapes (Hayes & Kolaczkowski, 1997)

The monolith or honeycomb reactor is a commonly used configuration in catalytic combustion as depicted in Figure 2.6. It consists of a number of parallel passageways through which the gas flows, with the catalysts being located on the channel walls. Major advantages of monolithic supports include high geometric surface area per unit volume (compactness), large open frontal area (low-pressure

drop) (Majewski & Khair, 2006) ; and excellent attrition resistance (Majewski & Khair, 2006) (Hayes & Kolaczowski, 1997) (Hans Bode, 1997). (Bartholomew and Farrauto, 2006).

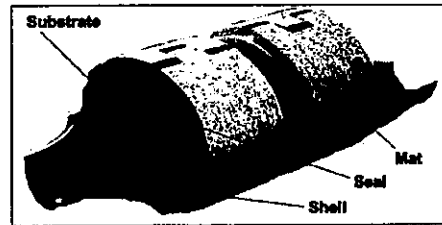


Figure 2.6: Ceramic monolith configuration (Majewski & Khair, 2006)

2.4.4 Ceramic foam

Ceramic foams are used commercially for filtration of molten metals, and attracting increasing attention as catalyst support due to high thermal stability, high porosity and capable to maintain pressure drop with respect to honeycombs.

Ceramic foams, sometimes referred to as reticulated ceramics are three-dimensional cellular structure in which the cells are connected by open windows giving high porosity of the order of 80-90 % void space as shown in Figure 2.7. Ceramic foam possess certain advantages compared with honeycombs; a much wide range of shape and the porosity which improves reactant mixing and favor surface reactant; and radial transport within the monolith is significantly improved.



Figure 2.7: Ceramic Foam (Patcas *et al.*, 2007)

2.4.5 Pellets in a Packed or Fluidized Bed

Many of the early automotive catalytic converters in the 1970s utilized pellet or bead-shaped supports. A volume of spherical particle (pellets) made of gamma-alumina, 2.5 to 5 mm in diameter, was placed into a steel shell and contained between two screens to form the catalytic converter. The noble metal catalysts were incorporated into the pellets (Majewski & Khair, 2006).

Normally, the application of pellets shape catalysts is popular in the chemical industry. The pellet structure is normally highly porous providing a large internal surface area on which the catalysts is dispersed (Hayes & Kolaczkowski, 1997). In gas phase combustion applications, there are two types of pellets configuration which is a fixed bed and a fluidization bed as shown in Figure 2.8 and 2.9. The gas flow through the channels between the pellets and reactants diffuse into the porous structure of the pellets where the catalytic reactions take place (Hayes & Kolaczkowski, 1997).

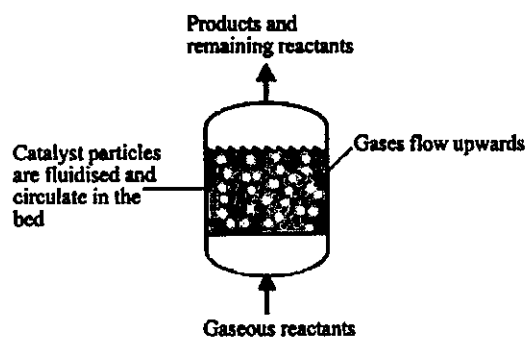


Figure 2.8: A Fluidization Bed Catalytic Reactor (Hayes & Kolaczkowski, 1997)



Figure 2.9: A Fixed bed Catalytic Reactor (Hayes & Kolaczkowski, 1997)

Particulate size distribution influences the packing of particulate catalysts in fixed-bed reactors and thus affects such process parameters as flow rates, reactant-catalyst contacting, temperature control and pressure drop, all of which influence product distribution. Large catalyst particle sizes favor low pressure drop but may not utilize contacting feed with catalyst (Hayes & Kolaczkowski, 1997) (Bartholomew and Farrauto, 2006) resulting in bypass. However, decreasing the size of particles to utilize the maximum contact surface between a gas and solid will increase the pressure drop.

Pellet catalysts (as in Figure 2.10) had several disadvantages including high-pressure drop and gradual catalyst loss due to attrition (Majewski & Khair, 2006) (Hayes & Kolaczkowski, 1997) (Bode, 2002) (Bartholomew & Farrauto, 2006). This is the reason for shortcomings of pellets supports. However, the pellet supports manage to penetrate the industrial production due to their heat transfer and radial mixing (Patcas *et al.*, 2007).

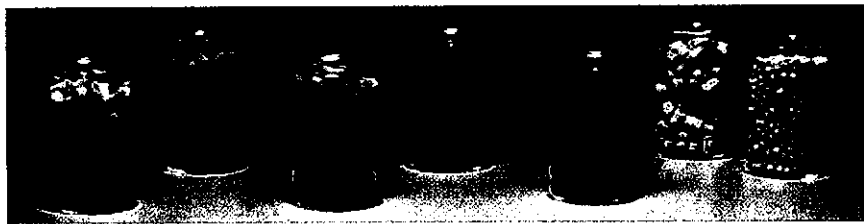


Figure 2.10: Examples of Catalyst Pellets with Various Shapes and Sizes (Hayes & Kolaczkowski, 1997)

2.5 Pressure Drop

2.5.1 Pressure Drop in Monolithic Substrate

The converter in the exhaust system produces pressure drop that has an immediate and counteractive effect on engine performance and fuel economy. This pressure change is related to the frictional loss across the honeycomb matrix, created by the cell wall thickness and cell pitch. Reducing the pressure drop is a function of

increasing the open frontal area and creating larger cells, which the thinner wall configurations, such as the 6 mil/400 cpsi substrate, can accomplish (Bode,1997).

The high filtration efficiencies of wall-flow filters are obtained at the expense of a relatively high pressure drop, which increases with the filter soot load. Under steady-state engine conditions the pressure drop buildup in a wall-flow monolith depends on the loading of the soot. Initially, the filter is clean and its pressure drop is at the ΔP_{clean} level. As the particulates start depositing within the pores in monolith wall, the pressure drop starts increasing with time in a nonlinear manner (Majewski & Khair, 2006).

After the filtration capacity of the pores becomes saturated, soot starts depositing as a layer inside the inlet monolith channels. The permeability and porosity of the monolith walls and soot layer can be assumed constant during this stabilized loading period (Majewski & Khair, 2006).

The pressure drop (as in Figure 2.11) of the clean filter (Diesel Particulate Filter) can be divided into three components (Majewski & Khair, 2006) (Konstandopoulos *et al.*, 2001)

- Pressure drop due to sudden contraction and expansion at inlet and outlet from the filter, $\Delta P_{\text{in/out}}$
- Pressure drop due to channel wall friction, ΔP_{ch}
- Pressure drop due to wall permeability, ΔP_{wall}

$$\Delta P_{\text{clean}} = \Delta P_{\text{in/out}} + \Delta P_{\text{ch}} + \Delta P_{\text{wall}} \quad (2.1)$$

The pressure drop of particulate loaded filter, $\Delta P = \Delta P_{\text{in/out}} + \Delta P_{\text{ch}} + \Delta P_{\text{particulate}} + \Delta P_{\text{wall}}$. The equation for pressure drop due to permeability of particulate layer, $\Delta P_{\text{particulate}}$ is same as ΔP_{wall} yet, replacing wall parameter with soot layer parameter (Majewski & Khair, 2006).

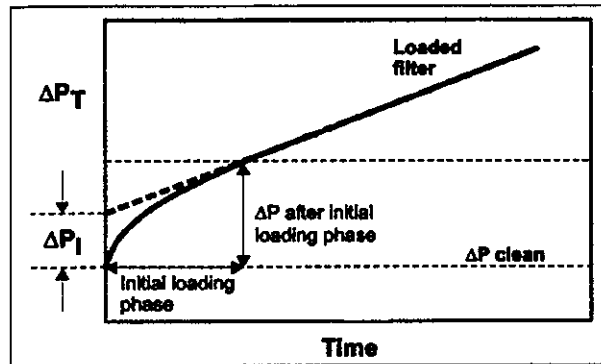


Figure 2.11: Pressure Drop Regimes (Majewski & Khair, 2006).

2.5.2 Catalyst Pressure Drop

The total pressure drop across the a catalyst substrate is a sum of three component: (1) pressure drop in a channels, ΔP_{ch} , (2) pressure loss at the channel entrance, ΔP_{in} , and (3) pressure loss at the channel exit, ΔP_{out}

$$\Delta P = \Delta P_{ch} + \Delta P_{in} + \Delta P_{out} \quad (2.2)$$

The channel inlet and exit losses are associated with the contraction and expansion of gas at the inlet and outlet catalyst face, respectively. The channel pressure drop is the most significant component in the total catalyst substrate pressure drop. The channel portion of substrate pressure drop is directly proportional to the gas flow rate. The inlet and outlet pressure drop contributes increase with the square of flow rate.

The frictional pressure drop of exhaust gases in substrate channels can be calculated using the Darcy equation (Majewski & Khair, 2006) (Bartholomew & Farrauto, 2006).

$$\Delta P_{ch} = 4f \left(\frac{L}{d_{ch}} \right) \frac{\rho v^2}{2} \quad (2.3)$$

The hydraulic diameter, d_h is used instead of d_{ch} for noncircular channel cross sections. The gas velocity, v , can be calculated as follows:

$$v = \frac{W}{\rho \cdot A_F} \quad (2.4)$$

The exhaust gas flow, which is always laminar inside channels, can be turbulent or transitional when outside of the catalyst substrate. The flow can be measured by Reynolds number, Re :

$$Re = \frac{v d_{ch} \rho}{\mu} \quad (2.5)$$

The laminar flow Fanning friction factor can be calculated as follows:

$$f = \frac{K}{Re} \quad (2.6)$$

The magnitude of K depends on channel cross section (Stratakis *et al.*, 2002). Few experimental data have published that relate specifically to catalyst substrate due to the inlet and outlet pressure losses insignificant in total catalyst pressure drop. The inlet and outlet pressure losses are likely to be influence by test equipment (Patcas *et al.*, 2007)(Stratakis *et al.*, 2002).

At a constant catalyst substrate volume, the exhaust gas pressure drop depends on the cell density, open frontal area, and substrate cross section (aspect ratio). The pressure drop increases with increasing cell density and with decreasing open frontal area. Therefore, substrates with thin walls, which yield high OFAs, are desirable to minimize catalyst pressure drop. The pressure drop can also be minimized by shortening the catalyst and increasing its cross-sectional surface area. This approached, however, is limited adverse effect on flow distribution, space constraints, and problem with canning of the monolith.

2.5.2.1 Inertial Filter Wall Pressure Losses

The pressure drop during flow through a porous filter wall for low velocities is governed by Darcy's law (Stratakis *et al.*, 2002). Pressure drop in the wall, ΔP_{wall} , is typically the most significant contribution to the total pressure drop. However, in substrate with long channels of small hydraulic diameter, the channel contribution (ΔP_{ch}) may also be significant. The pressure drop effects of inlet contraction and outlet expansion are small (Stratakis *et al.*, 2002).

2.5.2.2 Contraction and Expansion Losses

The pressure drop also developed due to inlet contraction and outlet expansion. Reasonable estimates of these additional pressure drop contributions are necessary for accurate predictions of overall filter pressure drop. For single sudden contraction of the flow, the pressure drop is given by Bardhan (1997);

$$\Delta P_{\text{contraction}} = \xi_{\text{cont}} \frac{\rho U^2}{2} \quad (2.8)$$

where ξ_{cont} is a constant that varies with the area contraction ratio and the Reynolds number. For the sudden expansion losses is given by

$$\Delta P_{\text{expansion}} = \left(1 - \frac{A_{\text{open}}}{A_{\text{total}}}\right)^2 \frac{\rho U^2}{2} = \xi_{\text{exp}} \frac{\rho U^2}{2} \quad (2.9)$$

Other researchers cite the following expression for the contraction losses (Bardhan, 1997).

$$\Delta P_{\text{contraction}} = \frac{1}{4} \frac{\rho U^2}{2} \quad (2.10)$$

and for the expansion losses

$$\Delta P_{\text{expansion}} = 1.098 \frac{1}{2} \rho U^{1.919} \left[\left(1 - \frac{A_{\text{open}}}{A_{\text{total}}} \right) \right]^{1.919} \quad (2.11)$$

2.5.3 Pressure Drop in Pellets Supports

2.5.3.1 Particle size and shape

In industrial processes, the shapes of the particles or pellets are irregular in spherical. Therefore, the solution to characterized the shape of particles and obtain the relevant and suitable value is the sphericity. The shape of the particle that non-spherical is measured by 'sphericity', ϕ (Kiricsi *et al.*, 1999)

$$\phi = \frac{\text{surface area of a sphere of the same volume as the particle}}{\text{surface area of the particle}} \quad (2.12)$$

2.5.3.2 Surface area of particles in a bed

The advantage of particulate beds for carrying out gas-to-solid reactions is the potentially very large surface area of solid which exposed to the gas. The surface area of a single, non-spherical particle, a_i , of sieve size d_i is given by (Kiricsi *et al.*, 1999);

$$A_s = \frac{6V_s}{\phi d_m} \quad (2.13 \text{ a}) \quad , \quad a_i = \frac{\pi d_i^2}{\phi} \quad (2.13 \text{ b})$$

2.5.3.3 Bed voidage

The voidage of a bed of particles, ϵ , is the fraction of the bed volume which is occupied by the space between the solid particles. It depends on the shape of the particles, the arrangement in the bed, the size range of the particles and the size of the bed (Kiricsi *et al.* 1999):

2.5.4 Pressure Drop across Pellets Packed bed

A general equation pressure drop which related to gas flow for pellets was refined by Ergun in 1952. The pressure drop is constant as the gas velocity increase from that minimum fluidization to that which significant particle entrainment occurs. The flow pattern through a fixed bed of particles is more complicated than that through a series of straight, parallel channels because the fluid flow paths through the voids are never straight, but have frequent changes in direction and repeated convergence and divergence of stream line.

2.6 Effect of Space Velocity (SV)

Space Velocity (SV) represents the inverse of residence time of gases on the catalyst bed (Patcas *et al.*, 2007; Makino and Kondo, 2001). Thus increase in SV reduces the residence time of gases on the catalyst bed and less time is available for the reactions among the gas molecules to occur, causing lower conversion of the gases. Again, very low SV for an existing engine requires large volume of catalyst bed which not only increases the cost of the catalytic converter but also causes greater pressure drop across the bed resulting degradation of engine performance. Hence, it is envisaged that an optimum SV is chosen considering the catalyst and engine economy and also the engine emission reduction performance of the catalysts (Grace Davison, 2008).

2.7 Effect on Back Pressure

Under the two-fold requirements of improved automobile performance and stringent allowable tail-pipe emissions, not only conversion efficiency but also back pressure or pressure drop across the catalyst bed is an important criterion for catalyst selection. The flow of exhaust gas through the catalyst bed is restricted by the catalyst particles which give rise to a pressure drop across the catalyst bed and this back pressure has negative effect on the engine performance (Grace Davison, 2008).

Research had been carried out in (Chun, 2003; Grace Davison, 2008) for pellets shape (Kiricsi *et al.* 1999) catalysts on different sizes associated with the SV. Figure 2.12 shows the variation of back pressure developed across a cylindrical packed catalyst bed of diameter of 50 mm and length 60 mm with different space velocities for two different sizes of catalyst pellets: one with diameter of 1.6 mm and the other with 3.0 mm. As expected, pressure drop increases continuously with increase in SV. As volume of catalyst bed is not altered, increase in SV is associated with increase in gas flow rate through the bed causing greater pressure drop. The rate of increase of pressure drop is also observed to be increasing with increase in SV. Maximum pressure drop of 200 mm of H₂O is observed at a SV of 67,500/h (Grace Davison, 2008).

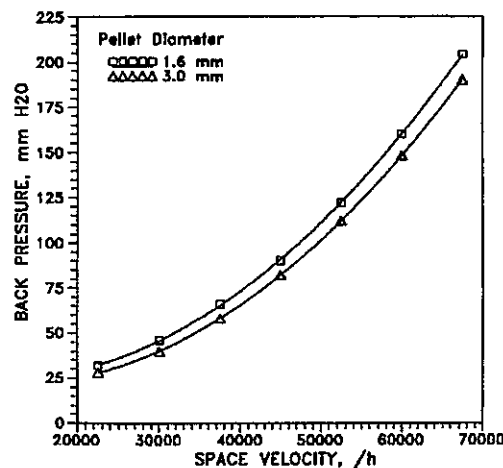


Figure 2.12: Back Pressure across the Catalysts Bed as a Function of Space Velocity (Kiricsi *et al.* 1999)

In (Chun, 2003); the pressure drop at different superficial velocities was reassured for pellets or beads, foam and honeycomb at the reaction temperature. For beads the Ergun equation was used:

$$\frac{\Delta P}{L} = \frac{150\eta(1-\varepsilon)^2}{d^2\varepsilon^3} w + \frac{1.75\rho(1-\varepsilon)}{d\varepsilon^3} w^3 \quad (2.15)$$

While for honeycomb the pressure drop was calculated by Hagen-Poiseuille equation:

$$\frac{\Delta P}{L} = \frac{32\eta}{d^2\varepsilon} w \quad (2.16)$$

The pressure drop for foam is estimated by using (Chun, 2003):

$$\frac{\Delta P}{L} = 3790w + 651w^2 \quad (2.17)$$

Figure 2.13 showed the effect on pressure drop with various types and shape of catalysts; beads, honeycombs and foam. The graph was obtained by calculation and experiment in (Chun, 2003) found the pressure drop increase in the sequence honeycomb < foam < pellets/beads. There is also reported in Patcas *et al* (2007) and Makino and Kondo (2001) that the pressure also increases with the length of the substrate as in Figure 2.14

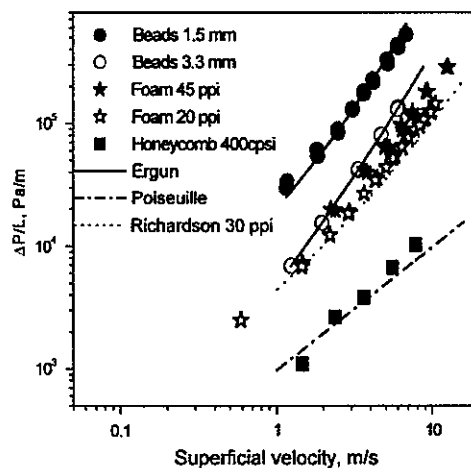


Figure 2.13: The Pressure Drop as Function of the SV Gas at Reaction Condition with Difference Shape and Size (Chun, 2003)

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