เบนซีน โทลูอีน และ ไซลีน ในไอเสียจากรถยนต์ที่ใช้น้ำมันเบนซิน

นายธีรเวช ทิตย์สีแสง

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BENZENE TOLUENE AND XYLENE IN EXHAUST FROM GASOLINE AUTOMOBILES

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นายธีรเวช ทิตย์สีแสง : เบนซีน โทลูอีน และ ไซลีน ในไอเสียจากรถยนต์ที่ใช้น้ำมันเบนซิน (BENZENE TOLUENE AND XYLENE IN EXHAUST FROM GASOLINE AUTOMOBILES) อ.ที่ปรึกษา : รศ.ดร. นพภาพร พานิช อ.ที่ปรึกษาร่วม : รศ.ดร. อมร เพชรสม; 135 หน้า ISBN 974-346-578-2

ทำการตรวจวัดหาสารมลพิษ เบนซีน โทลูอีน และ ไซลีน ในไอเสีย จากรถยนต์ที่ใช้น้ำมันเบนซิน ทั้งกลุ่มรถยนต์ที่มีการติดตั้ง และไม่ได้ติดตั้ง แคตตาไลติกคอนเวอร์ดเตอร์ ในสภาพรอบเครื่องยนต์เดินเบา ตัวอย่างไอเสียจะถูกเก็บโดยใช้ถุงชนิดเท็ดลาร์ ในกล่องสูญญากาศ โดยกลุ่มตัวอย่างรถยนต์จะถูกแบ่งออกเป็น 4 กลุ่ม ได้แก่ 1.กลุ่มรถใหม่ (มีอายุการใช้งานน้อยกว่า 5 ปี) ที่มีการติดตั้งแคตตาไลติกคอนเวอร์ดเตอร์ 2.กลุ่มรถกลางเก่ากลางใหม่ (มีอายุใช้งานระหว่าง 5-10 ปี) ที่มีการติดตั้งแคตตาไลติกคอนเวอร์ดเตอร์ 3. กลุ่มรถกลางเก่ากลางใหม่ (มีอายุใช้งานระหว่าง 5-10 ปี) ที่ไม่มีการติดตั้งแคตตาไลติกคอนเวอร์ดเตอร์ และ 4.กลุ่มรถเก่า (มีอายุการใช้งานมากกว่า10 ปี) ที่ไม่มีการติดตั้งแคตตาไลติกคอนเวอร์ดเตอร์ ค่าเฉลี่ยความเข้มข้นของเบนซีน โทลูอีน และ ไซลีน จะพบได้มากที่สุดในกลุ่มของรถเก่าที่ไม่มีการติดตั้งแคตตาไลติกคอนเวอร์ดเตอร์ โดยค่าเฉลี่ยความเข้มข้นของ เบนซีน โทลูอีน และ ไซลีน ในรถยนต์กลุ่มนี้ มีค่าเท่ากับ 12.11, 33.88 และ 8.55 ส่วนในล้านส่วน ตามลำดับ ในขณะที่ กลุ่มรถใหม่ที่มีการติดตั้งแคตตาไลติกคอนเวอร์ดเตอร์ จะพบความเข้มข้นของสารเหล่านี้น้อยที่สุด นอกจากนี้ยังพบว่าอัตราส่วนของสารเบนซีน โทลูอีน และ ไซลีน ในน้ำมัน และในไอเสียมีค่า 1 : 5.76 : 1.5 และ 1 : 1.92 : 0.55 ตามลำดับ

ในการทดสอบความสัมพันธ์ระหว่างการติดตั้งแคตตาไลติกคอนเวอร์ดเตอร์ กับ สารมลพิษในไอเสียที่ปล่อยออกมา ใช้สถิติทดสอบ t-test ผลจากการคำนวณโดยโปรแกรมทางสถิติ SPSS พบว่า ไม่มีความแตกต่างของความเข้มข้นสารมลพิษ ในไอเสีย ระหว่างรถยนต์ที่มีและไม่มีการติดตั้งแคตตาไลติกคอนเวอร์ดเตอร์ ที่ระดับนัยสำคัญ (α) 0.05 และยังพบว่าอายุของรถยนต์มีผลต่อปริมาณสารมลพิษที่ปล่อยออกมาในไอเสีย

ภาควิชา..... ลายมือชื่อนิสิต.....

สาขาวิชา..... ลายมือชื่ออาจารย์ที่ปรึกษา.....

ปีการศึกษา..... ลายมือชื่ออาจารย์ที่ปรึกษาร่วม.....

4072278123 MAJOR : ENVIRONMENTAL SCIENCE

KEY WORD : BENZENE / TOLUENE / XYLENE / EXHAUST / EMISSION / AUTOMOBILES / AIR POLLUTION

TEERAWET TITSEESANG : BENZENE TOLUENE AND XYLENE IN EXHAUST FROM GASOLINE AUTOMOBILES. THESIS ADVISOR : ASSOC. PROF. NOPPAPORN PANICH, D.Eng THESIS COADVISOR : ASSOC. PROF. AMORN PETSOM, Ph.D 135 pp. ISBN 974-346-578-2

The exhaust emissions of the air toxic Benzene, Toluene and Xylene from catalytic and non-catalytic equipped gasoline automobiles have been measured in the idle condition. The exhaust gas samples from tailpipe were collected by Tedlar bag in the vacuum box. The automobile samples were classified into 4 different groups as follow: 1.New catalytic car (less than 5 years old), 2. Moderate age catalytic car (5-10 years old), 3.Moderate age non-catalytic car (5-10 years old) and 4.Old non-catalytic car (more than 10 years old). The highest concentration was found in the old non-catalytic car group. The average concentrations of Benzene, Toluene and Xylene in old non-catalytic cars group were 12.11 ppm, 33.88 ppm and 8.55 ppm respectively. While the lowest concentrations of air toxic were found in the new catalytic cars group. Besides, the ratio of Benzene, Toluene and Xylene in gasoline and exhaust were 1 : 5.76 : 1.5 and 1 : 1.92 : 0.55, respectively.

The statistical t-test was used to determine the relationship between the catalytic converter and vehicle emission. The results from SPSS programming showed that there was no significant difference of pollutants emitted among car with and without catalytic converter at significant level (α) 0.05. It was also found that the age of engine has a strong influence on concentration of pollutants in vehicle exhaust.

Department…… Student's signature……..……..

Field of study…….. Advisor's signature……..

Academic year…….. Co-advisor's signature ……..

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CHAPTER 1

INTRODUCTION

1.1 General background

Air pollution constitutes an ominous threat to human health and welfare. Its adverse effects are pervasive and may be disaggregated at three levels - local, confined to urban and industrial centers, regional, pertaining to transboundary transport of pollutants, and global, related to build up of greenhouse gases. These effects have been observed globally but the characteristics and scale of the air pollution problem in developing countries are not known; nor has the problem been researched and evaluated to the same extent as in industrialized countries. Air pollution, however, can no longer be regarded as a local or a regional issue as it has global repurcussions in terms of the greenhouse effect and depletion of the ozone layer. At an international conference in Montreal , experts from 91 nations identified urban smog, acid rain, and global warming as the three most critical environmental concerns of the future.

Mobile sources, particularly motor vehicles, are a major cause of air pollution. In 1988, the global automobile population exceeded 400 million for the first time in history. Including commercial vehicles, over one half billion vehicles are now on the world's roads - ten times more than in 1950. While motor vehicles have increased mobility and flexibility for millions of people, created jobs, and enhanced many aspects of the quality of life, the benefits

have been at least partially offset by the air pollution generated by motor vehicles. (Faiz. et.al , 1990)

Motor vehicles emit carbon monoxide, hydrocarbons, nitrogen oxides, and other toxic substances such as fine particles and lead. Each of these pollutants has adverse effects on human health and welfare. It has been concluded that motor vehicles cause approximately 54-58 % of nationwide cancer cases associated with toxic air emissions in the USA. Pollutants emitted from vehicles that appear in the list of 189 air toxics identified in the 1990 amendment to the US clean air act include both particulate matter such as polyaromatic compounds and volatile organic compounds (VOCs) including 1,3-butadiene, benzene, toluene, the xylene, and aldehydes. (Kao cited in Duffy et.al 1998).

The growing vehicle population is a major contributor to air pollution problems; initially, these problems were most apparent in city centers but over the last two decades lakes and streams and even remote forests have experienced significant degradation. As evidence of anthropogenic impacts on the upper atmosphere accumulates, there is increasing concern over the role of the motor vehicle in global warming.

Emissions of non-methane hydrocarbons (NMHC) from vehicle exhausts are one of the largest anthropogenic sources of hydrocarbons (HCs). Although the HCs themselves are not usually a pollution problem, their participation in photochemical smog formation, in conjunction with the oxides of nitrogen (NO_x) has resulted in regulations being formulated for their control.

The determination of the individual HC composition of exhaust is useful for at least three reasons: 1) it enables an estimation of the relative contribution of vehicle exhaust to the total NMHC in an urban area. 2) it is essential for the development of realistic models of photochemical smog formation and 3) it should aid the development of models of HC emissions from internal combustion engines (Nelson and Quigley, 1984).

In an effort to reduce air pollution from mobile sources, emission rates from automobiles and other motor vehicles have been regulated by legislation in some industrialized countries for over two decades. As air pollution problems have spread in the wake of rapid motorization in the developing world, similar regulatory measures have been adopted in some developing countries, notably Brazil, Mexico, Republic of Korea, and Taiwan. However, the reduction in emissions per kilometer driven achieved through such measures is being more than offset by the rapid increase in the number of vehicles.

Although exhaust gas HC compositions have been determined in the past, few studies have used a wide range of vehicles and driving conditions. Most of the previous studies investigating speciated hydrocarbon emissions from motor vehicles have been performed in America and European cities, and there is little data available for the Thai car population. In this Thesis research the exhaust compositions of Benzene, Toluene, and Xylene of 35 vehicles in idle condition have been determined from measurements using Vacuum box. The results are compared with previous studies in both Thailand and other countries.

1.2 Objectives of the study

1. To assess the existing load of Benzene, Toluene and Xylene (that includes ortho-, meta-, and para- forms as total Xylene) concentrations in the automobile exhaust gas and in the gasoline.

2. To assess the effect of engine's age on the concentration of Benzene Toluene and Xylene (as total Xylene) in automobile exhaust gas.

3. To assess the concentration of Benzene Toluene and Xylene (as total Xylene) in the exhaust gases of non-catalytic equipped automobiles and catalytic equipped automobiles.

1.3 Scope of the study

In this study, the 4-stroke internal combustion engine automobiles are used to collect their exhaust gas as gas sample.

The pollutants in exhaust gas from automobile's tailpipe concerned are Benzene, Toluene and Xylene ; for xylene that includes ortho, meta, and para forms as total xylene.

The automobile samples are categorized into 3 different groups by the age of engine, 1) New car 2) Moderate age car and 3) Old car , which considered as :

1. The ages of new cars are less than 5 years old.

2. The ages of moderate age cars are in range of 5 to 10 years old.

3. The ages of old cars are more than 10 years old.

The automobiles are tested to collect the exhaust gas samples at idle mode condition only.

The limitation of this study is that can not be directly collected the gasoline samples from the fuel tank in automobiles. All gasoline samples in this study brought from the gasoline station in different gasoline's brands.

CHAPTER 2

LITERATURE REVIEW

2.1 Situation of urban air pollution in megacities of the world

In order to assess the problems of urban air pollution m a global context, the WHO and UNEP initiated a detailed study of air quality in 20 of the 24 megacities of the world. For the purposes of this study, megacities were defined as urban agglomerations with current or projected populations of 10 million or more by the year 2000 as shown in Figure 2.1 . The four megacities not chosen for inclusion in the study were Osaka (because of similarity to Tokyo) and Tehran, Lagos and Dacca because of a lack of data upon which to perform the study. The urban areas chosen included cities in all parts of the world-two in North America, four in Central and South America, one in Africa. 11 in Asia and two in Europe.

The megacities are not necessarily the world's most polluted cities. The primary reasons for singling out the megacities are that they already have serious air pollution problems; they encompass large land areas and many people (the total population of the 20 megacities in 1990 was estimated to be 234 million); and many other cities are heading for megacity status. In 2000, the United Nations estimate that there will be 59 "supercities" having over five million population and many of these will reach megacity status in the next century. This last point is of particular importance.

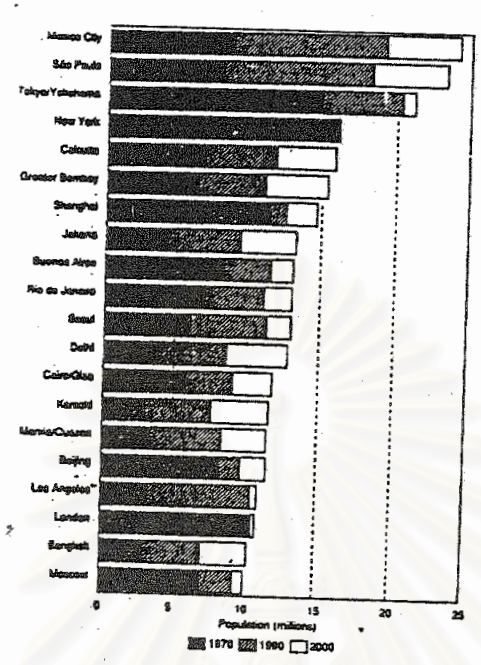

Figure 2.1 Estimated population of 20 megacities in 1970 and 1990 and projected population in 2000 (Source : Mage, 1996)

A review of the air pollution situation in the present-day megacitie and identification of their difficulties in finding solutions can serve as a warning in the problems facing rapidly growing urban areas, and act as a guide to solving and preventing some of them. Preventing pollution problems before they can occur is often the most cost-effective approach.

The first observation is that air pollution is wide spread across the megacities and is often most severe in cities in developing countries. But even in the others, health norms are being exceeded, although to a lesser degree.

Each of the 20 megacities has at least one major air pollutant which occurs at levels that exceed WHO health protection guidelines as shown in Figure. 2.2 ; 14 of these megacities have two such pollutants and seven have three or more. The last group consists of Beijing, Cairo, Jakarta, Los Angeles, Mexico City. Moscow and Sao Paulo. Five of these seven are located in the Pacific Basin. They are facing a variety of air pollution problems requiring comprehensive solutions, In the majority of the megacities, air quality is getting worse as the population, traffic, industrialization and energy use are increasing and there is much urgency in instituting control and preventive measures. (Mage, 1996)

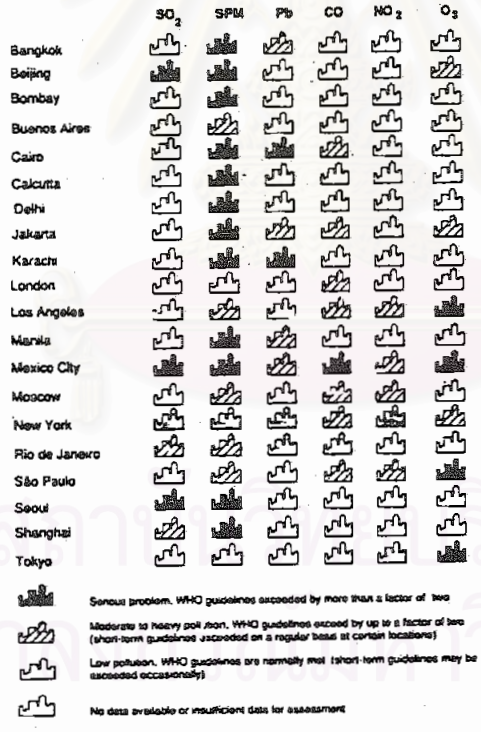

Figure 2.2 Overview of air quality in 20 megacities based on a subjective assessment of monitoring data and emissions inventories. (Source : Mage, 1996)

2.2 Major source of air pollution

Motor vehicle traffic is a major source of air pollution in the megacities. In half of them it is the single most important source. It is a major source of four of the six major air pollutants – CO, NO_x, HC and Pb—and contributes to the SPM concentration. Since 1950, the global vehicle fleet has grown tenfold and is estimated to double from the present total of 630 million vehicles within the next 20 – 30 years . Much of the expected growth in vehicle numbers is likely to occur in developing countries and in eastern Europe.

As cities expand into megacities. more people will drive more vehicles greater distances and for longer times, in the absence of controls, the automotive emissions will likewise increase. In Bangkok, for example, it is estimated that they will double by the year 2000. In cities where a substantial portion of the motor vehicle fleet is diesel-powered there are additional problems of black smoke and greater particulate emissions. Such a situation exists in Bangkok, Manila and Seoul. The implementation of automotive emission controls in the cities is paramount given the already high concentrations of automotive-related air pollutants, the rapid increase in motor vehicle traffic and the long time it takes for controls to take effect.

Indeed, many of these cities need to supplement technological automotive emission controls with administrative controls to reduce the vehicle kilometers traveled, such as better public transport systems. Several supercities have already begun using "incentive" approaches to securing improved air quality, especially indirect-based incentive policies. Gasoline taxes are a good example of such approaches.

From a review of trends in air quality in different cities it is quite evident that "history repeats itself". The experience of the current megacities in the developed countries is being repeated in the developing countries. As shown in Figure 2.3 , before rapid industrial development takes place, air pollution is mainly from domestic sources and light industry; concentrations are generally low and increase slowly as population increases. As industrial development and per capita energy use increase, air pollution levels begin to rise rapidly. Then urban air pollution becomes a serious public health concern and emission controls are introduced. Owing to the complexity of the situation, an immediate improvement in air quality cannot generally be achieved; at best the situation is stabilized, and serious air pollution persists for some time.

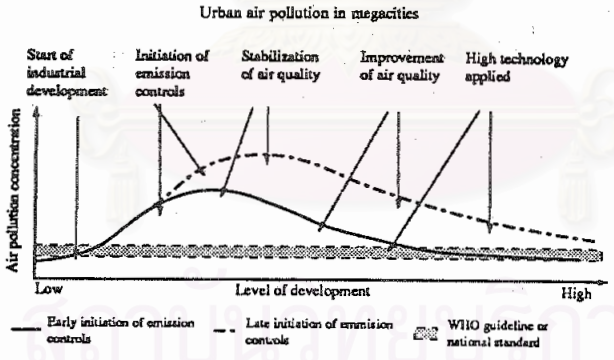

Figure 2.3 Development of air pollution problems in cities according to development status. (Source : Mage, 1996)

Several of the megacities studied are now in the situation where additional controls must be implemented without delay. Experience has shown that the introduction of emission controls has been followed by a staged reduction of air pollution as controls take effect. The earlier that integrated, enforceable air quality management plans are put into effect, the lower the maximum pollution levels that will occur. This is especially important for those cities of developing countries that are not yet of the size and complexity of present-day megacities. (Mage, 1996)

2.3 Air pollution from mobile source

Holman (1997) explained the situation of pollutant emissions from traffic that; in most urban areas of the United Kingdom traffic generated pollutants - nitrogen oxides (NO_x), carbon monoxide (CO), volatile organic compounds (VOCs) and particulate matter (PM) - have become the dominant pollutants. Although little long-term monitoring data on these pollutants exists, it is likely that urban concentrations have increased over the past three or four decades. In contrast, early concerns about lead in the atmosphere from car emissions have now been effectively tackled by reducing the maximum permitted lead level and encouraging the use of unleaded petrol. As a result concentrations are now down to about 20% of those in the 1970s .

Ozone is a regional scale pollutant formed from $N0_x$ and VOCs. The highest concentrations are typically found downwind of urban areas, although elevated levels are also observed in the summer in urban areas. In recent years carbondioxide has become an important pollutant as concern about its role in changing climate has increased. Although road transport is not the

major source of this pollutant, emissions from this sector are growing at a time when there is a Government commitment to stabilize emissions.

Table 2.1 shows the relative importance of different sources of sulfur dioxide (SO_2), black smoke (BS), NO_x, CO and VOCs in the United Kingdom in 1993. Black smoke is one constituent of airborne particulate matter. At a national level, road transport is the single most important source of most of these pollutants. The exceptions are SO_2 and VOCs. In urban areas the contribution from road transport is likely to be greater than indicated by national emission data. This is because there is typically more traffic and less industry in urban areas. In addition, emissions from traffic have a greater impact on local air quality as they are at a lower height than those from industrial sources.

Table 2.1 Sources of the principal pollutants 1993. (Source : Holman, 1997)

Source	% Total emission				
	Sulfur dioxide	Black smoke	Nitrogen oxide	Carbon monoxide	VOCs
Road transport	2	51	49	91	38
Power station	66	5	24	1	-
Other industry	24	4	14	2	55
Domestic	4	29	3	5	1
Other	5	11	9	1	5
Total in k tones	3188	444	2347	5641	2418

Cars are the dominant source of road transport emissions, contributing between 50 and 90 percent of the sector's share of CO, NO_x, VOC, SO_2, and CO_2 emissions. Cars are a less important source of PM and BS. The largest source of these pollutants is heavy duty vehicles (buses, coaches and lorries).

UK emissions from road transport increased rapidly during the 1980s. This is shown in Table 2.2 and was largely the result of the increase in traffic. Since the introduction of cars with three way catalytic converters, emissions have begun to decline. In general, road traffics emissions peaked around 1990 and since then have shown a small decrease. Despite forecasts of traffic increasing by 75% to 160% (depending on economic growth) over the next 30 years new technology is expected to result in a reduction in emissions of most pollutants, until some time in the second decade of the next century. Thereafter, unless there are further technological improvements, the growth in traffic will result in an upturn in emissions. For PM the upturn is likely to occur sooner as the reduction in new vehicle emissions has been smaller than for the gaseous pollutants.

Table 2.6 Increase in UK estimated emissions from road transport 1982-1993 (Source : Holman, 1997)

Pollutant	Percentage increase
Carbon monoxide (CO)	31
Nitrogen oxides (NO_x)	61
Volatile organic compounds (VOCs)	8
Black smoke (BS)	85
Sulfur dioxide (SO_2)	27
Carbon dioxide (CO)	43

2.4 The four-stroke internal combustion engine

The four-stroke IC gasoline engine has been the power source for most of the autos and small trucks ever built. It has withstood the challenges of all other types of engines because it is relatively light and small, durable, and moderately easy and relatively inexpensive to manufacture; has fairly good fuel efficiency; responds quickly and smoothly to changes in throttle setting; and can operate efficiently over fairly wide speed and load ranges. Other engine types can beat it at one or more of those attributes, but so far none has been able to beat it at enough of them to displace it.

Figure 2.4 shows, in very simplified form, a cross-sectional view of a typical auto engine. It shows only one piston and cylinder; most auto engines have four such pistons and cylinders, some have six or eight. In operation, the crankshaft rotates, causing the piston to move up and down, driven by the crank, connecting rod, and wrist pin. To begin a cycle, with the piston at the top (top dead center, TDC) during the first stroke the piston moves downward while the intake valve is open, so that an air-fuel mixture is sucked into the combustion chamber (the space within the cylinder, above the piston). When the piston is at the bottom (bottom dead center, BDC), the intake valve closes, ending the intake stroke.

As the piston rises again to the top during the compression stroke, both valves are closed, so that the air-fuel mixture is compressed. Near the top of that stroke the spark plug fires, igniting the air-fuel mixture. In its next downward travel, the power stroke, the piston is driven by the high-pressure combustion gases, which do the actual work of the engine. At the bottom of

the piston travel, the exhaust valve opens, and on its next upward travel the piston pushes the burned gases out into the exhaust system. The cycle is named for its four strokes - intake, compression, power, and exhaust. The spark plug fires every second upward travel of the piston. Power is produced only during the power stroke. Each of the other three strokes consumes power. The engine must have enough inertia so that the power produced in the power stroke will carry it through to the next power stroke. For a one-cylinder engine, this normally requires a large flywheel. For multi-cylinder engines the firing times of the cylinders do not coincide, so a much smaller flywheel is suitable. (Nerves, 1995)

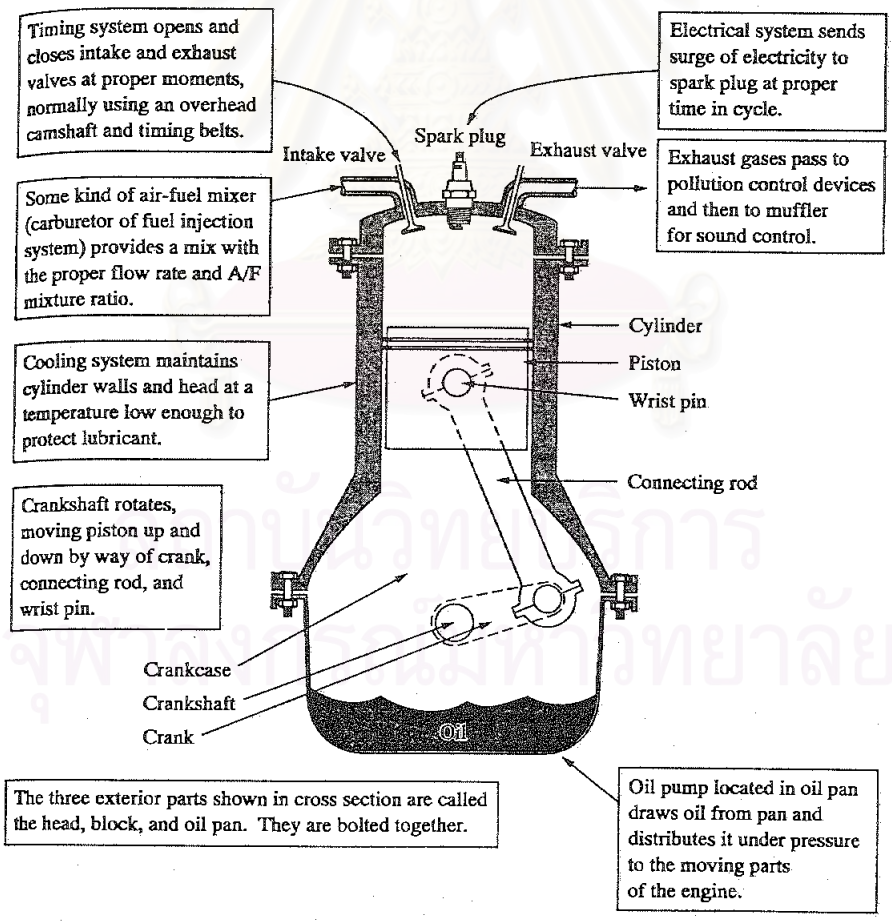

Figure 2.4 Very simplified schematic of one piston and cylinder of a 4 stroke gasoline IC engine (Source : Nevers, 1995)

2.5 Gasoline

Modern gasolines are blends of varying quantities of paraffins, olefins, naphthenes, and aromatics compounded to give the desired characteristics (of starting, accelerating, and so on) when burned in automobile engines. The composition varies from company to company and from one geographical region to another. For example, a gasoline designed for use in the winter of Minnesota will have a larger percentage of highly volatile constituents than will a gasoline for use in Florida in the summer. Examples of the hydrocarbon families are shown in figure 2.5. These include saturated straight and branched chains, and aromatic types.

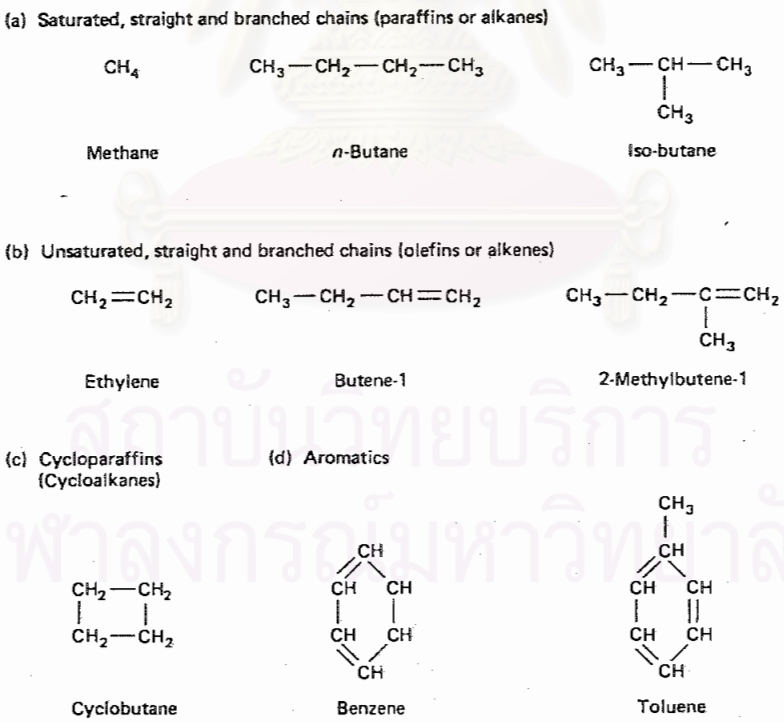

Figure 2.5 Examples of members of general hydrocarbon families.

(Source : Wark and warner, 1976)

The hydrocarbons have different boiling points, ignition temperatures, and combustion characteristics. For example, the ignition temperature of iso-octane is 1350 ^{0}F (730 ^{0}C), while that for n-octane is 880 ^{0}F (470 ^{0}C). Typical gasoline compositions are shown in table 2.3.

Table 2.3 Approximate composition of gasoline (Source : Wark and warner, 1976)

Component	Regular (%)	Premium (%)	Reactivity for Smog Formation
Aromatics	20	25	Slight
Olefins	22	17	High
Paraffins	58	58	Low

Extensive tests have shown that different gasoline when burned in a given engine will yield different unburned hydrocarbon exhaust products. Furthermore, the exhaust products vary from one engine to another when operating with the same gasoline. Over 200 different hydrocarbons have been identified in the exhaust products of one engine burning a given gasoline. The combustion phenomena occurring in an internal combustion engine are so complex that it has been impossible to develop a chemical reaction model which successfully predicts the composition of the exhaust products.

As an additional complicating factor, it has been found that the different unburned hydrocarbons have varying potentials for forming eye-irritating smog. This potential is termed reactivity. Thus one hydrocarbon has a higher reactivity than another, as illustrated in table 2.4. The reactivity of methane has been shown to be near zero. In light of the preceding discussion, it is not surprising that one of the methods proposed to reduce hydrocarbon emissions was to change fuels. Various compositions of gasolines were found to yield approximately the same total quantities of unburned hydrocarbons. (Wark and Warner, 1976)

Table 2.4 Reactivities of hydrocarbon based on ability to participate in Photooxidation of NO_x to NO_2 (Source : Wark and warner, 1976)

Hydrocarbon	Ranking	
	Altshuller and Cohen [12]	Glasson and Tuesday [13]
2,3-Dimethylbutene-2		10
2-Methyl-2-butene		3
trans-2-Butene[a]	2	2
Isobutene	1	
Propylene	1	0.5
1,3,5-Trimethylbenzene	1.2	1.2
m-Xylene	1	0.9
1,2,3,5-Tetramethylbenzene	0.9	0.7
o- and *p*-Xylene	0.4	0.4
o- and *p*-Diethylbenzene	0.4	0.4
Ethylene	0.4	0.3
Toluene	0.2	0.2
Benzene	0.15	0.04
3-Methylheptane	0.15	
n-Heptane		0.2
2,2,4-Trimethylpentane	0.15	0.15
Butanes		0.1
Acetylene	0.1	
Ethane		0.03
Methane		0.01

[a] Two ranking scales adjusted to give same value on both scales for *trans*-2-butene, for comparative purposes.

The octane number of a fuel is a measure of its anti-knock performance. A scale of 0-100 is devised by assigning a value of 0 to n-heplane (a fuel prone to knock), and a value of 100 to iso-octane (a fuel resistant to knock). A 95 octane fuel has the performance equivalent to that of a mixture of 95 percent iso- octane and 5 percent n-heplane by volume. The octane requirement of an engine varies with compression ratio, geometrical and mechanical considerations, and also its operating conditions. There are two commonly used octane scales, research octane number (RON) and motor octane number (MON), covered by British Standards 2637: 1978 and 2638: 1978 respectively (Stone,1985). Spiro (1996) summarised the properties of some components of gasoline in the table 2.5.

Table 2.5 properties of some components of gasoline (Source : Spiro, 1996)

Component	Research octane number (RON)	Motor octane number (MON)	Vapor pressure (psi @ 100°F)	PA*
butane			51	3.23
n-pentane	62	67	15.5	4.80
n-hexane	19	22	5.0	5.90
methyl propane			82	2.83
2-methylbutane	99	104	20	
2-methylpentane	83	79	6.6	5.82
2-methylhexane	41	42	2.2	6.85
iso-octane	100	110	1.65	3.15
1-butene	144	126	50	24.4
1-methylpropene	170	139	62	24.4
1-pentene	118	109	19	35.0
cyclohexane	110	97	3.3	8.50
methylcyclohexane	104	84	1.6	7.87
benzene	99	91	3.3	0.88
toluene	124	112	1.04	5.98
meta-xylene	145	124	0.33	22.8
ethanol	115†		17	3.3
methanol	123	93	60	1.0
Methyl *tert*-butyl ether (MTBE)	123	97	8	2.6
Ethyl *tert*-butyl ether (ETBE)	111†		4	8.1

*Photochemical activity measured as rate of reaction with OH radicals, units, cc/(molecule sec) × 10^{12}.

†Average (RON + MON).

Of the various fuel additives, those that increase octane numbers have greatest significance. In 1922 Midgely and Boyd discovered that lead-based compounds improved the octane rating of fuels. By adding 0.5 grams of lead per liter, the octane rating of the fuel is increased by about 5 units. The lead additives take the form of lead alkyls, either tetramethyl lead $(CH_3)_4Pb$, or tetraethyl lead $(C_2H_5)_4Pb$. (Stone, 1985).

Cause of the environmental and health concerns, Many countries have to restrict the amount of lead in gasoline severely. When gasoline lead content is either reduced or eliminated then, if octane quality is to be maintained, refineries have to resort to the increased use of certain components. Traditionally refineries have used aromatic components, which comprise mainly benzene, toluene, xylenes and ethyl benzene, from reforming processes to provide octane quality. These aromatic components or sometimes call volatile organic compounds (VOCs) are emitted in significant quantities from vehicles. Using of aromatics in unleaded gasoline is producing health and environmental dangers greater than that from lead itself when this fuel is used in cars not fitted with a catalyst. VOCs are precursors of photochemical smog and tropospheric ozone. Exposure to VOCs and other air toxics has been linked to adverse health effects. Specific VOCs, for instance, benzene may also lead to increases in diseases such as lung cancer and leukaemia. (Lertvisansak, 1996)

2.6 Catalytic converter

Most automobile manufacturers have concluded that they cannot meet current and future emission standards by engine modifications alone. Their

efforts to do that in the 1970s resulted in some very poorly performing automobiles. Instead, they have concluded that the most satisfactory solution is to modify the engine so that it produces the right mix of pollutants and then treat that mix catalytically to meet the emission standards. The first attempts used two catalysts, but since then automobile manufacturers have developed the "three-way catalyst" that promotes the following reaction:

$$NO + CO + HC \xrightarrow{\text{Platinum - rhodium catalyst}} N_2 + C0_2 + H_2O \qquad \text{Equation 1.}$$

This reaction requires very close control of the ratio of oxidizing agent (NO) to reducing agents (CO + HC). Figure 2.6 shows that with very close control of the A/F ratio, conditions can be found that lead to about 95 percent destruction of all three pollutants.

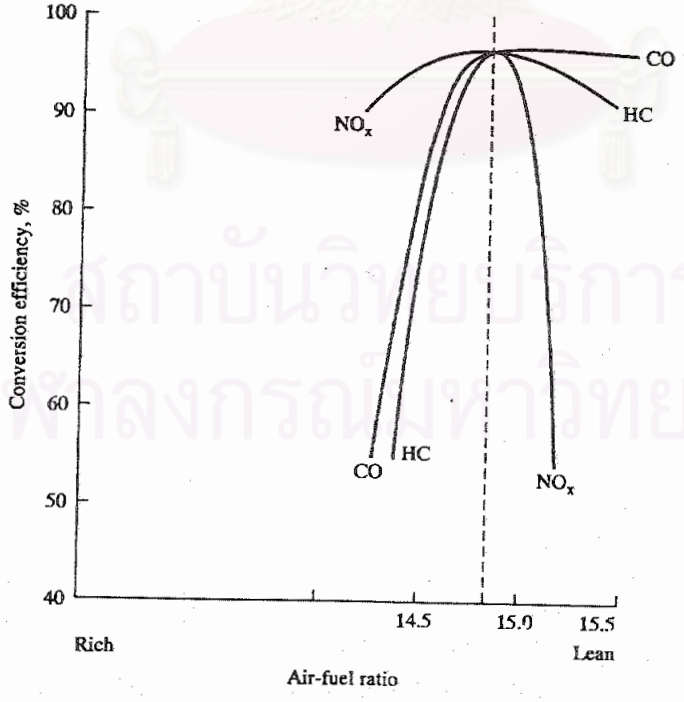

Figure 2.6 Conversion efficiency of a 3 way catalyst system as a function of A/F ratio.
(Source : Nevers, 1995)

The key to doing this successfully was the development of the doped zirconium dioxide oxygen sensor, shown in figure. 2.7. This consists of a closed cylinder of doped ZrO_2 that is coated on both sides with a platinum film and inserted into the exhaust manifold. The sensor is an electrolytic cell, with the ZrO_2 acting as a solid electrolyte; its output voltage is a strong function of the oxygen content of the exhaust gas. Using the measured value of the exhaust gas oxygen content, the engine computer can control the A/F ratio to stay within the ± 0.05 tolerance (ϕ tolerance of ± 0.003) needed to stay at the top of the curves in figure 2.6.

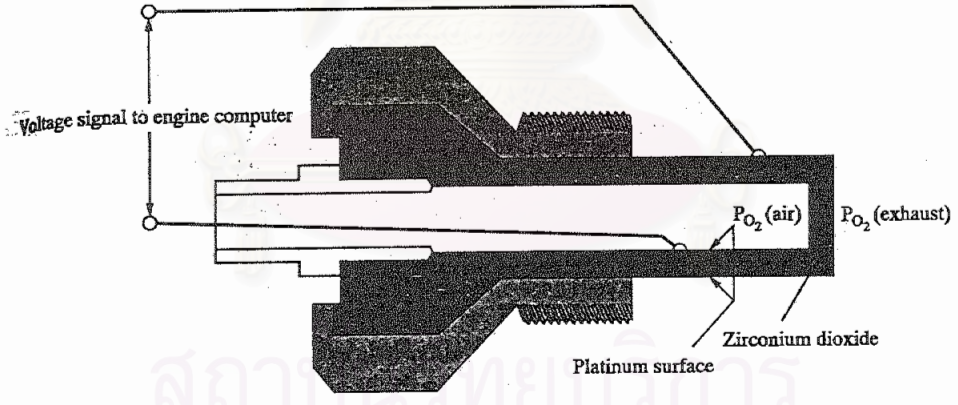

Figure 2.7 Schematic of doped zirconium dioxide exhaust gas oxygen sensor.
(Source : Nevers, 1995)

The typical automobile exhaust gas catalyst is a (5:1) mix of platinum or palladium with rhodium, supported on an Al_2O_3 layer that is deposited on a cheaper ceramic base. The requirements for an auto exhaust catalyst are these:

1. Produce at least 90 percent destruction of CO, HC, and NO_x, according to equation 1. in as small, lightweight, and inexpensive a package as possible. If possible, the catalyst should be formed in a pancake shape for easy installation under an auto.

2. Start to destroy CO, HC, and NO_x at as low a temperature as possible. Typical catalysts do not begin to promote the reaction until they are heated by the exhaust gas to their "light off" temperature of about 350 ^{0}C (662 ^{0}F). Thus they are inactive during the period of highest emissions, that is, during cold start.

3. Not have excessive heat flow to the surroundings or excessive surface temperatures, to prevent excessive heat flow to the passenger compartment of the car or the starting of grass fires. (Many cars have heat shields to solve this problem.)

4. Perform satisfactorily for at least 50,000 miles or five years (required by EPA regulations) in a very difficult environment (heat; cold; vibrations; varying input flow temperature, pressure, and chemical composition).

5. Have minimum pressure drop.

6. Cause the small amount of S in the gasoline to exhaust as SO_2 rather than the much smellier H_2S, but not oxidize the SO_2 to the more toxic SO_3 .

A typical modern auto catalyst does these things. It has a volume of about one liter and a noble metal content of about 1.5 g. Two mechanical arrangements are used. In the pellet arrangement (figure 2.8) the noble metal is dispersed on porous ceramic pellets about 1 cm in diameter, much like the pelleted catalysts widely used in the chemical industry and in petroleum refining. These are placed in a container the size and shape of a small textbook, whose sheet metal covers have multiple holes for the exhaust gas flow. This container is placed within an outer cover; baffles direct the exhaust gas along one side of the catalyst chamber, then through it in its narrowest dimension, then along its other side to leave the auto.

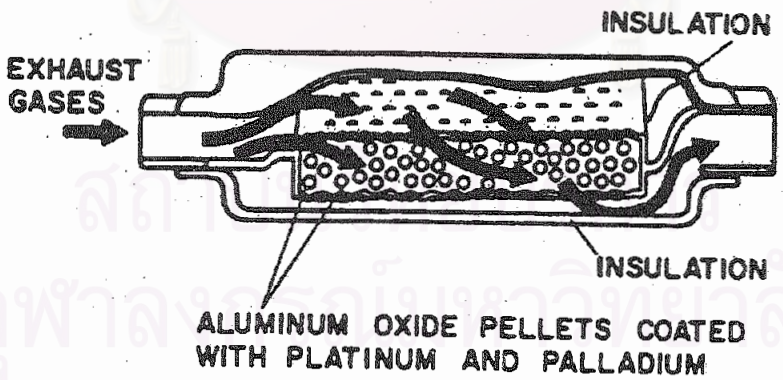

Figure 2.8 Mechanical and flow arrangements of a pellet-type catalytic converter. (Source : Nevers, 1995)

The other arrangement uses a single structure called a honeycomb monolith. This is a single ceramic piece, shaped like a honeycomb, with many straight passages through it, each about 1/20 of an inch wide (400 passages per $in.^2$) and about a foot long. The passages can be hexagonal, square, or triangular; most are square. It is packaged as shown in figure 2.9. In this design the basic ceramic piece serves only for strength, a thin layer of Al_2O_3 is deposited on it, and then the noble metal is deposited on the Al_2O_3. In both arrangements the metal parts are generally stainless steel, to provide long life in the high-temperature environment of the catalysts (Nevers, 1995)

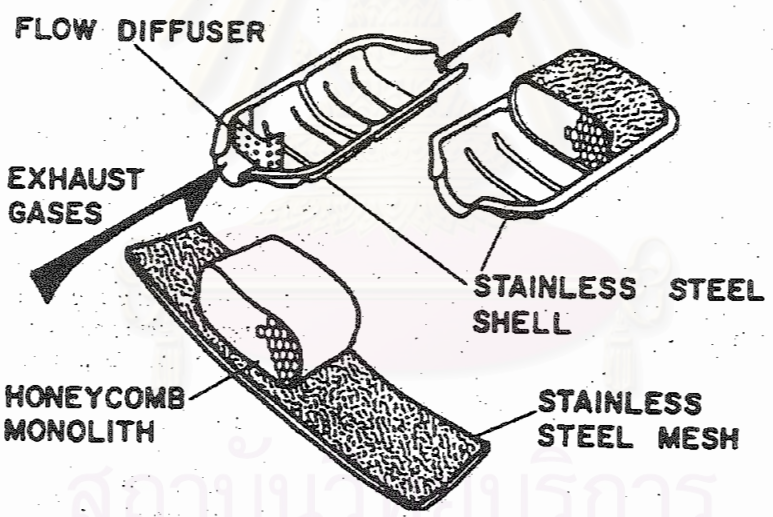

Figure 2.9 Mechanical and flow arrangements of a honeycomb monolith-type catalytic (Source : Nevers, 1995)

2.7 Exhaust emission

In 1968, U.S motor vehicles were responsible for 73 percent of the CO, 74 percent of the hydrocarbons, and 43 percent of the oxides of nitrogen. (Wark and Warner, 1976). While in the U.K on 1993 road transport was a source of 49 percent of the Nitrogen oxides, 91 percent of CO and 38 percent of VOCs (Holman, 1997). These percentages are larger because of the quantities of pollutants emitted by each car and the large number of cars in operation. In 1965 there were estimated to be 80 million cars in operation in the United States.

And in 1988, the global automobile population exceeded 400 million for the first time in history. Including commercial vehicles, over one half billion vehicles are now on the world's roads - ten times more than in 1950. (Wark and Warner, 1976 and Faiz, 1990). The effect of these cars upon the quantities of air pollutants is illustrated in figure 2.10, which presents the estimated hydrocarbon emission as a function of time. Similar diagrams are available for CO and NO_x.

An analysis of the automobile with no emission control by Springer and Patterson (1973) described the major sources of vehicle emission that, there are three sources of emissions from most automotive vehicles, as shown in figure 2.11. The fuel systems emission comes from the fuel tank and the carburetor and consists exclusively of hydrocarbons. Crankcase emission, also hydrocarbon (HC), comes mainly from the gas-air mixture which blows by the piston rings. The primary emissive source of automotive vehicles is the exhaust. Combustion is not complete. In addition to the exhaust products of

water, nitrogen, and carbon dioxide, other products including carbon monoxide, unburned hydrocarbons, partially burned hydrocarbons, hydrogen, oxides of nitrogen, and various particulates such as lead and sulfur compounds.

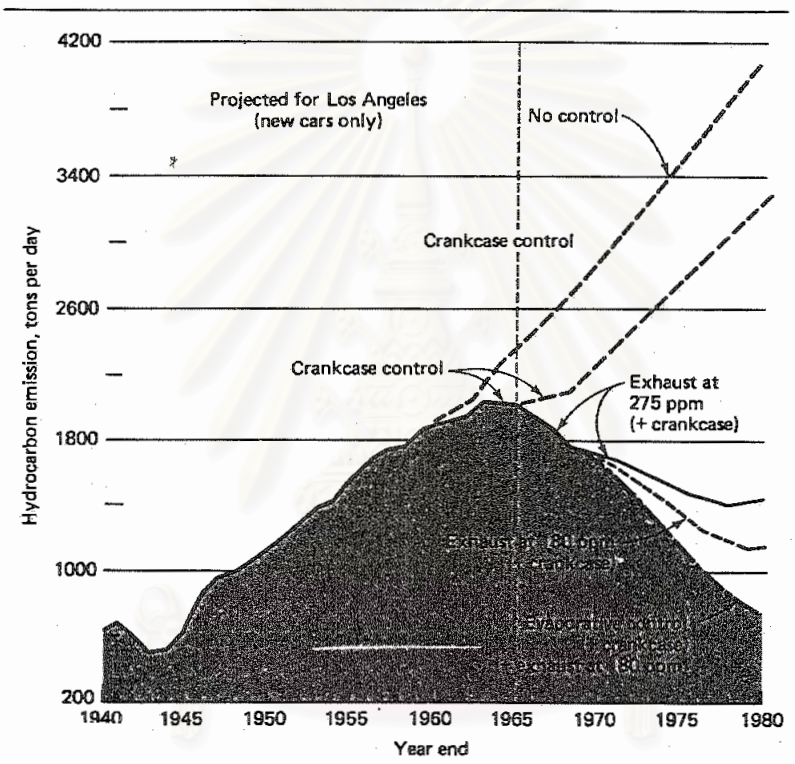

Figure 2.10 Forecasts of hydrocarbon emissions by cars in the city of Los Angeles. (Source : Wark and Warner, 1976)

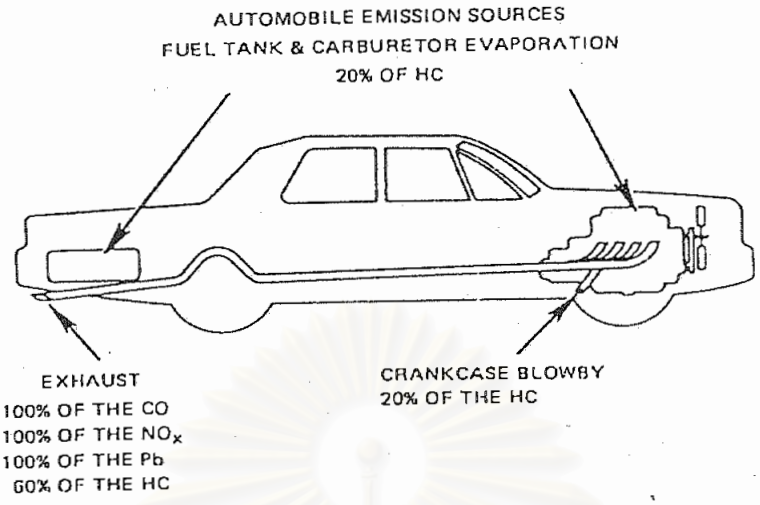

Figure 2.11 Sources of pollution from automobiles. (Source : Perkin, 1974)

As an additional complication, the mode of vehicle operation has a marked effect upon the emission as illustrated in figure 2.12. In 1960, the Motor Vehicle Pollution Control Board of the State of California was created to establish specifications on vehicle exhaust and evaporative emissions. The first automotive emission requirement was for the reduction of crankcase blow-by. The California Motor Vehicle Pollution Control Board adopted a resolution requiring that a positive crankcase ventilation system be installed on all new cars sold in California beginning with 1963 models. The result of this requirement is shown in figure 2.10 by the crankcase control line. The federal government, by an amendment to the Clean Air Act in 1965, specifically authorized the writing of national standards for emissions from all motor vehicles sold in the United States.

Condition	Exhaust				Blow-by[a] Flow[b]	Fuel System Flow[b,c]	
		Concentration					
Vehicle	Flow	HC	CO	NO_x		Tank	Carb.
Idle	Very low	High	High	Very low	Low	Average to moderate	Mod.
Cruise							
Low speed	Low	Low	Low	Low	Mod.		Small
High speed	High	Very low	Very low	Mod.	High		Nil
Acceleration							
Moderate	High	Low	Low	High	Mod.		Nil
Heavy	Very high	Mod.	High	Mod.	Very high		Nil
Deceleration	Very low	Very high	High	Very low	Very low		Mod.
Soak[d]							
Hot	None	—	—	—	None	High	High
Diurnal	None	—	—	—	None	Mod.	Very low

[a] Concentration of HC is high, CO is low, and NO_x is very low.
[b] Flows are at least one order of magnitude lower than the exhaust flow.
[c] Emission is nearly pure HC (no NO_x or CO).
[d] Engine stopped during this period.

Figure 2.12 Effect of vehicle mode of operation on emission. (Source : Wark and Warner, 1976)

2.8 Origin of exhaust emission

In the conventional spark ignition gasoline engine, a mixture of air and gasoline provided by the carburetor is inducted into the cylinder through the intake manifold and intake valve during the intake stroke, and then is

compressed and ignited by a spark from the spark plug during the compression stroke. The mixture burns, and the products of combustion expand as the piston travels downward during the expansion stroke. The combustion products are exhausted from the cylinder through the exhaust valves and manifold to the exhaust system during the exhaust stroke. An estimate of the theoretical quantity of air required to burn the fuel completely may be obtained by writing the complete chemical reaction equation employing a theoretical fuel to represent the actual gasoline blend of hydrocarbons. As an example, on a molar basis,

$$C_7H_{13} + 10.25\ O_2 + 38.54\ N_2 \rightarrow 7\ CO_2 + 6.5\ H_2O + 38.54\ N_2 \qquad \text{(eq.2)}$$

and on a mass basis such as pounds or kilograms,

$$97(\text{lb})\ C_7H_{13} + 328(\text{lb})\ 0_2 + 1080(\text{lb})\ N_2 \rightarrow 308(\text{lb})\ C0_2 + 1170(\text{lb})\ H_20 + 1080(\text{lb})\ N_2 \qquad \text{(eq.3)}$$

The complete or theoretical combustion, as shown by the above reactions, is defined as the complete conversion of carbon to CO_2 and hydrogen to H_2O. This is also frequently termed the stoichiometric reaction. It is useful to define a mixture ratio, or air-fuel ratio (A/F). This is the ratio of the mass of air required per unit mass of fuel for combustion. That is,

$$\text{Mixture ratio} = A/F = (\text{mass of air} / \text{mass of fuel}) \qquad \text{(eq.4)}$$

For comparative purposes we find that the stoichiometric air-fuel ratio is quite useful. In terms of equation 3. this is

$$(A/F)_{stoich} = (328 + 1080) / 97 = 14.5$$

This value is typical of the stoichiometric air-fuel ratios for many individual hydrocarbons or hydrocarbon mixtures. The fuel-air ratio (F/A) is the reciprocal value.

The ratio of the mass of air actually supplied to the mass of fuel may be larger or smaller than the stoichiometric ratio. It is common practice to employ the equivalence ratio, ϕ defined by equation 5. to express the actual air-fuel ratio.

$$\phi = (A/F)_{stoich} / (A/F)_{actual} = (F/A)_{actual} / (F/A)_{stoich}$$

When ϕ is less than 1, more air is being supplied than is required for complete combustion or an excess of air exists and the mixture is referred to as a lean mixture. Conversely, when the value of ϕ is greater than 1, the mass of air supplied is less than that required for complete combustion of the fuel and the mixture is said to be rich (an excess of fuel) (Wark and Warner, 1976).

The values presented in reaction 2. indicate that 52.04 moles of products are formed by the combustion of 1 mole of fuel. If 0.10 percent of the fuel is unburned and is exhausted with the combustion products as unburned hydrocarbon, the exhaust will contain approximately 20 ppm of unburned hydrocarbons. Should the quantity of unburned fuel be 1 percent, the exhaust

would contain roughly 200 ppm. The original emission standard for 1970 was 180 ppm of unburned hydrocarbons. Thus to satisfy the federal emission standards established from 1970 onward, practically complete combustion of the fuel must be attained. The detailed analysis of the combustion of hydrocarbons present in gasoline shows that many (25 to 100) separate competing chemical reactions may occur simultaneously and that the products of combustion vary depending upon the pressure and temperature existing at the time considered. A further complicating factor is the rate at which the chemical reactions occur, since the combustion process is a dynamic phenomenon. There may not be sufficient time for the complete combustion of some of the hydrocarbon species.

The combustion process is initiated by a spark. The combustion flame front then travels outward in all directions through the unburned mixture toward the walls of the combustion chamber. The surfaces of the combustion chamber are either air- or water-cooled. Consequently, the combustible mixture is cooled by contact with these cooler surfaces. This cooling action may lower the temperature of the air-fuel mixture in this region to such an extent that the flame goes out or is quenched before all of the fuel present is burned. This phenomenon is aggravated in combustion chambers which have a large surface-to-volume ratio.

In any case, a film of unburned hydrocarbons will exist along the wall of the cooled cylinder, causing a certain amount of unavoidable flame quenching. These unburned hydrocarbons are removed from the film along the cylinder walls and are exhausted with the combustion gases as the piston and its sealing surfaces (piston rings) move along the cylinder during the exhaust stroke.

Carbon monoxide, like unburned hydrocarbons, results from the incomplete combustion of the fuel. Consequently, those conditions which promote or enhance complete combustion tend to reduce the quantity of carbon monoxide in the exhaust gas of the engine. A major factor is the air-fuel ratio. Tests results presented in figure 2.13 show that as the air fuel ratio increases from 11 to 16, the CO in the exhaust gas decreases from 7.5 to 0.2 percent. The percent CO decreases somewhat more at even higher air-fuel ratios. Thus one method of reducing the CO emission is to operate the engine with lean-mixture ratios.

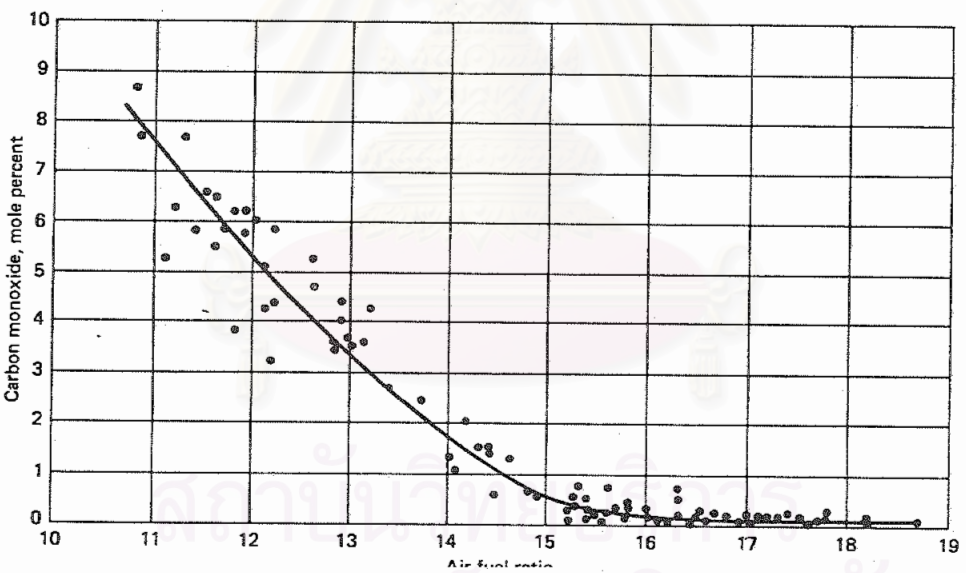

Figure 2.13 Effect of air-fuel ratio on exhaust gas CO concentrations. (Three engines – all data points.) (Source : Wark and Warner, 1976)

The value of the air-fuel ratio also exerts a major influence upon the quantity of unburned hydrocarbons emitted by a given engine. The results of experiments, as presented in figure 2.14, show that the value of unburned hydrocarbons in the exhaust gas first decreases as the air-fuel ratio is increased from 11 to approximately 16, and then increases as the air-fuel ratio increases further to 22.5. The increase in unburned hydrocarbons is attributed to what is known as misfire. The mixture is so lean that combustion does not always proceed from the ignition spark.

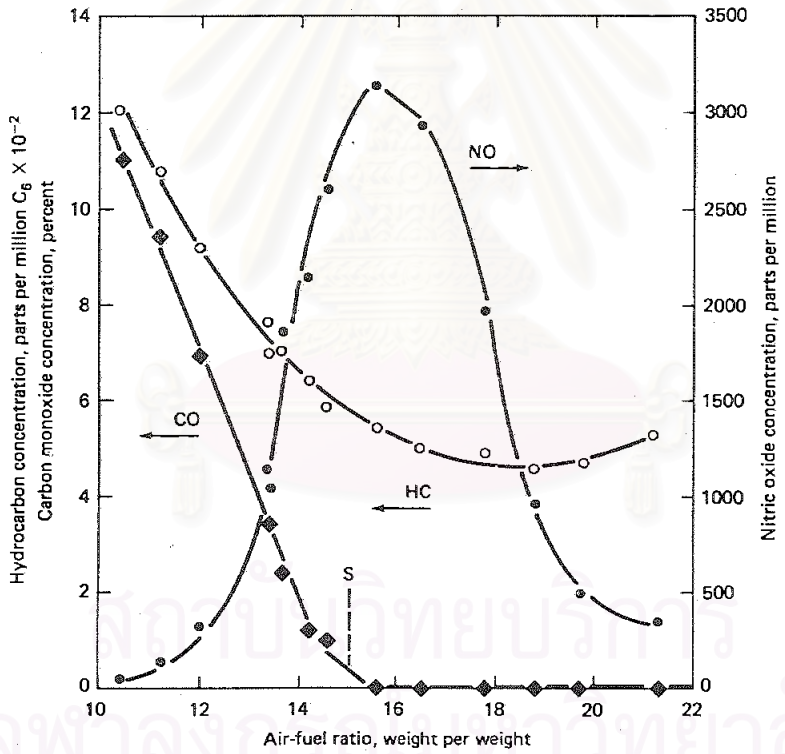

Figure 2.14 The effects of air-fuel ratio on HC, CO, and NO_x exhaust emissions. (Source : Wark and Warner, 1976)

The oxides of nitrogen are formed basically by reactions between atmospheric oxygen and nitrogen inducted into the engine. The major component of the oxides of nitrogen formed in the combustion zone is nitric oxide, NO. The quantities of the oxides of nitrogen formed are complicated functions of temperature, pressure, time of reaction, and the quantities of the reactants present. As indicated in the many experimental results, the following fact is well established: nitric oxide is formed within the combustion chamber during the time period that the maximum temperature exists, and it persists in above-equilibrium quantities during expansion and exhaust. The influence of the air-fuel ratio upon the quantity of NO in the exhaust gas of a typical gasoline engine is presented in figure2.15.

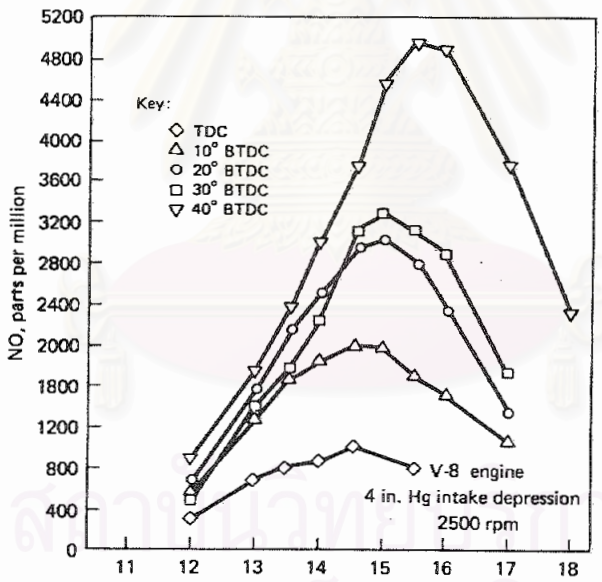

Figure 2.15 NO_x emissions at various air – fuel ratios and ignition timings.
(Source : Wark and Warner, 1976)

Note that the maximum amount of NO is obtained at an air-fuel ratio near stoichiometric.

Comparing the data presented in figures 2.13, 2.14, and 2.15, we can see that as the air-fuel ratio is increased from around 11 : 1, the unburned hydrocarbons and carbon monoxide concentrations decrease. The concentration of NO increases to a maximum at a value of the air-fuel ratio which gives a minimum of unburned hydrocarbons and carbon monoxide. A further increase in air-fuel ratio results in a reduction of NO but an increase in HC. Thus it may be concluded that minimum quantities of HC, NO, and CO cannot be attained concurrently by changes in the air-fuel ratio alone (Wark and Warner, 1976)

2.9 Factors Influencing emissions

If complete combustion of the fuel was possible, vehicle exhaust would contain only carbon dioxide and water vapor. However, as a result of a number of factors including the short time available for combustion in the engine, poor mixing of the fuel and air (e.g. due to unburnt fuel getting trapped in crevices in the engine) and the high temperature of combustion, vehicle exhaust also contains CO, VOCs, PM and NO_x (Holman, 1997)

The principal pollutants emitted from simple gasoline-powered internal combustion engines are carbon monoxide, hydrocarbons, and nitrogen oxides. All these are formed in all other combustion processes, e.g., fossil fuel power plants, kitchen stoves, campfires, and charcoal barbecues. Auto engines produce more of them per unit of fuel burned principally for the following reasons:

1. Auto engines are often oxygen deficient, which most other combustion systems are not.

2. Auto engines preheat their air-fuel mixtures, which most combustion systems do not.

3. Auto engines have unsteady combustion, in which each flame lasts about 0.0025 s. Almost all other combustion systems have steady flames that stand still while the materials burned pass through them.

4. Auto engines have flames that directly contact cooled surfaces, which is not common in other combustion systems. (Nerves, 1995).

The emissions of gasoline automobiles depend on a wide range of factors. The most important of these are discussed briefly in the following items.(Holman, 1997)

1. Fuel Used

Emissions depend on the fuel used to power the vehicle. For example, a car powered by petrol will emit more CO and VOCs and be less fuel efficient than a similar one powered by diesel. However, the diesel car will emit more NO_x and PM. Carbon dioxide emissions depend on fuel consumption and the carbon content of the fuel. Even though diesel is a more dense fuel, the carbon dioxide emissions from a diesel car are less than from a similar petrol car, but the benefit is smaller than the volumetric fuel consumption benefit.

The relative differences in emissions between petrol and diesel cars are shown in Table 2.6.

Table 2.6 Comparison of emission from petrol cars with three way catalysts and diesel cars. (Source : adapted from Holman, 1997)

Pollutant	Petrol without catalyst	Petrol with three way catalyst	Diesel without catalyst	Diesel with oxidation catalyst
Nitrogen oxide	4	1	2	2
Hydrocarbons	4	2	3	1
Carbon monoxide	4	3	2	1
Particulate matter	2	1	4	3
Aldehydes	4	2	3	1
Benzene	4	3	2	1
1,3-Butadiene	4	2	3	1
Polycyclic aromatic hydrocarbons	3	1	4	2
Sulfur dioxide	1	1	4	4
Carbon dioxide	3	4	1	2

1 = Lower emissions
2 or 3 = Intermediate
4 = Highest emissions

A range of alternative fuels such as compressed natural gas and electricity have been used in trials in the UK. These have their own emissions characteristics. Electric vehicles, for example, while being clean (and quiet) in use, contribute to emissions at the power station. These in turn depend on the fuel used to power the generators.

2. Engine Design / Pollution Control

Improvements to engine design and pollution control systems over the past twenty-five years has resulted in emissions from new vehicles now being more than an order of magnitude lower than those from unregulated vehicles.

For petrol engines one of the most important factors influencing emissions is the air to fuel ratio. Figure 2.16 shows that there is no ideal ratio at which all the main emissions are low and the engine power is at an acceptable level. Indeed, where CO and HC are at their lowest, the NO_x emission is at its maximum. A good compromise is found in the lean burn region, and small lean burn engines have been produced. However, their emissions are not as low as conventional petrol engines with a three way catalyst.

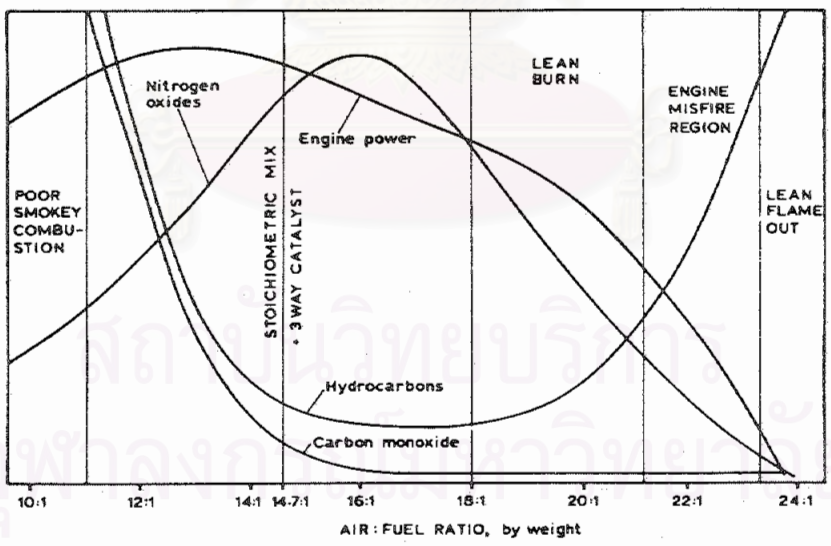

Figure 2.16 The effect of air/fuel ratio on engine operations. (Source ; Holman, 1997)

The greatest step in controlling emissions from road vehicles was the introduction of closed loop (or controlled) three way catalysts for petrol vehicles. These remove 80 to 90 percent of the emissions of CO, VOCs and NO_x. The reactions taking place on the catalyst are shown below :

Oxidation reaction

$$2CO + O_2 \rightarrow 2CO_2$$

$$HC + O_2 \rightarrow CO_2 + H_2O$$

Reduction reaction

$$2CO + 2NO \rightarrow 2C0_2 + N_2$$

$$HC + NO \rightarrow CO_2 + H_2O + N_2$$

Automotive catalysts are typically made from platinum and rhodium. For efficient removal of all three pollutants the air to fuel ratio needs to be close to the stoichiometric ratio (i.e. 14.7 to 1). Cars fitted with these catalysis require an oxygen sensor to monitor the exhaust gas composition and electronically controlled fuel management system to control the air to fuel ratio. The effect on catalyst efficiency of moving away from the stoichiometric air to fuel ratio (i.e. the equivalent ratio $\lambda = 1$) is shown in figure 2.17.

This technology cannot be used in the oxygen rich exhaust of a lean burn petrol or diesel engine. For these engines CO and HC emissions can be reduced using a simple oxidation catalyst. Currently no catalyst exists that is capable of removing NO_x from lean burn engines.

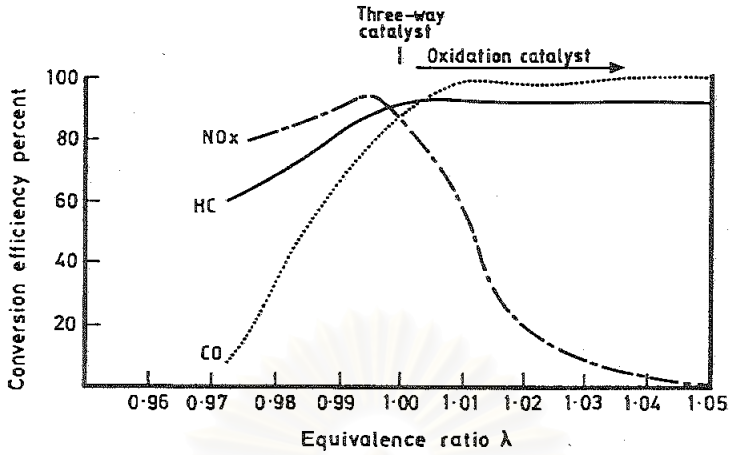

Figure 2.17 The effect on catalyst efficiency of moving away from the stoichiometric air to fuel ratio. (Source : Wark and Warner, 1976)

3. Maintenance.

Poorly maintained vehicles consume more fuel and emit higher levels of CO and VOCs than regularly serviced ones. It has been shown in a number of studies that a relatively small number of vehicles contribute a disproportionate amount of pollution. For example, in 1991, the RAC found that in London and Leicester 12 percent of vehicles were responsible for half the CO emissions. (Vanke cited in Holman, 1997).

In the Netherlands the government has systematically checked emissions of cars in service since 1987. Table 2.7 shows the percentage of different types of cars with excess emissions during the first five years of the programme. Most of the cars failing to meet the standards had excess carbon monoxide emissions. It should be noted that the data from the 6th year of the programme showed that only 3% of cars with newer closed loop catalysts

required tuning, suggesting that modern European catalyst cars are performing better in service than the early ones.

Table 2.7 Percentage of car failing to comply with standard (1987 – 1992)
(Source : Adapted from Holman, 1997)

Type of car	As received (%)
Non catalysts	68
Open loop catalysts	74
Close loop catalysts	9
Diesel	0

4. Driver Behavior / Traffic Congestion

Emissions are not constant but vary depending on how the vehicle is being driven. $N0_x$ emissions increase when the engine is under load such as during rapid acceleration and when travelling at high speeds, while CO and VOCs emissions will increase when it is necessary to run rich, for example, when the engine is cold, and during accelerations. Thus, in general, emissions will be lowest when a car is driven at a steady speed. In the stop-start driving conditions that characterize congested urban areas emissions will be higher than at the same average speed but under free flow conditions.

A recent Dutch study has showed that average emissions can increase by a factor of 3.5 for CO and two for $N0_x$ by driving aggressively due to excursions from the ideal air to fuel ratio during the frequent changes from

acceleration to deceleration and *vice versa,* compared with normal driving. (Heaton cited in Holman, 1997)

Emissions also vary with vehicle speed. For petrol cars without catalysts emissions of CO and VOCs decrease with increasing speed. Emissions are highest at the slow driving speeds characteristic of urban driving. For NO_x the opposite occurs; emissions increase with speed. Emissions from other types of vehicle (petrol with catalyst and diesel) typically have lowest values at medium speeds, with higher emissions at both low and high vehicle speeds.

5. Cold Starts

Most car journeys are very short and are in urban areas. Emissions from cars are particularly high when first driven from a cold start. The emissions penalty is greater (relative to those when hot) for petrol cars with catalysts than for non catalyst petrol and diesel cars, as it takes a few minutes for the catalyst to become fully operational.

The cold start penalty is dependent on the ambient temperature. The colder it is the greater the penalty. For example, it has been estimated that during the first kilometer of a journey in a three way catalyst petrol car the emissions of CO and VOCs arc 70% and 140% higher respectively when the temperature is 0^0 C compared to 10 ^{0}C. Cold start penalties for $N0_x$ for petrol and diesel engines are small. (Holman, 1997)

2.10 Hydrocarbon pollutants

The major sources of volatile organic compounds (which are mainly but not exclusively hydrocarbons) in the UK atmosphere are shown in Figure 2.18. It may be seen that these are rather more diverse than for many of the pollutants and include natural sources such as release from forest trees. In urban areas, road transport is probably the major contributor, although use of solvents, for example in paints and adhesives, can be a very significant source. Emissions from road transport include both the evaporation of fuels and the emission of unburned and partially combusted hydrocarbons and their oxidation products from the vehicle exhaust.

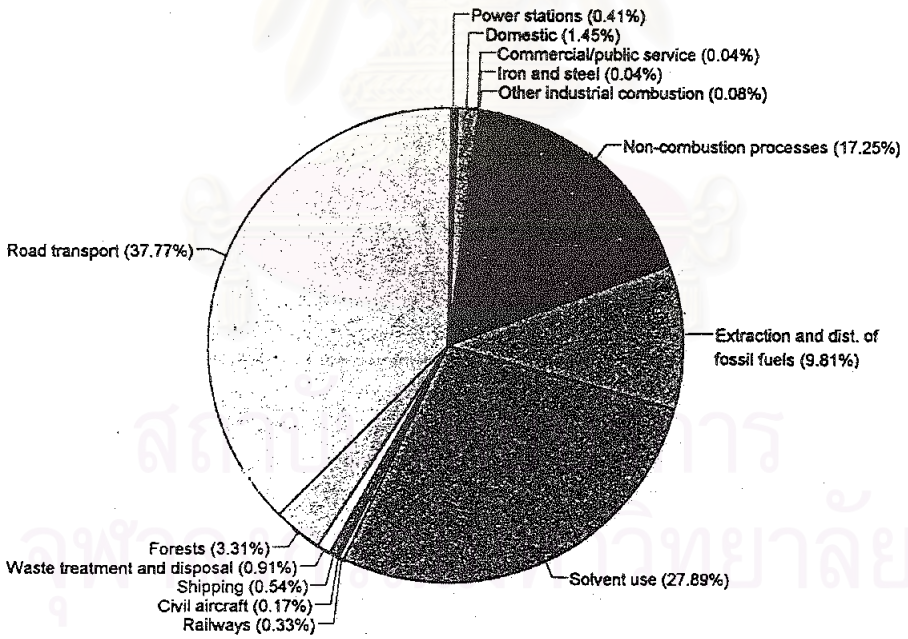

Figure 2.18 Estimated UK emission of volatile organic compounds by source category for 1993. (Source : Harrison, 1997)

Many sources emit a range of individual compounds and careful analytical work has shown measurable levels of in excess of 200 hydrocarbons in some ambient air samples. In the UK the Hydrocarbon Network, which makes automated hourly measurements of volatile organic compounds, reports data on some 26 individual hydrocarbons. A data summary for 1993 appears in Table 2.8.

Table 2.8 Hydrocarbon concentration in London, December 1994 (Source : Harrison, 1997)

	Average (ppb)	*Hour max* (ppb)
Ethane	1.93	13.7
Ethene	2.30	15.3
Propane	3.14	23.6
Propene	2.72	22.6
Ethyne	8.83	71.8
i-Butane	3.03	44.4
n-Butane	6.66	66.8
trans-2-Butene	0.46	5.4
1-Butene	0.65	6.9
cis-2-Butene	0.22	2.9
i-Pentane	3.50	44.4
n-Pentane	0.94	44.6
1,3-Butadiene	0.53	40.1
trans-2-Pentene	0.32	3.1
cis-2-Pentene	0.18	2.0
2-Methyl-pentene	1.15	14.5
3-Methyl-pentene	0.76	10.1
Isoprene	0.48	5.7
n-Hexane	0.35	7.3
n-Heptane	0.20	3.0
Benzene	1.92	22.5
Toluene	2.47	52.9
Ethylbenzene	2.52	38.3
m,p-Xylene	2.41	28.4
o-Xylene	1.10	11.4

Methane, which is not often measured, far exceeds the other hydrocarbons in concentration. The Northern Hemisphere background of this compound is approximately 1.8 ppm and elevated levels occur in urban areas as a result particularly of leakage of natural gas from the distribution system (Harrison, 1997).

There are two major reasons for interest in the concentrations of hydrocarbons in the polluted atmosphere. The first is the direct toxicity of some compounds, particularly benzene and 1,3-butadiene, both of which are chemical carcinogens. The UK Expert Panel on Air Quality Standards has recommended for benzene an ambient air quality standard of 5 ppb measured as a rolling annual average, with a longer term target of 1 ppb rolling annual average. The recommended standard for 1,3-butadiene is 1 ppb rolling annual average. The second cause of concern regarding hydrocarbons is due to their role as precursors of photochemical ozone (Harrison, 1997)

The most concern of chemicals in the ambient air which came from gasoline consumption are Benzene, Toluene and Xylene as we known “BTX”. Environmental inputs of benzene, toluene and the isomeric xylenes, are predominantly anthropogenic. The principal sources of BTX include chemical industry uses such as solvents, oil refineries, fuel oil/petrol combustion for industrial, transport and domestic purposes, the production and use of paints and glues and emissions from coke production facilities. Estimated annual UK emissions of BTX are currently as follows: benzene 13000 tones, toluene 69000 tones, and xylenes 46000 tones. With regard to emissions from motor vehicles; BTX compounds are released as unburnt components of the fuel and, additionally, as products from thermolytic dealkylation of higher

molecular weight monoaromatic compounds. Other sources associated with the use of motor vehicles include refueling of both individual vehicles and petrol stations (Harrad, 1997).

Source, amount and human health effects of BTX are illustrated in table 2.9. (Verschueren, 1977)

Table 2.9 BTX, characteristics and effects on human (Source : Verschueren, 1977)

	Benzene	Toluene	Xylene
Chemical formula	C_6H_6	$C_6H_5CH_3$	$(CH_3)_2C_6H_4$
Source	Petroleum refinery, Solvent recovery plant, Coal tar etc.	Petroleum refinery, Solvent recovery plant, Coal tar distillation etc.	Petroleum distillation, Coal tar distillation, organic chemical industry etc.
User and formation	Organic chemicals, pesticide, plastic and resin, rubber, gasoline, painting and coating etc.	Benzene derivative, gasoline, solvent for paint and coating, gum, resins, adhesive, etc.	Chemical manufacturer, rubber cement, Polyester industry, etc.
Threshold Limit Value (TLV) (ppm)	10 (in yr.1969)	200 (in yr.1974)	100 (in yr.1974)
• Acceptable Ceiling Concentration (ACC) (ppm)	25	300	-
• Acceptable maximum peak (AMP) (ppm)	50 (10 min)	500 (10 min)	-

To be continued

	Benzene	Toluene	Xylene
Man made source • Diesel engine of emitted HCs (%) • Rotary gasoline engine (%) • Reciprocating gasoline (%)	 2.4 1.3 2.2	 3.1 16.3 6.0	 1.9 (m+p xylene) 5.6 (m+p xylene) 1.3(m+p xylene)
% volume in gasoline	1.8 – 5	6 - 7	-
Expect ground level concentration in USA ambient air	Range to 10-50 ppb	Range to 10-50 ppb	-
In gasoline engine exhaust	0.1 – 42.3 ppm (partly methylvinylketone)	0.1 – 7.0 ppm (partly crotonaldehyde)	-
Effect on human • Severe toxic effect (ppm) • Symptoms of illness (ppm) • Unsatisfactory (ppm)	 1500 (60 min) 500 (60 min) 50 (60 min)	 1000 (60 min) 300 (60 min) > 100 (60 min)	 1000 (60 min) 300 (60 min) 100 (60 min)

2.11 BTX in exhaust gas

Emission of gasoline automobiles exhaust are one of the largest anthropogenic sources of Benzene , Toluene and Xylene as known as BTX. Many of studies considered the amount of BTX in exhaust emission from automobile. Unfortunately, most of these studies are investigated by the American, European and Australian researcher on their own country condition. Only a few researches on BTX in exhaust emission in Asian countries are studied. In this Thesis research, try to summarize the up to date research works on BTX in exhaust emission in both of Thailand and other countries and compare of the results on each study.

Duffy et.al (1999) studied on the speciated hydrocarbon profiles and calculated reactivities of exhaust and evaporative emission from 82 in-use light-duty Australian vehicles. On their research, Mass emissions of non-methane hydrocarbon (NMHC) from 26 pre-1986 and 56 post-1985 catalyst-equipped in-service vehicles were determined from measurements made on a chassis dynamometer using an urban drive cycle . The characteristics of vehicles tested are shown in table 2.10. The average mass emissions per ADR test (mg/km) for both the pre-1986 nc-lp vehicles and the post –1985 ce-ulp vehicles are given in table 2.11. While the average normalized composition for the exhaust emissions from both the pre-1986 nc-lp and the post –1985 ce-ulp vehicles are presented in table 2.12.

Table 2.10 Distribution by age and manufacture of the 82 vehicles tested for exhaust and/or evaporative hydrocarbon (Source: Duffy et. al,1999)

Year of manufacture	Manufacture					Total by year	No. with oxidative catalysts	No. with 3-way catalysts	Average odometer reading
	Ford	General Motors	Toyota	Mitsubishi	Nissan				
Pre-1986, non-catalyst-equipped, fuelled with leaded petrol									
1980	1	2	—	1	—	4	—	—	192852
1981	3	3	2	—	1	9	—	—	160839
1982	1	—	2	—	1	4	—	—	125843
1983	3	1	—	—	—	4	—	—	178453
1984	2	1	—	1	—	4	—	—	154141
1985	—	—	1	—	—	1	—	—	127046
Total	10	7	5	2	2	26			
Post-1986, catalyst-equipped, fuelled with unleaded petrol									
1986	3	—	2	1	1	7	4	3	134049
1987	3	3	—	3	—	9	4	5	123062
1988	2	—	1	2	1	6	3	3	85385
1989	3	—	1	4	—	8	5	3	73428
1990	4	2	2	—	1	9	4	5	86387
1991	3	5	5	—	4	17	3	14	58562
Total	18	10	11	10	7	56			

Table 2.11 Average per kilometer emission (mg/km) from the ADR test schedule for both pre –1986, non-catalyst-equipped vehicles fuelled with leaded petrol and post-1985, catalyst-equipped vehicles fuelled with unleaded petrol (Source: Duffy et. al,1999)

Compound	Pre-1986 vehicles				Post-1985 vehicles			
	Avg. emiss. per ADR test (mg/km)		No. Cars averaged	Ratio HT/CT emissions	Avg. emiss. per ADR test (mg/km)		No. Cars averaged	Ratio HT/CT emissions
	Mean	SD			Mean	SD		
Ethane	22	11	19	0.88	9.5	5	42	0.67
Ethene (ethylene)	135	94	19	0.68	35	45	42	0.40
Propane	3.2	3.9	23	0.44	1.1	0.8	56	0.58
Propene	96	39	23	0.81	18	20	56	0.40
Ethyne (acetylene)	159	93	19	0.94	24	43	42	0.10
Propyne	10	4	8	0.82	1.3	2.3	32	0.25
i-Butane	20	16	26	0.68	5.2	3.5	56	0.45
n-Butane	44	36	26	0.51	12	8	56	0.49
1-Butene + *i*-butene	42	16	26	0.80	8.4	8.8	56	0.36
trans-2-Butene	8.9	4.4	26	0.70	1.8	1.7	56	0.34
cis-2-Butene	6.2	2.6	26	0.66	1.5	1.3	56	0.29
Butyne	5.3	5.6	8	0.49	2.8	2.3	32	0.33
Cyclopentene	1.6	0.6	8	0.62	0.5	0.4	32	0.21
Cyclopentane	4.2	3.1	23	0.58	1.2	0.9	56	0.37
i-Pentane	133	98	26	0.58	39	26	56	0.44
n-Pentane	80	61	26	0.54	21	14	56	0.42
1,3-Butadiene	18	9	25	0.63	3.5	4.9	49	0.44
Isoprene	0.9	0.6	8	0.51	0.7	1.2	32	0.36
C5 unsaturates	32	23	26	0.50	5.4	5.2	56	0.26
Methylcyclopentane	18	14	18	0.52	4.1	3	24	0.35
Cyclohexane	3.3	2.4	15	0.69	0.5	0.4	24	0.31
2,3-Dimethylbutane	12	8	18	0.51	2.3	1.3	24	0.41
2-Methylpentane	48	31	26	0.52	15	11	56	0.37
3-Methylpentane	42	37	26	0.48	11	8	56	0.35
n-Hexane	36	27	26	0.49	10	8	56	0.35
C6 unsaturates	20	19	26	0.43	3	5.3	56	0.13
C7 cycloalkanes	5.8	4.2	15	0.46	1.3	1	24	0.32
2,4-Dimethylpentane	7.3	4.9	15	0.46	1.5	1.1	24	0.35
Methylcyclohexane	5.1	3.3	15	0.44	1	0.8	24	0.29
2- + 3-Methylhexane	45	31	18	0.47	10	9	24	0.32
n-Heptane	12	8	26	0.49	3.6	3	56	0.31
Benzene	149	64	26	0.65	42	35	56	0.36
2,2,4-Trimethylpentane	6.2	4.7	26	0.54	1.8	1.2	56	0.35
n-Octane	4.1	2.6	26	0.53	1.3	1.2	56	0.29
Toluene	259	124	26	0.60	62	66	56	0.30
Ethylbenzene	35	14	26	0.58	9	9.9	56	0.28
Nonane	1.2	0.8	8	0.53	0.7	0.7	32	0.25
m + *p*-Xylene	125	51	26	0.56	35	38	56	0.27
o-Xylene	46	26	26	0.60	12	12	56	0.28
Styrene	5.6	3.0	18	0.62	1	0.9	24	0.49
1,3,5-Trimethylbenzene + alkane	10	5	26	0.59	3.2	3.9	56	0.30
Decane	1.1	1.1	8	0.29	0.6	0.5	32	0.25
m + *p*-Ethyltoluene	32	15	18	0.64	5.7	6.4	24	0.32
n-Propylbenzene	7.2	5.8	18	0.50	1.4	2.7	24	0.41
o-Ethyltoluene	7.5	3.7	18	0.67	1.4	1.7	24	0.32
1,2,4-Trimethylbenzene	23	12	18	0.67	4.2	5.6	24	0.34
Unidentified hydrocarbons	96	101	23	0.64	12	20	56	0.26
Sum of identified HCs (g)	1.9			0.62	0.4			0.33
Criteria Pollutants (EPA)								
CO (g)	24	13	26		10	9	56	
CO_2 (g)	230	46	26		244	41	56	
NO_x (g)	2.5	0.9	26		1.3	0.8	56	
HC (g)	2.3	1.2	26	0.60	0.6	0.5	56	0.33

Table 2.12 The composition of exhaust based on average ADR mass emission compared to the average normalised composition of the exhaust for both pre-1985 and post-1985 vehicles. (Source: Duffy et. al,1999)

Compound	Pre-1986 nc-lp			Post-1985 cc-ulp		
	Composition based on avg. ADR mass emissions (%w/w)	Normalised Comp (%w/w)		Composition based on avg. ADR mass emissions (%w/w)	Normalised Comp (%w/w)	
		Mean	SD		Mean	SD
Ethane	1.2	1.2	0.4	2.1	2.9	1.1
Ethene (ethylene)	7.2	7.2	3.7	7.9	7.8	4.2
Propane	0.2	0.2	0.1	0.2	0.3	0.3
Propene	5.1	6.3	2.1	4.0	3.9	1.4
Ethyne (acetylene)	8.4	8.3	2.8	5.4	4.4	5.4
Propyne	0.5	1.0	0.4	0.3	0.2	0.2
i-Butane	1.1	1.1	0.5	1.2	1.6	0.9
n-Butane	2.4	2.5	0.9	2.7	3.6	1.9
1-Butene + *i*-butene	2.2	2.8	0.9	1.9	1.9	0.5
trans-2-Butene	0.5	0.6	0.3	0.4	0.4	0.1
cis-2-Butene	0.3	0.4	0.1	0.3	0.4	0.2
Butyne	0.3	0.4	0.3	0.6	0.5	0.5
Cyclopentene	0.1	0.2	0.0	0.1	0.1	0.0
Cyclopentane	0.2	0.2	0.1	0.3	0.3	0.1
i-Pentane	7.1	7.7	1.9	8.8	10.8	3.4
n-Pentane	4.2	4.5	1.0	4.6	5.6	1.5
1,3-Butadiene	1.0	1.2	0.6	0.8	0.7	0.7
isoprene	0.0	0.1	0.1	0.1	0.1	0.1
C5 unsaturates	1.7	1.8	0.4	1.2	1.4	1.3
Methylcyclopentane	1.0	0.9	0.2	0.9	1.2	0.3
Cyclohexane	0.2	0.2	0.1	0.1	0.1	0.0
2,3-Dimethylbutane	0.6	0.6	0.2	0.5	0.7	0.2
2-Methylpentane	2.6	2.8	0.6	3.4	3.9	0.9
3-Methylpentane	2.2	2.3	0.6	2.5	2.9	0.7
n-Hexane	1.9	2.0	0.4	2.2	2.6	0.5
C6 unsaturates	1.1	1.0	0.4	0.7	0.8	1.4
C7 cycloalkanes	0.3	0.3	0.1	0.3	0.4	0.1
2,4-Dimethylpentane	0.4	0.3	0.1	0.3	0.4	0.1
Methylcyclohexane	0.3	0.2	0.1	0.2	0.3	0.1
2- + 3-Methylhexane	2.4	2.2	0.5	2.3	2.8	0.4
n-Heptane	0.6	0.7	0.1	0.8	0.9	0.2
Benzene	7.9	9.4	1.8	9.3	10.4	2.5
2,2,4-Trimethylpentane	0.3	0.4	0.2	0.4	0.5	0.2
n-Octane	0.2	0.2	0.1	0.3	0.3	0.1
Toluene	13.8	16.1	2.8	13.9	14.2	3.1
Ethylbenzene	1.8	2.3	0.7	2.0	2.0	0.6
Nonane	0.1	0.1	0.0	0.1	0.1	0.1
m + *p*-Xylene	6.6	8.1	2.4	7.8	8.0	2.3
o-Xylene	2.5	2.8	0.7	2.6	2.7	0.8
Styrene	0.3	0.3	0.2	0.2	0.1	0.2
1,3,5-Trimethylbenzene + alkane	0.5	0.7	0.3	0.7	0.7	0.4
Decane	0.1	0.1	0.1	0.1	0.1	0.1
m + *p*-Ethyltoluene	1.7	1.7	0.7	1.3	1.4	0.4
n-Propylbenzene	0.4	0.4	0.2	0.3	0.3	0.2
o-Ethyltoluene	0.4	0.4	0.2	0.3	0.4	0.1
1,2,4-Trimethylbenzene	1.2	1.3	0.7	0.9	1.0	0.4
Unidentified hydrocarbons	5.1	4.5	3.5	2.6	3.2	3.9

As expected, the average per vehicle mass emissions of the individual HCs from the older pre-1986 vehicles were much higher (generally 4 - 7 times) than the emissions from newer, catalyst-equipped vehicles. The effect of the catalyst on the composition of the exhaust emission is also and important issue. Table 2.13 shows the ratio of the average composition for pre-1986 and post –1985 vehicles. Values greater than one indicate that the compound is more likely to be destroyed by the catalytic converter. On face value the data in table 2.13 would indicate that the substituted aromatics are more effectively removed by the catalyst than benzene. The order from least to most effectively removed was observed to be methane < saturated hydrocarbon < aromatics < unsaturated hydrocarbons.

Table 2.13 Ratio of the average exhaust compositions of the pre-1986 and post-1985 vehicles for selected hydrocarbons. (Source: Duffy et. al,1999)

Compound	Ratio of pre-1986 to post-1985 average normalised compositions
Ethane	0.43
Ethene (ethylene)	0.92
Propane	0.61
Propene	1.62
Ethyne (acetylene)	1.88
n-Butane	0.69
trans-2-Butene	1.46
n-Pentane	0.81
1,3-Butadiene	1.65
n-Heptane	0.75
Benzene	0.90
Toluene	1.13
o-Xylene	1.05
Styrene	3.28
m + *p*-Ethyltoluene	1.24
n-Propylbenzene	1.29
o-Ethyltoluene	1.02
1,2,4-Trimethylbenzene	1.29

About 54.8 % of the vehicles registered in the state of NSW and Victoria, Australia were manufactured prior to the introduction of catalytic converter technology. This value was used to weight the average ADR mass emission of

nc-lp and ce-lp vehicles to estimate the average emission from the entire vehicle fleet. The resultant mass emission were then used to determine the composition of exhaust emissions. This composition is presented in table 2.14.

Table 2.14 Composition of exhaust based on mass emissions weightted for the age distribution of the car fleet compared to that measured in the Sydney Harbour Tunnel (Duffy and Nelson, 1996) and the composition of 4 types of petrol. (Source: Duffy et. al,1999)

Compound	Composition based on weighted mass emiss. (%w/w NMHC)	Composition Sydney Harbour Tunnel[a] (%w/w NMHC)	Avg. petrol comp. (%w/w)			
			This study		Typical Sydney petrol[a]	
			Leaded	Unleaded	Leaded	Unleaded
Ethane	1.3	2.0	0.0	0.0	0.0	0.0
Ethene (ethylene)	7.3	6.3	0.0	0.0	0.0	0.0
Propane	0.2	4.4	0.1	0.1	0.2	0.2
Propene	4.9	5.2	0.0	0.0	0.0	0.0
Ethyne (acetylene)	7.9	6.7	0.0	0.0	0.0	0.0
Propyne	0.5	0.5	0.0	0.0	0.0	0.0
i-Butane	1.1	2.7	1.1	1.3	1.1	1.2
n-Butane	2.4	3.9	3.0	3.4	2.0	2.2
1-Butene + *i*-Butene	2.2	2.7	0.1	0.1	0.4	0.5
trans-2-Butene	0.5	0.7	0.2	0.2	0.5	0.5
cis-2-Butene	0.3	0.6	0.2	0.2	0.4	0.4
Butyne	0.3					
Cyclopentene	0.1	0.2			0.3	0.3
Cyclopentane	0.2					
i-Pentane	7.4	6.4	12.2	12.3	6.8	6.4
n-Pentane	4.3	2.5	7.2	6.5	3.5	3.3
1,3-Butadiene	0.9	1.1			0.0	0.0
Isoprene	0.1					
C5 unsaturates	1.6	2.8			3.9	4.1
Methylcyclopentane	1.0	1.0			1.6	1.6
Cyclohexane	0.2	0.4			0.4	0.2
2,3-Dimethylbutane	0.6		1.1	1.2		
2-Methylpentane	2.7	2.6	4.8	5.0	4.2	4.1
3-Methylpentane	2.3	1.7	3.3	3.4	2.7	2.6
n-Hexane	1.9	1.6	3.3	3.2	2.5	2.4
C6 unsaturates	1.0	2.1			3.1	3.5
C7 cycloalkanes	0.3	0.5				
2,4-Dimethylpentane	0.4	0.4			0.5	0.6
Methylcyclohexane	0.3	0.5			1.1	1.1
2- + 3-Methylhexane	2.4	2.3	1.7	1.8	4.5	4.3
n-Heptane	0.7	0.7	1.1	1.1	1.4	1.4
Benzene	8.1	5.2	5.7	5.0	3.5	3.0
2,2,4-Trimethylpentane	0.3					
n-Octane	0.2	0.3			0.7	0.8
Toluene	13.8	9.3	14.7	13.5	11.7	9.6
Ethylbenzene	1.9	1.3	2.1	2.0	1.9	1.6
Nonane	0.1					
m + *p*-Xylene	6.8	4.9	9.2	8.7	8.3	7.0
o-Xylene	2.5	1.8	3.0	2.9	3.1	2.6
Styrene	0.3					
1,3,5-Trimethylbenzene + alkane	0.6	0.4	0.8	0.8	0.9	0.8
decane	0.1					
m + *p*-Ethyltoluene	1.6	1.3			2.1	1.9
n-Propylbenzene	0.4					
o-Ethyltoluene	0.4	0.4			0.8	0.7
1,2,4-Trimethylbenzene	1.2	1.1	2.2	2.2	2.8	2.5
Unidentified hydrocarbons	4.7	8.5	23.1	25.0	21.5	27.0

[a] Duffy and Nelson (1996)

The latter finding let us to investigate whether the composition of the exhaust could be predicted from the petrol composition. In figure 2.19 shows the relationship between vehicle exhaust and petrol composition.

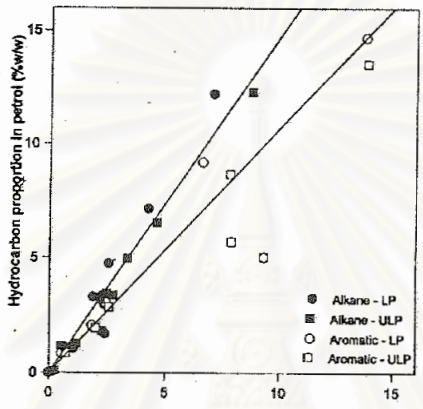

Figure 2.19 Relatioship between vehicle exhaust petrol composition. (Source : Duffy et.al, 1999)

Evaporative emissions were measured on a subset (4 pre-1986 and 8 post-1985) of these vehicles. Average ADK emissions (mg/km) of the individual HCs from the older pre-1986 vehicles were generally 4 - 7 times the emissions from newer catalyst-equipped vehicles. Evaporative emissions from the older vehicles are also much higher than those of newer vehicles. Exhaust

from newer catalyst-equipped vehicles had lower proportions of substituted aromatics and alkenes and higher proportions of lower molecular weight alkanes.

The effect of fuel type on the exhaust emissions was also investigated by refueling 9 of the pre 1986 vehicles with both unleaded and leaded petrol. A 20-40% reduction in HC mass emissions was observed when unleaded petrol was used instead of leaded petrol. The results of this are presented in table 2.15.

Reactivities of the emissions and the contributions from different classes of compounds are also reported. The specific reactivity of the exhaust emissions from newer vehicles was lower than that for older vehicles owing to the smaller proportions of highly reactive alkenes and substituted aromatic species. Moreover, as older vehicles have higher average mass emissions, when considered on a per-km basis, the pre-1986 vehicles have a greater ozone-forming potential than post-1985 vehicles. The specific reactivities of the NMHC (gO_3/gNMHC) of both the heat build and hot soak evaporative emissions were much lower than the exhaust emissions.

Table 2.15 Average emission (mg/km) during the ADR test schedule for the pre-1986 vehicles tested with both leaded and unleaded petrol, and the corresponding reduction in emissions observed by using unleaded petrol (Source: Duffy et. al,1999)

Compound	LEADED Avg. emiss. per ADR test (mg/km)		UNLEADED Avg. emiss. per ADR test (mg/km)		No. cars averaged	% Reduction ADR emissions
	Mean	SD	Mean	SD		
Ethane	20	5	19	5	6	6
Ethene (ethylene)	151	68	141	58	6	7
Propane	2.1	0.9	2.1	0.6	6	− 2
Propene	88	26	86	21	6	2
Ethyne (acetylene)	115	48	117	31	6	− 2
Propyne	11	5	10	4	3	6
i-Butane	19	9	19	18	9	0
n-Butane	38	21	29	9	9	33
1-Butene + *i*-Butene	39	11	39	7	9	0
trans-2-Butene	10	5	10	5	9	7
cis-2-Butene	7	2	6	1	9	14
Butyne	11	5	11	1	3	0
Cyclopentene	2.0	0.8	1.5	0.5	3	32
Cyclopentane	4.3	2.4	3.0	1.0	6	41
i-Pentane	136	79	101	26	9	34
n-Pentane	76	45	54	16	9	40
1,3-Butadiene	17	8	14	7	9	18
Isoprene	1.1	0.7	1.5	0.4	3	− 24
C5 unsaturates	30	18	24	7	9	23
Methylcyclopentane	12	6	10	3	6	23
Cyclohexane	3.9	2.8	3.0	3.8	3	28
2,3-Dimethylbutane	12	7	10	3	6	24
2-Methylpentane	48	22	39	11	9	25
3-Methylpentane	39	23	29	8	9	35
n-Hexane	35	20	26	7	9	36
C6 unsaturates	16	14	12	5	9	38
C7 cycloalkanes	4.7	3.8	3.2	0.9	3	50
2,4-Dimethylpentane	6.3	5.5	3.9	1.0	3	64
Methylcyclohexane	3.8	3.3	2.6	0.8	3	50
2- + 3-Methylhexane	39	24	29	7	6	33
n-Heptane	11	6	9	3	9	22
Benzene	149	44	124	30	9	20
2,2,4-Trimethylpentane	5.6	3.3	8	9	9	− 31
n-Octane	4.1	2.1	3.3	1.2	9	23
Toluene	269	87	220	58	9	22
Ethylbenzene	40	14	33	10	9	23
Nonane	2.0	0.7	1.4	0.8	3	40
m + *p*-Xylene	144	43	119	36	9	21
o-Xylene	47	15	39	10	9	23
Styrene	7	4	5	4	6	34
1,3,5-Trimethylbenzene + alkane	13	5	10	4	9	29
Decane	2.0	1.4	1.9	0.4	3	3
m + *p*-Ethyltoluene	35	9	31	11	6	12
n-Propylbenzene	9	8	4.5	3.1	6	88
o-Ethyltoluene	9	3	7	3	6	21
1,2,4-Trimethylbenzene	29	11	26	10	6	12
Unidentified hydrocarbons	86	124	54	61	6	59
Sum of identified HCs (g)	1.9	1.5				
Criteria pollutants (EPA)						
CO (g)	23	5	21	6	9	
CO_2 (g)	208	19	209	19	9	
NO_x (g)	2.2	0.6	2.3	0.6	9	
HC (g)	2.2	0.8	1.9	0.4	9	

Nelson and Quigley (1984) studied on the hydrocarbon composition of exhaust emitted from gasoline fueled vehicles. In their study, $C_2 - C_{12}$ HC concentrations were determined in the exhaust gas from the 67 vehicles. Average vehicle exhaust compositions were calculated from: (i) the individual compositions obtained for each vehicle by normalizing the concentrations on a weight basis and (ii) the individual compositions weighted according to the total HC concentration in the exhaust gas of each vehicle.

The second procedure of their work results in vehicles with higher HC mass emission rates having proportionately more influence on the average compositions, a situation which corresponds to exhaust emissions into an ambient atmosphere. However, as will be seen from a examination of the two averages (table 2.16) the exhaust HC composition is reasonably insensitive to variation in the mass emission rates. In general the HCs which are present in exhaust due to combustion of the fuel such as ethylene and propylene, are somewhat higher in the composition derived from equally weighting each vehicle, whilst the opposite is true for HCs which are components of the fuel. In any case the differences between the averages are well within the standard deviations observed for this vehicle population. The second average is probably a marginally better representation of the average vehicle exhaust composition, provided that the mass emission rates of these vehicles are compatible with those of the total population.

Table 2.16 Average exhaust hydrocarbon compositions (%w/w NMHC) for Sydney vehicles (Source : Nelson and Quigley, 1984)

Hydrocarbon	Composition (each vehicle equally weighted) Average	Standard deviation	Composition (weighted according to vehicle emission rates)
Ethane	1.4	0.5	1.2
Ethylene	11.2	3.2	10.1
Acetylene	8.7	2.7	8.9
Propane	0.1	0.1	0.1
Propylene	5.0	1.6	4.4
Methylacetylene	0.4	0.3	0.4
n-Butane	2.1	0.6	2.2
i-Butane	1.0	0.3	1.1
l-Butene	0.9	0.3	0.8
i-Butene	1.4	0.6	1.2
trans-2-Butene	0.6	0.4	0.6
cis-2-Butene	0.5	0.2	0.4
n-Pentane	3.0	0.7	3.3
i-Pentane	4.8	0.9	5.3
Cyclopentane	0.4	0.1	0.4
1-Pentene	0.2	0.1	0.2
trans-2-Pentene	0.3	0.2	0.3
cis-2-Pentene	0.3	0.2	0.3
2-Methyl-l-butene	0.3	0.2	0.3
2-Methyl-2-butene	0.5	0.2	0.5
n-Hexane	1.9	0.4	2.0
2-Methylpentane	2.3	0.4	2.4
3-Methylpentane	1.6	0.3	1.7
2,2-Dimethylbutane	0.3	0.2	0.4
2,3-Dimethylbutane	0.6	0.1	0.6
Methylcyclopentane	1.0	0.2	1.0
Cyclohexane	0.6	0.2	0.6
C_6 Olefins	0.7	0.2	0.7
Benzene	5.0	0.7	4.9
n-Heptane	0.8	0.2	0.9
2-Methylhexane	1.5	0.3	1.6
3-Methylhexane	1.2	0.3	1.3
2,4-Dimethylpentane	0.3	0.1	0.3
Methylcyclohexane	0.6	0.2	0.6
Other C_7 cycloalkanes	0.3	0.2	0.3
Toluene	10.2	0.9	10.2
n-Octane	0.4	0.1	0.4
2,2,4-Trimethylpentane	1.0	0.4	1.0
Other C_8 alkanes	3.2	0.7	3.2
Ethylbenzene	1.9	0.2	1.9
m,p-Xylenes	6.5	0.9	6.7
o-Xylene	2.5	0.4	2.5
n-Nonane	0.2	0.1	0.2
Other C_9 alkanes	1.7	0.4	1.7
n-Propylbenzene	0.4	0.1	0.5
i-Propylbenzene	0.2	0.1	0.2
1,2,4-Trimethylbenzene	1.9	0.3	2.1
1,3,5-Trimethylbenzene	0.7	0.1	0.8
m,p-Ethyltoluenes	2.0	0.3	2.1
o-Ethyltoluene	0.6	0.2	0.6
n-Decane	0.4	0.1	0.4
Other C_{10} alkanes and aromatics	0.9	0.4	0.9
C_{11} and C_{12} alkanes and aromatics	3.6	1.1	3.6

And they also found that ; emissions of compounds, which derive from the fuel, are relatively insensitive to the total mass emitted by the vehicle. There are slight decreases in the relative concentrations of these compounds with decreases in total emissions but they are not statistically significant. This is because the relatively small increases in the combustion-derived olefins are spread over a great number of fuel components.

Complete data for the emission of i-pentane, toluene and m,p-xylenes, the three most significant fuel-derived exhaust HCs, plotted against total emissions from the vehicles, are presented in figure 2.20 (a – c). Figure 2.20 demonstrates that the relative proportions of these components are almost independent of the total mass of HCs emitted by the vehicles.

The relationship between the composition of exhaust and the petrol used in Sydney was also examined in their study. The determination of the composition of the petrol has been described in brief in this study. Monthly samples were collected from each of the refineries. These were mix in accordance with the relative sales figure of the premium and regular grades and analyzed. The final average composition was derived from 115 separate samples.

In Figure 2.21 the proportions of 20 C_4-C_{10} alkanes and 10 C_6-C_9 aromatics in Sydney petrol are plotted against their % w/w NMHC in exhaust. The data fall on two lines: the alkane lie on one line and aromatic on another. The proportion of aromatics compared with alkanes is enriched in exhaust relative to that in petrol. There is thus, avery close relationship between fuel

and exhaust compositions but it not simply produced by emissions of totally unburnt petrol.

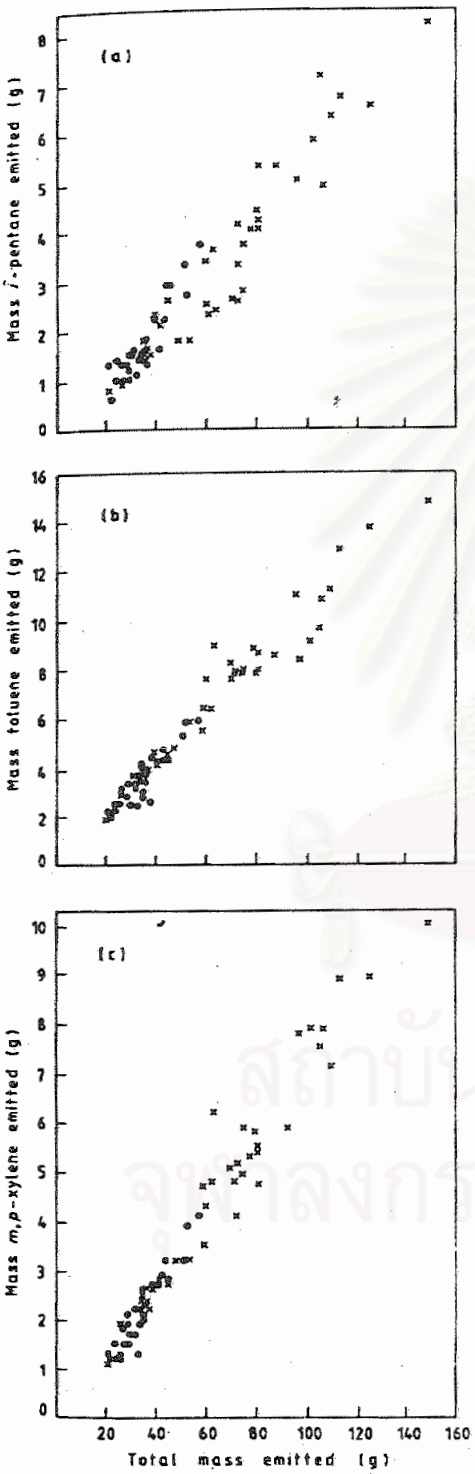

Figure 2.20 Mass of fuel components emitted by vehicles as a function of total hydrocarbon mass emitted by the vehicle during complete test cycles. (a) I-pentane, (b) toluene, (c) m,p-xylenes (combined) (X, pre-ADR 27A controls; ●, post-ADR 27A controls).
(Source : Nelson and Quigley, 1984)

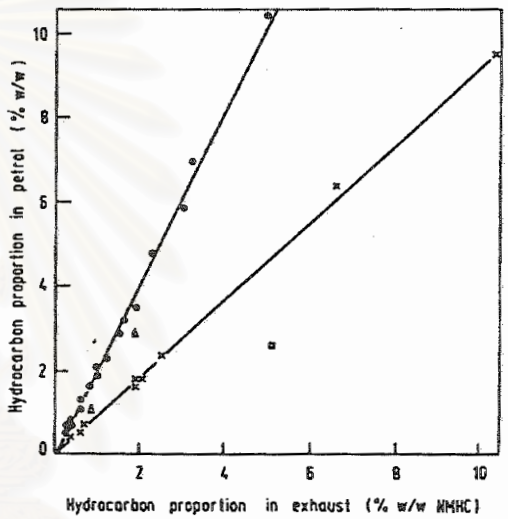

Figure 2.21 Relationship between the composition of vehicle exhaust and of petrol. (● , aliphatics (excluding butanes); ▲ butanes; X aromatics; □benzene).
(Source : Nelson and Quigley, 1984)

Duffy et.al (1998) investigated the emissions of Benzene, Toluene, Xylene and 1,3-Butadiene from a representative portion of the Australian car fleet. In this study, the exhaust emissions of the air toxics benzene, toluene, total xylenes and 1,3-butadiene have been measured in the cold transient (CT), cold stabilised (CS) and hot transient (HT) phases of the Australian Design Rule (ADR) 37/00 Drive cycle for 19 pre-1986 non-catalyst-equipped vehicles fuelled with leaded petrol, and 56 post-1985 catalyst-equipped vehicles fuelled with unleaded petrol. The details of the car samples are shown in table 2.17.

Table 2.17 Distribution by age and manufacture of the 75 vehicles tested for exhaust emissions of benzene, toluene, xylene and 1,3-butadiene using the ADR 37/00 drive cycle

(Source: Duffy et. al ,1998)

	Manufacture								
Year of manufacture	Ford	Holden	Toyota	Mitsubishi	Nissan	Total by year	No. with oxidative catalysts	No. with 3-way catalysts	Avg. odometer reading
				Pre-1986, non-catalyst-equipped, fuelled with leaded petrol					
1980	1	2	—	1	—	4	—	—	192,852
1981	3	1	2	—	—	6	—	—	157,640
1982	1	—	2	—	1	4	—	—	125,843
1983	1	1	—	—	—	2	—	—	195,413
1984	2	—	—	—	—	2	—	—	196,700
1985	—	—	1	—	—	1	—	—	127,046
Total	8	4	5	1	1	19			
				Post-1986, catalyst-equipped, fuelled with unleaded petrol					
1986	3	—	2	1	1	7	4	3	134,049
1987	3	3	—	3	—	9	4	5	123,062
1988	2	—	1	2	1	6	3	3	85,385
1989	3	—	1	4	—	8	5	3	73,428
1990	4	2	2	—	1	9	4	5	86,387
1991	3	5	5	—	4	17	3	14	58,562
Total	18	10	11	10	7	56			

Per vehicle exhaust emissions, averaged over the 3 phases of the ADR 37/00 test, of 1,3-butadiene, benzene, toluene, and total xylenes for the older vehicles were about 19, 139, 240 and 164 mg/km respectively . The corresponding emissions for the better 46 of the 56 post-1985 vehicles tested were 1.7,28.1,36.4, and 27.0 mg/km respectively. (table 2.18 and 2.19)

Table 2.18 Per vehicle exhaust emission (mg/km) of benzene, toluene, xylene and 1,3-butadiene calculates as aweighted average over the three phases of the ADR 37/00 Drive cycle for 19 pre-1986, nc-lp and 56 post-1985, ce-ulp motor vehicles (Source: Duffy et. al ,1998)

Vehicle group		Benzene Avg. ADR	Toluene Avg. ADR	Xylenes Avg. ADR	1,3-butadiene Avg. ADR
19 Pre-1986, nc-lp	Max	234.3	425.0	292.9	40.3
	Min	59.9	92.0	64.3	5.0
	Ratio Max to Min	3.9	4.6	4.6	8.1
	Average	139.1	240.5	164.0	18.7
	Std	52.3	94.2	60.4	9.9
56 Post-1986, ce-ulp	Max	146.4	281.5	238.5	24.6
	Min	8.8	11.8	8.4	0.4
	Ratio Max to Min	16.6	23.9	28.4	61.5
	Average (all 56)	41.8	61.9	46.5	3.6
	Std	34.7	65.7	50.4	5.2
	Average (better 46)	28.1	36.4	27.0	1.7
	Std	13.5	17.4	13.5	1.2
	Average (worst 10)	104.8	179.5	136.3	12.0
	Std	32.5	78.4	61.1	7.3
	Post-1986/Pre-1986 (%)	30.1	25.7	28.4	19.3
	Better 46 Post-1986/Pre-1986 (%)	20.2	15.1	16.5	9.1

Table 2.19 Comparison of previously reported exhaust emission (mg/km) of benzene, toluene, xylene ,and 1,3-butadiene with those recorded in the present study

Place	Vehicle age group	Type of study	Details	Fuel	Emissions (mg km) Benzene	Toluene	Xylenes	1,3-Butadiene	Reference
USA	1975	FTP	3 cars, year catalysts introduced	Regular grade	77.3	157.4	166.0	—	Sigsby *et al.* (1987)
	1976		4 cars		47.9	101.2	57.2	—	
	1977		4 cars		54.4	108.9	119.3	—	
	1978		5 cars		63.3	169.5	78.2	—	
	1979		5 cars		51.8	125.4	76.3	—	
	1980		7 cars		25.1	39.4	39.4	—	
	1981		12 cars		15.4	20.7	19.3	—	
	1982		6 cars		11.4	11.8	11.4	—	
	Average				36.0	65.3	50.6	—	
USA	In-use fleet	Roadside Tracer gas technique	site 1	In-use average	54.8	107.2	100.1	—	Zweidinger *et al.* (1988)
			site 2		81.6	177.2	149.5	—	
			site 3		111.7	222.1	198.8	—	
			site 4		113.9	235.3	204.9	—	
UK	Late 1980's vehicles Mostly 1986 As received	Mini portable CVS	ECE - cold start, 18.51 km hr^{-1}	Premium grade Leaded 97 octane	189.8	411.4	501.4	—	Bailey *et al.* (1990)
			ECE - hot start, 18.53 km hr^{-1}		163.8	356.9	430.4	—	
			On-road urban, 21.38 km hr^{-1}		195.6	453.5	599.6	—	
			On-road suburban, 41.73 km hr^{-1}		100.5	236.8	296.3	—	
			Cross-country rural, 54.53 km hr^{-1}		66.1	142.3	174.0	—	
			Motorway 1, 90.72 km hr^{-1}		46.2	91.6	93.0	—	
			Motorway 2, 111.36 km hr^{-1}		51.5	89.0	84.1	—	
USA	1989	FTP	20 newer vehicles	Industry average certification fuel	6.8	—	—	0.53	Gorse *et al.* (1991)
	1989				4.3	—	—	0.44	
	1983–1985		14 older vehicles	Industry average certification fuel	10.0	—	—	1.11	
	1983–1985				7.8	—	—	0.64	
USA	1989 Volvo	FTP	With three way catalyst	European 95 RON	12.1	—	—	0.64	Jemma *et al.* (1992)
	1989 Volvo		Without three way catalyst	European 95 RON	67.5	—	—	5.36	
	1990 Rover		High tech, non-catalyst car	European 95 RON	64.4	—	—	7.00	
	1987 VW		Carburettor, non-catalyst	European 95 RON	111.3	—	—	8.90	
USA	Non-catalyst		4 cars (1970–1978)	Average premium	97.6	211.5	—	1.85	Hoekman (1992)
	Oxidation catalyst		5 cars (1975–1982)		17.2	31.9	—	0.01	
	3-way catalyst		5 cars (1983–1990)		12.1	22.9	—	0.04	
	Adaptive learning		5 cars (1986–1989)		12.4	18.7	—	0.00	
USA	In-use fleet	Tunnel	Fort McHenry Tunnel	In-use average	14.9	28.7	32.8	1.76	Sagebiel *et al.* (1996)
	In-use fleet		Tuscarora Tunnel	In-use average	9.2	14.3	14.6	1.26	
Australia	In-use	US 1975 FTP	67 vehicles	In-use average	—	110–790	—	—	Nelson and Quigley, (1984)
Australia	In-use	FTP (ADR 37)	19, pre-1986 cars	Batch fuel representative of standard grade Australian petrols	139.1	240.5	164.0	18.7	This study
			56, post-1986 vehicles		41.8	61.9	46.5	3.6	
			10, worst post-1986 cars		104.8	179.5	136.3	12.0	
			46, best post-1986 cars		28.1	36.4	27.0	1.7	
	1986		7 cars		79.9	136.5	100.1	8.1	
	1987		9 cars		63.5	105.3	84.0	8.3	
	1988		6 cars		41.2	48.8	35.7	2.0	
	1989		8 cars		22.9	30.7	22.1	1.7	
	1990		9 cars		36.6	43.0	30.8	1.2	
	1991		17 cars		26.4	37.7	28.1	1.8	

(Source : Duffy et.al, 1998)

The remaining 10 high polluting post-1985 vehicles had emission rates comparable to those vehicles not equipped with catalytic converters, suggesting that about 20% of post-1985 vehicles have malfunctioning or poorly operating catalysts. For the non-catalyst-equipped, pre-1986 vehicles, CS and HT emissions were about 60% of the CT emissions. For the better 46 post-1985 vehicles, average emissions during the CS and HT phases were about 20-25%, 12-16%, 11-14%, and 7-13% of the CT emissions for benzene, toluene, the xylenes, and 1,3-butadiene, respectively. The emissions from a small number (9) of non-catalyst-equipped, pre-1986 vehicles were determined using unleaded and leaded petrol (table 2.20 and 2.21).

The emissions of all four target compounds were found to be significantly lower when unleaded petrol was substituted for leaded petrol. The greatest percentage emission reductions were observed for the CT phase, ranging from 25% for 1,3-butadiene to 35% for toluene. Emissions averaged over the 3 phases were reduced by 10% for 1,3-butadiene and by 16-18% for the aromatic compounds.

Table 2.20 Per vehicle exhaust emission (mg/km) of benzene, toluene, xylene and 1,3-butadiene during the cold transient (CT), cold stabilised (CS), and hot transient (HT) phase of the ADR 37/00 Drive Cycle (Source : Duffy et.al, 1998)

Vehicle group		Benzene					Toluene					Xylenes					1,3-butadiene				
		Emissions			Ratios		Emissions			Ratios		Emissions			Ratios		Emissions			Ratios	
		CT	CS	HT	CS/CT	HT/CT	CT	CS	HT	CS/CT	HT/CT	CT	CS	HT	CS/CT	HT/CT	CT	CS	HT	CS/CT	HT/CT
Pre-1986	Average	193.9	130.7	115.0	0.67	0.59	357.1	220.7	192.6	0.62	0.54	241.7	153.3	126.7	0.63	0.52	19.2	20.6	14.1	1.07	0.73
	Std	130.1	46.6	36.3			245.3	77.9	63.7			138.3	53.6	40.3			11.4	11.9	8.8		
Post-1986	Average (worst 10)	134.3	102.8	86.5	0.77	0.64	242.1	173.5	143.7	0.72	0.59	190.6	129.8	107.3	0.68	0.56	15.9	10.8	11.5	0.68	0.72
	Std	39.7	34.6	31.0			76.2	91.7	72.3			65.8	70.9	57.7			6.6	8.3	6.5		
	Average (all 56)	84.5	30.8	30.2	0.36	0.36	139.0	42.2	41.1	0.3	0.3	107.7	31.0	29.5	0.29	0.27	7.4	2.7	2.7	0.36	0.36
	Std	46.6	38.9	30.9			77.9	73.2	57.7			64.6	55.2	44.2			5.8	5.6	5.1		
	Average (better 46)	73.7	15.2	18.0	0.21	0.24	116.6	13.7	18.8	0.12	0.16	89.7	9.5	12.5	0.11	0.14	5.7	0.4	0.7	0.07	0.12
	Std	40.9	14.3	10.8			58.1	14.4	13.5			48.8	8.6	8.9			3.8	0.6	0.7		

Table 2.21 Emission of toluene, xylene and 1,3-butadiene relative to those of benzene determined in the present study compared to those reported in a recent study of the Sydney Harbour Tunnel (Source : Duffy et.al, 1998)

	Ratio to Benzene		
	Toluene	Xylenes	1,3-Butadiene
Pre-1986, nc-lp cars	1.73	1.18	0.13
Worst 10 post-1985, ce-ulp cars	1.71	1.30	0.11
All 56 post-1985, ce-ulp cars	1.48	1.11	0.09
Better 46 post-1985, ce-ulp cars	1.30	0.96	0.06
Sydney Harbour Tunnel study (Duffy and Nelson, 1996)	1.79	1.29	0.21

Per vehicle total (heat build and hot soak) evaporative emissions of 1,3-butadiene, benzene, toluene and xylenes from pre-1985 vehicles during the Sealed Housing Evaporative Determination tests were 36, 646, 679 and 260 mg per test, respectively. Corresponding values for the post-1985 vehicles were much lower at 14, 76, 131 and 65 mg per test, respectively. Heat build evaporative emissions of the four air toxics from pre-1986 vehicles were greater than those from the newer vehicles by factors ranging from 2.8 for 1,3-butadiene to 16 for benzene. The corresponding values for hot soak emissions were 1.8 and 5.2 respectively (table 2.22 and 2.23).

Table 2.22 Per vehicle exhaust emission of benzene, toluene, xylene and 1,3-butadiene from 9 pre-1986 vehivles when fuelled with either lead or unleaded petrol (Source : Duffy et.al, 1998)

		Benzene				Toluene				Xylenes				1,3-butadiene			
	Petrol	CT	CS	HT	AVG ADR	CT	CS	HT	AVG ADR	CT	CS	HT	AVG ADR	CT	CS	HT	AVG ADR
Average	LP	216.7	135.5	116.8	146.6	418.3	234.0	203.5	262.6	279.7	166.8	141.3	182.7	18.9	16.4	11.5	15.5
Std		154.2	33.7	19.0	44.5	295.3	59.8	39.3	87.4	141.0	47.9	31.9	54.3	12.6	7.9	9.3	8.7
Average	ULP	143.7	123.2	106.2	122.8	269.9	210.8	183.6	215.6	193.0	147.6	124.3	150.6	14.1	15.9	10.4	14.0
Std		36.0	37.1	22.7	30.8	73.8	65.2	45.8	58.9	49.8	46.4	34.3	41.0	7.5	7.9	6.7	7.2
% reduction using ULP		34	9	9	16	35	10	10	18	31	12	12	18	25	3	9	10

Table 2.23 Heat build and hot soak evaporative emission (mg/test) of benzene, toluene, xylene, 1,3-butadiene for 4 pre-1986, nc-lp and 8 post-1985, ce-ulp vehicles (Source : Duffy et.al, 1998)

Compound	Heat Build		Hot soak		Total	
	Mean	Std	Mean	Std	Mean	Std
			Pre-1986, nc-lp cars			
Benzene	365.2	199.6	280.5	102.3	645.7	188.4
Toluene	334.8	77.6	343.7	127.1	678.5	78.7
Xylenes	96.6	34.6	163.0	75.1	259.6	104.0
1,3-butadiene	26.5	17.1	9.2	4.0	35.6	19.2
			Post-1985, ce-ulp cars			
Benzene	22.4	17.1	53.7	43.8	76.0	52.0
Toluene	34.3	24.3	96.2	48.0	130.5	59.1
Xylenes	17.3	11.1	47.8	19.4	65.2	25.3
1,3-butadiene	9.4	7.6	5.0	7.9	14.4	9.9

Jerry (1996) studied on in-use vehicle hydrocarbon speciation: the impacts of fuel types, driving cycles and emission status on the reactivity of vehicle emissions. His project examined the relative significance of three emission factors (fuel, cycle and emission status) on in-use vehicle exhaust reactivity. Nineteen in-use vehicles were tested with randomly assigned seven fuel types and two driving cycles.

The specific reactivity was used to compare the exhaust reactivity among tests. For each exhaust speciation profile, three different compound classes were analyzed: lightened HC, midrange HC, and carbonyls. The primary analysis focused on the effects of three emission factors on the total exhaust reactivity. The difference in total exhaust reactivity between the FTP and UC cycles was not statistically significant ($p > 0.05$). However, exhaust reactivity was a strong function of fuel type. On average, for Bag 1 the exhaust reactivity for California Phase 2 fuel was the lowest (16% below the highest fuel type). The mean SR for high emitting vehicles was significantly higher than for low emitting vehicles for Bags 2 and 3 (11% and 15% higher than low emitters, respectively). In general, exhaust emissions were the highest in Bag 1 because the catalyst had not reached its optimal operating temperature. Thus, catalyst was critical in reducing the exhaust SR in Bags 2 and 3 for low emitting vehicles. The secondary analysis concentrated on the effects of three emission factors on the three compound classes. The mean SR differences between the FTP and UC cycles for Bag 2 lightened HC and carbonyls were statistically significant ($p < 0.05$). There was a significant fuel effect on the mean SR for the midrange HC ($p < 0.05$), but not for lightened HC and carbonyls ($p > 0.05$). Emission status showed a significant effect on the mean SR for all three compound classes.

A further detailed analysis evaluated the effects of three emission factors on the weight percent of individual hydrocarbon species emitted. In general, the weight percent of the exhaust species from the lightened HC and midrange HC fuel fractions were significantly affected by the choice of fuel, while driving cycle and emission status had minimal effects. The weight percents for lightened HC species (non-fuel fraction) from low emitting vehicles were significantly lower than for the high emitting vehicles in Bags 2 and 3 (p-value < 0.05). The results of this research highlight the importance of including exhaust reactivity in current mobile source emission inventory model.

David (1995) studied on the determination of the effects of speed, temperature, and fuel factors on exhaust emissions (automobile emissions, fuel economy). This study provided a comprehensive approach to examining the relative significance and possible synergistic effects of speed, temperature, and fuel on mobile source emissions modeling. Eleven passenger vehicles from three fuel delivery system control groups were tested, namely, three from carburetor (CARBU), three from throttle body injection (TBI), and five from multi-port fuel injection (MPFI) group. A minimum of 90 tests were conducted on each vehicle with a random combination of three fuel types (Phase 1, Phase 2, and Indolene), three temperatures (50 F, 75 F, and 100 F), and ten speed cycles. Each vehicle was repeated for ten speed cycles (75 F and Indolene). In general, exhaust emissions descended in the order of CARBU, TBI, and MPFI. All vehicles in the CARBU group contained a "dead" catalyst, which probably explained why vehicles in CARBU were "high emitters.". Results from the paired t-test indicated that exhaust emissions difference between Phase 1 and Phase 2 fuels for all vehicles was significant.

The net exhaust emissions reduction of Phase 2 over Phase 1 fuel for HC and NO_x was 21% and 12%, respectively; which is in good agreements with the CARB projected 17% HC (including evaporative and exhaust emissions) and 11% CO emissions reduction based on 1996 calendar year when Phase 2 fuel is introduced.

Temperature had minimal effects on exhaust emissions especially the test cycles were in hot-stabilized mode. Nevertheless, exhaust emissions from cold-start mode were higher than hot-start mode because the catalyst had not reached to optimal operating temperature during the cold-start mode. The relative contributions of speed, temperature, and fuel to exhaust emissions were determined using analysis of variance (ANOVA) and it was found interaction terms among fuel, speed, and temperature were statistically insignificant. Individually, the temperature and fuel factor played a minor role in exhaust emission modeling. Speed and vehicle type were the two dominant factors determining exhaust emissions.

Sripruetkait (1996) studied on the application of oxidation catalytic converter in a carburetted engine. The objective of his research is to study engine performance and emission control in a carburetted engine between the difference of an installed and uninstalled oxidation catalytic converter. Each experiment was tested at constant speed which varied from 1,000 to 3,000 rpm.

From the experiment, the result of the installed oxidation catalytic converter causes litter reduction in the engine performance. The averages of brake specific fuel consumption (bsfc) increase 0.001-0.08 kg/kw.hr. The

averages of thermal efficiency decrease 0.05-2.0%. The averages of fuel consumption increase 0-2.0 l/hr. The maximum power at each speed decrease 0.15-2.0 kw. CO and HC reduce depending on the operating condition. As for the exhaust gas treatment, the parameters that can reduce CO and HC emission depend on the temperature inside the oxidation catalytic converter and A/F ratio. The effective temperature is greater than 407 ^{0}C and effective A/F ratio is greater than 14.4.

Garivait (1995) The determination of hydrocarbon composition in exhaust gas from 4-stroke gasoline engine was studied in this research. The exhaust gas samples are collected in 20-L Tedlar bags from 30 new vehicles before delivery with regard to the gasoline used (Leaded gasoline; LG and Unleaded gasoline; ULG) and the type of emission system (Non-Catalytic converter and Catalytic converter). The exhaust gas was collected at idle stage and hot start. The sample was determined by using gas chromatograph that equipped with cryofocussing system. Cryofocussing technique has been applied in chemically bonded fused silica capillary column (CBP-1 50m x0.22m I.D x 0.25 m) ,this technique can separate hydrocarbon composition more than 100 compounds and can be classified into 4 groups i.e. paraffins olefins naphthenes and aromatics.

The result from this study showed that in the case of the type of emission System ; the cars equipped with catalytic converter can apparently reduce the quantity of hydrocarbons in paraffins olefins napthenes and aromatics groups but the percentage of hydrocarbon compositions in napthenes groups is not so reduce when comparing the cars wihtout catalytic converter. It was also found that in the case of the gasoline used; the percentage of olefins and

aromatics groups in car exhaust from the cars using unleaded gasoline are higher than the cars using leaded gasoline.

Dasch and Williams (1991) investigated the benzene exhaust emissions from in-use General Motors vehicles. In their study, Benzene emission were measured from the exhaust of 73 in-use, light-duty vehicles. Benzene averaged 27 mg/mile for 1981/1982 model year cars and decreased to 9.4 mg/mole for 1983-1987 cars. Hydrocarbon emissions also decreased after 1982 as closed-loop systems and fuel control improved. Benzene emissions showed a modest increase with mileage: the base-line benzene was 6.6 mg/mile with an increase of 1.0 mg/mile for each additional 10000 miles of travel. Lower levels of benzene were emitted from dual-bed catalysts than from three way catalysts. However, since many engine modifications were made during the period when dual-bed catalysts were replaced with three-way catalysts, a direct comparison is difficult. In a recent EPA paper, benzene emissions were calculated to be 102-119 mg/mile for the 1986 vehicle fleet. Based on the in-use values measured in this study of 9.4 mg/mile for 1983-1987 vehicles, substantial decreases in the fleet average are expected as these newer vehicles dominate the vehicles dominate the vehicle fleet.

Suksomsankh (1990) investigated the exhaust gas from gasoline engines, which registered in Bangkok. The vehicle sample in this study including passenger cars, 2 and 4 stroke motorcycles, taxies and 2 stroke tricycles. Gas sample were collected directly from the exhaust pipes of motor vehicles at 5 different speeds : idling speed which usually found in traffic jam condition, 10, 18, 28 kms / hour which were averaged travelling speed in Bangkok, and 60 kms / hour which was a city limit of Bangkok. Concentration

of CO, NO_x, Total hydrocarbons and composition of hydrocarbons in gas samples were analyzed. Results from this study showed that the highest concentrations of CO and HC were found in gas samples from 2 and 4 stroke motorcycles. The highest levels of oxides of nitrogen were emitted from passenger cars taxies. Concentrations of HC components in gas samples from 2 stroke engine motorcycles were higher than those from 4 stroke motorcycles. Benzene, Toluene, and Xylene, which are strongly toxic to human health, were major aromatic hydrocarbons found in gas samples from both 2 and 4 stroke engine motorcycles. The results of amount of Benzene, Toluene and Xylene from exhaust gas samples at idle condition are shown as

Type of vehicles	Type of pollutant and concentration (ppm)							
	Benzene		Toluene		Meta and Para Xylene		Ortho Xylene	
	Mean	range	Mean	range	Mean	Range	Mean	range
Passen-ger cars	53.44	10.29-240.63	175.35	17.06-1359.11	467.91	14.22-2153.58	41.43	4.03-262.09
2-Stroke motorcy-cles	355.51	93.62-787.89	866.11	225.23-1722.26	621.05	170.21-1399.20	221.82	49.37-428.64
4-Stroke motorcy-cles	145.48	7.07-777.37	468.80	25.15-2673.43	371.21	25.45-2050.34	117.37	9.35-644.99

Lertvisansak (1996) studied benzene concentration in vehicle emission using unleaded gasoline. The benzene in exhaust gas was measured from 12 used cars in this study. The exhaust gas from car was evaluated to determine the correlation between benzene concentration versus mileage, and model

year. The charcoal tubes were used to collect the sample of exhaust gas. Samples were collected from the car under two conditions, one was collected on chassis dynamometer and the other was collected at idle mode.

There was a modest increase in benzene emission with older model year but there was not found the correlation with the mileage. The maximum benzene emission was found to be 28.68 mg/m^3 from Toyota model year 1990. The lowest level of benzene emission was found in 3 new cars (1 Toyota and 2 Nissan) with installation of catalytic converter. The average benzene concentration of exhaust gas from Toyota, Nissan and Mitsubishi are 0-17.4 , 0-22.02 and 0.76-18.26 mg/m^3 respectively. The concentrations of benzene from old model car (1990-1992) were 4.4-22.02 mg/m^3 while the same for new model car was 0-4.14 mg/m^3. The results of benzene emission when the car was performed on chassis dynamometer were calculated from total hydrocarbon (THC) and benzene concentration was estimated to be 3 % of THC.

Moschonas and Glavas (1996) examined the fifty-seven C_3-C_{10} paraffins, olefins and aromatics were identified and quantified in the atmosphere of Athens in samples collected in electropolished canisters in the early morning hours of summer months. Aliquots of air were cryocollecled in glass beads and cryofocused prior to separation in a capillary column and analyzed by GC-MS. The aromatic fraction predominates with maximum benzene and toluene concentrations of 19 and 39 ppbv, respectively. Through comparison with NMHC emission profiles of other cities (that shown in table 2.23) it is inferred that vehicle emissions and paint solvents are the two main sources of the observed NMHC.

Table 2.24 NMHC in Athens and other urban centers, unit ppbv

(Source : Moschonas and Glavas, 1996)

Hydrocarbon	Vienna	Hamburg	Sydney	Chicago	Osaka	Athens[a] average	Athens[a] range
Ethane	28.3[b]		7.5	6.4	24.3[c]	NM	NM
Ethylene		5.3	12.5	3.5	23.3	NM	NM
Acetylene		8.8	10.1	4.1		NM	NM
Propylene	6.3[d]	2.9	7.4	1.4	6.1	3.9	0.7–12.6
Propane		2.1	5.9	3.2	8.9	1.2	0.4–2.6
Isobutane	1.8	3.8	4.7	1.2	5.1	1.1	0.3–3.1
Isobutene + 1-butene	2.5		2.4		3.6	0.9	0.2–3.0
n-Butane	4.9	7.8	7.5	6.0	11.0	2.1	0.4–6.4
trans-2-Butene	1.8		1.1		1.1	0.4	0.1–0.8
cis-2-Butene	0.9		1.0		0.9	0.3	0.1–0.8
Isopentane	6.9	6.4	9.0	4.1	10.6	11.7	4.6–25.6
1-Pentene			0.4		0.4	0.4	0.1–1.1
n-Pentane	4.5	5.1	5.0	3.8	7.7	4.2	1.0–11.6
1,3-Pentadiene						0.2	0.05–0.5
1,1-Dimethyl-cyclopropane						0.7	0.2–2.5
2-Methyl-1-butene			0.5		0.7	0.4	0.1–1.1
2-Methyl-2-butene			1.3		0.5	1.4	0.4–4.0
2,2-Dimethyl-butane			0.5			0.8	0.3–1.6
Cyclopentene			0.8			0.2	0.05–0.5
1-Ethyl-1-methyl-cyclopropane						0.1	0.1–0.2
2,3-Dimethyl-butane			0.9		0.8	0.6	0.2–1.5
2-Methyl-pentane	3.2		2.6	2.4	3.9	3.3	1.3–6.9
3-Methyl-pentane	1.9		1.6	2.4	3.1	2.3	0.9–4.7
1-Hexene				2.4		0.2	0.1–0.5
n-Hexane	2.2	3.8	2.1	2.0	5.5	1.6	0.6–4.2
2-Methyl-2-pentene						0.3	0.2–0.7
cis or *trans*-3-Methyl-2-pentene						0.2	0.1–0.3
trans-3-Hexene						0.2	0.1–0.3
cis-3-Methyl-2-pentene						0.3	0.2–0.7
Methyl-cyclo-pentane	1.4		1.2		1.7	0.7	0.3–1.4
Benzene	6.0	3.2	2.6	2.4	5.1	5.0	0.8–18.7
Cyclohexane	0.6		0.9		0.8	0.3	0.1–0.8
2-Methyl-hexane	1.1		1.2		1.5	1.8	0.6–5.7
2,3-Dimethyl-pentane			0.7		0.6	0.3	0.1–0.8
3-Methyl-hexane	1.1		0.8		1.7	3.5	1.0–8.7
n-Heptane	1.4		0.7		2.0	2.4	0.4–7.8
Methyl-cyclohexane	0.5		0.6		0.7	1.8	1.0–3.5
Toluene	10.9	8.2	8.9	3.8	31.1	14.3	3.4–39.0
2-Methyl-heptane					0.6	2.3	0.4–8.2
3-Methyl-heptane	0.5				0.7	0.8	0.4–2.2
n-Octane	0.4		0.4		0.6	0.6	0.4–1.2
Ethyl-benzene	1.8	2.2	1.3	0.6	3.8	2.7	0.6–8.1
m + *p*-Xylenes	5.7	5.2	3.9	1.5	7.7	12.1	2.6–29.8
3-Methyl-octane						1.0	0.5–1.5
o-Xylene	2.3	1.8	1.5	0.4	2.8	3.7	1.4–6.4
Nonane	0.2		0.4		0.7	1.7	0.5–2.7
2,3,7-Trimethyl-octane						0.9	0.8–1.0
Propyl-benzene	0.5		0.4			1.1	0.4–1.6
1-Ethyl-3-methylbenzene + 1-ethyl-4-methylbenzene	2.1		1.1		3.1	9.5	2.5–14.9
1,2,3-Trimethyl-benzene					0.6	3.3	0.9–5.4
3-Methyl-nonane						1.0	0.8–1.1
1-Ethyl-2-methyl-benzene	0.6		0.4		0.7	2.2	0.9–3.2
1,3,5-Trimethyl-benzene	0.7		0.5		1.2	9.2	2.8–14.2
Decane	0.6		0.5		0.9	3.1	0.8–5.0
1,2,4-Trimethyl benzene	2.4		1.3		2.9	3.9	0.9–6.6
1-Ethenyl-2-methyl-benzene						0.9	0.8–1.0
1-Methyl-3–propyl-benzene						1.3	0.3–2.1
2-Diethyl-benzene						2.3	0.7–3.5
1-Methyl-2-propyl-benzene						0.4	0.3–0.4
2-Ethyl-1,4-dimethyl-benzene						1.8	1.6–2.0
Sum of paraffins, ppbC	221.0	133.0	250.1	131.5	353.5	217.2	56.9–670.4
Sum of olefins, ppbC	58.5	36.9	100.4	33.8	143.9	28.2	7.7–74.9
Sum of aromatics, ppbC	247.4	150.2	164.8	61.0	439.2	479.1	63.8–1138.3

Note: Vienna = Lanzerstorfer and Puxbaum (1990); Hamburg = Bruckmann *et al.* (1988); Sydney = Nelson and Quigley (1982); Chicago = Aronian *et al.* (1989); Osaka = Tsujino and Kuwata (1993).

[a] This work.

[b] Sum of C_2 hydrocarbons.

[c] 10% ethane and 90% acetylene.

[d] Sum of C_3 hydrocarbons.

Heeb et.al (1999) studied on the fast and quantitative measurement of benzene, toluene and C_2-benzenes in automotive exhaust during transient engine operation with and without catalytic exhaust gas treatment. In their study, the Time-Resolved Chemical Ionization Mass Spectrometry (CIMS) has been used to investigate the emission profiles of benzene, toluene and the C_2-benzenes (xylenes and ethyl benzene) in automotive exhaust during transient engine operation. On-line emission measurements with a frequency of 1-5 Hz clearly identitied the critical driving conditions that are mainly responsible for the overall aromatic hydrocarbon emissions.

The passenger car, equipped with a catalytic converter showed significant BTXE-emissions only in the first part of the New European Driving Cycle (NEDC) due to sub-optimal catalyst temperature. On the same car without a catalytic converter, emissions of aromatic hydrocarbons were detected over the entire test run and the benzene toluene mixing ratios of the exhaust gas were rather constant. The concentrations of BTXE in diluted exhaust gas are presented in figure 2.22, figure 2.23 and table 2.25

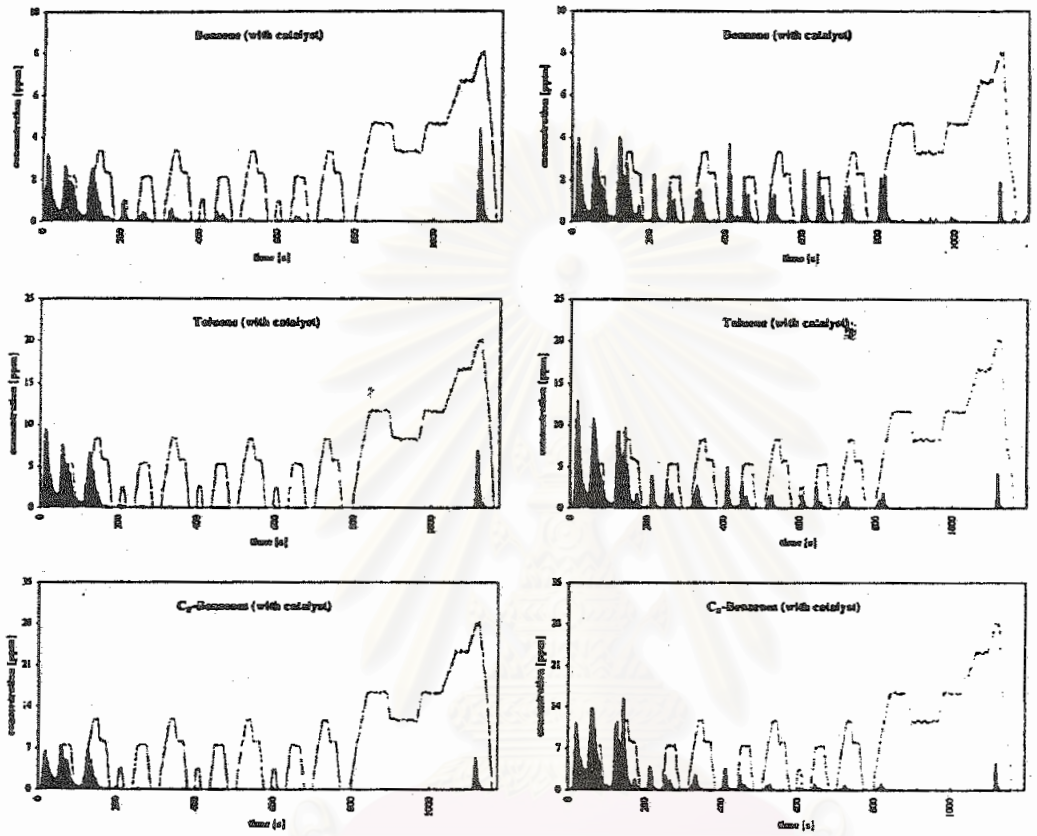

Figure 2.22 Concentration of benzene, toluene, and C_2 – benzene (ppm) in diluted exhaust gas as a function of cycle time from two test runs with a compact passenger car equipped with an operational three-way catalyst. (Source : Hebb et.al, 1999)

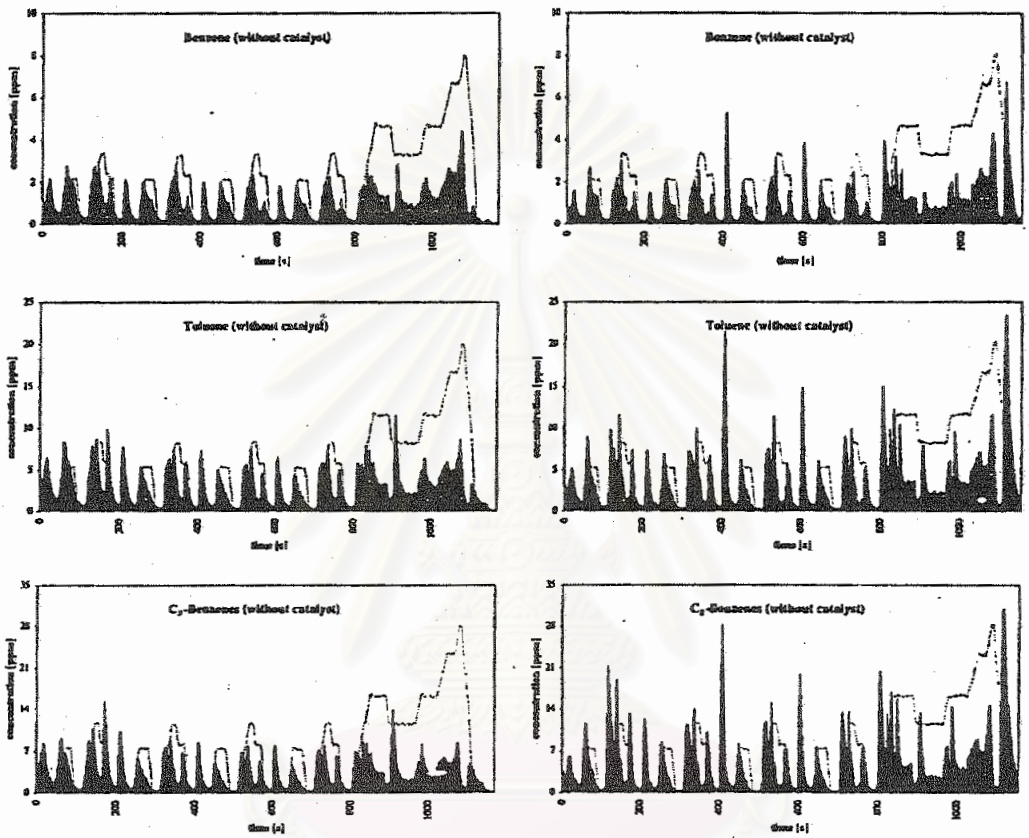

Figure 2.23 Concentration of benzene, toluene, and C_2– benzene (ppm) in diluted exhaust gas as a function of cycle time from two test runs with a compact passenger car without exhaust gas treatment. (Source : Hebb et.al, 1999)

Table 2.25 Average emission factor (mg/km) for individual aromatic hydrocarbons and the total hydrocarbon group of compounds with and without catalytic exhaust gas treatment.

(Source : Hebb et.al, 1999)

Cycle or part of cycle	Average velocity ($km\,h^{-1}$)	Benzene without converter ($mg\,km^{-1}$)	Benzene with converter ($mg\,km^{-1}$)	Efficiency of conversion[a]	Toluene without converter ($mg\,km^{-1}$)	Toluene with converter ($mg\,km^{-1}$)	Efficiency of conversion[a]	C_2-Benzenes[b] without converter ($mg\,km^{-1}$)	C_2-Benzenes[b] with converter ($mg\,km^{-1}$)	Efficiency of conversion[a]	T.HC[c] without converter ($mg\,km^{-1}$)	T.HC[c] with converter ($mg\,km^{-1}$)	Efficiency of conversion[a]
NEDC	33.3	62.9	19.7	0.69	227.2	43.6	0.81	332.2	55.2	0.83	1682	283	0.83
ECE	18.4	92.0	27.0	0.49	351.9	119.1	0.66	521.0	139.7	0.73	2680	694	0.74
EUDC	62.4	46.1	3.8	0.92	155.1	6.1	0.96	223.2	6.1	0.97	1104	44	0.96
1 km	17.3	113.5	117.8	−0.04	426.4	378.8	0.11	650.9	469.4	0.28	4456	2832	0.36
2 km	18.5	87.2	28.4	0.67	336.1	43.2	0.87	494.8	44.1	0.91	3264	403	0.88
3 km	18.3	88.0	24.0	0.73	340.0	32.2	0.91	491.6	27.6	0.94	3183	324	0.90
4 km	17.6	85.7	20.4	0.76	334.0	20.1	0.94	486.5	13.0	0.97	2826	164	0.93
5 km	55.2	58.6	5.2	0.91	227.4	5.9	0.97	339.3	5.3	0.98	2221	99	0.96
6 km	57.5	34.1	0.3	0.99	128.9	1.1	0.99	188.1	1.3	0.99	1112	15	0.99
7 km	56.7	38.3	0.8	0.98	127.2	1.1	0.99	178.6	1.3	0.99	1012	18	0.89
8 km	72.2	34.8	0.2	0.99	109.5	0.5	> 0.99	147.5	0.6	> 0.99	827	11	0.99
9 km	95.4	42.9	0.2	0.99	120.5	0.6	0.99	161.3	1.2	0.99	934	18	0.98
10 km	106.6	54.0	7.6	0.86	140.5	15.7	0.89	184.2	15.8	0.91	1006	44	0.96
11 km[d]	52.0	53.6	8.1	0.85	206.5	16.8	0.92	333.2	17.8	0.95	1821	135	0.93

[a] Conversion efficiency of the three-way catalyst was calculated according to formula (1- te-factor (with cat.) e-factor (without cat.))].

[b] Quantitation of C_2-benzenes (*o*- *m*-, *p*-xylenes and ethyl benzene) was done using the detector response of *o*-xylene present in the calibration gas.

[c] Quantiative T.HC measurements were done using a detector response of *n*-propane and asuming an average hydrogen carbon ratio of 1.85.

[d] The calculated emission factors represent the average emission on the last 0.8 km of the New European Driving Cycle.

To study the temperature dependency of the observed cold start behaviour in the case of 3 way catalyst, 3 additional test runs were performed with a comparable passenger car. Figure 2.24 showed the benzene and toluene emission profile of the 3 test runs with variable engine and catalyst conditions.

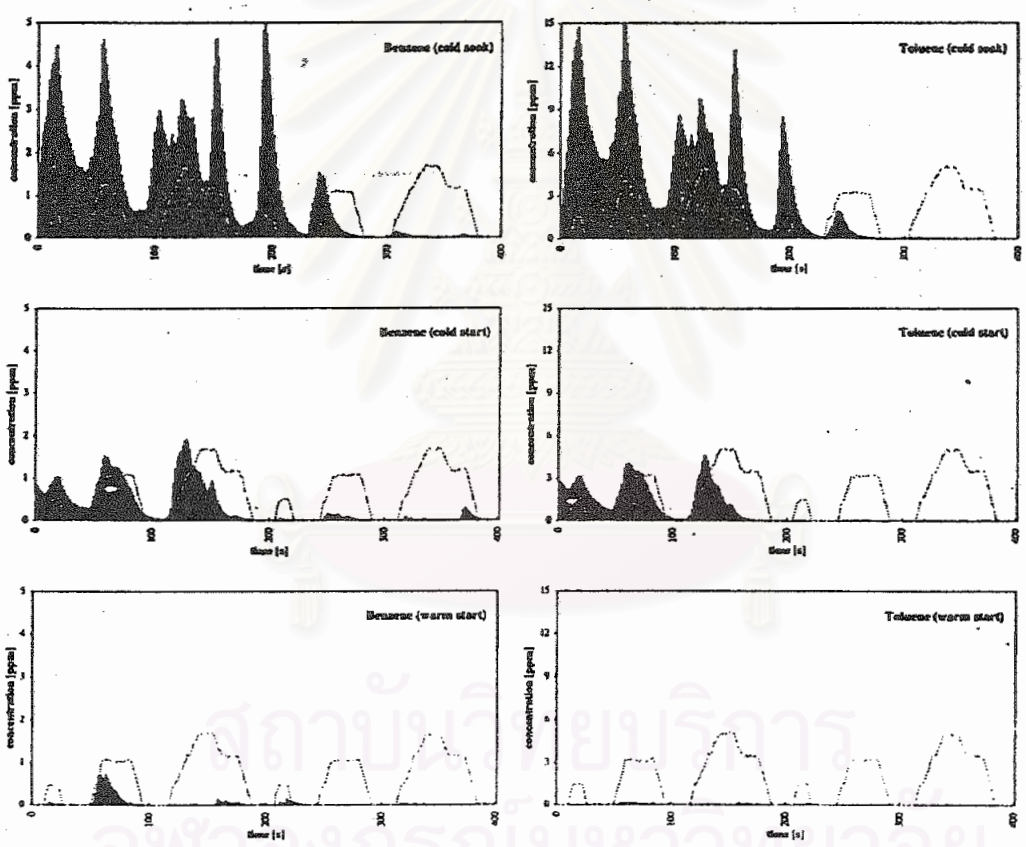

Figure 2.24 Temperature dependent emission of benzene and toluene (ppm) as a function of cycle time from a passenger car equipped with a three way catalyst during three test runs. (Source : Hebb et.al, 1999)

With catalytic exhaust gas treatment the observed benzene-toluene mixing ratios varied to a greater extent reflecting predominantly different catalytic converter conditions. The average molar ratio of benzene over toluene rose from 0.33 to 0.53 upon exhaust gas treatment. With catalytic converter the emissions during extra urban (EUDC) driving repeatedly showed benzene toluene mixing ratios > 1 and an average molar benzene/toluene ratio of 0.74 was detected during the EUDC part of the driving cycle. Whereas the total hydrocarbon (T.HC) emissions were decreased by 83% upon exhaust gas treatment the overall reduction of the benzene emissions was only 70%. The results of these are presented in figure 2.25, table 2.26 and figure 2.26.

CHAPTER 3

EXPERIMENT

3.1 Automobiles selection

Regular in-use automobiles with capacity in ranges of 1300 to 2200 CC were selected in this study by interviewing the car owner. The questionnaire used in this study that was shown in Appendix B. The automobile samples were classified into 3 groups by using age of engines. The first group was new automobiles (less than 5 years), the second group was moderate age automobiles (5 – 10 years) and the last group was old automobiles (more than 10 years).

3.2 Material for sampling collection

1. Tedlar bag of which size in 20 liter as a sampling bag
2. Black plastic bag
3. Purified nitrogen gas (N_2) (99.999%)
4. Temperature detector
5. Vacuum box
6. Air pump
7. Teflon tube
8. Moisture trap scrubber with Magnesium perchlorate ($Mg(ClO_4)_2$)
9. Three ways valve

The picture of materials was illustrated on the figure 3.1.

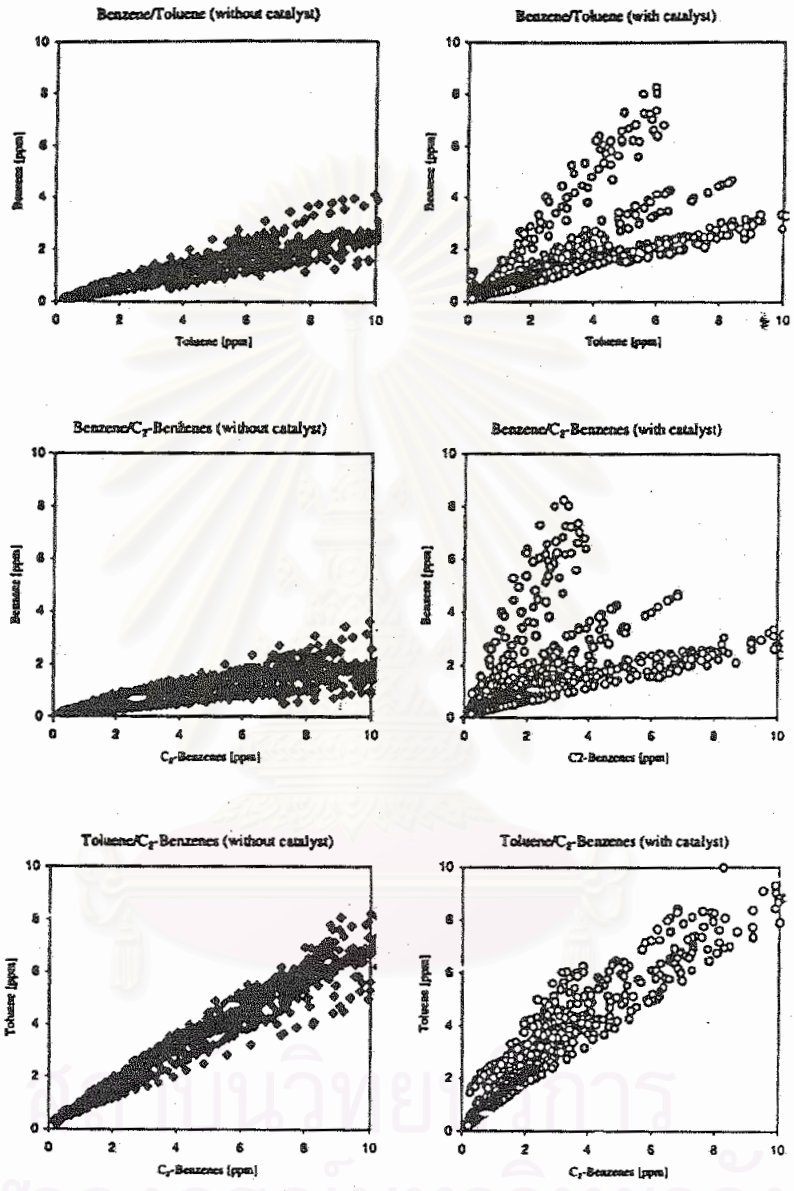

Figure 2.25 Correlation diagrams of the concentrations of aromatic hydrocarbons (ppm) determined in dilute exhaust gas of the passenger car during four test runs. (Source : Hebb et.al, 1999)

Table 2.26 Average molar ratio (mol mol^{-1}) of individual aromatic hydrocarbons in dilute exhaust gas with and without catalytic exhaust gas treatment (Source : Hebb et.al, 1999)

Cycle or part of cycle	Average velocity ($km\ h^{-1}$)	Molar ratio [Benzene]/[Toluene]		Molar ratio [Benzene]/[C_2-Benzenes][a]		Molar ratio [Toluene]/[C_2-Benzenes][a]	
		Without converter (mol mol^{-1})	With converter (mol mol^{-1})	Without converter (mol mol^{-1})	With converter (mol mol^{-1})	Without converter (mol mol^{-1})	With converter (mol mol^{-1})
NEDC	33.3	**0.33**	**0.53**	**0.26**	**0.49**	**0.79**	**0.91**
ECE	18.4	**0.31**	**0.47**	**0.24**	**0.46**	**0.78**	**0.98**
EUDC	62.4	**0.35**	**0.74**	**0.28**	**0.85**	**0.80**	**1.15**
1 km	17.3	0.31	0.37	0.24	0.34	0.75	0.93
2 km	18.5	0.31	0.77	0.24	1.87	0.78	1.13
3 km	18.3	0.31	0.88	0.24	1.18	0.80	1.34
4 km	17.6	0.30	1.20	0.24	2.14	0.79	1.78
5 km	55.2	0.30	1.04	0.23	n.r.	0.77	n.r.
6 km	57.5	0.31	n.r.	0.25	n.r.	0.79	n.r.
7 km	56.7	0.36	n.r.	0.29	n.r.	0.82	n.r.
8 km	72.2	0.38	n.r.	0.32	n.r.	0,86	n.r.
9 km	95.4	0.42	n.r.	0.36	n.r.	0.86	n.r.
10 km	106.6	0.45	0.57	0.40	0.66	0.88	1.15
11 km[b]	52.0	0.31	0.57	0.22	0.62	0.71	1.09

[a] Quantitation of C_2-benzenes (*o*-, *m*-, *p*-xylenes and ethyl benzene) was done using the detector response of *o*-xylene present in the calibration gas.
[b] The calculated emission factors represent the average emission on the last 0.8 km of the New European Driving Cycle.
n.r.: Not reported, due to increased uncertainty, no molar ratios are reported where conversion efficiency of the three-way catalyst exceeded 98%.

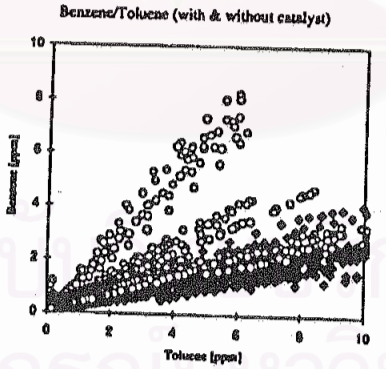

Figure 2.26 Comparison of the benzene/toluene correlation data with (O) and without (◆) the catalytic converter during test runs. (Source : Hebb et.al, 1999)

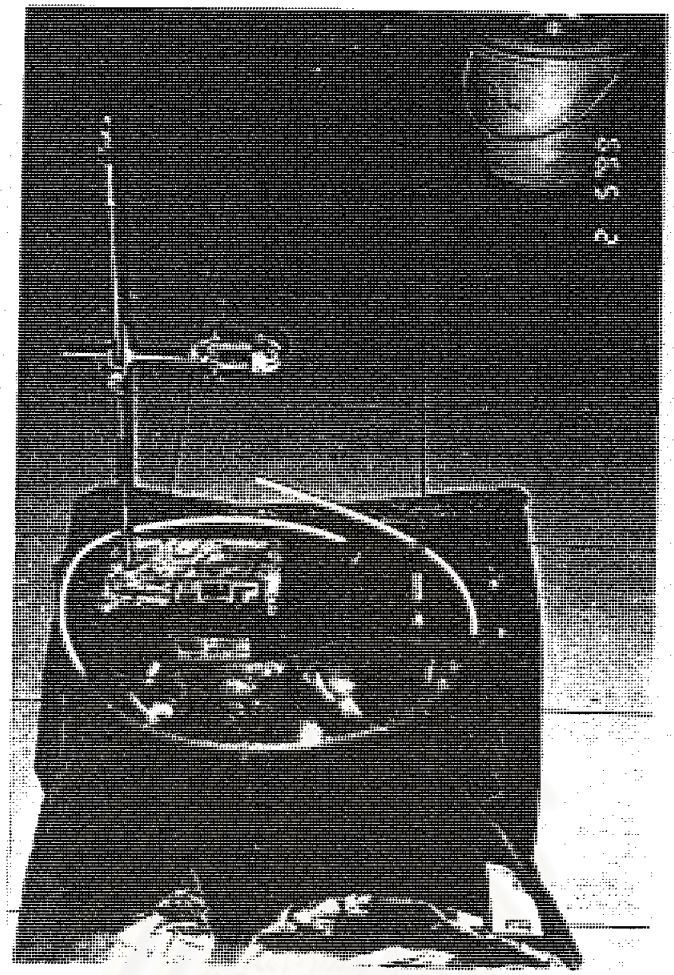

Figure 3.1 Materials for the sampling

3.3 Sampling method

In this study, The exhaust gas samples from automobile tailpipe was collected while the car was operated at idle mode. A sampling method consisted of the 20 liter Tedlar bag and also covered by a black plastic bag to prevent photo-oxidation reaction inside the Tedlar bag. The exhaust gas sample was held in the bag. Before each collection and measurement, the automobile was warm up for at least 10 minutes and the temperature of exhaust gas need to reach 60 ^{0}C or more. The exhaust gas was collected by a vacuum box as shown in Figure 3.2. The Tedlar bag must be washed by purified N_2 (99.999%) at least 3 times every time before sampling.

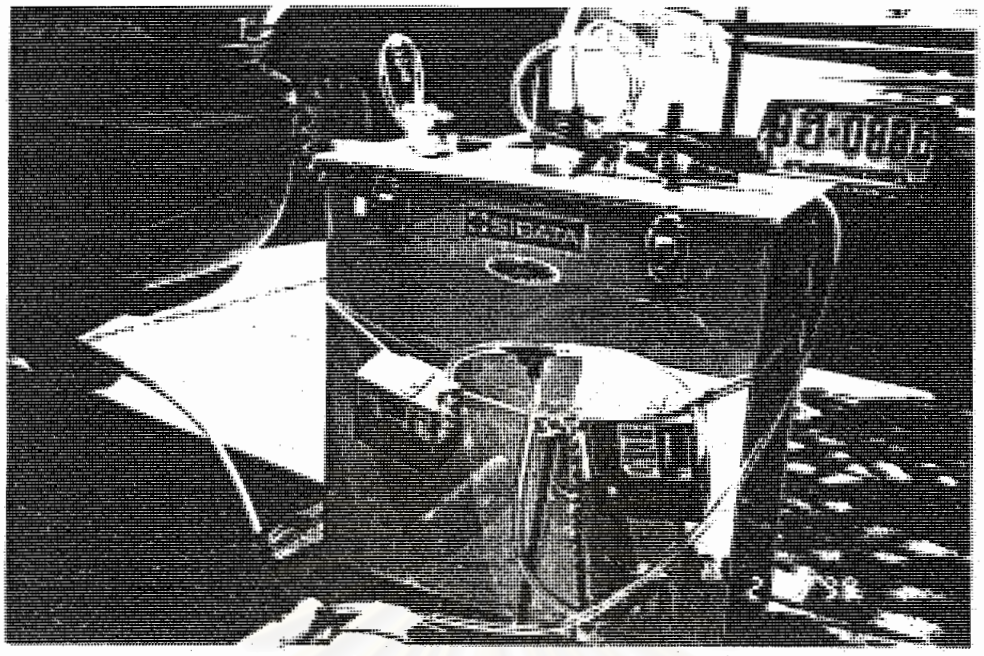

Figure 3.2 The exhaust gas collector

The 3 major hydrocarbon pollutants in the exhaust; Benzene, Toluene and Xylene (in form of total Xylene that includes ortho-, meta-, and para- form) were investigated. All of the concentration of Benzene, Toluene and Xylene were calculated in both Part Per Million (ppm) and Milligram per Cubic Meter (mg/m^3) units.

Due to the limitation of the study, the gasoline sample was not collected from the car fuel tank directly. The unleaded gasoline that includes the octane number both 91 (regular grade) and 95 (premium grade) from the gasoline station was used instead. Approximately 5 ml of sample was collected and then kept in the refrigerator at 20 ^{0}C for laboratory analysis later.

3.4 The sampling procedure

The procedures of exhaust gas sample collection were operated as follows:

1. The end of Teflon tube and temperature detector were inserted deeply into the exhaust tailpipe and the other end of Teflon tube was connected to the moisture-trapped scrubber.

2. The other Teflon tube was connected from the moisture trapped scrubber to the three ways valve. From one end of the valve, it was connected to sampling bag in vacuum box, while the other end was separated from the vacuum box.

3. The valve on the bottom of the vacuum box was connected to the air pump.

4. Stopcock 1 was closed and stopcock 2 was opened while the vacuum pump was operated. The air in the box was drained so that a vacuum condition occurs in the box.

5. Stopcock 1 was still closed, while the stopcock 3 was opened to ventilated the exhaust gas from tailpipe until the temperature of exhaust gas from tailpipe reached to 60^{0}C.

6. Stopcock 3 is then closed while stopcock 1 was opened immediately. (The stopcock 2 was remain opened to continued the vacuum condition in the box). Then, the exhaust gas from tailpipe flow into the bag immediately by the vacuum force.

7. After the exhaust gas was collected approximately 5 minutes or the volume of exhaust gas in bag was about 10 liter. Stopcock 1 and 2 are then closed respectively and then the air pump was off. The bag was taken out for an analysis in the laboratory within 3 hours after collection.

The diagram of sample collection using vacuum box was shown in Figure 3.3. And the figure 3.4 illustrated the sampling of the exhaust gas from car.

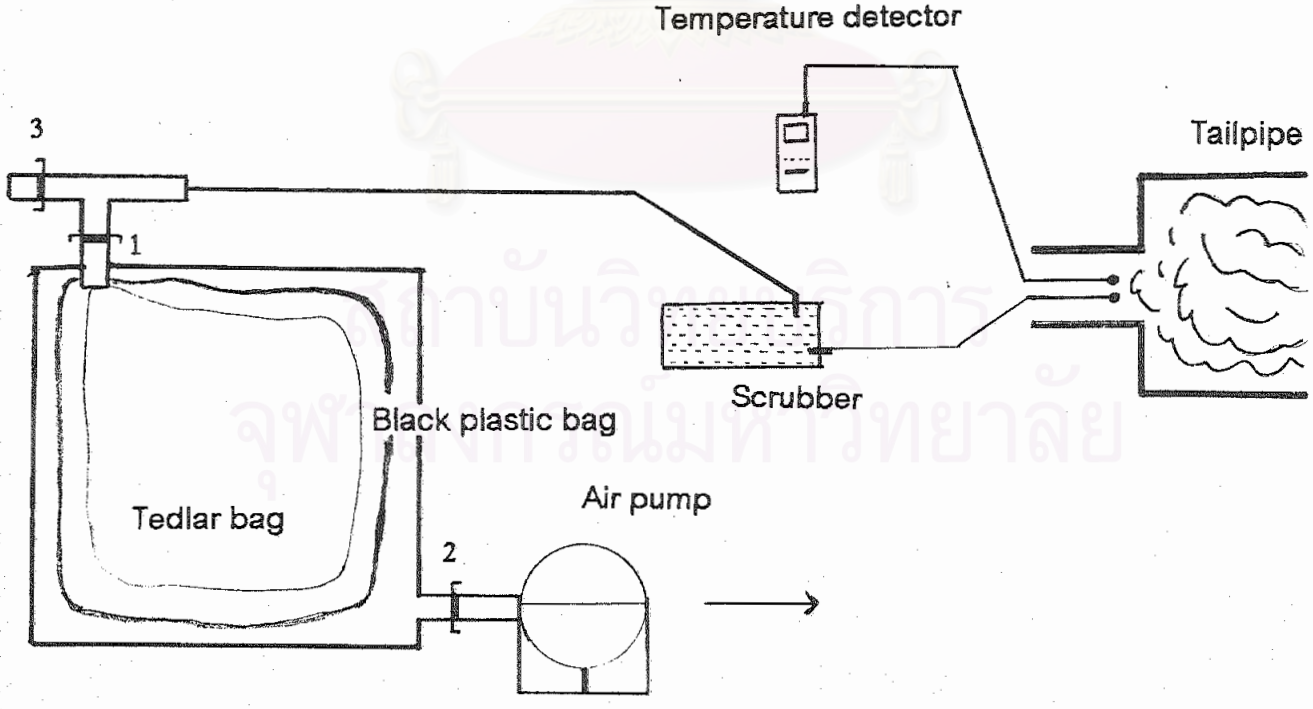

Figure 3.3 Vacuum box and valves of connection

Figure 3.4 Sampling probe inserted into the exhaust pipe

3.5 Analytical method

After sampling, the exhaust gas sample in the Tedlar bag and the gasoline sample in vial were brought to the laboratory for analyzed the quantities of Benzene, Toluene and Xylene by high resolution Gas Chromatography with Flame Ionization Detection (GC/ FID). The Gas Chromatography is shown in figure 3.5 and the experimental condition of GC was listed in below :

1. Brand of GC	Hewlett – Packard 5890 series II
2. Type of Column	DB-1
3. Carrier gas	Purified N_2 (99.999%)
4. Temperature program	30^0C, hold for 2 min.
	10^0C per min.to100^0C, hold for 1 min.

5. Temperature at injection port	200^{0}C
6. Detector	Flame ionization detector (FID) (heated to 300^{0}C)
7. Exhaust gas sample used	1 ml.
8. Gasoline sample used	1 µl.
9. Standard BTX used	1 µl.

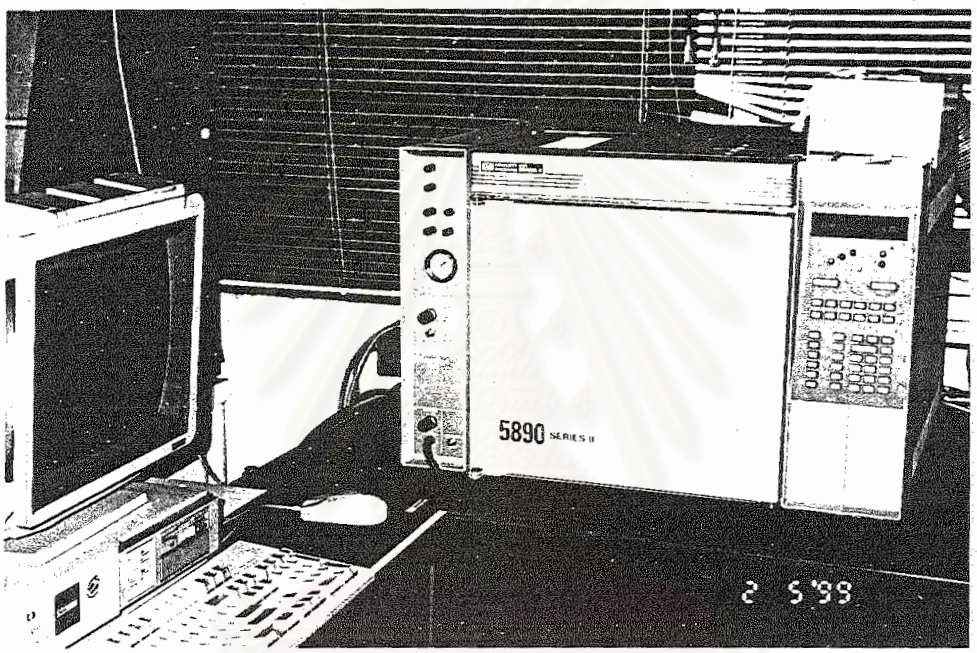

Figure 3.5 Gas Chromatography

3.6 Preparation of standard solution

All reagents that used in this preparation must be Analytical Reagent grade (AR grade). The following reagents were added into the 250 ml Acetone (CH_3COCH_3) in order 125 µl Benzene (C_6H_6), 75 µl Toluene ($C_6H_5CH_3$)

and 50 μl Xylene ($(CH_3)_2C_6H_4$). Then, shake all reagents to mix well, and keep the mixed reagent in the refrigerator at 20 ^{0}C for use as standard solution.

3.7 Calculation

3.7.1 The concentrations in mg/m^3 unit

The standard solution, with Acetone 250 ml, Benzene 125 μl, Toluene 75 μl and Xylene 50 μl had a total volume as 250250 μl. The amount of 1 μl standard solution, 1μl gasoline sample and 1 ml exhaust gas sample were used to calculate for the concentration of each substance.

From Weight of substance (g) = Volume (cm^3) x Density (g/cm^3)

Density of Benzene is 0.8787 g/cm^3

Density of Toluene is 0.8660 g/cm^3

Density of Xylene is 0.8647 g/cm^3

The weight of Benzene, Toluene and Xylene in standard solution

Benzene	=	4.3891×10^{-4}	mg
Toluene	=	2.5954×10^{-4}	mg
Xylene	=	1.7227×10^{-4}	mg

When the standard solution or the samples, with Benzene, Toluene, and Xylene components, were injected into the Injection port of Gas Chromatography (GC) at temperature 200 ^{0}C. All hydrocarbon components were evaporated immediately and moved into the column by the carrier gas (N_2) in the state of gases. After detected by the Flame Ionization Detector (FID), the peak areas of Benzene, Toluene, and Xylene were shown as known as the chromatogram

If,

1.Standard solution

Peak area of Benzene in standard solution is = X

Peak area of Toluene in standard solution is = Y

Peak area of Xylene in standard solution is = Z

2.The sample

Peak area of Benzene in the samples = X_1

Peak area of Toluene in the samples = Y_1

Peak area of Xylene in the samples = Z_1

The concentrations of Benzene in the exhaust gas sample were calculated by comparing with Benzene in standard solution that known the exact concentration.

Concentration of Benzene in exhaust gas is $\frac{(438.91) \times X_1}{X}$ .mg/m^3

Concentration of Toluene in exhaust gas is $\frac{(259.54) \times Y_1}{Y}$ mg/m^3

Concentration of Xylene in exhaust gas is $\frac{(172.77) \times Z_1}{Z}$ mg/m^3

Concentration of Benzene in gasoline sample is $\frac{(4.3891 \times 10^5) \times X_1}{X}$ mg/m^3

Concentration of Toluene in gasoline sample is $\frac{(2.5954 \times 10^5) \times Y_1}{Y}$ mg/m^3

Concentration of Xylene in gasoline sample is $\frac{(1.7277 \times 10^5) \times Z_1}{Z}$ mg/m^3

3.7.2 Concentrations in ppm unit

As the same as above, the concentration of gasoline sample as was calculated by comparing with standard solution.

Concentration of Benzene in gasoline sample is = $\frac{(499.50) \times X_1}{X}$ ppm

Concentration of Toluene in gasoline sample is = $\frac{(299.70) \times Y_1}{Y}$ ppm

Concentration of Xylene in gasoline sample is = $\frac{(199.80) \times Z_1}{Z}$ ppm

For the exhaust gas sample, the concentration of Benzene, Toluene and Xylene in ppm unit was calculated by using the gas's law.

From the gas's law defined that 1 g - mole of vapor or gas has volume 22.4 liters at 20 ^{o}C and 760 mmHg (1 atm).

At the room temperature (25 ^{0}C), the volume of vapor is 24.45 liter.

Molecular weight of Benzene = 78.11

Molecular weight of Toluene = 92.13

Molecular weight of Xylene = 106.16

At room temperature (25 ^{0}C) and atmospheric pressure 760 mmHg.

Benzene 1 g-mol has weight = 78.11 g

It can be defined that:

Concentration of Benzene in exhaust gas is $\frac{(137.39) \times X_1}{X}$ ppm

Concentration of Toluene in exhaust gas is $\frac{(68.88) \times Y_1}{Y}$ ppm

Concentration of Xylene in exhaust gas is $\frac{(39.79) \times Z_1}{Z}$ ppm

CHAPTER 4

RESULTS AND DISCUSSION

Before detailing the results of this work, it was important to put the relative contributions of vehicle exhaust and hydrocarbon pollutants distribution in to perspective. Many studies showed that there was the strong relationship between the mobile emission source and amount of hydrocarbon in ambient air in many megacities of the world. Many researchers from America, Australia and European countries tried to examine these relationship, for instance, Duffy et.al (1998 and 1999), Heeb et.al (1999), Nelson (1984) and Moschonas and Glavas (1996). In Thailand, only a few of studies that determined the relationship between emission from mobile source and distribution of hydrocarbons in the ambient air. In this study, comparison of Benzene, Toluene and Xylene's concentrations that emitted from cars in Bangkok and the concentration of these hydrocarbon in the ambient air both Thailand and other countries were shown. Duffy et.al (1998) explained that the fraction of evaporative to total motor vehicle emission in the atmosphere of urban cities ranges from 0.3-0.57.

There were many types of data presented in the body of text. The idle condition of car samples and types of car samples specify a procedure for collecting the exhaust gas sample in this study. The method of the study has a limitation on the car samples that presented in the table below.

Ages of car engine	Types of car samples	
	Catalytic equipped car	Non-catalytic equipped car
Old car (more than 10 years old)	X	✔
Moderate age car (5-10 years old)	✔	✔
New car (less than 5 years old)	✔	X

✔ = Able to use in this study

X = Unable to use in this study

According to the new regulation that came into force in recent years was not allowed the unequipped catalytic converter car sold in Thailand. The new non-catalytic converter equipped cars were unable to find in this study. In addition, the expensive cost of catalytic converters and people's ignorance in pollution from motor vehicles were a major problem which old catalytic equipped cars were hardly found. In this research, The effects of catalytic converter equipment on the exhaust pollutants was examined by the comparison of hydrocarbon pollutant concentrations between 2 different groups, catalytic equipped moderate age car and non-catalytic equipped moderate age car. The effect of engine's ages on the exhaust pollutants was studied by comparison of pollutants' concentration in 2 different groups. The first group was comparison between non-catalytic equipped old cars and non-catalytic equipped moderate age cars. The second group was comparison between catalytic equipped moderate age cars and catalytic equipped new cars.

4.1 Concentration of BTX in exhaust gas and gasoline

4.1.1 Benzene's concentration

In this study, it was found that the average concentrations of Benzene in old non-catalytic cars group was the highest when compare with others. The average concentration of Benzene in non-catalytic cars group was 12.11 ppm, on the contrary, the lowest Benzene concentration was found in new catalytic cars group. All samples in this group, it can not be quantified the amount of Benzene in exhaust gas sample cause of the quantities of Benzene was less than the detection limit of Gas Chromatography. Moreover, it was discovered that the amount of Benzene in non-catalytic cars was greater than the catalytic cars. The average concentrations of Benzene were 7.49 ppm and 6.74 ppm, respectively. The detail of Benzene concentrations was presented in table 4.1.

4.1.2 Toluene's concentration

It was discovered that the highest Toluene concentration was found in old non-catalytic car whereas the lowest concentration less 10 times than the highest was found in new catalytic cars group. The average concentrations of Toluene in old non-catalytic car group and new catalytic cars group were 33.88 and 3.69 ppm, respectively. The detail of Toluene concentrations was shown in table 4.2.

4.1.3 Xylene's concentration

Like the Benzene and Toluene's concentration, the highest concentration of Xylene was also found in old non-catalytic car group. The average concentration in this group was 7.69 ppm while 1.95 ppm was the average concentration of new catalytic converter cars group. The detail of Xylene concentration was presented in table 4.3.

Table 4.1 Benzene concentrations in exhaust gas

	Car No.	Catalytic		Non-catalytic	
		mg/m^3	Ppm	mg/m^3	ppm
Old cars (Higher than 10 years old)	1	X	X	22.79	7.14
	2	X	X	38.86	12.16
	3	X	X	41.52	13.00
	4	X	X	43.55	13.63
	5	X	X	25.94	8.12
	6	X	X	45.88	14.36
	7	X	X	52.31	16.38
	Mean	X	X	38.69	12.11
	SD	X	X	10.68	3.34
	Variance	X	X	114.06	11.17
	Range	X	X	29.52	9.24
	SE of mean	X	X	4.03	1.26
Moderate age cars (5-10 years old)	1	27.44	8.59	28.11	8.80
	2	19.89	6.23	10.11	3.17
	3	22.11	6.92	26.81	8.39
	4	21.63	6.77	28.26	8.85
	5	29.66	9.29	37.12	11.62
	6	24.10	7.54	21.14	6.62
	7	35.18	11.01	16.11	5.04
	8	10.01	3.14	X	X
	9	12.02	3.76	X	X
	10	13.30	4.17	X	X
	Mean	21.53	6.74	23.95	7.49
	SD	8.08	2.50	8.92	2.79
	Variance	65.29	6.99	79.76	7.81
	Range	25.16	7878	27.05	8.45
	SE of mean	2.55	0800	3.34	1.05
New cars (Less than 5 years old)	1	N.D	N.D	X	X
	2	N.D	N.D	X	X
	3	N.D	N.D	X	X
	4	N.D	N.D	X	X
	5	N.D	N.D	X	X
	6	N.D	N.D	X	X
	7	N.D	N.D	X	X
	8	N.D	N.D	X	X
	9	N.D	N.D	X	X
	10	N.D	N.D	X	X
	11	N.D	N.D	X	X
	Mean	-	-	X	X
	SD	-	-	X	X
	Variance	-	-	X	X
	Range	-	-	X	X
	SE of mean	-	-	X	X

Table 4.2 Toluene concentrations in exhaust gas

	Car No.	Catalytic		Non-catalytic	
		mg/m^3	ppm	mg/m^3	ppm
Old cars (Higher than 10 years old)	1	X	X	134.92	35.81
	2	X	X	165.56	43.94
	3	X	X	84.10	22.32
	4	X	X	136.66	36.27
	5	X	X	108.06	28.68
	6	X	X	145.90	38.72
	7	X	X	118.53	31.46
	Mean	X	X	127.68	33.88
	SD	X	X	26.66	7.078
	Variance	X	X	711.25	50.09
	Range	X	X	81.45	21.61
	SE of mean	X	X	10.08	2.67
Moderate cars (5-10 years old)	1	81.50	21.63	71.70	19.03
	2	76.75	20.37	16.39	4.35
	3	38.29	10.16	39.62	10.52
	4	77.47	20.56	40.85	10.84
	5	94.52	25.09	108.89	28.90
	6	35.64	9.46	66.02	17.52
	7	94.22	25.01	31.73	8.42
	8	26.35	6.99	X	X
	9	22.59	6.00	X	X
	10	38.25	10.15	X	X
	Mean	58.56	15.54	53.60	14.22
	SD	28.79	7.64	30.98	8.22
	Variance	828.89	58.35	959.82	67.69
	Range	71.91	19.09	92.48	24.54
	SE of mean	9.14	2.41	11.71	3.10
New cars (Less than 5 years old)	1	10.94	2.79	X	X
	2	4.28	1.31	X	X
	3	8.017	2.13	X	X
	4	13.55	3.60	X	X
	5	8.50	2.26	X	X
	6	13.89	3.67	X	X
	7	14.80	3.93	X	X
	8	25.54	6.78	X	X
	9	9.47	2.51	X	X
	10	20.38	5.56	X	X
	11	22.78	6.07	X	X
	Mean	13.04	3.69	X	X
	SD	6.49	1.75	X	X
	Variance	44.21	3.15	X	X
	Range	20.60	5469	X	X
	SE of mean	2.00	0532	X	X

Table 4.3 Xylene concentrations in exhaust gas

	Car No.	Catalytic		Non-catalytic	
		mg/m^3	ppm	mg/m^3	ppm
Old cars (Higher than 10 years old)	1	X	X	34.67	7.99
	2	X	X	38.94	8.97
	3	X	X	41.85	3.64
	4	X	X	49.74	11.46
	5	X	X	37.84	8.72
	6	X	X	39.10	9.01
	7	X	X	17.80	4.10
	Mean	X	X	37.13	8.55
	SD	X	X	9.73	2.22
	Variance	X	X	94.77	5.26
	Range	X	X	31.99	7.35
	SE of mean	X	X	3.69	0.84
Moderate age cars (5-10 years old)	1	22.95	5.29	23.93	5.53
	2	27.04	6.23	N.D	.00
	3	8.13	1.87	11.18	2.57
	4	36.39	8.38	11.93	2.75
	5	16.92	3.90	40.76	9.39
	6	9.86	2.27	26.60	6.13
	7	28.76	6.63	10.08	2.32
	8	6.65	1.53	X	X
	9	7.06	1.63	X	X
	10	13.28	3.06	X	X
	Mean	17.70	4.07	20.75	4.78
	SD	10.51	2.42	12.07	2.78
	Variance	110.56	5.86	145.68	7.72
	Range	29.74	6.85	30.68	7.06
	SE of mean	3.32	0.76	4.92	1.13
New cars (Less than 5 years old)	1	N.D	N.D	X	X
	2	N.D	N.D	X	X
	3	6.94	1.60	X	X
	4	13.63	3.14	X	X
	5	3.70	0.85	X	X
	6	N.D	N.D	X	X
	7	N.D	N.D	X	X
	8	N.D	N.D	X	X
	9	N.D	N.D	X	X
	10	9.64	2.22	X	X
	11	8.47	1.95	X	X
	Mean	8.47	1.95	X	X
	SD	3.64	0.83	X	X
	Variance	13.26	0.70	X	X
	Range	9.92	2.28	X	X
	SE of mean	1.62	0.37	X	X

4.1.4 BTX concentrations in gasoline

One of the most important problems in this study was that the gasoline sample can not be collected from the car fuel tank directly and most of the car sample owners did not remember the exact fuel's octane number and brand of fuel they used. The gasoline samples were brought from the gasoline station in different brand and octane number (91 or regular grade gasoline and 95 or premium grade gasoline). The samples were stored in the refrigerator at 20 ^{0}C for analysis in the laboratory. The concentrations of Benzene, Toluene and Xylene in gasoline samples were presented in table 4.4.

Table 4.4 BTX concentrations in gasoline

Type of pollutants	Type of gasoline (Octane number)			
	Gasoline No.	Brand	Octane No.95 ppm	Octane No.91 ppm
Benzene	1	Shell	14359.38	16537.96
	2	PTT	15939.00	18373.28
	3	ESSO	15614.14	21763.86
	4	PTT	13606.77	20406.52
	Mean		11293.13	19270.41
Toluene	1	Shell	80756.18	85651.59
	2	PTT	85622.10	97107.38
	3	ESSO	85470.81	100221.3
	4	PTT	79393.47	90610.26
	Mean		82810.64	93397.65
Xylene	1	Shell	26060.76	18622.84
	2	PTT	23091.53	16642.41
	3	ESSO	25026.40	21464.22
	4	PTT	34812.20	17706.23
	Mean		27247.73	18608.93

From the details of table 4.4 the ratio of Benzene, Toluene and Xylene in gasoline were 1 : 7.33 : 2.41 and 1 : 4.84 : 0.97 for the gasoline octane number 95 and 91 respectively. In addition, the average concentrations of Benzene, Toluene and Xylene in total gasoline were 15281.77 ppm, 88104.14 ppm and 22928.33 ppm, respectively and the ratio of Benzene, Toluene and Xylene in total gasoline was 1 : 5.76 : 1.5.

The ratio of Benzene, Toluene and Xylene in exhaust gas and gasoline were shown in table 4.5. It was found that the ratio of Benzene, Toluene and Xylene in exhaust was different from the ratio in gasoline.

Table 4.5 Ratio of Benzene, Toluene and Xylene in exhaust and gasoline

Pollutants	Exhaust		Gasoline	
	Concentration (ppm)	Ratio	Concentration (ppm)	Ratio
Benzene	8.78	1	15281.77	1
Toluene	16.83	1.92	88104.14	5.76
Xylene	4.84	0.55	22928.33	1.5

4.2 Effects of catalytic converter on exhaust gas

Although the average concentrations of Benzene and Xylene in the catalytic equipped cars were less than the non-catalytic equipped cars. While the concentration of Toluene was greater in catalytic cars (see in figure 4.1). It does not mean that the 2 different car groups have different rate of air toxic pollutants emission.

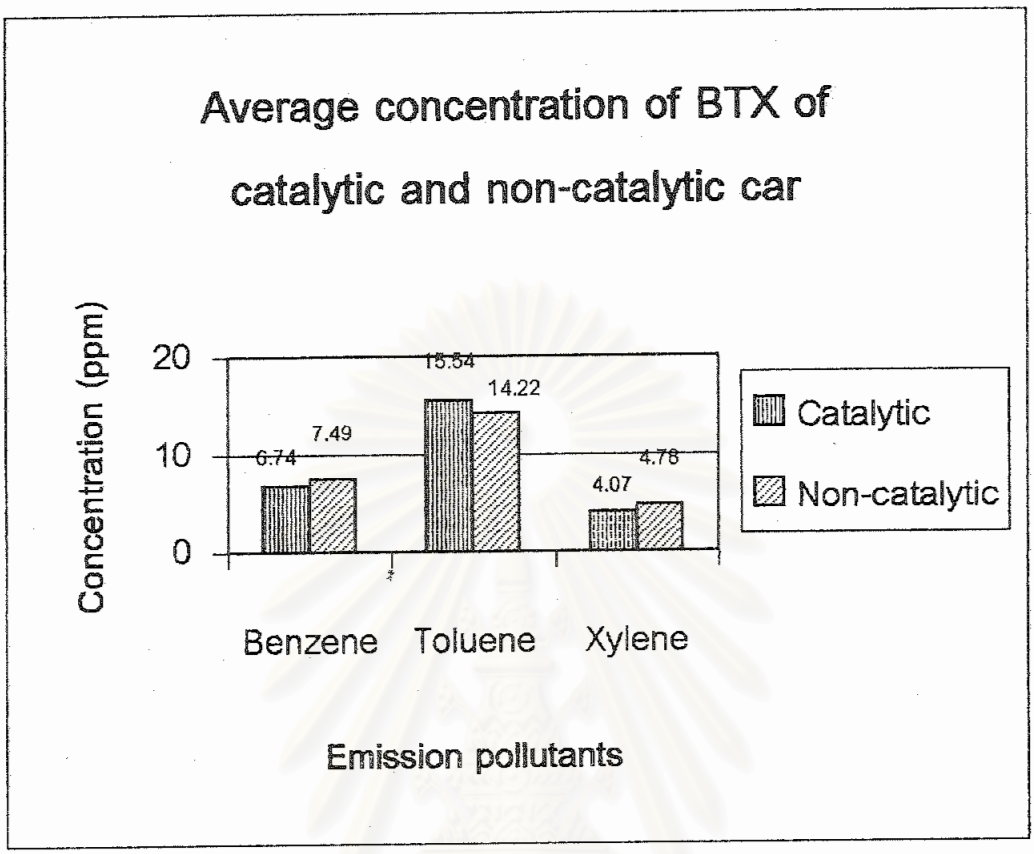

Figure 4.1 Average emission concentration of BTX from catalytic and non-catalytic car

In this study, The statistical t-test was used for independents sample to calculate the statistic relation of car pollution emitted between the car with and without catalytic converter. The SPSS programming version 6.0 for MS windows was used to prove the hypothesis that it has no significant difference of pollutants emitted between the catalytic and non-catalytic cars. After finishing the data processing by SPSS programming the results was shown in table 4.6.

Table 4.6 T-test for BTX of catalytic and non-catalytic cars

Benzene concentration				
Variance	t-value	df	2-Tail Sig	SE of Diff
Equal	-.58	15	.569	1.300
Toluene concentration				
Variance	t-value	df	2-Tail Sig	SE of Diff
Equal	.34	15	.739	3.883
Xylene concentration				
Variance	t-value	df	2-Tail Sig	SE of Diff
Equal	-.53	14	.603	1.320

The result from table 4.6 showed that there was no significant difference of Benzene, Toluene and Xylene concentrations in exhaust gas between car with and without catalytic converter at significant level (α) 0.05.

While, many studies on the effects of catalytic converter on car emission presented their results in directly opposite this study. Hebb et.al (1999) studied on the emission of BTXE (Benzene, Toluene, Xylene and Ethyl benzene) from the passenger car equipped with a catalytic converter and without catalytic converter. The catalytic car showed significant BTXE emissions lesser than the same car without catalytic converter. Lertvisansak (1996) tested the benzene emission from passenger cars. He found that the lowest level of benzene emission was found in 3 new cars with installation of

catalytic converter. Garivait et.al (1995) determined the hydrocarbon composition in exhaust gas from new 4 stroke gasoline engine. Their results showed that the cars equipped with catalytic converter apparently reduced the quantity of hydrocarbon in paraffin, olefin, napthene and aromatic groups.

The conflict of this study and other studies was explained by the age of catalytic converter. In this study, the moderate age cars have period of use in range of 5-10 years old. The age of catalysts in the catalytic equipped cars was over than 5 years old. It may be possible that the potential and efficiency of catalysts in catalytic converter came to an end.

The supportive of this explanation was confirmed by Duffy et.al (1998). They studied on the effect of the catalyst on the composition of the exhaust emission and found that the average BTX's concentrations of the best catalyst post-1986 vehicles were higher (generally 3-5 times) than the worst catalyst post-1986 vehicles. David (1995) determined the effect of some factors on exhaust emissions and he found that all vehicles in the CARBU group of his car samples that contained "dead" catalyst emitted high pollutants than other sample groups.

4.3 Effects of engine's ages on exhaust gas

Figure 4.2 and 4.3 presented that the average concentrations of Benzene, Toluene and Xylene in the older cars were greater than the newer cars. This phenomenon showed the possibility of the effect of engine's ages on pollutant concentrations in motor vehicle exhaust.

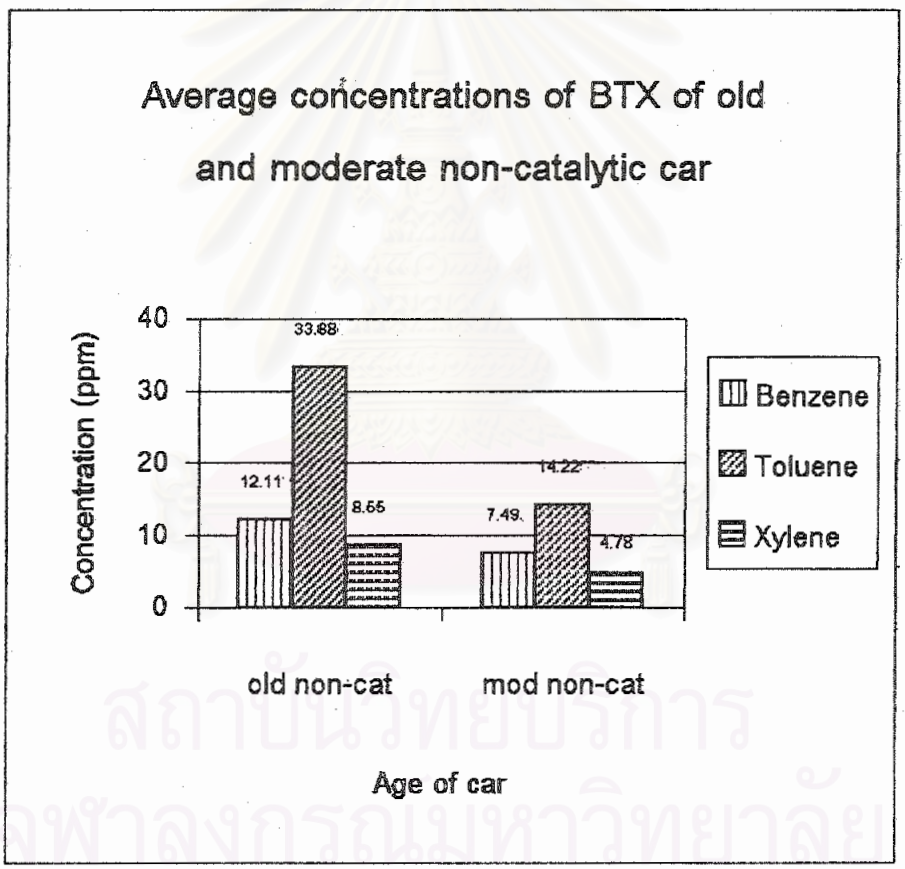

Figure 4.2 Average emission concentration of BTX from old and moderate age non-catalytic car

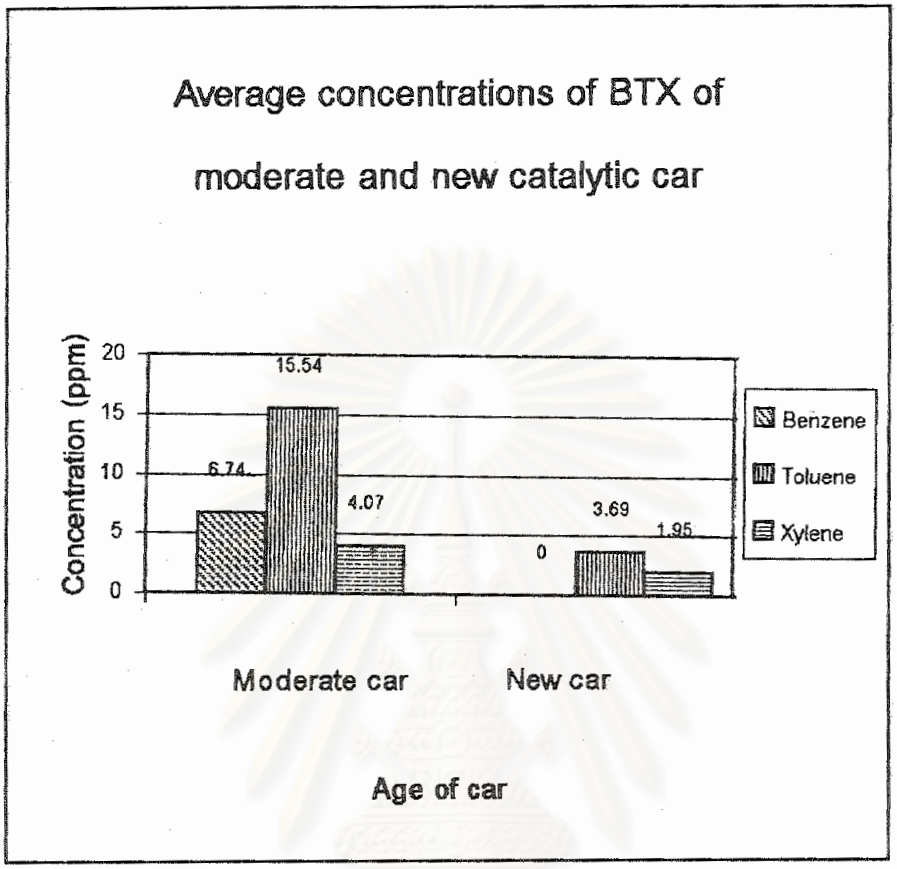

Figure 4.3 Average emission concentration of BTX from moderate age and new catalytic car

The statistical t-test for independent samples was used to examine the effects of engine's ages on concentration of Benzene, Toluene and Xylene in exhaust gas . The comparison of pollutants' concentration was applied into 2 different groups. The first group was the comparison between non-catalytic old car and non-catalytic moderate age car. The other group was comparison among catalytic moderate age car and catalytic new car. The results of benzene data processing by SPSS programming were displayed in table 4.7.

Table 4.7 T-test for effect of engine age on Benzene concentration

Benzene concentration				
Non-catalytic old and non- catalytic moderate				
Variance	t-value	df	2-Tail Sig	SE of Diff
Equal	2.80	12	.016	1.647
Catalytic moderate and catalytic new				
Variance	t-value	df	2-Tail Sig	SE of Diff
Unequal	8.43	9	.000	.800

The result from table 4.7 can be interpreted that there was significant difference of Benzene concentrations in exhaust gas emission between old and new cars at significant level (α) 0.05 or the age of engine has a strongly effected on Benzene concentrations in exhaust. The older emitted Benzene concentration higher than the newer ones.

In the same way, the results of Toluene and Xylene data processing by SPSS programming were presented in table 4.8 for Toluene and table 4.9 for Xylene. These tables showed the statistical t-test for independents sample that was used to prove the assumption that engine's ages had influenced on concentration of Toluene and Xylene in vehicle emission.

Like benzene, the comparison of Toluene and Xylene concentration were applied into 2 different groups. The first one was the comparison between non-catalytic old car and non-catalytic moderate age car. The other one was comparison between catalytic moderate age car and catalytic new car.

Table 4.8 T-test for effect of engine age on Toluene concentration

Toluene concentration				
Non-catalytic old and non- catalytic moderate				
Variance	t-value	df	2-Tail Sig	SE of Diff
Equal	4.79	12	.000	4.101
Catalytic moderate and catalytic new				
Variance	t-value	df	2-Tail Sig	SE of Diff
Unequal	4.79	9.87	.001	2.474

Table 4.9 T-test for effect of engine age on Xylene concentration

Xylene concentration				
Non-catalytic old and non- catalytic moderate				
Variance	t-value	df	2-Tail Sig	SE of Diff
Equal	2.71	11	.020	1.391
Catalytic moderate and catalytic new				
Variance	t-value	df	2-Tail Sig	SE of Diff
Unequal	2.49	12.25	.028	.853

The result from table 4.8 and 4.9 can be explained that there was significant difference of Toluene and Xylene concentrations in exhaust emission between two different age of car at significant level (α) 0.05. The age of engine strongly influenced on Toluene and Xylene concentrations in exhaust emission. The older car emitted air pollutants higher than the newer car. Because the older had an incomplete engine function while the engine's operation in the newer was better than the older. Vanke (1992) cited in Holman(1997) explained that the poorly maintained vehicles consume more fuel and emit higher levels of CO and VOCs than regularly serviced ones.

The results of relationship between age of engine and amount of air toxic in exhaust in this study were consistent with other studies. Lertvisansak (1996) studied on Benzene concentration in vehicle emission using unleaded gasoline. In his study, the exhaust gas was evaluated to determine the correlation between Benzene concentration versus mileage, and model year. He found that there was a modest increase in Benzene emission with older model year but there was no correlation with the mileage. Gorse et.al (1991) cited in Duffy et.al (1998) showed that the emission concentrations of Benzene and 1,3- Butadiene of newer vehicles were 6.8 and 0.53 mg/km. While Benzene and 1,3- Butadiene concentrations of older vehicles were 10.00 and 1.11 mg/km respectively. Dasch and Williams (1991) reported the concentrations of Benzene in car exhaust in their study. Benzene averaged 27 mg/mile for 1981/1982 model year cars and decreased to 9.4 mg/mile for 1983-1987 model year cars.

4.4 Comparison with previous studies

The hydrocarbon pollutants have harmful effect on both environment and human health; in fact these air toxic came from many sources. The best solution for the hydrocarbon problem was to restrict the major sources that had emitted the huge quantities of pollutants. Duffy et.al (1998) pointed that motor vehicles are recognized as a major contributor to the atmospheric burden of hydrocarbons in many urban areas.

The summary of selected research work in Benzene, Toluene and Xylene emission from vehicle from many countries was shown in table 4.10. The result from this study was compared with the other studies from Thailand, U.S.A, Europe, and Australia.

There was a rapid decrease in the average concentrations of Benzene, Toluene and Xylene when compared with the pervious studies. Due to the new standard of gasoline engine vehicles (safety requirements; emission from engine, level 6) from Thailand Industrial Standard Institute, Ministry of Industry, came to force in November 1999. And the new standard of unleaded gasoline from Ministry of commerce which declared on September 1992, has forced the petroleum refineries to reduce the aromatic hydrocarbon composition in gasoline from 50 % (by volume) to 35 % since January, 1st 2000.

Table 4.10 Comparison of previously reported researches and this study

Researchers and Place	Type of study	Details	Concentration					
			Benzene		Toluene		Xylene	
			mg/m^3	ppm	mg/m^3	ppm	mg/m^3	ppm
This study Bangkok, Thailand	1.Exhaust emission 2.Test on Idle condition 3.Bag sampling	Non-catalytic old cars	38.69	12.11	127.68	33.88	37.13	8.55
		Non-catalytic moderate cars	23.95	7.49	53.60	14.22	20.75	4.78
		Catalytic moderate cars	21.53	6.74	58.56	15.54	17.70	4.07
		Catalytic new cars	N.D	N.D	13.04	3.69	8.47	1.95
Duffy et.al (1998) Australia	1.Exhaust emission 2.Federal Test Procedure (FTP) 3.ADR 37/00 Drive Cycle	Pre-1986 non-catalytic cars	139.1 mg/km		240.5 mg/km		164.0 mg/km	
		Post-1986 catalytic cars (All)	41.8 mg/km		61.9 mg/km		46.5 mg/km	
		Post-1986 catalytic cars (Better catalysts)	28.1 mg/km		36.4 mg/km		27.0 mg/km	
		Post-1986 catalytic cars (Worst catalysts)	104.8 mg/km		179.5 mg/km		136.3 mg/km	
Suksomsankh (1990) Bangkok, Thailand	1.Exhaust emission 2.Test on Idle condition 3.Bag sampling	Passenger cars used in Bangkok	-	53.44	-	175.35	m- and p-xylene 467.91 ppm	o-xylene 41.43 ppm
Lertvisansak (1996) Bangkok, Thailand	1.Exhaust emission 2.Test on idle condition 3.Sampling by Charcoal tube	New model cars (1994-1995)	0 - 4.14 mg/m^3		0 - 6.26 mg/m^3		-	
		Old model cars (1990-1992)	4.40 - 22.02 mg/m^3		11.5 - 44.75 mg/m^3		-	

To be continued

Researchers and Place	Type of study	Details	Concentration			
			Benzene	Toluene	Xylene	
Hebb et.al (1999) Switzerland	1.Exhaust emission 2.New European Driving Cycle (NEDC)				C_2-Benzene (Xylene and Ethyl benzene)	
		Cars without catalytic converter	62.9 mg/km	227.2 mg/km	332.2 mg/km	
		Cars with catalytic converter	19.7 mg/km	43.6 mg/km	55.2 mg/km	
Dasch and Williams (1991) U.S.A	1.Exhaust emission 2.Cars tested under the Cooperative Test Program (CTP) and General Motors in-use emissions performance program (GM)	1981/1982 model year cars	27 mg/mile	46 mg/mile	-	
		1983-1987 model year cars	9.4 mg/mile	27.8 mg/mile	-	
Moschonas and Glavas (1996)	Non methane hydrocarbon in Ambient air of urban centers	Concentration units ppbv			m+p-xylene	0-xylene
		Name of cities				
		1.Vienna	6.0	10.9	5.7	2.3
		2.Hamburg	3.2	8.2	5.2	1.8
		3.Sydney	2.6	8.9	3.9	1.5
		4.Chicago	2.4	3.8	1.5	0.4
		5.Osaka	5.1	31.1	7.7	2.8
		6.Athens	5.0	14.3	12.1	3.7

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 Conclusions

The exhaust gas was collected at idle condition using Tedlar bag and analyzed for Benzene, Toluene and Xylene. The car samples were classified into 4 different groups as follow: 1.New catalytic car 2. Moderate age catalytic car 3.Moderate age non-catalytic car and 4.Old non-catalytic car. Based on the results obtained from this study, the following conclusions could be made:

1. The average concentrations of Benzene, Toluene and Xylene in old non-catalytic cars group were the highest when compared with other groups

2. The lowest concentrations of Benzene, Toluene and Xylene were found in the new catalytic cars group.

3. The ratio of Benzene, Toluene and Xylene in gasoline and exhaust are 1 : 5.76 : 1.5 and 1 : 1.92 : 0.55, respectively.

4. The statistic t-test was used to determined the relationship between the catalytic converter and vehicle emission. The result from SPSS programming showed that there was no significant difference of pollutants emitted among car with and without catalytic converter at significant level (α) 0.05. It may be possible that the potential of

catalysts in catalytic converter, which age over 5 years, has been dead.

5. The age of engine has a strongly influenced on amounts of pollutants in vehicle exhaust. This assumption was proved by statistic t-test at significant level (α) 0.05.

5.2 Recommendations for future work

1. This study investigates hydrocarbon in exhaust emission only 3 major pollutants, Benzene, Toluene and Xylene. Therefore, the other hydrocarbons in the vehicle exhaust should be studied to support the effect of motor vehicle emission on ambient air quality.

2. The determination of pollutant concentration in this study based on the vehicle idle condition only. The driving cycle mode for vehicle in Bangkok should be studied to estimate the real emission load.

3. The effect of emission from other vehicles such as motorcycles and diesel engine on ambient air quality should be studied to evaluate the real emission load from mobile sources to atmospheric environment.

4. The relationship between catalytic converter ages and emission pollutant reduction efficiency should be studied to find the optimum period of use of catalytic converter.

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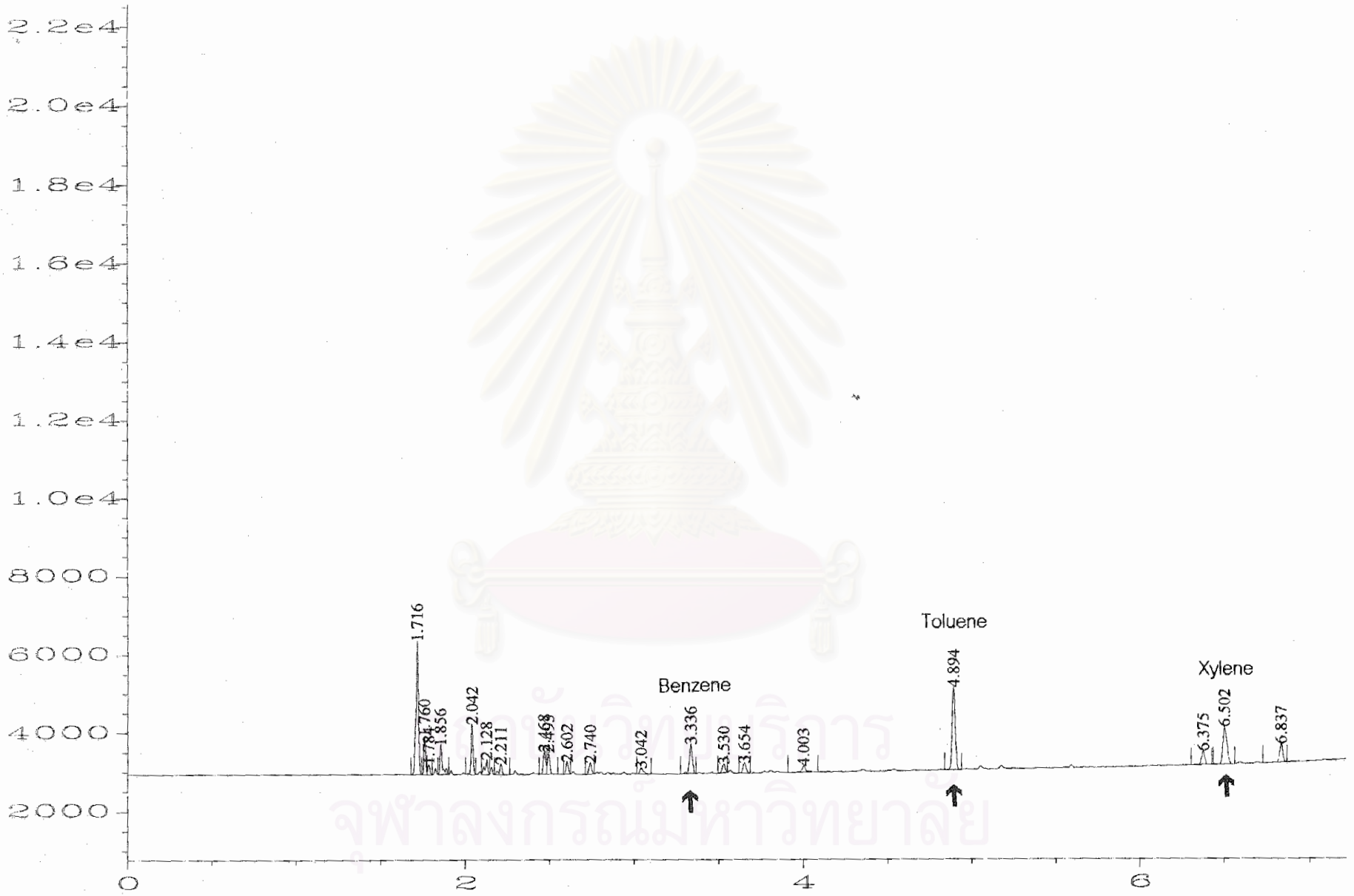
APPENDIX A

Chromatogram of exhaust gas sample



Sampling number _____

Type of sample O car O motorcycle

Name of owner and Telephone. No. _____.

Date _____ time _____ Pump model Gilian Model 3

General information

1.ยี่ห้อ และรุ่น / Trade mark and model year_____.

2.ชนิดของเครื่องยนต์ / Engine type_____.

3.จำนวนและความจุของกระบอกสูบ(ซี ซี) / No.of cylenders and capacity_____.

4.อายุการใช้งาน (ปี) / Period of use_____.

5.เลขไมล์ (ก.ม) / Mileage_____.

6.ป้ายทะเบียน / Car plate number_____.

7.ชนิดของน้ำมัน (ค่าออกเทน) และยี่ห้อ / Octane type and brand of fuel_____.

8.สภาพการใช้งาน

O ใช้งานน้อย / Rarely use (น้อยกว่า 20 ชั่วโมงต่อสัปดาห์ / Less than 20 hr./week)

O ใช้งานตามปกติ / Moderately use (20-40 ชั่วโมงต่อสัปดาห์ / 20-40 hr./week)

O ใช้งานมาก / Frequenly use (มากกว่า 40 ชั่วโมงต่อสัปดาห์ / More than 40 hr./week)

9.การบำรุงรักษา / Maintainace

O ดี / Good O ปานกลาง / Moderate O แย่ / Poor

Please specify_____

For car only

10.แคตตาลิกคอนเวอร์เตอร์ / Catalytic converter O มี / Yes O ไม่มี / No

ถ้ามีโปรดระบุชนิด / If yes please specify_____.

(ถ้าทราบ / If know)

For motorcycle only

11.น้ำมันออโตลูปที่ใช้ / Lubricating oil_____.

12.ระบบการระบายความร้อนของเครื่องยนต์ / Engine heat exchange_____.

Sampling Information

1.ระยะเวลาที่เก็บตัวอย่าง(นาที) / Sampling period_____.

2.อุณหภูมิท่อไอเสีย / Tailpipe Temp_____.

3.อุณหภูมิบรรยากาศ / Ambient Temp_____.

4.สถานที่ ที่เก็บตัวอย่าง / Place of sampling_____.

APPENDIX B

Questionnaire used in this study

APPENDIX C

Details of car samples used in this study

Catalytic equipped cars

	Number	Trade Name	Engine Capacity cc	Period of use (years)	Octane No. of gasoline	Frequency of use	Main-tenance
Old	1	x	X	x	x	x	x
	2	x	x	x	x	x	x
	3	x	x	x	x	x	x
	4	x	x	x	x	x	x
	5	x	x	x	x	x	x
	6	x	x	x	x	x	x
	7	x	x	x	x	x	x
Mod-erate	1	TOYOTA	1600	6	95	2	2
	2	NISSAN	1600	5	95	1	1
	3	NISSAN	1600	5	91	2	1
	4	MITSUBISHI	1500	5	91	2	2
	5	NISSAN	1600	5	91	2	3
	6	NISSAN	1600	6	91	1	1
	7	FORD	1300	5	95	2	1
	8	MITSUBISHI	1500	5	91	2	1
	9	MAZDA	1500	6	91	2	2
	10	TOYOTA	1600	6	95	1	1
New	1	HONDA	1600	3	91	2	2
	2	TOYOTA	1600	4	95	2	2
	3	MITSUBISHI	1500	3	95	2	2
	4	BMW	1800	3	95	1	1
	5	TOYOTA	1600	4	95	2	2
	6	BMW	1600	3 months	95	2	2
	7	HONDA	1500	4 months	91	1	1
	8	TOYOTA	1500	2	95	1	1
	9	HONDA	2000	4.5	95	2	1
	10	VOLVO	2400	4	95	1	1
	11	TOYOTA	1800	1	95	2	1

Explanation: Frequency of use 1 = Rarely use, 2 = Moderately use, 3 = Frequently use

Maintenance 1 = Good, 2 = Moderate, 3 = Poor

Non-catalytic equipped cars

	Number	Trade Name	Engine Capacity cc	Period of use (years)	Octane No. of gasoline	Frequency of use	Main-tenance
Old	1	BMW	1600	12	95	1	2
	2	HONDA	1600	11	91	1	1
	3	NISSAN	1300	12	95	2	1
	4	TOYOTA	1300	11	95	2	1
	5	TOYOTA	2000	11	95	2	1
	6	NISSAN	1300	11	91	2	2
	7	BMW	1800	13	95	2	1
Mod-erate	1	HONDA	1600	7	95	1	2
	2	MITSUBISHI	1500	8	95	1	2
	3	MITSUBISHI	1300	10	95	2	2
	4	BMW	2000	8	95	1	1
	5	HONDA	1300	7	91	2	2
	6	HONDA	1600	10	95	1	1
	7	HONDA	2000	10	91	1	1
	8	x	X	x	x	x	x
	9	x	x	x	x	x	x
	10	x	x	x	x	x	x
New	1	x	x	x	x	x	x
	2	x	x	x	x	x	x
	3	x	x	x	x	x	x
	4	x	x	x	x	x	x
	5	x	X	x	x	x	x
	6	x	x	x	x	x	x
	7	x	x	x	x	x	x
	8	x	x	x	x	x	x
	9	x	x	x	x	x	x
	10	x	x	x	x	x	x
	11	x	x	x	x	x	x

Explanation: Frequency of use 1 = Rarely use, 2 = Moderately use, 3 = Frequently use

Maintenance 1 = Good, 2 = Moderate, 3 = Poor

APPENDIX D

SPSS Programming output

19 Aug 00 SPSS for MS WINDOWS Release 6.0

t-tests for independent samples of Benzene concentration of
Catalytic moderate and Noncatalytic moderate

Variable	Number of Cases	Mean	SD	SE of Mean
Benzene concentration (ppm)				
Cat moderate	10	6.7415	2.529	.800
Non-cat moderate	7	7.4981	2.795	1.056

Mean Difference = -.7566

Levene's Test for Equality of Variances: F= .120 P= .734

t-test for Equality of Means Variances	t-value	df	2-Tail Sig	SE of Diff	95% CI for Diff
Equal	-.58	15	.569	1.300	(-3.529, 2.016)
Unequal	-.57	12.18	.578	1.325	(-3.644, 2.131)

T-test for Benzene of catalytic moderate and non-catalytic moderate cars

20 Aug 00 SPSS for MS WINDOWS Release 6.0

t-tests for independent samples of Toluene concentration of
Catalytic moderate and Non-catalytic moderate

Variable	Number of Cases	Mean	SD	SE of Mean
Toluene concentration (ppm)				
Cat moderate	10	15.5420	7.641	2.416
Non-cat moderate	7	14.2251	8.222	3.108

Mean Difference = 1.3169

Levene's Test for Equality of Variances: F= .098 P= .758

t-test for Equality of Means Variances	t-value	df	2-Tail Sig	SE of Diff	95% CI for Diff
Equal	.34	15	.739	3.883	(-6.961, 9.595)
Unequal	.33	12.42	.744	3.937	(-7.263, 9.896)

T-test for Toluene of catalytic moderate and non-catalytic moderate cars

20 Aug 00 SPSS for MS WINDOWS Release 6.0

t-tests for independent samples of Xylene concentration of
Catalytic moderate and Non-catalytic moderate

Variable	Number of Cases	Mean	SD	SE of Mean
Xylene concentration (ppm)				
Cat moderate	10	4.0783	2.422	.766
Non-cat moderate	6	4.7807	2.780	1.135

Mean Difference = -.7024

Levene's Test for Equality of Variances: F= .097 P= .761

t-test for Equality of Means					95%
Variances	t-value	df	2-Tail Sig	SE of Diff	CI for Diff
Equal	-.53	14	.603	1.320	(-3.533, 2.129)
Unequal	-.51	9.50	.620	1.369	(-3.800, 2.396)

T-test for Xylene of catalytic moderate and non-catalytic moderate cars

19 Aug 00 SPSS for MS WINDOWS Release 6.0

t-tests for independent samples of Benzene concentration of
Non-catalytic old and non-catalytic moderate

Variable	Number of Cases	Mean	SD	SE of Mean
Benzene concentration (ppm)				
Non-cat old	7	12.1119	3.343	1.263
Non-cat moderate	7	7.4981	2.795	1.056

Mean Difference = 4.6137

Levene's Test for Equality of Variances: F= .170 P= .688

t-test for Equality of Means Variances	t-value	df	2-Tail Sig	SE of Diff	95% CI for Diff
Equal	2.80	12	.016	1.647	(1.025, 8.203)
Unequal	2.80	11.63	.016	1.647	(1.025, 8.203)

T-test for Benzene of non-catalytic old and non-catalytic moderate cars

19 Aug 00 SPSS for MS WINDOWS Release 6.0

t-tests for independent samples of Benzene concentration of
Catalytic moderate and Catalytic new

Variable	Number of Cases	Mean	SD	SE of Mean
Benzene concentration (ppm)				
Cat moderate	10	6.7415	2.529	.800
Cat new	11	.0000	.000	.000

Mean Difference = 6.7415

Levene's Test for Equality of Variances: F= 18.516 P= .000

t-test for Equality of Means Variances	t-value	df	2-Tail Sig	SE of Diff	95% CI for Diff
Equal	8.86	19	.000	.761	(5.149, 8.334)
Unequal	8.43	9.00	.000	.800	(4.932, 8.551)

T-test for Benzene of catalytic moderate and catalytic new cars

20 Aug 00 SPSS for MS WINDOWS Release 6.0

t-tests for independent samples of Toluene concentration of
Non-catalytic old and non-catalytic moderate

Variable	Number of Cases	Mean	SD	SE of Mean
Toluene concentration				
Non-cat old	7	33.8860	7.078	2.675
Non-cat moderate	7	14.2251	8.222	3.108

Mean Difference = 19.6609

Levene's Test for Equality of Variances: F= .220 P= .647

t-test for Equality of Means Variances	t-value	df	2-Tail Sig	SE of Diff	95% CI for Diff
Equal	4.79	12	.000	4.101	(10.724, 28.598)
Unequal	4.79	11.74	.000	4.101	(10.724, 28.598)

T-test for Toluene of non-catalytic old and non-catalytic moderate cars

20 Aug 00 SPSS for MS WINDOWS Release 6.0

t-tests for independent samples of Toluene concentration of
Catalytic moderate and catalytic new

Variable	Number of Cases	Mean	SD	SE of Mean
Toluene concentration (ppm)				
Cat moderate	10	15.5420	7.641	2.416
Cat new	11	3.6898	1.765	.532

Mean Difference = 11.8522

Levene's Test for Equality of Variances: F= 66.368 P= .000

t-test for Equality of Means Variances	t-value	df	2-Tail Sig	SE of Diff	95% CI for Diff
Equal	5.01	19	.000	2.365	(6.901, 16.803)
Unequal	4.79	9.87	.001	2.474	(6.338, 17.367)

T-test for Toluene of catalytic moderate and catalytic new cars

20 Aug 00 SPSS for MS WINDOWS Release 6.0

t-tests for independent samples of Xylene concentration of
Non-catalytic old and non-catalytic moderate

Variable	Number of Cases	Mean	SD	SE of Mean
Xylene concentration (ppm)				
Non-cat old	7	8.5527	2.242	.847
Non-cat moderate	6	4.7807	2.780	1.135

Mean Difference = 3.7721

Levene's Test for Equality of Variances: F= .925 P= .357

t-test for Equality of Means Variances	t-value	df	2-Tail Sig	SE of Diff	95% CI for Diff
Equal	2.71	11	.020	1.391	(.709, 6.835)
Unequal	2.66	9.63	.024	1.416	(.615, 6.929)

T-test for Xylene of non-catalytic old and non-catalytic moderate cars

20 Aug 00 SPSS for MS WINDOWS Release 6.0

t-tests for independent samples of Xylene concentration of
Catalytic moderate and Catalytic new

Variable	Number of Cases	Mean	SD	SE of Mean
Xylene concentration (ppm)				
Cat moderate	10	4.0783	2.422	.766
Cat new	5	1.9524	.839	.375

Mean Difference = 2.1259

Levene's Test for Equality of Variances: F= 7.562 P= .017

t-test for Equality of Means Variances	t-value	df	2-Tail Sig	SE of Diff	95% CI for Diff
Equal	1.88	13	.083	1.133	(-.322, 4.574)
Unequal	2.49	12.25	.028	.853	(.267, 3.984)

T-test for Xylene of catalytic moderate and catalytic new cars

BIOGRAPHY

Mr. Teerawet Titseesang was born on December 14, 1971 in Bangkok, Thailand. He obtained many degrees in several fields; B.Sc. (2^{nd} class Honours) in General science from Chulalongkorn University, Thailand B.Pol.Sc (International relations and Comparatives Government and Politics), B.A (Information Science), B.Ed (Educational Administration), Cert. In English for Specific Career (Teaching) from Sukhothai Thammathirat Open University, Thailand

He has received His Majesty King Bhumibol scholarship award from the writing composition contest in title "The implementation of Thailand's international relationship policy to the neighbor countries after 100 years the Thai politic reformation" organized by Chulalongkorn University. He also received a reward for his academic outstanding from Faculty of Science, Chulalongkorn University in 1994 and 1995 and from the Professor Tab Neelanithi Foundation in 1996.

He was granted a scholarship from National Science and Technology Development Agency (NSTDA) for graduate's study at Chulalongkorn University. And he also received a fellowship from Foreign Commonwealth Office (FCO) for Air Pollution training at Urban Pollution Research Centre (UPRC) Middlesex University, London U.K.