



## CHAPTER I

### INTRODUCTION

Volatile organic compounds (VOCs) are emitted from many industrial processes and mobile sources. They are recognized as major contributors to air pollution, either directly through their toxicity or malodorous nature, or indirectly as ozone precursors, smog precursors, acid rain and finally global warming (Papaethimiou *et al.*, 1997). VOCs can enter to the human body by respiration or touching. The effect of their emissions on the human health such as respiration can be caused more severe problems to the lungs and lower resistance to respiratory infections. According to the effects on human health, the weak irritation can be initiated until become the most severe symptom. The effects of short-term exposure are still unclear, but continue or frequent exposure to high concentrations may cause incidence of acute respiratory disease. The other human health effects include premature death, effects on breathing, respiratory illness, alterations in the lung's defenses, and aggravation of existing cardiovascular disease.

VOCs have long been a major source of air pollution. A variety of industrial manufacturing processes have been considered for emission of volatile organic compounds. Table 1.1 illustrates the volatile organic compounds from various industries obtained from Pollution Control Department of Thailand. The emission of trace VOCs from the previous processes is of considerable concern due to their harmful environmental effects. The common VOCs in air pollution found in the atmosphere are for example, carbon monoxide, sulfur dioxide, nitrogen oxide, ozone, particulate matters, hydrocarbons, and etc. These VOCs are important precursors to both ozone and acidic precipitation (acid rain) and they can affect both terrestrial and aquatic ecosystems.

Table 1.1 Summary listing of organic compounds for some industries.

Industry	Effluent stream	Major compounds
Steel	Coke-oven gas scrubbing operation	NH <sub>3</sub> , sulfides, cyanides, phenols
Petroleum refining	Primary distillation process	Hydrocarbons
Organic chemical manufacture	Intermediate organic chemicals and by products	Hydrocarbons, cyanides, NH <sub>3</sub> , etc.
Pharmaceutical manufacture	Recovery and purification	Alcohols, ketones, benzene, xylene, toluene, etc.
Pulp and paper	Washing operation	Phenols, organic sulfur compounds
Textile and fiber manufacture	Wash water, deep discharges	organic solvents, surfactants
Food processor	Washing operation	Amines, NH <sub>3</sub>

*Source: Pollution Control Department, Thailand*

Amines are classified as nitrogenated volatile organic compounds. These compounds can be found in many industrial processes especially for food industry. The toxicity can be characterized by a pungent smell like as fishy odor while at higher concentrations the odor is more reminiscent of ammonia. Amines are also flammable and have high vapor pressure at ordinary temperatures. Its vapor can cause irritations of mucous membranes, eyes, and skin. The seriousness of human exposure to the amines is reflected in the low threshold limit values (TLV) suggested by the American Conference of Governmental and Industrial Hygienists (ACGIH) as shown in Table 1.2:

Table 1.2 ACGIH threshold limit values (Othmer and Kroschwitz, 1992).

Alkylamine	Concentration (ppm)
Methylamine	10
Dimethylamine	10
Trimethylamine	10
Ethylamine	10
Diethylamine	10
Isopropylamine	5
n-Butylamine	5
Diisopropylamine	5

There are various methods for abating VOC emissions in the air pollution control. A variety of techniques that are usually used for VOC abatement are shown the major advantages and disadvantages of their performances in Table 1.3. Among the several methods used for VOC abatement, the combustion processes are unique in that they combine in one step the function of capture, destruction and final disposal of the materials responsible for the problems. The combustion of toxic or malodorous compounds present in gaseous process emissions is an accepted air pollution control technique because it is capable for high destruction efficiency. The combustion is a controlled oxidation process, which used for destruction of VOC emissions from industrial waste gases. Many of the odorant vapors and gases are organic compounds that can be completely oxidized in air, at elevated temperature, to odorless carbon dioxide and water vapor (Wasfi *et al.*, 1978). Since energy requirements for thermal combustion are rather high, catalytic combustion is often seen to offer a promising alternative and economical operation.

Table 1.3 Performances of some VOCs abatement in air pollution control (Noyes, 1991).

Technology	Advantage	Disadvantage
Adsorption	- provides many surfaces for organic molecules in a gas stream, resulting in a high rate of organic removal.	- has a finite adsorption when the adsorbate becomes saturated. It needs a regeneration unit.
Absorption	- high degree of gas liquid mixing and high particulate removal performance.	- requires high pressure and have relatively short contact times. Thus, this method is also restricted to high solubility gases.
Thermal combustion	- currently available at the commercial scale because the generated heat can be further used in other units.	- requires a high operating temperature. So, the addition of supplemental fuel is needed to maintain the desired temperature.
Catalytic combustion	- higher destructive efficiency at lower temperature as compared to the thermal combustion. - can reduce the amount of pollutants from combustion, the complete combustion products are desirable. - have a potential saving in fuel costs resulting in less cost.	- more expensive for the catalyst. - have some limited applications for liquid and not applicable for solid wastes disposal.
Membrane	- useful for treating vent gases that are difficult to treat by using conventional processes.	- have a temperature limitation for organic polymeric membranes, it's a major difficulty.

Catalytic combustion of trace concentration of gaseous VOCs is more economical because the reaction can be carried out at lower temperatures. It can be controlled to produce lower temperatures and, as a result, to produce significantly lower amounts of the unwanted oxides such as carbon monoxide (CO). According to the potential advantages over other abatement technologies, this method has been developed in such the way that provides the higher performance and economically available. Catalytic combustion is known to be applicable to many of the stationary and mobile sources of organic emissions. It also becomes most popular and has potentially advantages because, in many cases, it is more versatile and economical for the low concentrations of organic emissions (i.e., < 5,000 ppm) (Heck *et al.*, 1989). The primary advantage of catalytic combustion over thermal combustion is that the complete oxidation process, common to both types of combustion, takes place at a lower temperature in a catalytic unit. The temperature in the catalytic combustion needed to obtain high conversions of organic compounds in waste gas stream is usually between 200 and 500 °C, whereas the thermal combustion requires temperatures of roughly 750 °C to 1,100 °C. The operating temperatures as shown in Table 1.4 are used for catalytic abatement of organic compounds. These temperatures are hardly dependent on the type of pollutant in gas stream, concentrations, and type of catalysts. The catalyst initiates reaction at lower temperatures. This demonstrates the major advantage of catalyzed processes, which is that they proceed faster than non-catalytic reactions, allowing lower temperatures for the same amount of conversion. Normally, the combustion products contain a variety of components rather than a single component in the mixture of organic compounds. This mixture is typically analyzed for carbon, hydrogen, oxygen, and other elements so that an empirical formula can be developed which represents the mixture. However, there are some limited applications for liquid and not applicable for solid waste disposal.

Table 1.4 Operating temperatures for catalytic abatement of some VOCs  
(Bonacci *et al.*, 1989).

Name of chemical	Chemical formula	Concentration (PPM)	Operating temperature (°C)
Acetaldehyde	CH <sub>3</sub> CHO	240	350
Acetic acid	CH <sub>3</sub> COOH	590	350
Acetone	CH <sub>3</sub> COCH <sub>3</sub>	410	350
Benzene	C <sub>6</sub> H <sub>6</sub>	380	210
Butyl acetate	CH <sub>3</sub> COOC <sub>4</sub> H <sub>9</sub>	480	350
Butyl alcohol	C <sub>4</sub> H <sub>9</sub> OH	330	260
Carbon monoxide	CO	4,000	150
Diethylamine	(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> NH	300	278
Triethylamine	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N	300	256
Ethyl acetate	CH <sub>3</sub> COOC <sub>2</sub> H <sub>5</sub>	350	350
Ethyl alcohol	C <sub>2</sub> H <sub>5</sub> OH	550	350
Formaldehyde	HCHO	410	150
Methyl alcohol	CH <sub>3</sub> OH	830	150
M-xylene	C <sub>6</sub> H <sub>4</sub> (CH <sub>3</sub> ) <sub>2</sub>	270	210
Phenol	C <sub>6</sub> H <sub>5</sub> OH	380	300
Toluene	C <sub>6</sub> H <sub>5</sub> CH <sub>3</sub>	320	210

Catalytic combustion of such a mixture of organic compounds containing carbon, hydrogen, and oxygen is described by the overall exothermic reaction:



The products of the complete combustion,  $\text{CO}_2$  and  $\text{H}_2\text{O}$ , are generally considered to be less objectionable than the waste components, making catalytic combustion as an attractive waste disposal method (Van der Vaart *et al.*, 1991). When chlorinated or sulfur-containing compounds are presented in the mixture, the complete combustion products include the acid components,  $\text{HCl}/\text{Cl}_2$  or  $\text{SO}_2/\text{SO}_3$ , respectively in addition to  $\text{CO}_2$  and  $\text{H}_2\text{O}$ . In case of the catalytic combustion of one or more volatile nitrogen-containing organic compounds, the suitable catalyst promotes the oxidation reaction to selectively produce nitrous oxide ( $\text{N}_2\text{O}$ ), nitrogen ( $\text{N}_2$ ), carbon dioxide ( $\text{CO}_2$ ), and water vapor ( $\text{H}_2\text{O}$ ) without generating significant amounts of nitrogen oxides ( $\text{NO}_x$ ). This reaction is performed to permit the reaction products to be vented directly into the atmosphere (Rossin and Campell, 1998).

Most industrial effluent gases consist of dilute mixtures of VOCs in air. VOCs content is found to be very low. Excess oxygen and some auxiliary fuel are usually required for complete combustion. The suitability of combustion as a control technique for waste gases depends on the “flammability” of the VOCs involved. Flammability is characterized by two limits: the lower explosive level (LEL) and the upper explosive limit (UEL). These limits represent, respectively, the smallest and largest amounts of VOCs, which are mixed with air, will burn without a continuous application of external heat. To avoid the potential explosion, VOCs content of industrial waste gases released to the atmosphere is normally outside the flammability limits. Table 1.5 presents the flammability limits for some selected VOCs. Care should be taken to make sure that mixtures of compounds with air, oxygen, or nitrogen dioxide, do not form explosives although each compound may be non-explosive by itself and then the catalytic combustion will be successfully used on an industrial scale. Lower concentrations of VOCs with a very large stoichiometric excess of oxygen are passed over a catalyst maintained at a temperature high enough to favour total oxidation.

Table 1.5 Flammability limits for some organic compounds in air ( 298 K and 101.3 kPa) (Benitez, 1993).

VOC	LEL (%)	UEL (%)
Acetaldehyde	4.0	6.0
Acetone	2.6	12.8
Acetonitrile	4.4	16.0
Benzene	1.3	7.1
n-Butane	1.9	8.5
n-Butanol	1.4	11.2
Carbondisulfide	1.3	50.0
Chlorobenzene	1.3	7.1
Diethylamine	1.8	10.1
Ethane	3.0	12.5
Ethanol	3.3	19.0
Ethyl acetate	2.2	11.0
Heptane	1.0	6.7
Hexane	1.1	7.5
Isobutane	1.8	10.0
Isopropanol	2.0	12.0
Methane	5.4	15.0
Methanol	6.7	36.0
Propane	2.2	9.5
Toluene	1.2	7.1
Trichloroethane	12.5	90.0

For the commercial catalysts that are usually used for the combustion of volatile organic compounds, they can be classified into the following categories: supported noble metals, and based metal oxides. The catalysts are either in pellet or ceramic monolith form. The noble metal catalysts and based



metal oxide catalysts are defined herein as metals and oxides of metals occurring in group VIII and III-B to II-B of the periodic table, respectively. Generally, metal catalyst possesses greater activity than oxide catalyst for complete combustion, contributing to the reduction of operating costs despite their higher manufacturing. The based metal oxide catalysts are generally less active than supported noble metals, but they are somewhat more resistant to poisoning (Spivey, 1997). This poison resistance may be due to the high active surface area of metal oxides compared with supported noble metals. The catalyst manufacturers try to solve many of the problems inherent in noble metal and based metal catalyst systems. Perhaps, the most promising development in catalysts for combustion application is the concept of active monoliths.

The objectives of the present study are to investigate the catalytic activity in terms of the light off temperature of three commercial-honeycombed monolith catalysts used for the catalytic combustion of nitrogenated volatile organic compound. Diethylamine was chosen as a model compound. The catalysts used for this study are commercial-honeycombed monolith catalysts with three noble metals, platinum (Pt), palladium (Pd), and rhodium (Rh), supported on the alumina washcoat. All catalysts will be investigated their activities and then the most active catalyst will be further used for reaction rate and kinetic studies. Before the experiment, the catalysts were characterized the surface area, physical dimension, and cell densities. In this study, the kinetic parameters such as reaction orders, activation energy will be determined in the expression of power rate law equation.