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ELIMINATION OF VOLATILE ORGANIC COMPOUNDS BY NON-THERMAL PLASMA COUPLED WITH PHOTOCATALYSIS

Miss Hathairat Muangsaen

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By	Miss Hathairat Muangsaen
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Thesis Advisor	Assistant Professor Varong Pavarajarn, Ph.D.

Accepted by the Faculty of Engineering, Chulalongkorn University in Partial Fulfillment of the Requirements for the Master's Degree

....Dean of the Faculty of Engineering

(Professor Bundhit Eua-arporn, Ph.D.)

THESIS COMMITTEE

....Chairman

(Associate Professor Tawatchai Charinpanitkul, D.Eng.)

....Thesis Advisor

(Assistant Professor Varong Pavarajarn, Ph.D.)

....Examiner

(Assistant Professor Apinan Soottitantawat, D.Eng.)

....External Examiner

(Busarakam Charnhattakorn, D.Eng.)

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การย่อยสลายโทลูอีนซึ่งใช้เป็นตัวแทนของสารอินทรีย์ไอระเหย โดยใช้พลาสมาอุณหภูมิต่ำร่วมกับการเร่งปฏิกิริยาด้วยแสงได้ถูกศึกษาในที่นี้ การย่อยสลายเกิดในเครื่องปฏิกรณ์แบบท่อที่มีลวดอะลูมิเนียมวางตัวอยู่ตรงกลางท่อ ผนังด้านในของเครื่องปฏิกรณ์จะเคลือบไว้ด้วยตัวเร่งปฏิกิริยาด้วยแสงไทเทเนียมไดออกไซด์ พลาสมาอุณหภูมิต่ำถูกสร้างขึ้นภายในเครื่องปฏิกรณ์ด้วยวิธีการปล่อยประจุแบบโคโรนา อากาศชื้นที่ถูกผสมกับไอโทลูอีนถูกจ่ายให้เครื่องปฏิกรณ์ ในขณะที่แก็สขาออกจะถูกนำไปวิเคราะห์ด้วยแก๊สโครมาโทกราฟี เมื่อศึกษาผลของกระแสไฟฟ้าขาเข้าที่มีต่อประสิทธิภาพการกำจัดโทลูอีน พบว่า การย่อยสลายมีประสิทธิภาพเพิ่มขึ้นเมื่อเพิ่มกระแสไฟฟ้า โดยมีการเสริมกันของปฏิกิริยาที่เร่งด้วยแสงและพลาสมาอุณหภูมิต่ำ ยิ่งไปกว่านั้นออกซิเจนและน้ำมีบทบาทสำคัญในทั้งสองกระบวนการ โดยปกติแล้วออกซิเจนเกี่ยวข้องกับปฏิกิริยารีดักชันในปฏิกิริยาที่เร่งด้วยแสงในการเป็นตัวรับอิเล็กตรอน ในขณะที่น้ำจะมีส่วนร่วมในการเกิดขึ้นของอนุมูลที่ไวต่อปฏิกิริยา อย่างไรก็ตามปริมาณน้ำที่มากจะส่งผลในทางลบเนื่องจากน้ำจะไปแย่งการดูดซับบนพื้นผิวของตัวเร่งปฏิกิริยาด้วยแสง และยังจะเกิดความเป็นพิษกับตัวเร่งปฏิกิริยาอีกด้วย นอกจากนี้ยังพบว่ากระบวนการเร่งปฏิกิริยาด้วยแสงจะช่วยเพิ่มผลได้ร้อยละของคาร์บอนไดออกไซด์อีกด้วย

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Degradation of toluene vapor, which was used as representative for volatile organic compounds (VOCs), by combination of non-thermal plasma and photocatalytic reaction, was investigated in this study. The degradation took place in a tubular flow reactor with an aluminum wire aligned at the center of the tube. The inner wall of the reactor was loaded with titanium dioxide photocatalyst. Non-thermal plasma was generated as corona discharge within the reactor. Wet air mixed with toluene vapor was supplied to the reactor, while the gas at the outlet of the reactor was analyzed by GC. The impact of the input electrical current on toluene removal efficiency was investigated. The degradation was found to improve with an increase in the electrical current. Synergistic effect can be obtained from the combination of photocatalytic reaction and non-thermal plasma. Moreover, both oxygen and water play a considerable role in both processes. Oxygen is regularly related in the photocatalytic reduction as the electron acceptor whereas water participates in the formation of more highly reactive radicals. However, large amount of water gives negative results due to the competitive adsorption on the photocatalyst surface and also poisons the photocatalyst. Additionally, it was found that the photocatalytic process also increased carbon dioxide yield.

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CHAPTER I
INTRODUCTION

In the Earth's atmosphere, there are many different global environmental issues caused by human activities. Air pollution seems to be one of the world's most serious problems in this century. Volatile organic compounds (VOCs) are recognized as major sources of air pollution which exist widely in both indoor and outdoor environments. The presence of VOCs in the atmosphere is emitted by various industrial and agricultural processes and its effects are increasing environmental and public health concerns over the last several years. VOCs cause a relevant contribution to many critical environmental problems, such as the production of tropospheric ozone or ground level ozone, the depletion of the stratospheric ozone layer and the global warming effects [1]. Many VOCs are known to be toxic and considered to be carcinogenic, mutagenic, or teratogenic [2]. Depending on the exposure level, VOCs can cause various severely adverse health effects in both short-term and long-term including allergic skin reactions, eye, nose and throat irritation, dry cough, headache, loss of coordination, nausea, dyspnoea, liver, kidney, and central nervous system damage, cancer and other health problems [3, 4]. The BTEX group of contaminants, which consists of benzene, toluene, ethylbenzene and three isomers of xylene, are the most cited VOCs. All of them are colourless liquids, immiscible with water but miscible with organic solvents. Ordinarily, these organic chemicals are found in petroleum hydrocarbon products and other environmental contaminants. Their effluents in some industries, such as rubber, glue and adhesives, paints, paint thinners, lacquers, fingernail polish, building materials and furnishings and some printing and leather tanning processes.

Numerous treatments have been developed to remove VOCs in the environment such as adsorption, incineration, scrubbing, biotechnology, catalytic oxidation and non-thermal plasma. Among the air-cleaning technologies, adsorption by activated carbon or activated charcoal seems to be the most popular traditional method. However, this removal technique only transfers the contaminant molecules from gaseous phase to absorbent surface instead of eliminating them. Additional chemical treatments or handling procedures are subsequently required for a destruction of absorbed VOCs [5]. In last few years, the pollution control technique using non-thermal plasma treatment has been widely studied since it is one of the promising technologies with higher efficiency and lower energy consumption. The main advantages of non-thermal plasma over conventional technologies are the ability to generate highly energetic electrons while keeping the background gas close to room temperature, easy operations, short residence times, less NO_x formation, etc. [6-9]. In the non-thermal plasma process, highly reactive species are created with no additional energy needed for gas heating as in thermal processes. The energetic electrons were excited and perform an ionization of the gas molecules which further produce chemically active species [6]. There are plenty of variations in the types of non-thermal plasma reactors that are currently investigated as follows: dielectric-barrier discharge (DBD) reactor, corona discharge reactor, surface discharge (SD) reactor, etc. [10]. However, quite a few undesirable by-products like ozone and NO_x are produced in non-thermal plasma technology. To overcome the by-products formation and to increase energy efficiency, non-thermal plasma could take advantage of its synergetic effect through combination with heterogeneous catalysts in the same reactor [6, 7].

An alternative remediation technology, which offers a number of advantages over conventional technologies, is the application of photocatalytic oxidation (PCO). Photocatalysts are semi-conductor substances with electrical conductivity in between that of a conductor and an insulator. The photocatalysts are capable to conduct electricity under some specific conditions and are activated by the irradiation of light. Titanium dioxide (TiO_2) is one of the most efficient photocatalysts for VOCs treatment with good performances in photocatalytic degradation of organic molecules, good chemical stability, absence of toxicity and relatively low price. Titanium dioxide has been used in various applications including solar cells, thin-film optical devices, and gas sensor [11]. In the photocatalysis process, electron–hole pairs are created, inducing oxidation or reduction reactions with adsorbed polluted molecules at the surface of the material. The photocatalysts are able to induce the degradation of a broad range of contaminants, at low or room temperature, into non-toxic final products without significantly high energy input and yields a very high CO_2 selectivity [12]. Hence, the reasons for combining non-thermal plasma technology and photocatalysis system are the following: (i) plasma treatment is expected to improve the kinetics of the reaction, (ii) photocatalysis is expected to improve significantly the carbon dioxide selectivity, and (iii) plasma generated UV is supposed to activate photocatalytic material [13].

In this study, the result of coupling non-thermal plasma with photocatalysis for VOCs vapor degradation in investigated experimentally by using a tubular reactor. Non-thermal plasma generated in this process is produced by a DC-corona discharge. A very particular advantage of this discharge type is the fact, that a highly reactive discharge medium is created, while the bulk gas is at ambient temperature and pressure. Therefore, pulsed corona promises higher efficiency than other advanced oxidation processes. The VOCs removal efficiency as well as the yield of carbon dioxide are concerned in this study.

Objectives of the study are to investigate the results of combination of non-thermal plasma treatment and photocatalytic degradation on degradation of volatile organic compounds vapor as well as carbon dioxide yield.

The thesis is consisted of five chapters as follows:

Chapter I suggests the motivation and introduction of this work.

Chapter II presents the basic theory about definition of volatile organic compounds as well as health and environmental effects, principle of non-thermal plasma and types of reactor systems, chemical and physical properties of titanium dioxide photocatalyst, photocatalysis reactions. Literature surveys of previous works relating to this research are also given in this chapter.

Chapter III shows chemicals, reactor apparatus, experimental schematic and analytical instruments.

Chapter IV describes the experimental results and discussion of the research.

Chapter V states the overall conclusions of this research

CHAPTER II

FUNDAMENTAL THEORY AND LITERATURE SURVEYS

Fundamental theory and literature surveys relating to definition, properties and health and environmental effects of volatile organic compounds, non-thermal plasma technique, photocatalysis and coupling non-thermal plasma and photocatalysis are described as follows.

2.1 Volatile Organic Compounds (VOCs)

Volatile Organic Compounds (VOCs) are a large group of carbon-based chemicals that easily evaporate at room temperature. Generally, VOCs exist extensively in both indoor and outdoor environments because they have become essential ingredients in many products and materials. Some of them can be detrimental to the health of people and the environment.

2.1.1 Definition of Volatile Organic Compounds

Volatile organic compounds (VOCs) are liquids or solids that contain organic carbons (carbon bonded to carbon, hydrogen, nitrogen, or sulfur), excluding carbon monoxide, carbon dioxide, carbonic acid, metallic carbides or carbonates, and ammonium carbonate, which vaporize at significant rates under normal atmospheric conditions of temperature and pressure [14]. Since the boiling point is proportional to the volatility of a compound, the volatile organic compounds are sometimes defined and classified by their normal boiling points. According to the definition of the World Health Organization (WHO), VOCs are referred as all organic compounds in the boiling point range of 50 - 260 °C, and excluding pesticides [2].

2.1.2 Health Effects of Volatile Organic Compounds

Volatile organic chemicals are probably the second-most widespread and diverse class of emissions after particulates. Some of them are toxic and carcinogenic, and are regulated individually as hazardous pollutants. They can cause a variety of different health effects depending on the chemical. There are two types of health effects that are commonly heard about when discussing VOCs; acute and chronic effects. Acute health effects are based upon a single exposure to a significant amount of the chemical, while chronic effects are based upon exposure to small amounts over a long period of time. Typical VOCs and their health effects are shown in Table 2.1 [15].

At present, the control of VOCs in an atmosphere is a major health and environmental problem. The methods of VOCs removal have been continuously developed such as absorption, adsorption, incineration, membrane separation, biotechnology, condensation, catalytic oxidation and non-thermal plasma.

Table 2.1 Typical VOCs and the health effects. Threshold value TLV in ppm [15].

VOC	Formula	Effects
Acetone	CH_3COCH_3	Carcinogen
Benzene	C_6H_6	Carcinogen
Butyl Acetate	$CH_3COOC_4H_9$	Carcinogen
Carbon Tetrachloride	CCl_4	Probable carcinogen
Dichloroethane	CH_2ClCH_2Cl	Paralysis of nerve centers
EGM	$(CH_2OH)_2(C_2H_5)_2C$	Birth defects
Ethylbenzene	$C_6H_5C_2H_5$	Probable carcinogen
Formaldehyde	HCHO	Sore throat dizziness and headache
Methyl chloride	CH_2Cl	Carcinogen
Methyl ethyl ketone	$CH_3COC_2H_5$	Carcinogen
Perchloroethylene	C_2H_5Cl	Probable carcinogen
Phenol	C_6H_5OH	Headache, dizziness
Styrene	$C_6H_5CH=CH_2$	Probable carcinogen
Tetrachloroethylene	$CCl_2=CCl_2$	Probable heart and liver disease
Toluene	$C_6H_5CH_3$	Headache, dizziness
Trichloroethane	$CH_2ClCHCl_2$	Probable birth defects, heart problems
Trichloroethylene	$CHCl=CCl_2$	Liver and kidney disease, paralysis of nerve centers
Vinyl chloride	$CH_2=CHCl$	Carcinogen
Xylene	$C_6H_4(CH_3)_2$	Headache, dizziness

2.1.3 Environmental Effects of Volatile Organic Compounds

The VOCs are also key contributors to environmental impact, primarily in the form of air pollution (petrochemical smog) and, to a lesser degree, in the form of greenhouse gases. They also have harmful environmental effects such as crop, vegetation and materials damage and reduced visibility when they chemically interact with oxides of nitrogen and sunlight to form ground-level ozone. Troposphere ozone or ground-level ozone is a harmful photochemical oxidant that significantly contributes to the formation of smog. Troposphere ozone is regularly measured as an indicator of smog levels in the atmosphere. Also VOCs react with stratospheric ozone causing destroying in this sphere and increasing the depletion of the ozone layer which protect plants, animals and humans from ultra violet rays. This will expose people to dangerous ultra violet rays and cause eyes and skin cancer [16].

2.2 Plasma Technique

2.2.1 Characteristics of Plasma

Plasma, which is considered to be the fourth state of matter, is a mixed state of atoms, molecules, positive and negative ions, electrons and radicals, which can be produced by supplying sufficient energy to a neutral gas. Energized electrons or photons collide with the neutral atoms and molecules in the feed gas (electron-impact ionization or photoionization) causing an electrified gas with the formation of a large number of different charge carriers in the ground or any higher state of any form of excited species as illustrated in Figure 1 [17, 18]. There are various methods to supply that essential energy to a neutral gas at low-pressure or atmospheric pressure for plasma generation such as mechanical, thermal, chemical, radiant, nuclear, electrical and electromagnetical methods [17].

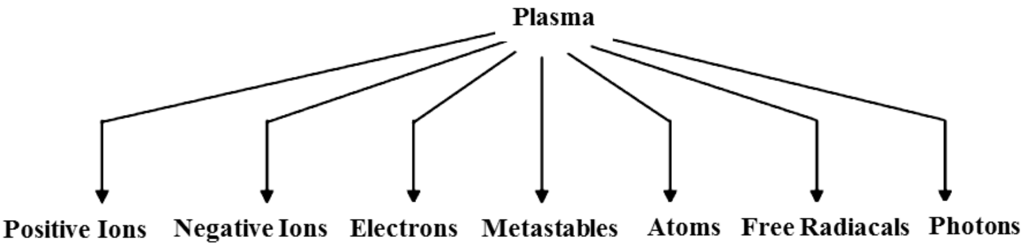

Figure 2.1 Constituents of Plasma.

2.2.2 Classification of Plasma

On the basis of relative temperature between electrons, ions, and neutrals, plasmas can be distinguished into three main groups as thermal equilibrium or fusion plasmas, local thermal equilibrium (or quasi equilibrium), and non-thermal equilibrium [17, 19].

Thermal equilibrium plasma implies that the temperatures of all species (electrons, ions and neutral species) are identical in a thermal equilibrium state. This is attributed to the frequent collisions between electrons and ions/neutrals inside high temperature and high density plasma. Examples include the natural fusion reactor (Sun), a magnetic field (of Tokamak design), or inertial (laser) confinement of plasma.

Local thermal equilibrium (LTE) plasma is also called quasi-equilibrium plasma. The electron, ion, and neutral temperature are in the same range (3,000-10,000 K). Thermal energy is regularly provided to the gas by a flame, where exothermic chemical reactions of the molecules are used as the prime energy source. This type of plasma can be generated by DC and RF arcs, or by an inductively coupled torch.

In the non-thermal equilibrium plasma or cold plasma, the energy input to generate the non-thermal plasma is very small and the temperature increase of the background gas or the reactor is quite low compared with that in the equilibrium and quasi-equilibrium plasma.

2.2.3 Generation of Plasma

In the plasma production, two types of plasma sources, which are electric fields and beams of electrons and photons, are ordinarily used.

2.2.3.1 Plasma Production Using Electric Fields

Plasma production using external electric fields utilizes the electrical breakdown of a neutral gas creating the charge carriers which are accelerated in the electric field. These kinds of species subsequently transfer their energy into the plasma when collide with other gaseous molecules. Due to their small mass, electrons maintain most of energy in collisions with atoms and molecules. Discharges are classified as DC discharges, AC discharges, or pulsed discharges on the basis of the temporal behaviour of the sustaining electric field [18].

In addtion, the different types of discharges and plasmas can be obtained depending on the applied voltage and the discharge current as shown in Figure 2.2.

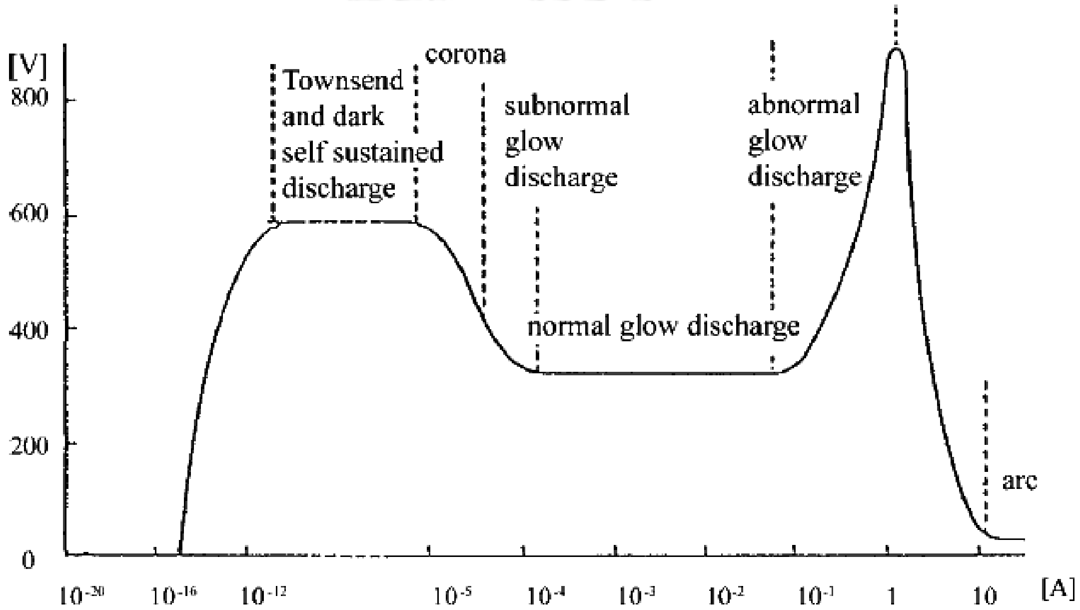

Figure 2.2 The dependence of voltage upon current for various kinds of DC discharges. (Ne,1.3 mbar, flat copper electrodes 10 cm^2, electrode distance 50 cm) [18].

The Townsend discharge is a self-sustained discharge characterized by a low discharge current. The transition to a sub-normal glow discharge and to a normal glow discharge is marked by a decrease in the voltage and an increase in the current. An abnormal glow discharge develops as the current is increased even further. Finally, at very high currents, the discharge undergoes an irreversible transition down into an arc (glow-to-arc transition).

2.2.3.2 Plasma Production Using Beam

Plasma generation using beams is most frequently accomplished by the use of electron beams and laser beams. Collective effects of the beam produce turbulent high-amplitudes plasma oscillations. The heating of the plasma electrons in this turbulent field is sufficient to sustain the beam-produced discharge plasma. Up to 70% of the beam energy can be transferred to the plasma. Plasma with high degree of ionization is possible to create in low-pressure environments. The plasma properties may be controlled by the electron beam current, the acceleration voltage, the gas pressure, and by the shape of the beam. Electron-beam generated plasmas are being used for large-area material processing [20]

2.3 Non-thermal Plasma

The non-thermal plasma includes almost electric discharge plasma except arc (or thermal plasma). The electrons temperature is considerably higher than in ions and neutrals. The temperature increase of the background gas or the reactor is quite low compared with that of the electron. In some cases, the temperature increase caused by the non-thermal plasma is only a few degrees [4, 15, 21-23]. Figure 2.3 is a typical example of the non-thermal plasma which shows that the temperature of the plasma is low enough to touch by a finger.

Ordinarily, non-thermal plasma is generated by applying a sufficiently strong electric field to ensure the dissociation of a neutral gas. The majority of the discharge energy goes into the production of energetic electrons, rather than heating any other particles. High-energy free electrons are generated and subsequently activate various radicals. This creates a quasi-neutral environment containing neutrals, ions, radicals, electrons, UV photons, etc. [24]. Ions and molecules can either be fragmented and degraded into new, smaller species or lead to the formation of activated chemical species which can undergo further reactions with neutrals or toxic contaminant molecules [4, 25].

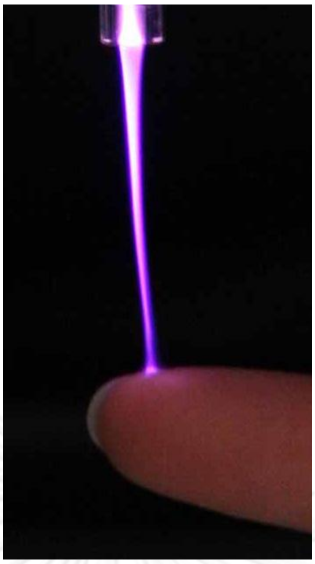

Figure 2.3 Typical example of the non-thermal plasma demonstration [21].

Non-thermal plasmas used in the removal of hazardous pollutants have been typically produced by either an electron beam method or various electrical discharge methods. There are many types of non-thermal plasma reactor frequently used in air purifying systems exemplified as follows [21].

2.3.1 Electron Beam

Figure 2.4 shows schematic representation of electron beam source. In an electron beam method, the electrons are generated by high voltage in the vacuum region outside the reaction chamber and are injected into the gas stream chamber. Energy of the electron beam is directly used for dissociative ionization, dissociation, radiative and dissociative attachments and excitation of the background gas. These inelastic reactions, as well as the electrons thermalized by elastic collisions, will further produce a large volume of plasma that can be used to initiate the removal of various types of pollutant molecules such as NO_x, SO_x and VOCs [15, 21].

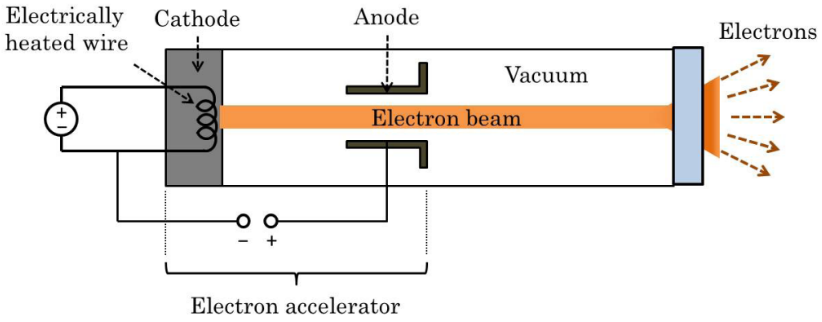

Figure 2.4 Schematic representation of electron beam source [21].

2.3.2 Dielectric Barrier Discharge

In DBD reactor, high AC voltage is typically applied to electrodes, one or both of which are covered with a thin dielectric layer that helps prevent spark discharges between metal electrodes. Glass, quartz, mica, and alumina are commonly used as the dielectric barrier. The gap distance between the electrodes is a few hundred of μm to several mm order. A schematic representation of typical DBD electrodes is shown in Figure 2.5.

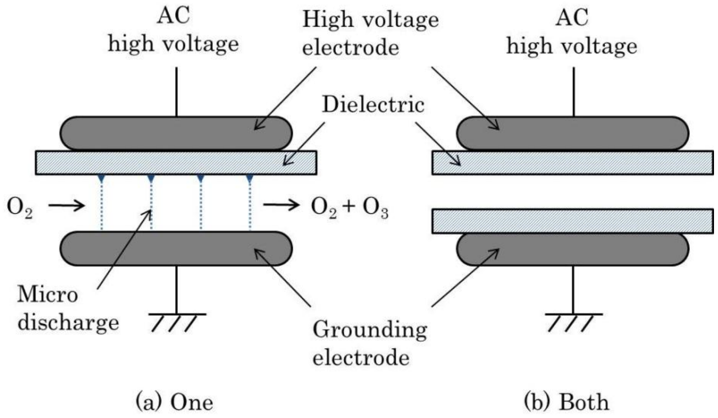

Figure 2.5 Dielectric barrier discharge electrode [21].

The barrier discharge is characterized by millions of small pulsed micro discharge which occurs repetitively in gas space. Because energetic electrons are generated in this micro discharge, various radicals and ions are produced by the collision between electrons and gas molecules. These radicals defuse into the barrier discharge space and react with background gas. As a result, ozone generation and NOx or VOCs removal are realized [15, 21, 25].

2.3.3 Corona Discharge

Corona discharges are relatively low power electrical discharges that take place at or near atmospheric pressure. The corona is invariably generated by strong electric fields under many electrode configurations such as small diameter wires, needles, or sharp edges on an electrode. In the case of for instance a positive point-to-plane geometry under DC or pulsed power supply, the discharge can have either a mono-filamentary structure for DC power supply or a branching structure for pulsed power supply [26-28].

In the DC corona discharge, the stable current and voltage are applied to the system to generate the non-thermal plasma. The construction of the reactor is simple, typically consisting of an anode plate and a cathode containing sharp metallic pin. By pumping the gas through the discharge volume, a stationary discharge can be established without overheating the gas [21].

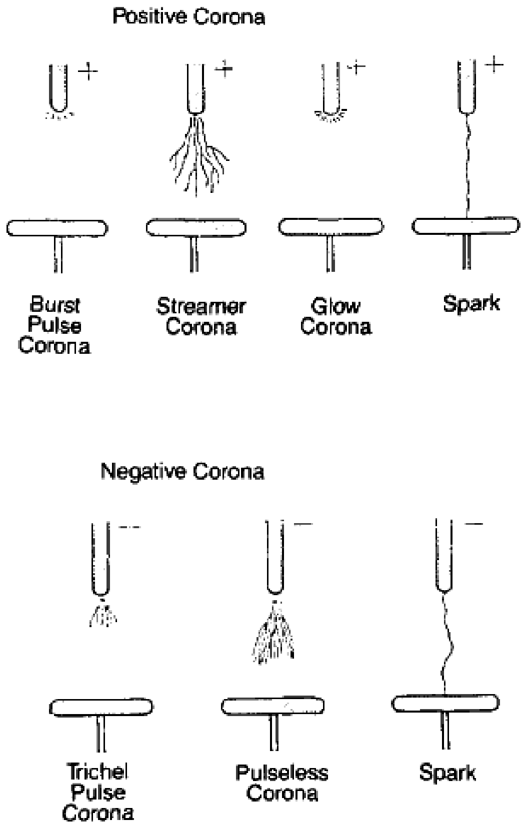

Figure 2.6 Schematic of DC corona discharges [28].

A pulsed corona discharge is energized with a pulse power supply with a fast voltage rising time of several tens of nanoseconds. The reactors used for the pulsed discharge are of two types: either with or without a dielectric barrier. The discharge mode in the pulsed corona discharge is usually the streamer mode, where the ionization zone is spread over the entire gap. Therefore, the electrode gaps can be set at around 10 cm or more, which is highly favourable for large-scale application and reducing the pressure drop. One of the distinctive characteristics of the pulsed corona discharge is the use of a short-duration pulse voltage. Due to the short duration of the applied voltage, the energy dissipation by ions can be minimized, resulting in the enhancement of energy efficiency. Figure 2.7 shows a pulsed corona discharge reactor [15, 21, 29].

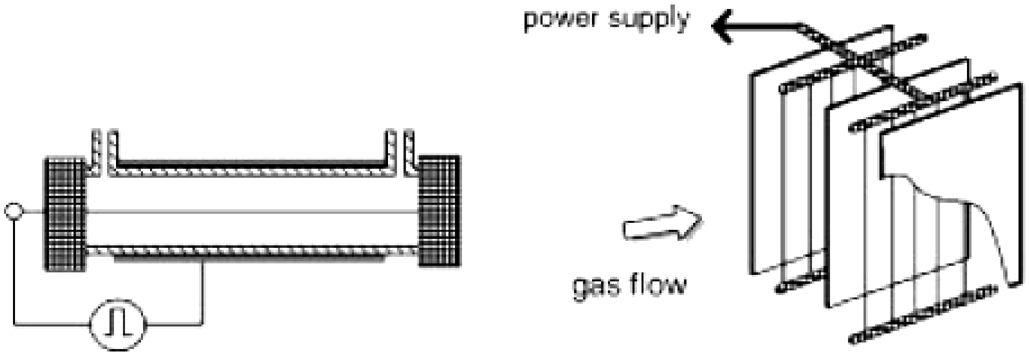

Figure 2.7 Pulse corona discharge reactor [15].

2.3.4 RF and Microwave Discharges

Discharges excited and sustained by high-frequency electromagnetic fields are of increasing interest for technical and industrial applications. RF discharges usually operate in the frequency range $f = \omega/2\pi$ of 1–100 MHz. The corresponding wavelengths (λ = 300–3 m) are large compared to the dimensions of the plasma reactor. For microwaves the most commonly used wavelength is 12.24 cm, corresponding to a frequency of 2.45 GHz. This wavelength is roughly comparable to the dimensions of a typical microwave reactor. For lower frequencies, the ions accelerated in the field move towards the electrodes and produce secondary electrons, similar to what happens in a DC discharge. As the frequency increases, the ions and subsequently also the electrons can no longer reach the electrode surface during the acceleration phase of the exciting external field [18, 30]. The example of the RF plasma system for plasma processing is illustrated in Figure 2.8.

In general, for the remidiation of contaminated air, uniform discharge is desirable for high energy efficiency compared with localized strong plasma which consumes greater amount of energy but is not so effective in enhancing total removal capability.

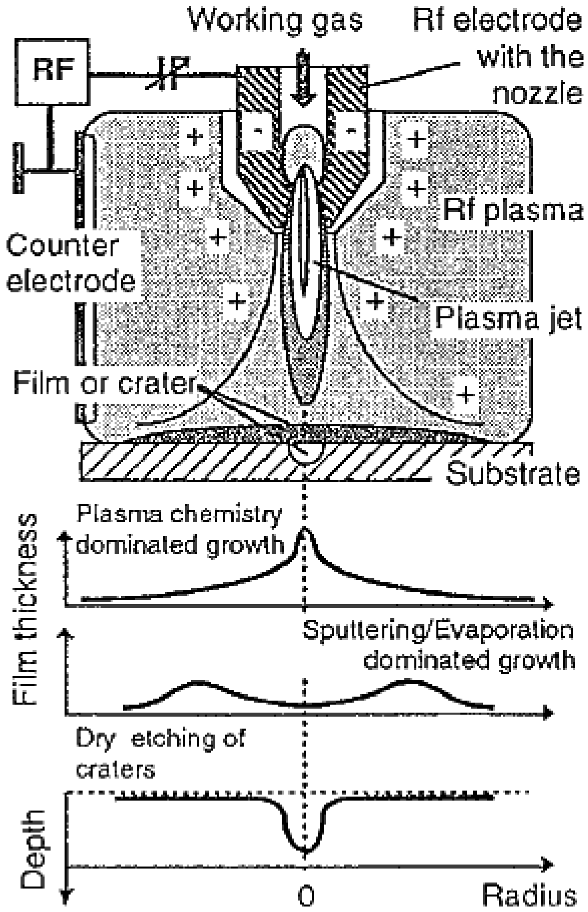

Figure 2.8 Schematic representation of the RF plasma jet system for plasma processing [18].

For the degradation of toluene by non-thermal plasma treatment, Huang et al. studied the effect of humidity on toluene decomposition using wire-plate dielectric barrier discharge as a plasma source. The results indicated that water plays a very important role in the reaction since it decomposes into OH and H free radicals inside the plasma system, resulting in a higher removal efficiency. However, water also has an adverse effect on toluene removal due to its electronegative characteristics. Increasing the humidity limits the electron density in the system and quench the activated chemical species [31].

2.4 Photocatalysis

Titanium dioxide has been widely used as a photocatalyst for the oxidation of organic pollutants due to its high photostability, commercial availability, low cost and relatively good activity. Titanium dioxide can crystallize in three structures, i.e. rutile (tetragonal), anatase (tetragonal) and brookite (orthorhombic) as shown in Figure 2.9. Rutile is thermodynamically the most stable, whereas anatase and brookite are metastable and transform to rutile upon heating. Among these crystalline forms, brookite occurs rarely compared to the anatase form of TiO_2 and exhibits no significant photocatalytic activity under daylight irradiation. Rutile and anatase have more industrial applications. Rutile has the smallest band gap, i.e. 3.0 eV, while anatase has a slightly higher band gap of 3.2 eV. Both band gaps are close to the limiting wavelength between UV-A light (320–400 nm) and visible light (400–700 nm). For the photocatalysis application, anatase is superior to rutile for the reasons as follows: (a) the conduction band location for anatase is more favorable for driving conjugate reactions involving electrons, and (b) very stable surface peroxide groups can be formed on the anatase during photo-oxidation reaction but not on the rutile surface [5, 32-35]. Among the different sources of TiO_2, Degussa P25 TiO_2 (Germany) has effectively become a research standard [1].

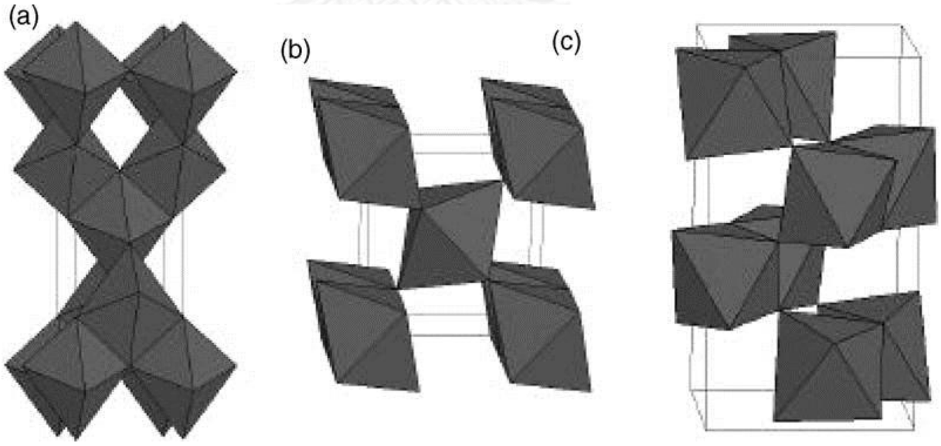

Figure 2.9 Crystal structures of (a) anatase (b) rutile and (c) brookite [33].

Titanium dioxide is a semiconductor material which has an electronic structure characterized by a filled valence band (VB) and an empty conduction band (CB). When the energy provided (photon) matches or exceeds the band gap, an electron (e^-) is raised from the VB to the CB leaving a hole (h^+) behind. A portion of this photo-excited electron-hole pairs diffuses to the photocatalyst surface of and takes part in chemical oxidation and reduction reactions with e.g. adsorbed water, oxygen and pollutant molecules. Hereby, highly reactive species like the hydroxyl radical ($^{\bullet}OH$) and the superoxide radical-anion ($O_2^{\bullet -}$) are formed, showing strong ability to degrade different micro-organisms as well as organic and inorganic pollutants. Common light sources used for photocatalysis are the ultra-violet (UV) lights [5, 34-38]. Figure 2.10 shows the schematic of the PCO process using TiO_2 as the catalyst.

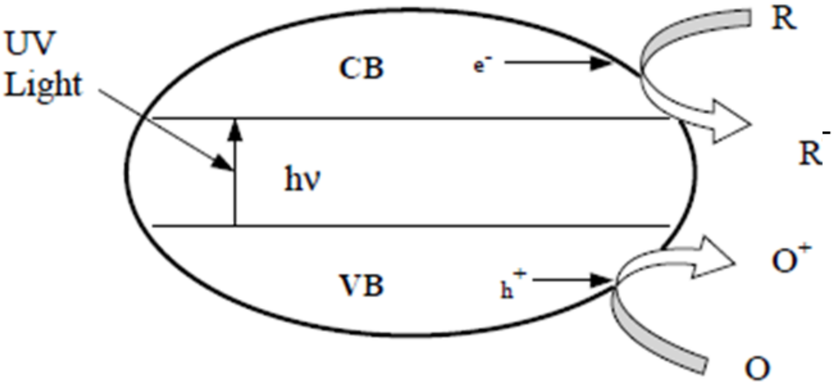

Figure 2.10 The schematic of TiO_2 UV photo-excitation process (R = reduction; O = oxidation) [5].

2.5 Non-thermal plasma coupled with photocatalysis

Discharge plasma as a driving force of photocatalyst furnished a mess of UV light. Fridman discovered that plasma is a source of UV radiation at different wavelength [39]. Four relevant ranges of the UV wavelengths can be specifically indicated:

1. Vacuum ultraviolet (VUV) radiation between 10-100 nm
2. UV-C radiation between 100 and 280 nm
3. UV-B radiation between 280 and 315 nm
4. UV-A radiation between 315 and 400 nm

However, the intensity of UV generated from the non-thermal plasma is dependent with the experiment configuration including reactor apparatus, type of power generator, amount of power applied, shape of electrode, etc.

In the photocatalytic degradation on TiO_2, The initial reaction step consists of electron-hole pair creation by exposing photocatalyst with light having energy content higher than the energy difference between the lowest energy level of the conduction band and the highest energy level of the valence band, the so-called band gap. For anatase and rutile TiO_2, the band gap energy are 3.2 eV and 3.0 eV, respectively, corresponding with wavelengths of 388 nm and 410 nm [40]. Thus, major of UV that emit from non-thermal plasma is potentially capable to activate TiO_2 photocatalyst.

The use of a catalyst located within the plasma zone has been reported to improve the efficiency in VOCs removal and CO_2 formation. A synergistic effect seems to occur when the non-thermal plasma and the photocatalysis are coupled in the same reactor [7].

The experimental results when the plasma and the photocatalysis are combined have shown a higher efficiency in a conversion than using either the plasma or the photocatalyst alone as investigated by Maciuca et al. [7] and Thevenet et al. [13, 41]. The nature of this effect could be due to several mechanisms occurring when the non-thermal plasma is present since the plasma produces various species such as high energy electrons, excited molecules or radicals. These molecules can activate the surface of TiO_2 or interact directly with reactant molecules. Additionally, Zhu et al. concluded that decomposition efficiency increases with increasing electrostatic field strength since more high energy electrons are generated [42, 43]. A similar result of the influence of input power was obtained from the literature conducted by Thevenet et al. [13] as well.

To explain the observed behavior when non-thermal plasma and photocatalysis are combined, Maciuca et al. [7] proposed several hypothesis as discussed below.

1. Activation of TiO_2 under high energy electrons generated by plasma can form the same electron–hole pairs as in photocatalysis, increasing then the number of reactive sites.

2. Formation of specific active species on the TiO_2 catalyst by the action of active species generated by non-thermal plasma on the electron hole pairs formed by UV.

3. Plasma favoring desorption of intermediary products of oxidation leading to an increase in the turn-over of the catalytic sites.

CHAPTER III
EXPERMIENTAL

This chapter describes about the experimental procedures of volatile organic compounds elimination using non-thermal plasma coupled with photocatalysis method. It is divided into four parts, i.e., chemicals, reactor apparatus, catalyst loading, experimental schematic and analytical instruments.

3.1 Chemicals

The photocatalyst powder of titanium dioxide used in this research is Degussa P-25 (80% anatase, 20% rutile, surface area 35-65 m^2/g (BET)) obtained from Sigma-Aldrich. Liquid toluene, purchased from local vender, is from Merck Millipore. Analytical grade magnesium nitrate hexahydrate ($Mg(NO_3)_2.6H_2O$) obtained from Ajax Finechem was used as reagents in humidifier solution. Carrier gases are air zero and ultra-high purity (UHP) nitrogen procured from Labgaz and TIG, respectively.

3.2 Tubular Reactor Apparatus

The reactor used in this experiment is made from a stainless steel tube, with 3/8 inch outer diameter and wall thickness of 0.035 inch, and a center-aligned aluminum wire. The wire alignment is controlled by adding rubber stoppers at each end of the reactor tube. The tube and wire, which were both connected to a high voltage power generator as displayed in Figure 3.2, acted as plasma electrodes. When the non-thermal plasma was created, electrons were driven directly from the centered wire (negative electrode) to the tube wall (grounding electrode) resulting in the 10 cm fixed-length non-thermal plasma region. In this area, the TiO_2 photocatalyst was loaded on the inner wall surface of the stainless steel tube. The illustration of the reactor apparatus is shown in Figure 3.1

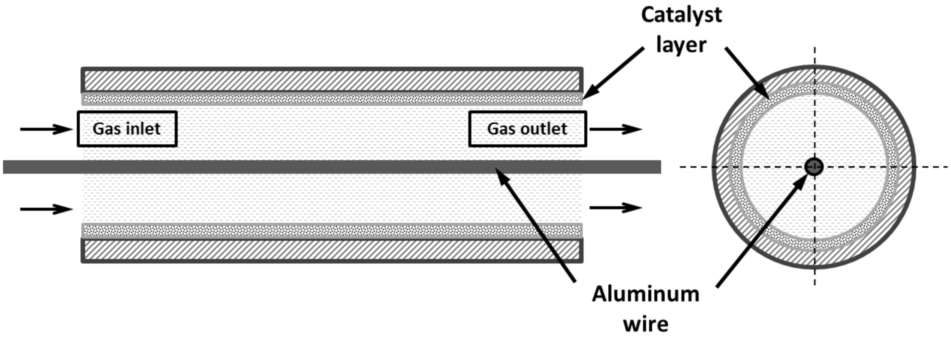

Figure 3.1 The apparatus of the tubular reactor

Upon the application of potential in the range of 1.2 - 4.5 kV between the wall of the reactor and the wire, non-thermal plasma was generated as corona discharge within the reactor. The electrical current was ranged from 0.5 - 5 mA which are the minimum and maximum proper value of the equipment limitations.

Figure 3.2 The high voltage power generator

3.3 Catalyst Loading

To load the catalyst onto a substrate, 0.5 g of the TiO_2 photocatalyst was suspended in 10 mL of ethanol. The suspension was stirred to disperse the photocatalyst effectively. The catalyst was coated on the reactor inner wall via rinsing the tube with the catalyst suspension. More layers of thin film of TiO_2 nanoparticles could be coated on the substrate by repeating the above-mentioned operation. In this experiment ten catalyst layers were surfaced on the tube wall. The reactor tube was then oven-dried at 80°C for 24 hr. The amount of TiO_2 coated on the substrate was estimated from the difference in the weight of the substrate before and after coating. Average TiO_2 photocatalyst weight measured in each experimental run was 5-7 mg.

3.4 Experimental Schematic

A schematic of the experimental set-up for the elimination of VOCs in vapor phase is shown in Figure 3.3. A stream supplied from a pressurized dry air cylinder was divided into two minor streams. The first stream was dry air at the calibrated flow rate of 4.8 mL/min that was alternatively humidified by bubbling it through DI water or saturated $Mg(NO_3)_2$ solution at room temperature (30°C) to obtain 100% relative humidity and 52.9% humidity, respectively [44]. The second stream was loaded with toluene vapor in similar way at 0.3 mL/min. The contaminated air was produced by mixing two air streams together and then supplied to the reactor, giving the residence time of 55 seconds and the toluene concentration of 20,000 ppm, approximately. Ultra high purity nitrogen was used to substitute dry air in the study of the effect of oxygen on photocatalyst degradation.

Inlet and outlet air sample was periodical taken by 0.1 mL pressurized storage microsyringe with built-in push-button valve obtained from Valco instruments Co. Inc. The sample was taken every 10 minutes in the first hour, every 30 minutes for next 2 hours and hourly until the system reached steady state.

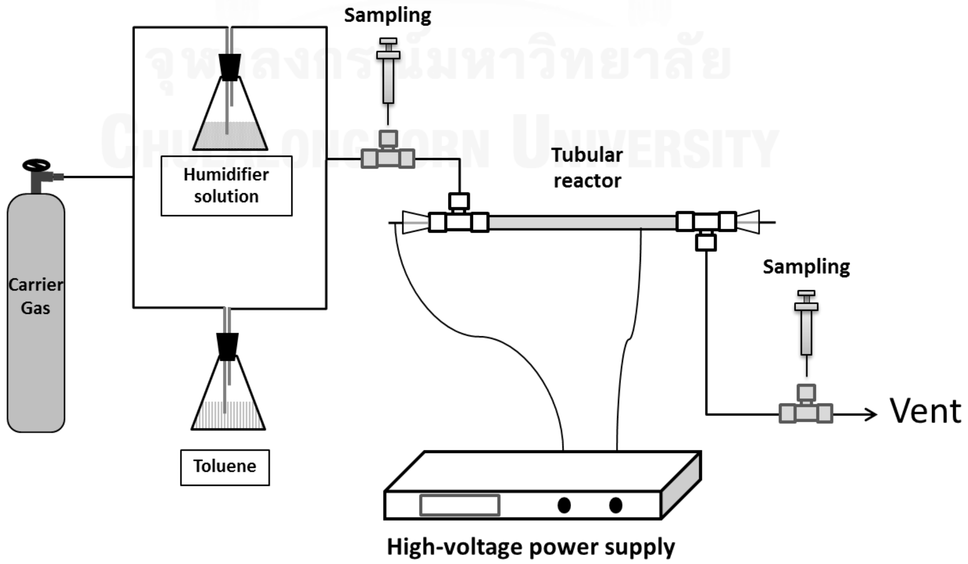

Figure 3.3 Schematic of the experimental set-up

3.5 Kinetics Studies

The first-order kinetic model was applied to explain the characteristic of the reaction in this experiment. The rate law is expressed as following:

$$\frac{-dC}{dt} = kC \tag{3.1}$$

The integrated form is described as

$$ln\frac{C_0}{C} = kt \tag{3.2}$$

Where	C_0	is the initial concentration of the reactant
	C	is the concentration of the reactant at a particular time
	k	is the first-order rate constant

The first-order rate constant can be obtained from the slope of the plot of $ln\frac{C_0}{c}$ versus residence time. The total flow rates were set to 5.1, 7.7, 10.3 and 12.8 mL/min to obtain 100, 75, 50 and 25% of the residence time in the reactor, respectively. The flow rate of each air streams was adjusted properly to maintain the toluene concentration.

3.6 Analytical Instruments

Removal efficiency of VOCs was analyzed by Shimadzu Gas Chromatograph (GC-14B) with a PE-WAX capillary column (Algilent, USA), equipped with a flame ionization detector (FID). The column initial temperature, injection temperature and detector temperature are 40°C, 150°C and 280°C, respectively. The yield of carbon dioxide was tested by Shimadzu Gas Chromatograph (GC-8A) with TCD detector. The column temperature was initially 40°C and then increased to 70°C at the progress rate 5°C/min. The injector and detector temperature were identically set to 50°C.

CHAPTER IV
RESULTS AND DISCUSSION

The combination of non-thermal plasma treatment and photocatalytic reaction was applied to a VOC contaminated air remediation. The effects of various degradation conditions on toluene vapor elimination were investigated. The synergistic results from the associated method are analyzed and discussed in this chapter.

4.1 Effect of Various Parameters on Toluene Degradation Performance

Although, non-thermal plasma technique has been commonly used in the VOCs elimination system, coupling with photocatalyst seems to get extremely more attention from researchers. To study the influence of the photocatalysis when combine with non-thermal treatment in airflow system, several parameters were examined in this experiments to obtain the explanation about the factors that affect the reaction attribute resulting to the differences in toluene degradation.

The toluene removal efficiency is defined as follow:

$$\%eff = \frac{C_{in}-C_{out}}{C_{in}} \times 100 \qquad (4.1)$$

4.1.1 Effect of Electric Current

Basically, the characteristics of toluene destruction in non-thermal plasma process only and combined process when supplying different amounts of electrical energy is reported. The values of average electric current, average potential, calculated input power and energy density provided to the reaction process are reported in Table 4.1. The energy density can be obtained by using following evaluation criteria [45]:

$$Energy\ Density\ (kJ/L) = \frac{Discharge\ Power\ (W)}{Gas\ Flow\ Rate\ (mL/min)} \times 60 \qquad (4.2)$$

The total volumetric flow rate of the air stream used in this experiment was set to 5.13 mL/min calibrated by water replacement method. The stability of the flow rate in each minor streams were controlled using two mass flow controllers.

Table 4.1 Average current, average potential, input power and electron density supplied to the reactor in different conditions.

Average Current (mA)	Average Potential (kV)	Input Power (W)	Electron Density (kJ/L)
0	0	0	0
0.5	3.9	1.95	22.79
1	2.95	2.95	34.47
3	1.8	5.4	63.10
5	1.5	7.5	87.64

The electric current in the range of 1-5 mA was applied to the reactor to generate non-thermal plasma. The toluene removal efficiency at steady-state conditions in non-thermal plasma system and combined system are compared, as shown in Table 4.2. The results of applying different amount of electricity indicate that the degradation efficiency is significantly improved with increasing the amount of electrical power supplied to the reactor in all cases.

As a result of higher electrical power input, the electron intensity generated within the reactor channel is raised which is helpful for the formation of greater number of electrons with higher energy [45]. More active species are excited and further react with the toluene molecules while flowing through the reactor tube. Thus, removal efficiency of toluene are proportional to the density of electrons [43]. The reasons for describing the differences in the degradation performance of toluene between the two mentioned methods will be subsequently discussed.

Table 4.2 The steady state toluene removal efficiency in combined method compared with non-thermal plasma system at different electric currents.

Current (mA)	% Removal	
	Non-thermal plasma	Combined method
0.5	55.72	70.70
1	75.23	82.20
3	89.31	90.87
5	95.61	94.57

4.1.2 Effect of Photocatalysis

According to experimental results, applying TiO_2 photocatalyst on the reactor wall together with non-thermal plasma plays a considerable role on the degradation of toluene. The synergistic effects are founded in almost all cases with different applied input electric currents as mentioned previously in Table 4.2. However, as demonstrated in Figures 4.1-4.4, it can be seen that there are dissimilarities in the reaction dynamic of the toluene decomposition in each experiment before the operation reaches steady state. The results indicate that the photocatalyst apparently enhances the degradation reaction. It could be suggested that this synergy is due to two factors: the photocatalytic reaction as the mainly influential factor and the adsorption process.

Firstly, in the non-thermal plasma process, low current and high voltage discharge are widely used. As the voltage applied across the two electrodes is increased, the current suddenly increases sharply at a threshold voltage required for sufficiently intensive electron avalanches. These energetic electrons then bombard the gas molecules or atoms resulting to a development of ionized derivatives including atoms, ions, radicals, neutrals and UV photons. As stated in chapter 2, plasma is a source of UV with different wavelengths. Four relevant ranges of UV wavelengths specially can be indicated: VUV, UV-C, UV-B, and UV-A [39].

In the photocatalytic degradation on TiO_2, the electron-hole pair is primarily generated after the photocatalyst is exposed by light with energy higher than the band gap energy. For anatase and rutile TiO_2, the band gap energy are 3.2 eV and 3.0 eV, respectively, corresponding with wavelength of 388 nm and 410 nm [40]. For the TiO_2 photocatalyst used in this experiment (Degussa P-25), the compositions of anatase and rutile are 80% and 20%, respectively. Thus, major of UV that emit from non-thermal plasma is potentially capable to activate TiO_2 photocatalyst. The occurrence of UV was detected by photometer using UV-sensor probe which confirmed that there is UV generation in this process.

When photon energy exceeds the energy of the band gap, and electron (e^-) is excited from the valence band to the conduction band, leaving the hole (h^+) behind. In electrically conducting materials, the charged carriers produced from such operation are instantaneously recombined. Nonetheless, in semiconductor materials a portion of this photo-excited electron-hole pairs diffuse and are trapped at the photocatalyst surface leading to a participation in the chemical reaction with the absorbed donor (D) or acceptor (A) molecules.

The activation of TiO_2 by UV light can be written as:

$$TiO_2 + light \rightarrow h^+ + e^- \tag{4.3}$$

Two types of reaction probably occur on the photocatalyst surface in the photocatalytic degradation process, which are oxidation and reduction reaction. The holes regularly perform an oxidation with absorbed donor molecules whereas the electron can reduce acceptor molecules as follows:

$$D + h^+ \rightarrow D^{\cdot +} \tag{4.4}$$

$$A + e^- \rightarrow A^{\cdot -} \tag{4.5}$$

Commonly, in photocatalysis process, water favourably acts as electron donor while oxygen prefers to accept electron. Thus, when there is a presence of water or oxygen molecules, the reactions take place introducing a formation of energetic hydroxyl and superoxide radicals as follows:

For water $$h^+ + H_2O \rightarrow OH^\bullet + H^+ \tag{4.6}$$

or $$h^+ + OH^- \rightarrow OH^\bullet \tag{4.7}$$

For oxygen $$O_2 + e^- \rightarrow O_2^{\bullet -} \tag{4.8}$$

However, water vapour was not supplied to the reactor. Therefore, apart from the non-thermal plasma process, the elimination of toluene was partially done by the reduction reaction of superoxide radicals when there was a presence of oxygen molecules as mentioned above leading to the improvement of the degradation performance [5, 46, 47]. Moreover, strongly-energized particles, such as electrons, excited molecules, and radicals may also transfer their energy to TiO_2 by bombardment when TiO_2 photocatalyst is placed in a non-thermal plasma reactor [9].

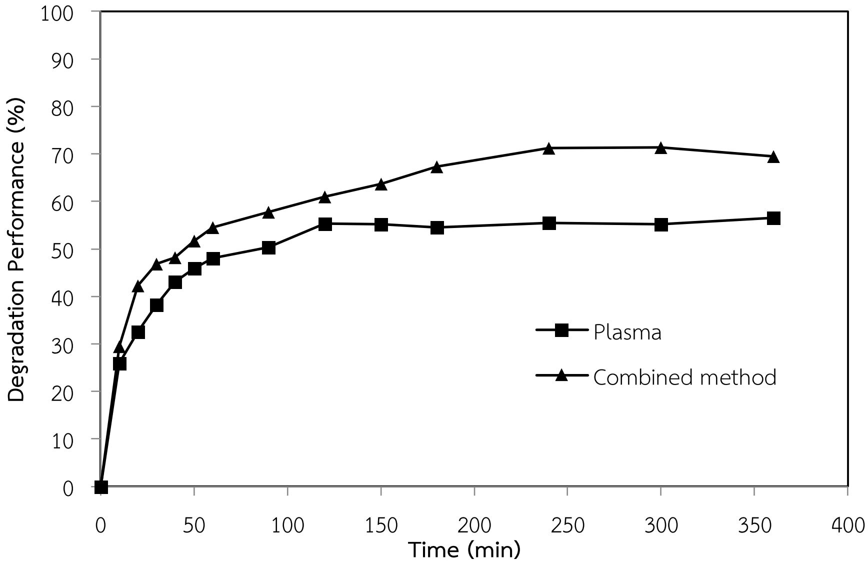

Figure 4.1 The degradation performance of toluene in plasma system and combined system at 0.5 mA electric current.

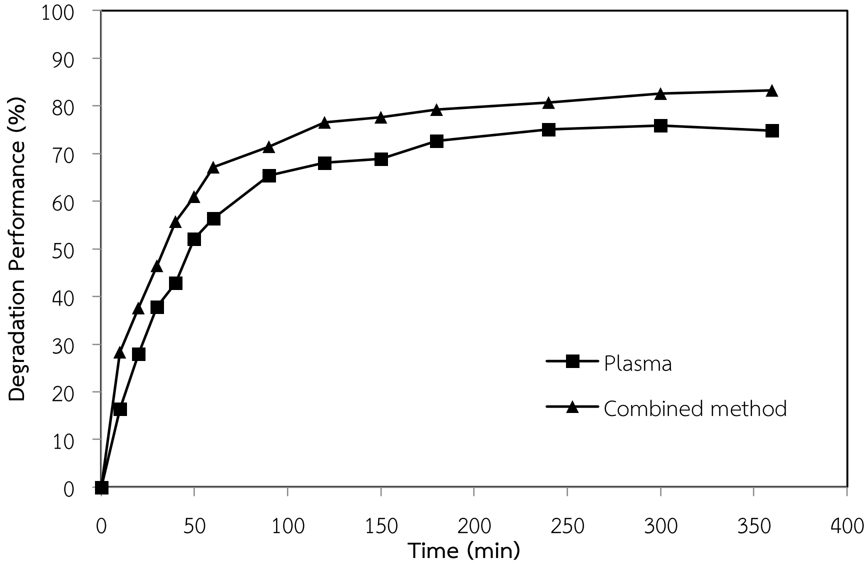

Figure 4.2 The degradation performance of toluene in plasma system and combined system at 1 mA electric current.

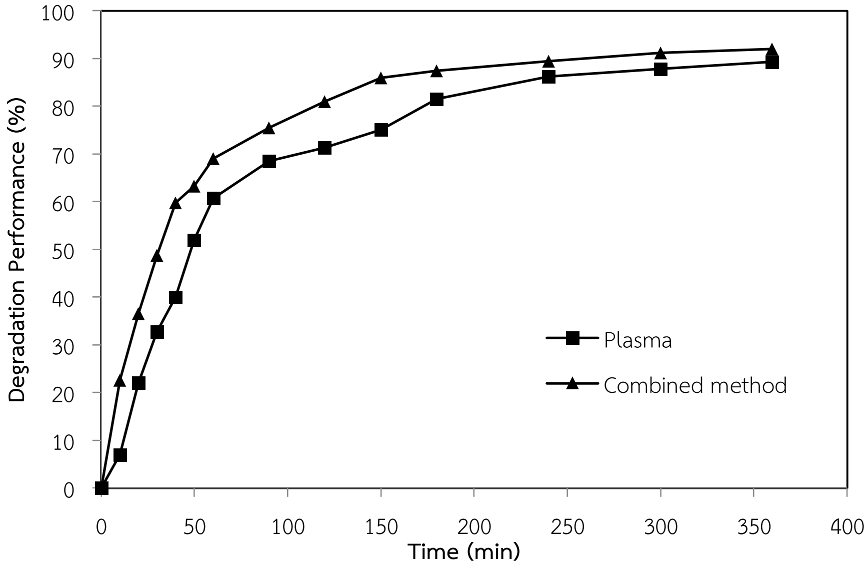

Figure 4.3 The degradation performance of toluene in plasma system and combined system at 3 mA electric current.

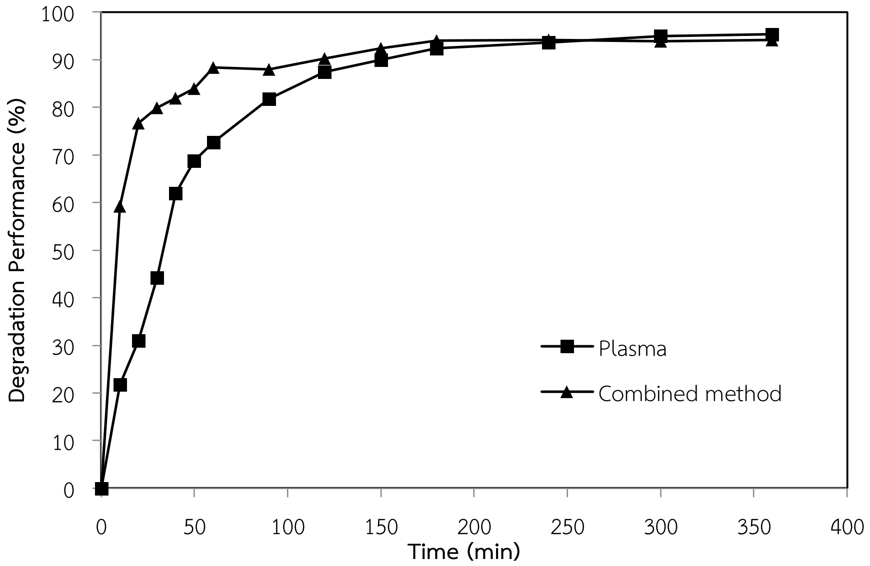

Figure 4.4 The degradation performance of toluene in plasma system and combined system at 5 mA electric current.

On the other hand, adsorption process normally takes place when there is a presence of photocatalyst. As a result, toluene molecules, moving randomly in gas stream might be trapped on the TiO_2 photocatalyst surface leading to enhance a possibility in colliding with charge particles. In addition, if the catalyst has a significant adsorption capacity for pollutant molecules, it prolongs the pollutant retention time in the reactor [24].

However, it is found that when 0.5 mA discharge current was utilized as a non-thermal plasma source, the magnitude of the differences of the degradation efficiency between plasma and combined method is much greater compared with the result obtained from 1, 3 and 5 mA currents. It is indicated that, for this process, loading TiO_2 photocatalyst in the plasma reactor play a significant role when apply with small electric discharge current. When conducting the experiments, it was noticed that the electric current were inversely proportional to the electric potential, as can be seen in Table 4.1. The electric potential directly affects the electron potential energy whereas the number of electrons are limited by the electric current. Although the amount of electrons is at the minimum, the potential energy of each is maximized resulting in the higher energy stored in electrons and charged particles which can transfer much more energy to photocatalyst.

Considering when the reaction gets close to steady state, only small amount of toluene was remained in the reactor. Most of toluene molecules are moving along the reactor channel in bulk phase where the plasma occurred, only a few of them migrated to TiO_2 layer. When providing large amount of electricity during the reaction, which corresponds to a large number of electrons, the probability of collision between the neutral molecule and electron is raised. The majority of toluene molecules could be destructed, either by plasma-generated derivatives or direct hit from electron rather than undergoing photocatalytic process. Hence, the impact of the toluene degradation done by plasma treatment in bulk is absolutely higher than that of photocatalytic reaction performing at the catalyst surface. It could be concluded that the difference between these two methods in the degradation efficiency is found to decrease with increasing energy density.

4.1.3 Effect of Oxygen

In order to investigate the participation of oxygen in photocatalytic degradation of toluene, dry air which was used as carrier gas was substituted by ultrahigh purity nitrogen and supplied to the reactor, loading with toluene vapour in the similar way. The results are presented in Figures 4.5-4.8 indicating that the effects between non-thermal plasma and plasma-photocatalysis method are not dramatically different. The degradation efficiencies seems to be nearly the same as can be seen in all cases. As the result, it is confirmed that oxygen is the influential factor in combining photocatalysis with plasma technique. Accordingly, oxygen regularly takes part in the photocatalytic reduction as the electron acceptor as expressed in equation (4.8).

However, when the results of the uses of only non-thermal plasma and coupled method are taken into deliberate consideration, it is found out that there are noticeable dissimilarities in the reaction progress of the two conditions before each process reaches steady state. The destruction of toluene in coupled method is a bit better than the original one. In this part, oxygen and water were not supplied to the reaction section. Since the carrier gas was composed of only nitrogen molecules, the effect of photocatalytic reaction was negligible. The influence of adsorption of is considered instead.

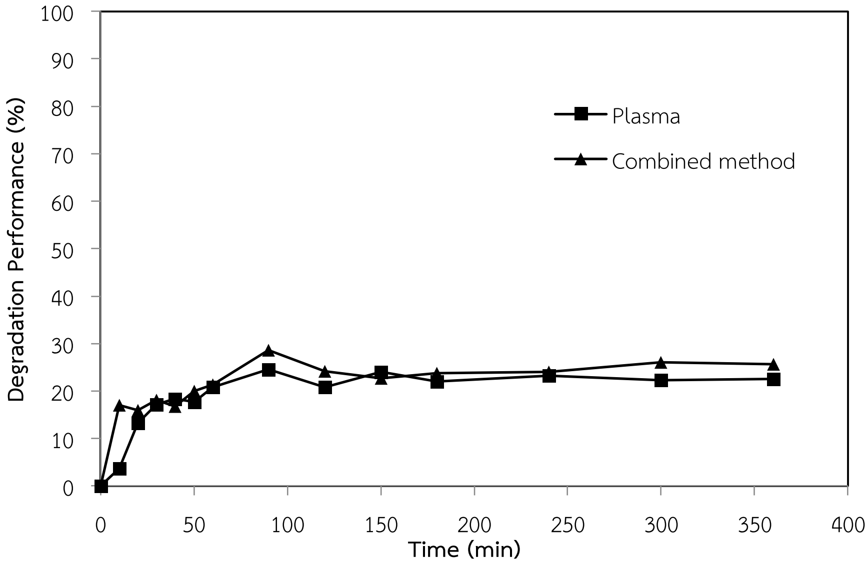

Figure 4.5 The degradation performance of toluene in plasma system and combined system using N_2 carrier gas at 0.5 mA electric current.

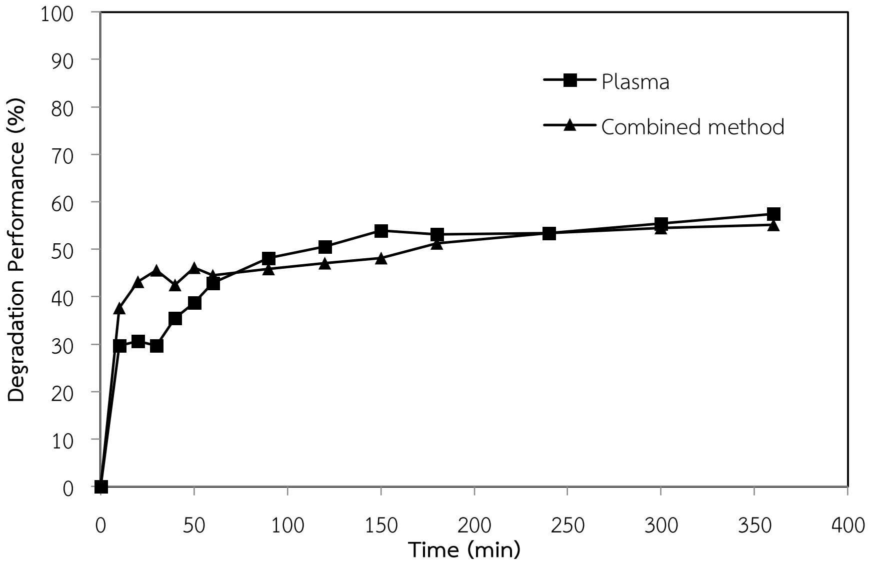

Figure 4.6 The degradation performance of toluene in plasma system and combined system using N_2 carrier gas at 1 mA electric current.

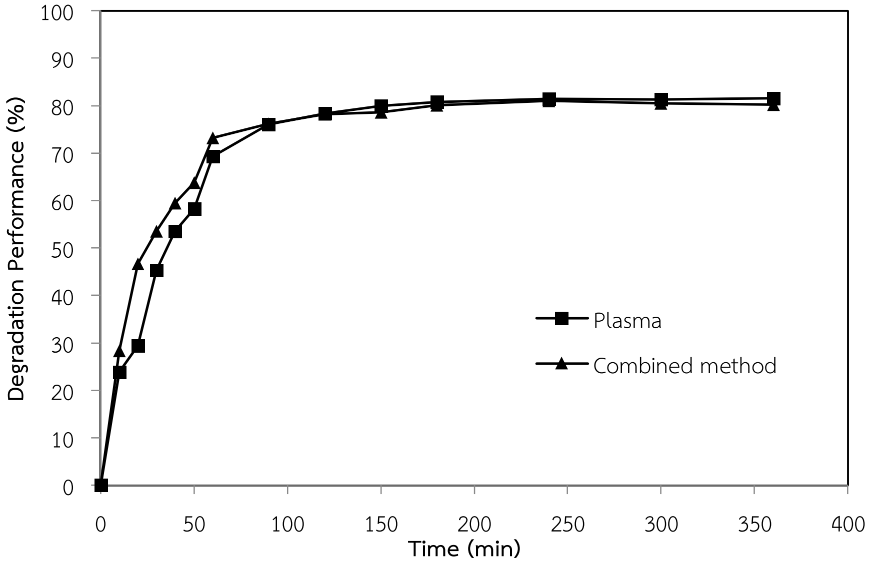

Figure 4.7 The degradation performance of toluene in plasma system and combined system using N_2 carrier gas at 3 mA electric current.

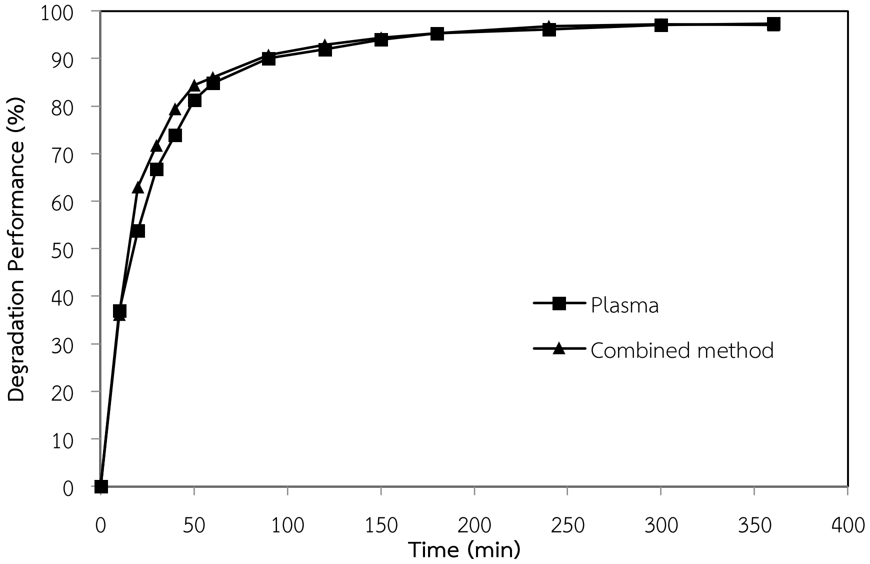

Figure 4.8 The degradation performance of toluene in plasma system and combined system using N_2 carrier gas at 5 mA electric current.

When loading TiO_2 photocatalyst in non-thermal plasma reactor, adsorption process certainly takes place. As a result, certain part of toluene molecules are adsorbed and trapped on the catalyst surface and are set as fixed targets in electron and excited particle bombardment leading to additional opportunities to be involved in plasma reaction. Therefore, adsorption site would be helpful during the reaction operation. Additionally, before all experiments were started, contaminated air was flow through the reactor for hours, until the concentration of inlet and out let to be identical. Thus, the process was definitely let to reach equilibrium.

The comparisons of the toluene removal performance when using dry air and nitrogen as a carrier gas are represented in Table 4.3. It is mainly found that the degradation of toluene using nitrogen gas are less efficient, compared with dry air which is composed of 80% nitrogen and 20% oxygen. The removal efficiency drops approximately by 40%, 25% and 10% when 0.5, 1, 3 mA electric currents were applied, respectively, but seems to be similar when the highest energy density was supplied. This is related to the difference in ionization of the gas atoms and molecules in plasma generation.

At a certain kinetic energy, the background gas atoms or molecules can be ionized. In air, most charges in a non-thermal plasma discharge are initially produced by the direct ionization of oxygen and nitrogen by electron according to the following reactions:

$$O_2 + e^- \rightarrow O_2^+ + 2e^- \tag{4.9}$$

$$N_2 + e^- \rightarrow N_2^+ + 2e^- \tag{4.10}$$

The threshold ionization energy of nitrogen is 15.58 eV while oxygen has the threshold ionization energy of 12.07 eV [48]. Resulted from the higher threshold ionization energy, nitrogen demands more energy to be excited so applying small amount of electrical power may be sufficient to ionize only a few part of nitrogen molecules in gas stream compared with using air stream which composed of nitrogen and oxygen. However, when the electricity is high enough nitrogen can be charged and ionized as well.

Table 4.3 The steady state toluene removal efficiency in non-thermal plasma and combined method when using dry air as a carrier gas compared with nitrogen at different electric currents.

Current (mA)	% Removal			
	Air		Nitrogen	
	Plasma	Combined	Plasma	Combined
0.5	55.72	70.70	22.72	25.21
1	75.23	82.20	55.39	54.36
3	89.31	90.87	81.44	80.55
5	95.61	94.57	96.81	96.99

4.1.4 Effect of Water

This part covers both the effects of water in plasma-only process and plasma coupled with photocatalysis. The steady state degradation efficiency of toluene with different relative humidity are summarized in Table 4.4. Basically, it could be concluded that the water vapour improves the toluene destruction in non-thermal plasma process. When 0.5 mA was applied to plasma generation, the results convince that the degradation enhancement proportionally raises with increasing water content. The efficiency was found to improve by 25% with the provided electric current of 0.5 and 6% increase with 1 mA current at 100% relative humidity.

It could be suggested that large amount of water vapour probably facilitate the formation of strong oxidant such as hydroxyl radical leading to the increase in reactive radicals. Hydroxyl radical is a second type of radical that is important in non-thermal plasma process and especially found in moist gases by the following expression [49]:

$$H_2O + e^- \rightarrow H^\bullet + OH^\bullet + e^- \tag{4.11}$$

Water also plays a very important role in the reaction since it decomposes into OH and H free radicals inside the plasma system as expressed in this equation [31]:

$$H_2O \rightarrow H, OH^\bullet, e^-, H_2, H_2O_2, H_3O^+, OH^- \tag{4.12}$$

Moreover, several secondary reactions between water molecule and particles generated from air are also believed to play an important role in the production of the hydroxyl radicals given as follows:

$$H_2O + O(D) \rightarrow 2OH^\bullet \tag{4.13}$$

$$H_2O + N_2(A) \rightarrow OH^\bullet + H^\bullet + N_2(X) \tag{4.14}$$

where $O(D)$ is an excited state of oxygen atom

$N_2(A)$ is a metastable nitrogen molecule

$N_2(X)$ is a nitrogen molecule in the ground state

According to above equations, it is expected that equation (4.11) occurs only in the ionization phase, while subsequent equations also occur in the recombination phase when the electron temperature is equal to the gas temperature [48]. It could be summarized that water vapour assists the addition of hydroxyl radicals that importantly participate in toluene elimination.

Table 4.4 The toluene removal efficiency in non-thermal plasma process with various water content at steady state.

Current (mA)	**% Removal**		
	Dry	**52% RH**	**100% RH**
0.5	55.72	62.52	66.76
1	75.23	80.18	81.27
3	89.31	88.63	91.90
5	95.61	93.25	94.17

On the other hand, there is no considerable dissimilarities obtained at 3 mA and 5 mA electric currents. Since the large amount of electricity was used which proportionate to high energy density, the process then had more capability in highly energetic particles generation. Although, a lot more particles are developed in a bulk gas, this also led to a higher recombination rate of charged derivatives, forming more stable matters resulting in a decrease of reactive species available for toluene degradation. Consequently, addition of water vapour seems not to be assistant in non-thermal plasma process with plenty of electrons in small volume of reaction unit.

When taking into a consideration in the reaction dynamic, Figures 4.9-4.12 indicate that the effects of water occurred in all conditions applied but the enhanced effects reduce with the enlargement of electric power. Because of the mentioned mechanism, insertion of humidity to non-thermal plasma air reactor will play a significant role with high toluene concentration due to the multiplication of strongly reactive particles that involve in the degradation reaction. At the same time, these particles also more frequently collide with each other when there are not many toluene molecules left within the plasma zone. This leads to an insignificant enhancement of water at steady state.

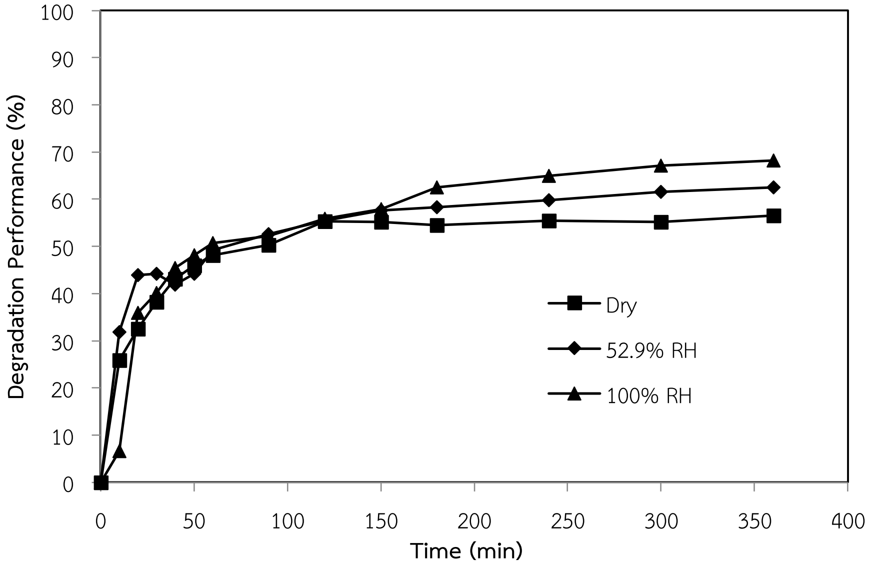

Figure 4.9 The degradation performance of toluene in plasma system with various water content at 0.5 mA electric current.

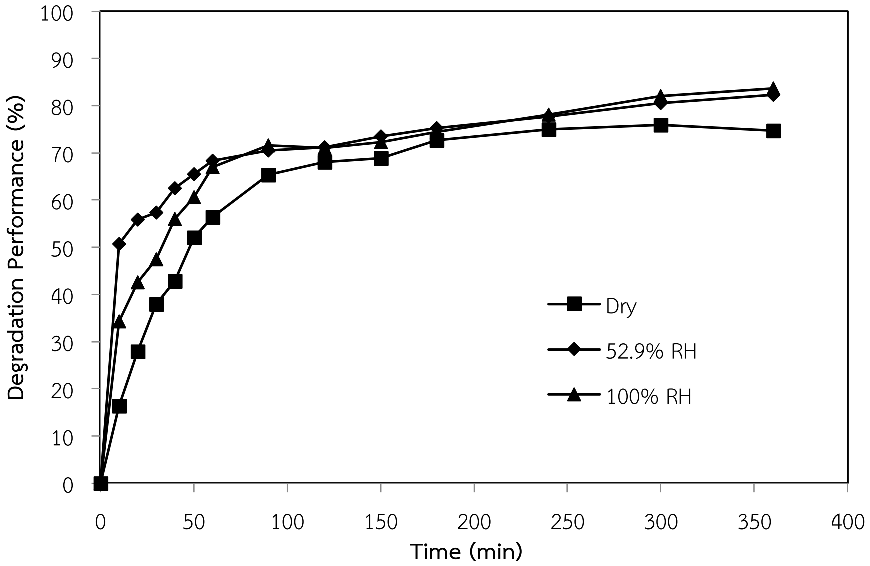

Figure 4.10 The degradation performance of toluene in plasma system with various water content at 1 mA electric current.

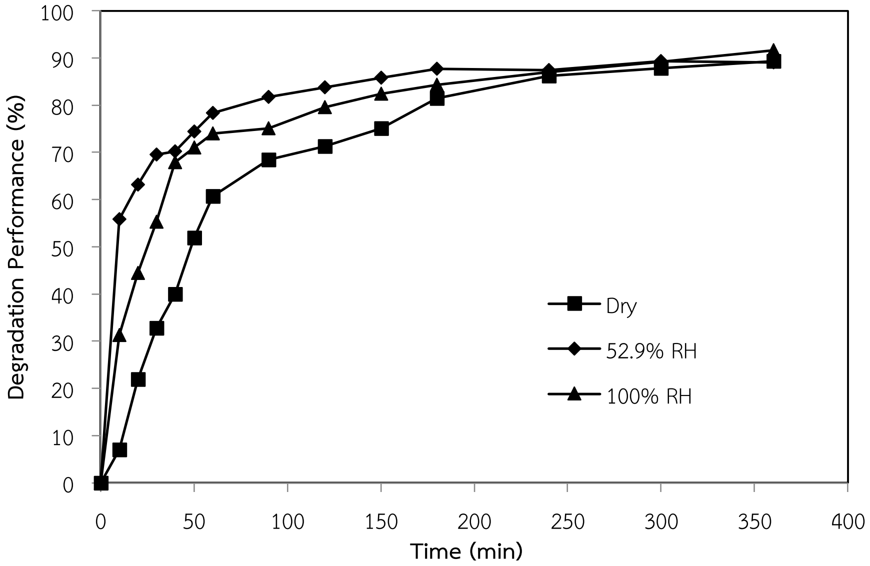

Figure 4.11 The degradation performance of toluene in plasma system with various water content at 3 mA electric current.

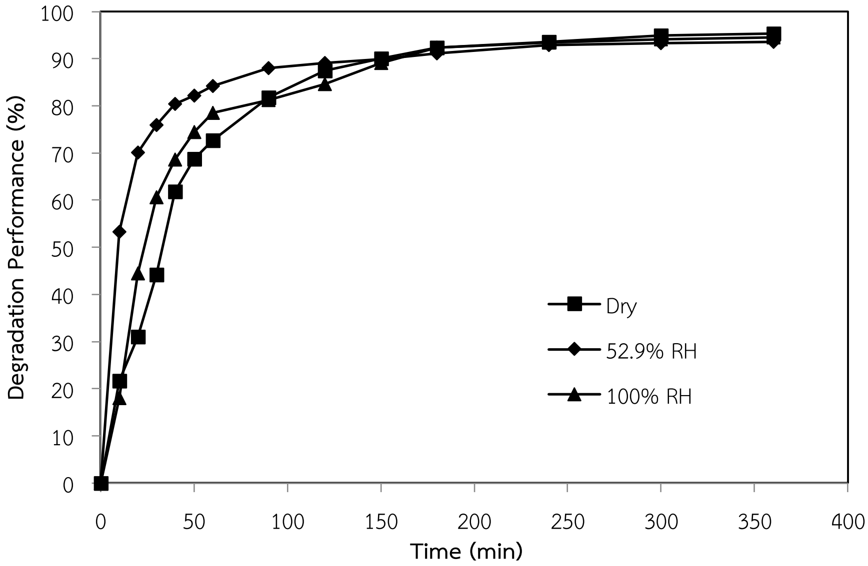

Figure 4.12 The degradation performance of toluene in plasma system with various water content at 5 mA electric current.

Additionally, it is suggested that water also has an adverse effect on toluene removal due to its electronegative characteristics. Increasing the humidity limits the electron density in the system and quench the activated chemical species. Therefore, controlled humidity is essential for toluene destruction [31].

In combining photocatalysis with non-thermal plasma operation, feeding water is found to be positive when the relative humidity is at 52% but the negative results shows in toluene elimination at 100% relative humidity compared with dry air stream. As demonstrated in Table 4.5. The positive and negative effects display when 0.5 mA and 1 mA electric currents was used but for 3 mA and 5 mA, no important difference can be noticed.

Humidity is a critical parameter in plasma-catalytic processes. Water vapour prevents the adsorption of toluene on the catalyst because of competitive adsorption of water. The adsorption of water on the photocatalyst surface results in a decrease of the reaction probability of the toluene with the photocatalyst surface and therefore reduces the photocatalyst activity. Moreover, it also poisons the photocatalyst by occupying catalytic active sites [24, 31, 50, 51]. As a result, the performance of toluene decomposition decreased with increasing humidity in the plasma-photocatalyst process.

Table 4.5 The toluene removal efficiency in non-thermal plasma process coupled with photocatalysis with and without the addition of water.

Current (mA)	**% Removal**		
	Dry	**52% RH**	**100% RH**
0.5	70.70	73.51	66.52
1	82.20	84.17	81.57
3	90.87	90.79	87.88
5	94.57	93.34	94.57

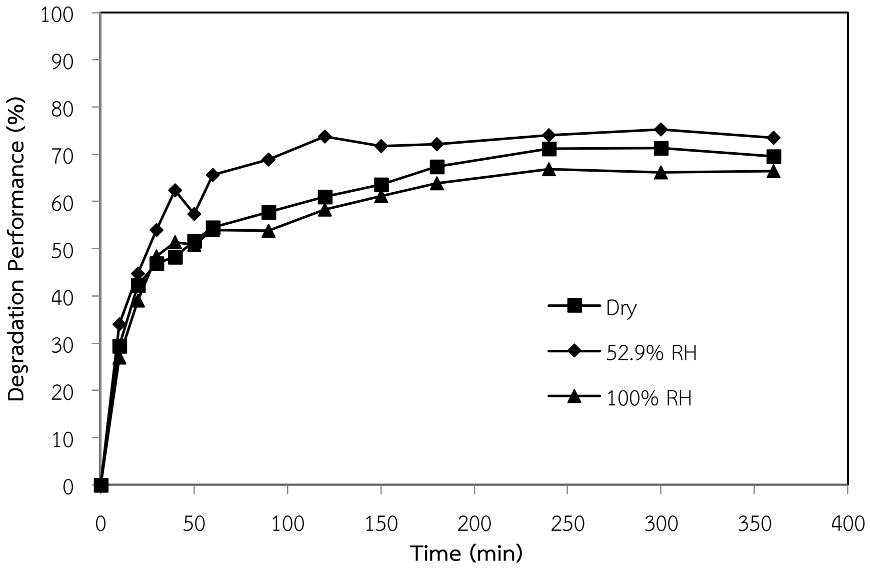

Figure 4.13 The degradation performance of toluene in plasma system coupled with photocatalysis with various water content at 0.5 mA electric current.

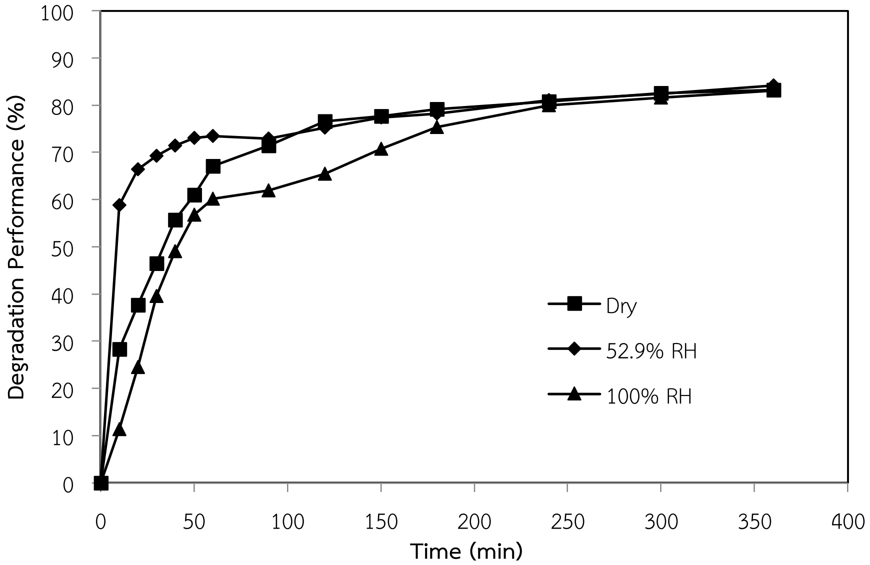

Figure 4.14 The degradation performance of toluene in plasma system coupled with photocatalysis with various water content at 1 mA electric current.

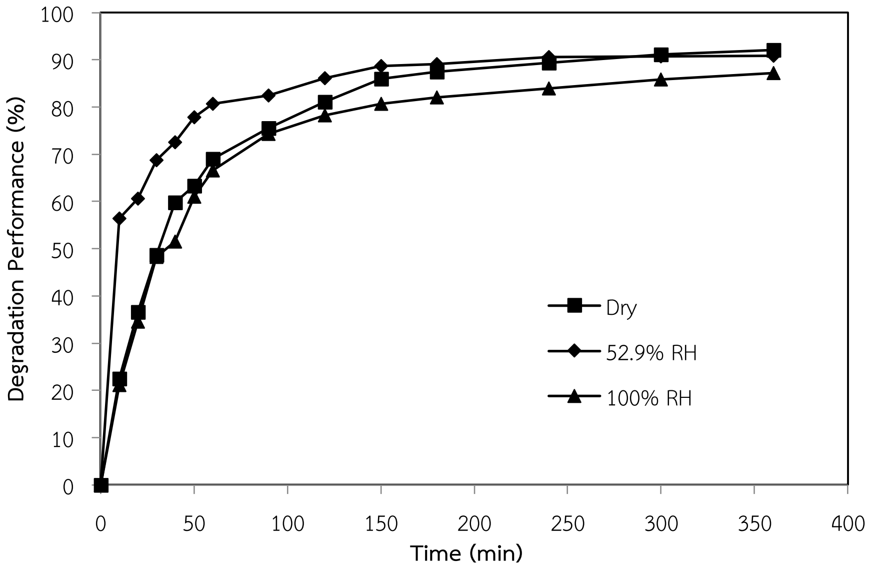

Figure 4.15 The degradation performance of toluene in plasma system coupled with photocatalysis with various water content at 3 mA electric current.

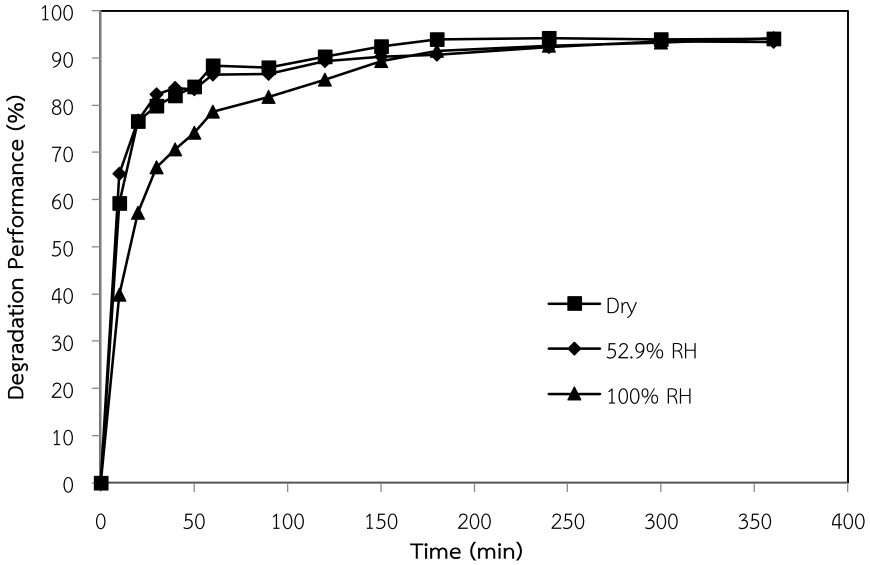

Figure 4.16 The degradation performance of toluene in plasma system coupled with photocatalysis with various water content at 5 mA electric current.

4.1.5 Kinetic Model Studies

In general, the degradation rate of organic compounds is suggested to be explainable by the first order kinetic indicating that the rate of reaction is a function of reactant concentration. The reaction equation could be expressed as following:

$$r = kC_A = -\frac{dC_A}{dt} \tag{4.15}$$

Where *r* is the degradation rate, C_A is the concentration of reactant A, *k* is the rate constant, *t* is the residence time. Equation (4.15) can be integrated to Eq. 4.16 when C_0 is initial concentration of the reactant.

$$ln\frac{C_0}{C_A} = kt \tag{4.16}$$

Table 4.6 The rate constant (*k*) for the toluene degradation using non-thermal plasma method and combined method with different electric currents.

Current (mA)	Plasma		Combined	
	k	R^2	k	R^2
0.5	0.0183	0.6412	0.0251	0.8453
1	0.0283	0.9048	0.0326	0.9491
3	0.0481	0.7211	0.0518	0.7025
5	0.0649	0.8355	0.0639	0.7438

Kinetics studies will be evaluated from the change in the concentration of the toluene as a function of residence time. The rate constant can be determined from the slope of the plotted curve. The rate constants of all experiments with different conditions are illustrated in Figure 4.17 for only-plasma operation and in Figure 4.18 for combined method. The rate constants obtained from the plot curves are also summarized in Table 4.6.

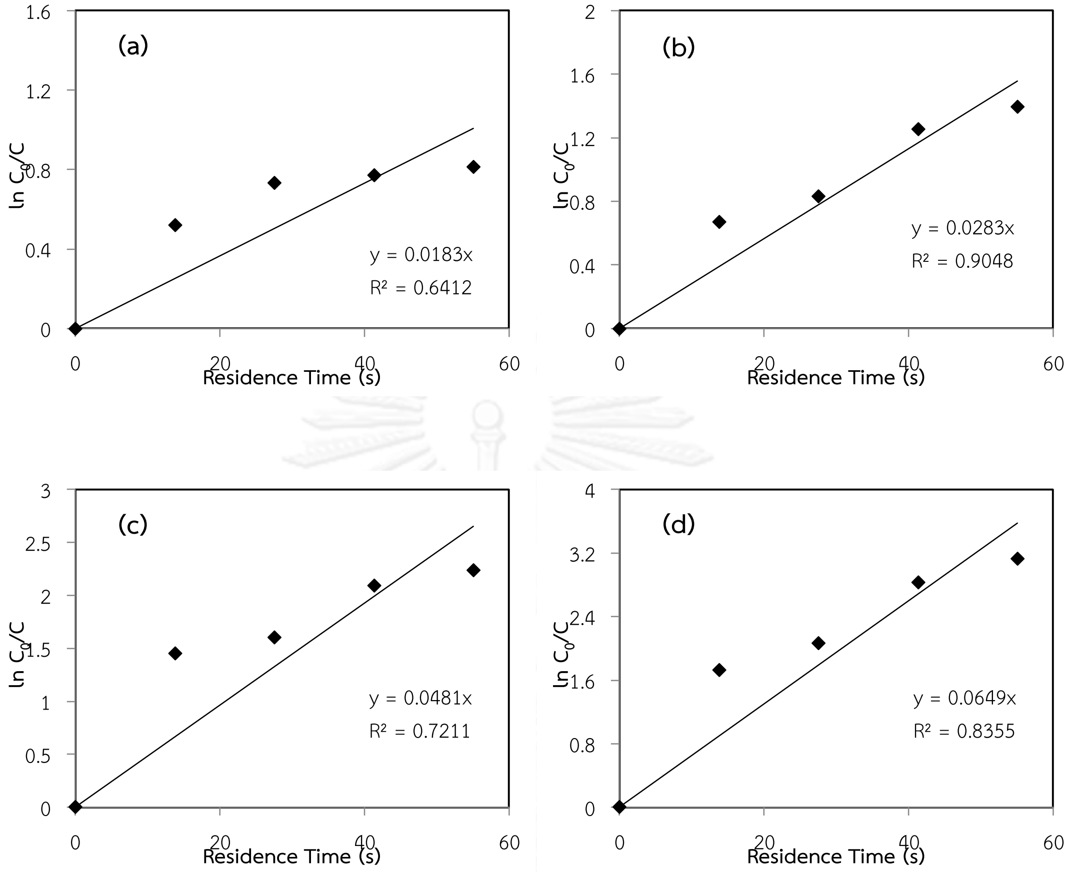

Figure 4.17 First-order linear transform plot of the toluene degradation in non-thermal plasma process with various electric currents: (a) 0.5mA, (b) 1mA, (c) 3mA and (d) 5mA.

According to Table 4.6, the rate constants of the reaction utilizing non-thermal plasma method and the combination of non-thermal plasma and photocatalysis are compared. The difference in rate constant are found to abate with increasing supplied electrical power. It is indicated that there must be some differences in reaction mechanism between these two processes which conform to the effects of influential parameters described previously.

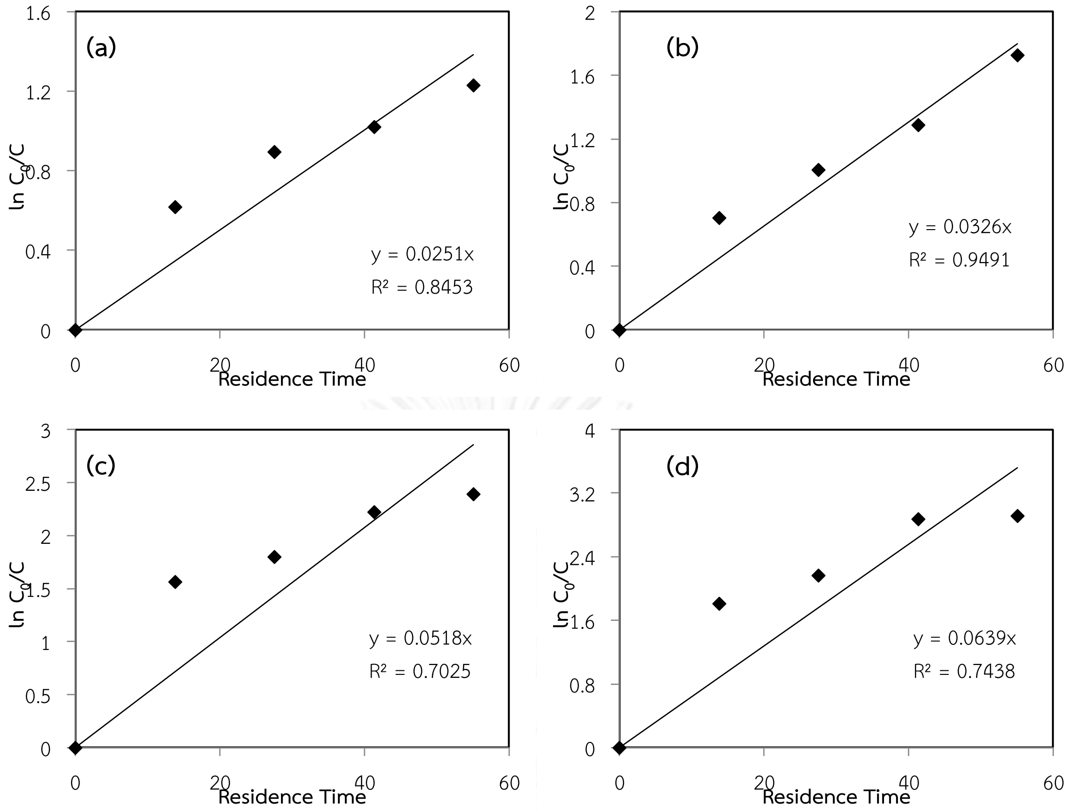

Figure 4.18 First-order linear transform plot of the toluene degradation in non-thermal plasma coupled with photocatalysis process with various electric currents: (a) 0.5mA, (b) 1mA, (c) 3mA and (d) 5mA.

However, according to the degradation data as s function of time shown in Figure 4.19-4.20, it could be seen that the residence time does not limit the degradation reaction. The C/C_0 ratio does not decrease linearly with the prolongation of the residence time. It seems that, the longer residence time, the less in degradation escalation. After the optimal point, increasing the time in the reactor does not give any effect to the degradation efficiency.

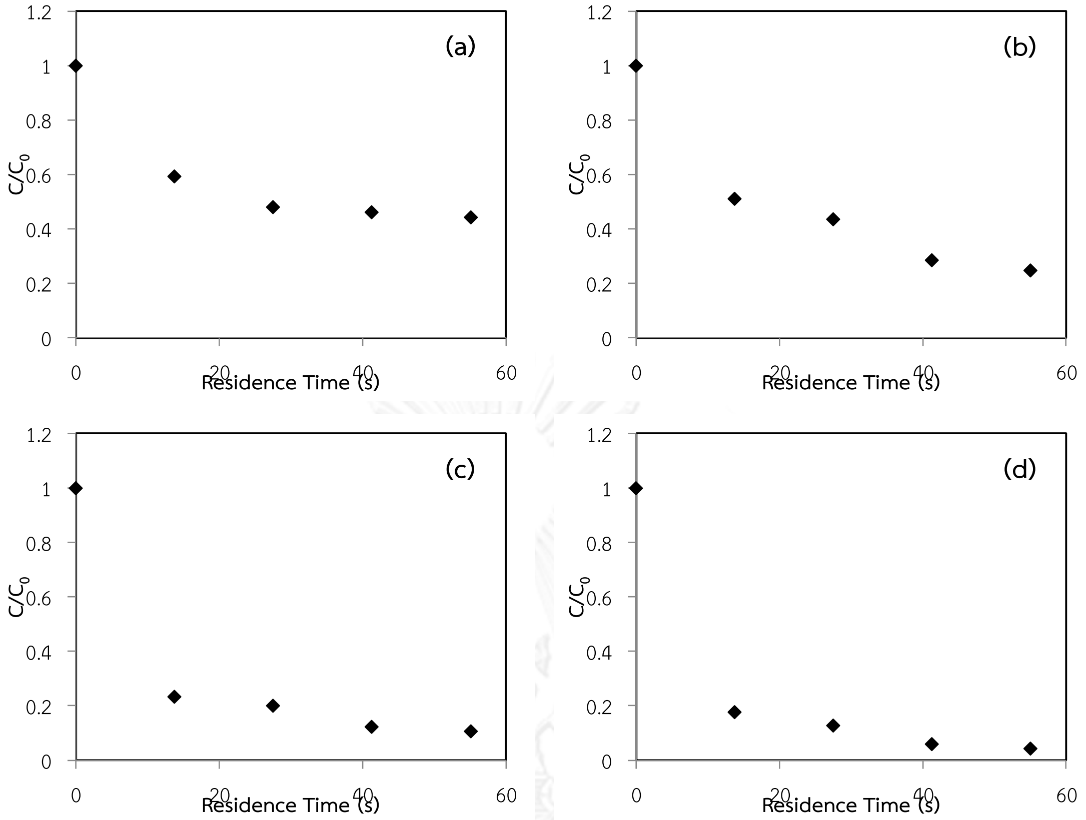

Figure 4.19 The toluene degradation as a function of time in non-thermal plasma process with various electric currents: (a) 0.5mA, (b) 1mA, (c) 3mA and (d) 5mA.

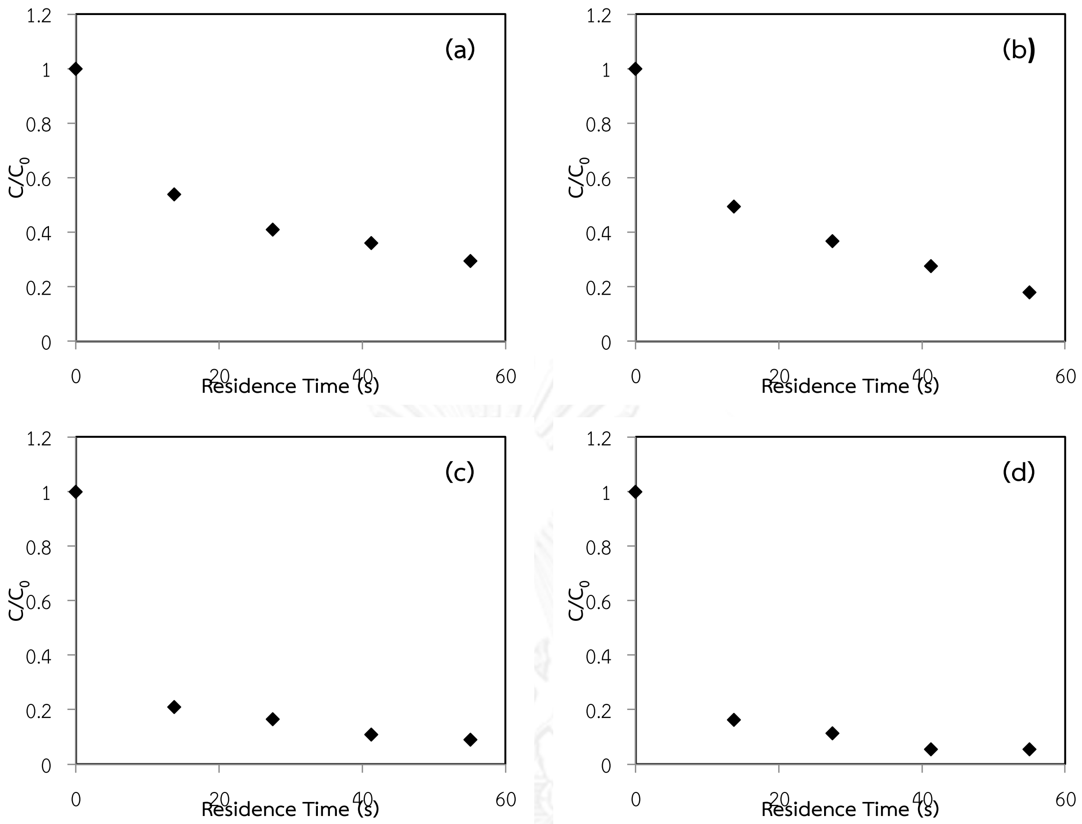

Figure 4.20 The toluene degradation as a function of time in non-thermal plasma process coupled with photocatalysis with various electric currents: (a) 0.5mA, (b) 1mA, (c) 3mA and (d) 5mA.

4.1.6 Carbon Dioxide Yield

One of the advantages of applying photocatalysis combining with the non-thermal plasma treatment in organic compound degradation is that the photocatalyst has great promise to enhance carbon dioxide yield. For toluene, the calculation of carbon dioxide yield could be expressed by the following equation:

$$CO_2\ Yield\ (\%) = \frac{[CO_2]}{7([Toluene]_0 - [Toluene]} \times 100 \tag{4.17}$$

According to Figure 4.21 and 4.22, it could be summarized that addition of photocatalyst improves carbon dioxide yield compared with traditional non-thermal plasma process. The increased results can be found in the processes with and without humidifying. In addition, the selectivity of CO_2 seems to be independent of electric field strength.

CO_2 yield indicates the degree of complete mineralization of pollutants. High CO_2 yield indicates the high conversion of toluene into CO_2. Generally, the photocatalyst considerably improves the mineralization of organic by-products. Not only toluene that is reacted with photocatalyst, some organic intermediates and secondary products generated from toluene destruction probably deposit on the photocatalyst surface and could subsequently perform reaction with the TiO_2 surface coated on reactor tube wall. As a result, the yield of CO_2 is enhanced [9, 42, 45].

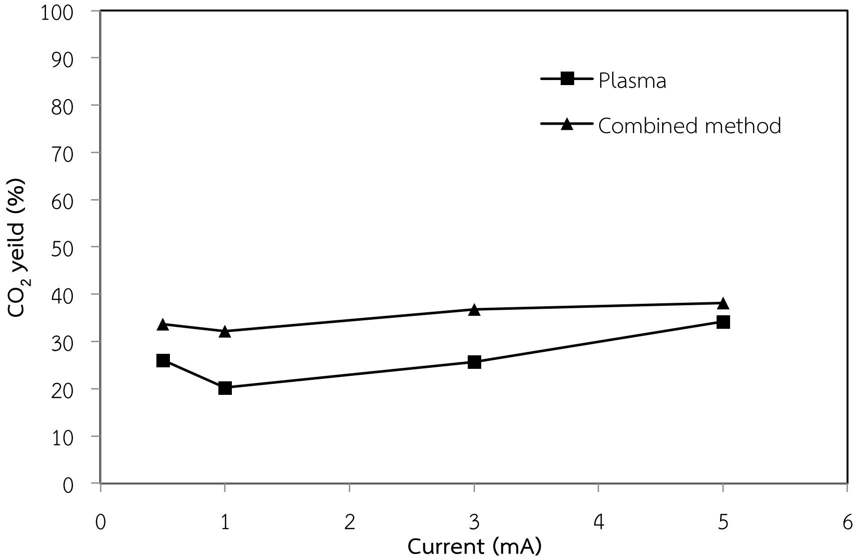

Figure 4.21 The carbon dioxide yield in non-thermal plasma and combined process using dry air as a carrier gas without water.

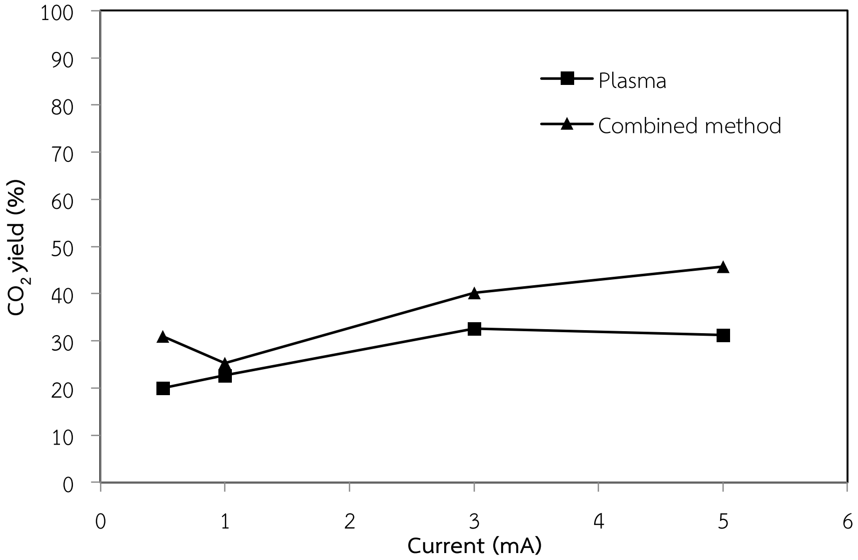

Figure 4.22 The carbon dioxide yield in non-thermal plasma and combined process using dry air as a carrier gas with water.

CHAPTER V
CONCLUSIONS AND RECOMMENDATIONS

5.1 Summary of Results

The summary of the results of the present research is the following:

1. The degradation efficiency are significantly improved with increasing the amount of electrical power supplied to the reactor in both non-thermal plasma and coupled method.

2. Loading TiO_2 photocatalyst on the reactor wall together with non-thermal plasma plays a considerable role on the degradation of toluene. The synergistic effects are founded in almost all cases with different applied input electric currents due to occurrences of photocatalytic reaction as well as adsorption process.

3. Oxygen is the influential factor in combining photocatalysis with plasma technique. It regularly takes part in the photocatalytic reduction as the electron acceptor. The effects between non-thermal plasma and plasma-photocatalysis method are not dramatically different when using nitrogen as a carrier gas.

4. Water vapour improves the toluene destruction in non-thermal plasma process suggesting that large amount of water vapour probably facilitate the formation of strong oxidant such as hydroxyl radical leading to the increase in reactive radicles.

5. The performance of toluene decomposition is decreased with increasing humidity in the plasma-photocatalyst process. The competitive adsorption of water on the photocatalyst surface results in a decrease of the reaction probability of the toluene with the surface and also poisons the photocatalyst by occupying catalytic active sites.

6. The photocatalytic process increases carbon dioxide yield in the process with and without water vapour. However, the carbon dioxide could not be detected in the process with the used of nitrogen gas.

5.2 Conclusions

Degradation of toluene vapour by combination of non-thermal plasma and photocatalytic reaction was investigated in this study. The impact of the input electrical current indicates that the degradation was found to improve with an increase in the electrical current. The synergistic effects are founded when adding TiO_2 photocatalyst on the reactor wall. Moreover, oxygen and water both play a considerable role in non-thermal plasma process and combined process. Oxygen regularly takes part in the photocatalytic reduction as the electron acceptor whereas water facilitates the formation of strong oxidant such as hydroxyl radical. However, large amount of water results in the competitive adsorption on the photocatalyst surface and also poisons the photocatalyst. Additionally, coupling non-thermal plasma with the photocatalytic process has a capability to increase carbon dioxide yield.

5.3 Recommendations

1. The electrical currents should be varied narrowly in the range of 1-3 mA to obtain more obvious results

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2. The suggested reaction mechanisms are able to be proved using GC-MS as an analytical instrument.

3. The relative humidity should be studied to find the optimizing value.

REFERENCES

[1] Demeestere, K., et al., *Gas–solid adsorption of selected volatile organic compounds on titanium dioxide Degussa P25.* Chemical Engineering Science, 58, 11 (2003): 2255-2267.

[2] Wang, S., H.M. Ang, and M.O. Tade, *Volatile organic compounds in indoor environment and photocatalytic oxidation: State of the art.* Environment International, 33, 5 (2007): 694-705.

[3] Debono, O., et al., *Toluene photocatalytic oxidation at ppbv levels: Kinetic investigation and carbon balance determination.* Applied Catalysis B: Environmental, 106, 3–4 (2011): 600-608.

[4] Schmid, S., M.C. Jecklin, and R. Zenobi, *Degradation of volatile organic compounds in a non-thermal plasma air purifier.* Chemosphere, 79, 2 (2010): 124-130.

[5] Zhao, J. and X. Yang, *Photocatalytic oxidation for indoor air purification: a literature review.* Building and Environment, 38, 5 (2003): 645-654.

[6] Quoc An, H., et al., *Application of atmospheric non thermal plasma-catalysis hybrid system for air pollution control: Toluene removal.* Catalysis Today, 176, 1 (2011): 474-477.

[7] Maciuca, A., C. Batiot-Dupeyrat, and J.-M. Tatibouët, *Synergetic effect by coupling photocatalysis with plasma for low VOCs concentration removal from air.* Applied Catalysis B: Environmental, 125, 0 (2012): 432-438.

[8] Kim, H., A. Ogata, and S. Futamura, *Complete oxidation of volatile organic compounds (VOCs) using plasma-driven catalysis and oxygen plasma.* International Journal of Plasma Environmental Science and Technology, 1, (2007): 46-51.

[9] Zhu, T., *Removal of VOCs Using Nonthermal Plasma Technology.*

[10] Hyun-Ha, K., et al., *Comparative assessment of different nonthermal plasma reactors on energy efficiency and aerosol formation from the decomposition of gas-phase benzene.* Industry Applications, IEEE Transactions on, 41, 1 (2005): 206-214.

[11] Bettinelli, M., et al., *Photocatalytic activity of TiO2 doped with boron and vanadium.* Journal of Hazardous Materials, 146, 3 (2007): 529-534.

[12] Guaitella, O., et al., *C2H2 oxidation by plasma/TiO2 combination: Influence of the porosity, and photocatalytic mechanisms under plasma exposure.* Applied Catalysis B: Environmental, 80, 3–4 (2008): 296-305.

[13] Thevenet, F., et al., *Oxidation of acetylene by photocatalysis coupled with dielectric barrier discharge.* Catalysis Today, 122, 1–2 (2007): 186-194.

[14] Code of Federal Regulations, 40: Chapter 1, Subchapter C, Part 51, Subpart F, 51100. http://cfr.vlex.com/vid/19784887 accessed 8 February 2009, and EPA's Terms of Environment Glossary, Abbreviations, and Acronyms.

[15] Urashima, K., et al., *Removal of volatile organic compounds from air streams and industrial flue gases by non-thermal plasma technology.* Dielectrics and Electrical Insulation, IEEE Transactions on, 7, 5 (2000): 602-614.

[16] Ismail, O.M.S. and R.S.A. Hameed, *Environmental effects of volatile organic compounds on ozone layer.*

[17] Nehra, V., A. Kumar, and H. Dwivedi, *Atmospheric non-thermal plasma sources.* International Journal of Engineering, 2, 1 (2008): 53-68.

[18] Conrads, H. and M. Schmidt, *Plasma generation and plasma sources.* Plasma Sources Science and Technology, 9, 4 (2000): 441.

[19] Chu, P.K. and X. Lu, *Low Temperature Plasma Technology: Methods and Applications*. 2013: CRC Press.

[20] Meger, R., et al., *Beam-generated plasmas for processing applications.* Physics of Plasmas (1994-present), 8, 5 (2001): 2558-2564.

[21] Matsumoto, T., et al., *Non-Thermal Plasma Technic for Air Pollution Control.* (2012).

[22] Foest, R., M. Schmidt, and K. Becker, *Microplasmas, an emerging field of low-temperature plasma science and technology.* International Journal of Mass Spectrometry, 248, 3 (2006): 87-102.

[23] Oda, T., *Non-thermal plasma processing for environmental protection: decomposition of dilute VOCs in air.* Journal of Electrostatics, 57, 3 (2003): 293-311.

[24] Vandenbroucke, A.M., et al., *Non-thermal plasmas for non-catalytic and catalytic VOC abatement.* Journal of Hazardous Materials, 195, (2011): 30-54.

[25] Oda, T., *Non-thermal plasma processing for environmental protection: decomposition of dilute VOCs in air.* Journal of Electrostatics, 57, 3–4 (2003): 293-311.

[26] Yousfi, M., et al., *Non thermal plasma sources of production of active species for biomedical uses: analyses, optimization and prospect.* (2011).

[27] Penetrante, B.M. and S.E. Schultheis. *Non-thermal plasma techniques for pollution control*. in *NATO Advanced Research Workshop on Non-Thermal Plasma Techniques for Pollution Control (1992: Cambridge, England)*. 1993: Springer-Verlag.

[28] Chang, J.S., P.A. Lawless, and T. Yamamoto, *Corona discharge processes.* Plasma Science, IEEE Transactions on, 19, 6 (1991): 1152-1166.

[29] Kim, H.-H., *Nonthermal Plasma Processing for Air-Pollution Control: A Historical Review, Current Issues, and Future Prospects.* Plasma Processes and Polymers, 1, 2 (2004): 91-110.

[30] Bárdoš, L., S. Berg, and H. Baránková, *Radio frequency plasma jet applied to coating of internal walls of narrow tubes.* Journal of Vacuum Science & Technology A, 11, 4 (1993): 1486-1490.

[31] Yu-fang, G., et al., *Humidity effect on toluene decomposition in a wire-plate dielectric barrier discharge reactor.* Plasma chemistry and plasma processing, 26, 3 (2006): 237-249.

[32] Fujishima, A., X. Zhang, and D.A. Tryk, *TiO2 photocatalysis and related surface phenomena.* Surface Science Reports, 63, 12 (2008): 515-582.

[33] Carp, O., C.L. Huisman, and A. Reller, *Photoinduced reactivity of titanium dioxide.* Progress in Solid State Chemistry, 32, 1–2 (2004): 33-177.

[34] Ramirez, A.M., et al., *Titanium dioxide coated cementitious materials for air purifying purposes: Preparation, characterization and toluene removal potential.* Building and Environment, 45, 4 (2010): 832-838.

[35] Maira, A.J., et al., *Gas-phase photo-oxidation of toluene using nanometer-size TiO2 catalysts.* Applied Catalysis B: Environmental, 29, 4 (2001): 327-336.

[36] Hoffmann, M.R., et al., *Environmental Applications of Semiconductor Photocatalysis.* Chemical Reviews, 95, 1 (1995): 69-96.

[37] Fujishima, A., T.N. Rao, and D.A. Tryk, *Titanium dioxide photocatalysis.* Journal of Photochemistry and Photobiology C: Photochemistry Reviews, 1, 1 (2000): 1-21.

[38] Fujishima, A. and X. Zhang, *Titanium dioxide photocatalysis: present situation and future approaches.* Comptes Rendus Chimie, 9, 5 (2006): 750-760.

[39] Fridman, A., *Plasma chemistry*. 2008: Cambridge University Press.

[40] Rezaee, A., et al., *Photocatalytic decomposition of gaseous toluene by TiO2 nanoparticles coated on activated carbon.* Iranian Journal of Environmental Health Science & Engineering, 5, 4 (2008).

[41] Thevenet, F., et al., *Comparison of the plasma-photocatalyst synergy at low and atmospheric pressure.*

[42] Zhu, T., et al., *Gaseous phase benzene decomposition by non-thermal plasma coupled with nano titania catalyst.* Int. J. Environ. Sci. Tech, 6, 1 (2009): 141-148.

[43] Zhu, T., et al., *Decomposition of benzene by non-thermal plasma processing: Photocatalyst and ozone effect.* Int. J. Environ. Sci. Tech, 5, 3 (2008): 375-384.

[44] Rockland, L.B., *Saturated salt solutions for static control of relative humidity between 5° and 40° C.* Analytical Chemistry, 32, 10 (1960): 1375-1376.

[45] Huang, H., et al., *Byproducts and pathways of toluene destruction via plasma-catalysis.* Journal of Molecular Catalysis A: Chemical, 336, 1 (2011): 87-93.

[46] Zhu, T., et al., *Volatile organic compounds decomposition using nonthermal plasma coupled with a combination of catalysts.* International Journal of Environment Science and Technology, 8, 3 (2011): 621-630.

[47] Huang, H., et al., *Photocatalytic destruction of air pollutants with vacuum ultraviolet (VUV) irradiation.* Catalysis Today, 175, 1 (2011): 310-315.

[48] Nijdam, S., et al., *An Introduction to Nonequilibrium Plasmas at Atmospheric Pressure.* Plasma Chemistry and Catalysis in Gases and Liquids, (2012).

[49] Itikawa, Y. and N. Mason, *Cross sections for electron collisions with water molecules.* Journal of Physical and Chemical reference data, 34, 1 (2005): 1-22.

[50] Cho, C.-H. and S.-K. Ihm, *Development of new vanadium-based oxide catalysts for decomposition of chlorinated aromatic pollutants.* Environmental science & technology, 36, 7 (2002): 1600-1606.

[51] Pengyi, Z., et al., *A comparative study on decomposition of gaseous toluene by O< sub> 3</sub>/UV, TiO< sub> 2</sub>/UV and O< sub> 3</sub>/TiO< sub> 2</sub>/UV.* Journal of Photochemistry and Photobiology A: Chemistry, 156, 1 (2003): 189-194.

APPENDICES

APPENDIX A
TOLUENE CARIBRATION CURVE

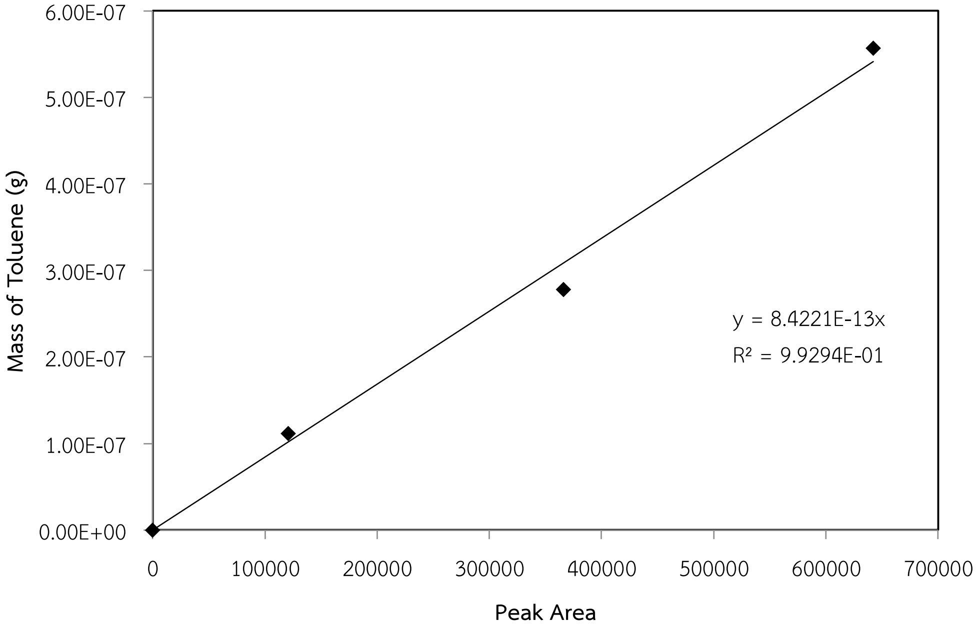

Figure A.1 The calibration curve of toluene.

APPENDIX B

CARBON DIOXIDE CARIBRATION CURVE

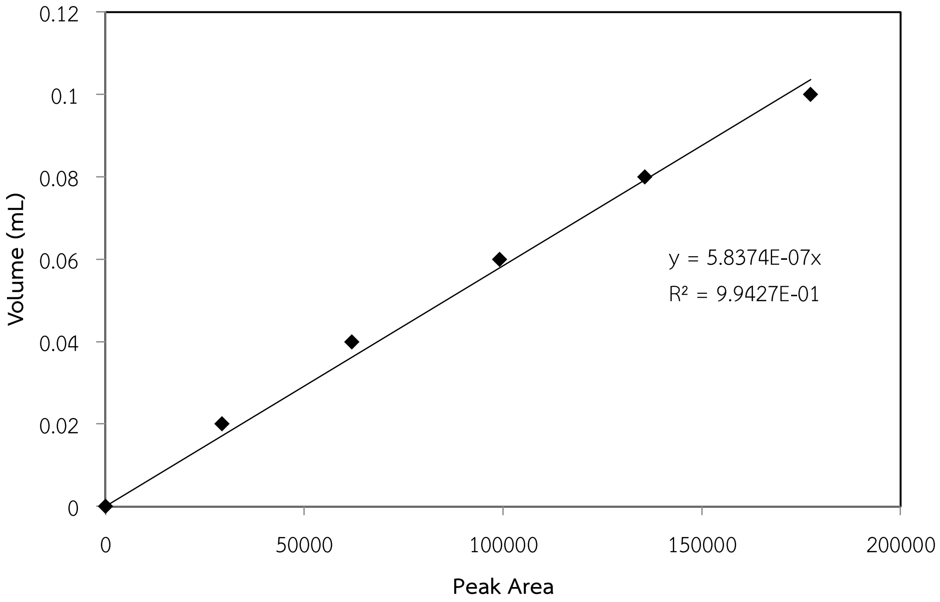

Figure B.1 The calibration curve of carbon dioxide.

APPENDIX C
LIST OF PLUBLICATION

1. Hathairat Musngsaen and Varong Pavarajarn. “DEGRADATI OF VOLATILE ORGANIC COMPOUNDS BY NON-THERMAL PLASMA COUPLED WITH PHOTOCATALYSIS”. Proceedings of the Pure and Applied Chemistry International Conference 2014, Khon Kaen, Thailand, January 8 – 10, 2014.

VITA

Miss Hathairat Muangsen was born on April 19, 1989 in Bangkok, Thailand. She received the Bachelor Degree of Chemical Engineering from Faculty of Engineering, Chulalongkorn University in 2011. She continued her Master’s study at Chulalongkorn University in June, 2011.