REVIEW

Decomposition of greenhouse gases by plasma

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Abstract The topic of decomposition and reduction of greenhouse gases is becoming an important issue in tackling the global warming effect since several years ago. Several technologies, including plasma-utilized process, were proposed to improve the treatment ability for the destruction of green house gases usually emitted by industrial activities. In this review paper, the application of plasma to reduce the emission of greenhouse gases was briefly summarized.

Keywords Non-thermal plasma · Green house gases ·
Pollution control

Introduction

The emission from various industrial areas into ambient environment causes problems to the environment (Shah and Singh 1988). Those emissions usually contain greenhouse gases, such as carbon dioxide (CO_2), methane (CH_4), and chlorinated volatile organic compounds (CVOCs), e.g., methylene chloride (CH_2Cl_2), chloroform ($CHCl_3$), and carbon tetrachloride (CCl_4). Among all greenhouse gases, however, CO_2 together with CH_4 contributes the most of man-made greenhouse effects. Numerous amounts of CO_2 were released into the environment, estimated to be around 2×10^{15} g per annum, and industrial sector has been suspected as the main contributor (Kiani et al. 2004; Yabe 2004). Chlorinated VOC emissions, caused by degradation

of chlorine-containing chemicals, could be the source of chloric acid (HCl) and suspected to contribute in the acid rain problem (Sanhueza 2001). Some studies reported that these compounds, in stratosphere, could produce highly active chlorine radicals due to solar radiation reactions and could possibly to react and reduce the ozone molecules (US EPA 2002). However, the most significant problem related to the emission of chlorinated VOCs are remained on its high toxicity and carcinogenicity (International Agency for Research on Cancers 1987).

Concerning this situation, Kyoto protocol obligates industrialized countries to cut their greenhouse gas emissions by an average 5.2% between 2008 and 2012. This will deliver a strong message to us for finding effective methods for eliminating these industrial wastes (Frosch 1995). In this discussion, we would like to address the issue of the use of plasma technology as an alternative way to reduce or decompose gaseous emissions. The topic will not stress too much on the physical-theoretical or mathematical terms but on the application of plasma for environmental purposes.

Plasma in general

The discovery of plasma and its application have been known for more than a century (Roch 1995). Electric-created plasma-assisted chemical process has been intensively studied in the way of finding some potential applications for new chemical synthesis or other purposes. Moreover, worldwide application and industrial large-scale process using plasma are getting famous, e.g., ozone production and surface treatment (Kogelschatz 2003; Fridman et al. 1999). One of the main advantages of the plasma method is that the plasma is able to produce very high

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density discharge species compared to other methods, e.g., electrochemical (Raizer 1997) and combustion.

In general, based on the flame temperature, plasma can be divided into two major parts, thermal and cold (non-thermal) plasma (Roch 1995). Thermal plasma, sometimes called very high temperature plasma ($T > 10,000$ K), is widely used to decompose (strong bond) toxic chemicals and solid particle synthesis. This type of plasma has very high-energy species, able to destroy stable or strong chemical-bond of the compounds. Some of them, e.g., thermal-arc, torch or supersonic plasma, can handle high input flow rates with very short reaction time. The second type of plasma is called non-thermal or non-equilibrium plasma. Although it is not as strong as thermal plasma, cold (non-thermal) plasma is much favorable for the application in gaseous chemical synthesis type reactions, such as methane conversion for synthesis gas production. Non-thermal plasma refers to the temperature of the bulk gas which is usually as low as room temperature. The examples are quite many and some of them are already being applied in industrial scale (Roch 1995), such as corona, dielectric barrier discharge, microwave plasma, and radio frequency plasma for ozone production and solid surface treatment.

Instead of their physical characteristics, the consideration to choose the plasma used for its application also depends on other aspects. Table 1 shows the general comparison between thermal and cold plasma in some non-physical factors. This table clearly shows some advantages and some limitations of each division. Thermal plasma consumes high energy and the installation and/or the operating cost is expensive. On the other hand, the cold plasma has a main problem related to the low conversion of the reactants, especially for toxic gas decomposition when the concentration levels are higher than hundred of ppm. Compared to thermal plasma, the maintenance and operation cost are relatively easy and cheap. Moreover, regardless of the type of plasma that we use, optimization is necessary in order to obtain better performance with lower cost to meet the market requirements. Currently, the remaining key point for plasmachemical methods to be

Table 1 General comparison between thermal and non-thermal plasma

Characteristic	Thermal plasma	Cold plasma
Temperature (K)	>10,000	5,000–10,000
Discharged volume	High	Low
Reaction conversion	High	Low
Input flow rate	High	Low
Difficulty to handle	Difficult	Easy
Safety	Relative dangerous	Relative save
Installation cost	Expensive	Cheap

acceptable as a chemical-advanced process is how to optimize the condition to produce profitable reactions.

Plasma for chemical synthesis offers a wide spectrum of possible application. In particular, depending on the physical characteristics of the plasma produced by different ionization systems, three types of processes can be classified: (1) destruction of toxic/harmful materials; (2) modification of existing materials, e.g., surface treatment for catalyst; (3) creation of new materials (Bonizzoni and Vassallo 2002). For the first point, many researches have been conducted by decomposing many industrial emissions, such as H_2S (Dalaine et al. 1998), N_2O (Krawczyk and Mlotek 2001), $CHCl_3$ and CCl_4 (Krawczyk and Ulejczyk 2003, 2004). High percentage of destruction efficiency have been claimed using plasma. However, in this discussion, we would like to focus the discussion on the decomposition of three industrial gaseous: chlorinated volatile organic compounds, methane (CH_4) and carbon dioxide (CO_2).

Decomposition of chlorinated volatile organic carbons

The most widely adopted or common technique for the treatment of chlorinated volatile organic carbon emission was thermal combustion or incineration (Lou and Chang 1997). This method was mostly used due to its easiness and simplicity by reacting directly to the reactants with air under high-temperature condition, ca. 800–1,100 °C. It was reported that when the combustion does not occur perfectly (incomplete combustion), the reactions tend to produce a large amount of complex chlorinated products (Taylor and Dellinger 1988) which could be more toxic than the reactant itself. To avoid side stream reactions, some possibilities to control the reactions by introducing metal and/or metal oxide catalyst have also been investigated. Using this method, the decomposition rate could be faster and the product selectivity was very good, but the catalyst became easily deactivated by impurities and by the presence of solid products (Alberici and Jardim 1997). This method also, requires elevated temperatures to achieve the appropriate catalyst temperature and reaction rate. Another limitation to apply this method for industrial plants is the input flow rates were very small.

Currently, many studies were carried out on the application of combined process or new alternative methods such as plasma-assisted technology, which could overcome the above mentioned problems. Plasma-assisted technology for environmental purposes, such as radio frequency plasma (Lee et al. 1996), surface discharge reactors (Oda et al. 2002), dielectric barrier discharge reactors (Tonkyn et al. 1996), pulsed discharge reactors (Yamamoto et al. 1992), capillary-tube type discharge reactors (Kohno et al. 1998), and gliding arc (Krawczyk and Ulejczyk 2003,
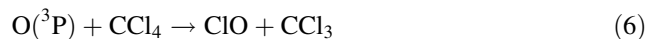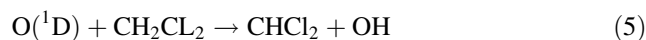
2004) have been studied and developed. Lee et al. (1996) tried to decompose 1,1-dichloroethylene (DCE) using RF plasma. It showed that below 10% DCE (diluted in oxygen) at gas flow rate of 15 cm^3, the DCE was totally removed. The products were dominated by CO and CO_2 were the concentration reached 50% at high oxygen feeds. This method, however, has a major drawback that at higher O_2 injections, instead of raising the CO_2 concentration, the concentration of $COCl_2$ (phosgene) was also increasing (Lee et al. 1996). This phenomenon could happen due to the reaction between chloride molecules with oxygen (Lee et al. 1996; Indarto et al. 2005a; 2006a)

$$CHCl_2 + O \rightarrow COCl_2 + H \qquad (1)$$

$$CHCL_3 + O \rightarrow COCl_2 + HCl \qquad (2)$$

$$CCl_3 + O \rightarrow COCl_2 + OCl \qquad (3)$$

$$CCl_3 + O \rightarrow Cl_2 + Cl. \qquad (4)$$

Using dielectric barrier discharge, Oda et al. (2002) tried to remove trichloroethylene (TCE) and mentioned that the presence of some packed materials could save energy and reduce the power supplied to the reactor. Toykyn et al. (1996) observed that the reduction mechanism was likely a synergistic effect that involves changes in the plasma density, scavenging of low energy secondary electrons, and possible surface passivation. This point, which could be the advantage of plasma-assisted process, could be the important factor on the decomposition process and the energy density supplied from electrical generator should be measured in order to control the strength of the energy for the reaction. This idea was supported by Yamamoto et al. (1992), who performed the decomposition of various VOCs, including DCE and trichlorotrifluoroethane (known as CFC-113). They concluded that the plasma process strongly depended on the energy strength of the electron. The experiment itself was able to remove the reactants up to ca. 67% and the presence of noble gases could help increasing the decomposition rate by halogen-collision mechanism with atom carbon of the VOC molecules. Kohno et al. (1998) also conducted experiments to remove some VOCs using capillary column plasma. The authors claimed that they were able to remove the VOCs as high as 90% under a short residence time (3.8 ms) with a destruction energy efficiency of up to 95 g of compound/kWh. Following this promising result, the authors proposed to use this system for the semiconductor clean-room environment. Currently, a series of experiment to decompose VOCs has been conducted by Indarto et al. (Indarto et al. 2005a, 2006a, b, c, d, 2007a, b). Using gliding arc plasma and another type of non-thermal plasma which produced arcs from two or more electrode blades. Compared to the other non-thermal plasmas, gliding arc plasma produced higher flame temperatures, stronger powers, and was able to handle higher input flow rates

(Fridman et al. 1999). This type of plasma is currently becoming famous and it has better possibility to be utilized for industrial chemical applications.

Kinetic model of chlorinated methane compound decomposition in dry air (mostly, VOCs were presented together with atmospheric air) under plasma conditions has been investigated also (Indarto et al. 2005a; 2006a; 2007b; Penetrante et al. 1995; Koch et al. 1995; Nichipor et al. 2000). The theoretical model suggested that the main product could be Cl_2, $COCl_2$, CO, CO_2, $ClNO_3$ and ClO_3. Decomposition of chlorinated methane compound itself consists of two kinds of reaction mechanism (Penetrante et al. 1995). The mechanism took place when chlorinated carbon compounds collide with dissociated species, such as ground state atomic oxygen $O(^3P)$ and excited atomic oxygen $O(^1D)$,

$$O(^1D) + CH_2CL_2 \rightarrow CHCl_2 + OH \qquad (5)$$

$$O(^3P) + CCl_4 \rightarrow ClO + CCl_3 \qquad (6)$$

$$O(^1D) + CCl_4 \rightarrow CCl_3 + ClO_2 \qquad (7)$$

The second mechanism occurred through the secondary electrons. The secondary electrons could dissociate CVOCs, e.g., CCl_4, to produce CCl_3 and negative ion Cl^-.

$$e + CCl_4 = CCl_3 + Cl^-. \qquad (8)$$

The presence of chlorine atom could act as an auto-catalyzing agent for further decomposition reaction when this species collides with chlorinated molecules. Moreover, radical ClO and CCl_3 were detected as the most important intermediate species in the formation of products and the O and Cl atoms has mostly responsible on the radical reactions both during initiation and termination reaction. CO, Cl_2 and CO_2 could be formed by dissociative process of $COCl_2$ (phosgene) by electron according to (Lee et al. 1996; Nichipor et al. 2000):

$$e + COCl_2 = CO + Cl_2 \qquad k = 10^{-7} cm^3/mol \qquad (9)$$
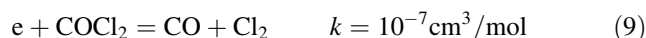
and CO could react continuously into CO_2:

$$CO + ClO = CO_2 + Cl. \qquad (10)$$

More detailed mechanism for specific VOC molecules, e.g., chloroform ($CHCl_3$), carbon tetrachloride (Indarto et al. 2005a, 2006b, 2007b; Penetrante et al. 1995; Koch et al. 1995; Nichipor et al. 2000), and dichloro methane (Indarto et al. 2006d), can be found in the references.

Methane conversion

Instead of being an energy source, methane could be the potential source of green house gases. The man-made activities, e.g., gas flaring in mining sites, petrochemical

industry, and natural decomposition of organic compounds have converted methane into the second largest global warming-caused emissions. Conversion of methane into usable energy and/or higher-price compounds, such as hydrogen, synthesis gas, acetylene, and other higher hydrocarbons or black carbon is still posing a challenge (Lunsford 2000). Together with carbon dioxide (CO_2), many studies have been done intensively for several decades, especially for direct methane conversion. The main problem that we are facing so far so is the inertness of the molecule to any kinds of reaction.

Many research groups used thermal-catalytic method to activate the methane molecule and reported some interesting results. The activation of methane on the surface of catalyst is the key point of the process. However, the results were still not satisfying when further problems appeared. Carbon solid deposition on surface, produced by fragmentation of C–H bond, reduced the catalyst performance. Moreover, the catalyst required a specific temperature operation range which is usually ca. 100–200 °C higher than room temperature. Small flow of injected raw gas is another barrier to apply this process in industrial scale.

Nowadays, plasma-assisted processes, both thermal and non-thermal plasmas, have been studied for methane conversion. Generally, many researches were focused on the utilization of high concentration methane for industrial purposes in order to reduce the methane released to the atmosphere. This technology was targeted to be in-situ process, built in the same location where the source of methane was found, such as gas mining facilities, or petrochemical plants. One of the interesting point of using plasma technology is that the different plasmas and operation conditions, used in the process, could produce different products distribution. This characteristic made it suitable for chemical synthesis selection. Methane utilization using glow discharge (Diamy et al. 2001; Legrand et al. 1997, 1999), dielectric barrier discharge (Kado et al. 2004; Zhang et al. 2003; Hwang et al. 2003, Kim et al. 2003a; 2003b, Jeong et al. 2001, Larkin et al. 2001), corona (Legrand et al. 1997, Liu et al. 1997), spark (Legrand et al. 1997), arc plasma-jet (Coltrin and Dandy 1993), radio frequency plasma (Savinov et al. 2004, Lee et al. 2001) and thermal plasma (Fabry et al. 2001, Kim 2004) have been investigated already. Other parameters of plasma methane reaction, such as plasma power generator (Yao et al. 2001, Song et al. 2004a), catalyst process-assisted (Kim et al. 2004, Song et al. 2004b), water vapor injection (Hijikata et al. 1999) were also investigated experimentally.

The conversion of CH_4 will produce higher hydrocarbons (HCs), especially when non-thermal plasmas are used. Higher energy plasma or thermal plasma will convert CH_4 mainly into carbon (C) and hydrogen (H_2) (Indarto et al. 2006e)

$$CH_4 + Energy \rightarrow C + H_2 \tag{11}$$

Higher HCs could be formed by coupling reactions of methyl radical (Indarto et al. 2008) or carbon with radical species (Diamy et al. 2001).

$$CH_2 + CH_3 \rightarrow C_2H_6 \tag{12}$$

$$C + CH_2 \rightarrow C_2H_2 \tag{13}$$

The same coupling reactions also occurred in temperature-based reactions (Choudhary et al. 2003). In some particular cases, the reaction between carbon and radical shows important role, especially in the case when the concentration of acetylene is the highest among other products (Diamy et al. 2001). Legrand et al. (1997, 1999) the investigation have investigated methane conversion using dielectric barrier discharge. Using IR spectroscopy to analyze the excitation of N_2, they proposed that the reactions were not initiated by electron, but by the existence of excited nitrogen compounds. This result is interesting, but arguable since in the absence of N_2, the conversion of methane can be obtained in a higher rate by increasing the supplied power. Raising the supplied power could increase the population of electron inside the reactor. Based on the (movement) speed comparison, electron is much faster than other species such as ion, radical, or excited molecule (Roch 1995) which means electron could play a dominant role in the reactions. Moreover, apart from these two different arguments, the formation of metastable N_2 as well as noble gases, e.g., Ar, Ne, and He, could help the decomposition rate of the reactants.

In the case of non-thermal plasmas, numerous research papers have been published which show very diverse results. Diamy et al. (2001; Legrand et al. 1997, 1999) found that the acetylene formed the majority of the products when corona-like discharge was used. Other groups (Kim et al. 2003a, 2003b; Jeong et al. 2001; Indarto et al. 2008) found ethane (C_2H_6) as the major products although the distribution could be different with some process manipulations or optimization. By kinetic calculation, Indarto et al. (2005b) showed that the concentration of ·CH_3 radical (·CH_3) and hydrogen atom (H) was increased sharply just after the initiation of plasma reaction, then ·CH_3 was consumed and reacted to form higher mass molecules. An interesting result from Kim et al. (2003a, 2003b), and majority of papers (Indarto et al. 2006f, 2008), is that the coupling reactions occurred and would be followed by dehydrogenation reactions.

$$C_2H_6 \rightarrow C_2H_4 \rightarrow C_2H_2 \tag{14}$$

The coupling reactions would compete with H radical attack to ·CH_3 to form hydrogen molecule (H_2) and lone-pair CH_2. Near the electrode part, the reaction would be dominated by methane fragmentation similar to

reaction 11. Later on, atom carbon, with lone pair electron, could react with planar $\cdot CH_3$ to form acetylene by $C + \cdot CH_3 \rightarrow C_2H_2 + H$. This reaction together with the final result of reaction 14 could be the reason why the concentration of acetylene in the products in some plasma experiments was the highest. This could only occurr when the electrode surface has enough power to fully decompose methane into carbon. Again, as there is still no evidence of the real detailed analysis of this mechanism, the idea is still arguable.

From the transition region between non-thermal and thermal plasma, e.g., gliding arc (Indarto et al. 2006e), the reaction was dominated by total fragmentation of CH_4 into carbon and hydrogen (H_2), similar to the thermal cracking (Indarto et al. 2006f). As CH_4 can be converted into various products, the important factors in the consideration of the choosing the best method is the energy efficiency and instrumentation. Some power supplies, due to the different wave power, have different energy efficiencies.

Decomposition of CO_2

Emission of carbon dioxide (CO_2) into the atmosphere has been known as the major reason for the global warming effect. CO_2 initiated and participated in ozone-depleting reactions (US Environmental Protection Agency 2002; Shah and Singh 1988). The increasing amounts of CO_2 released into the environment by transportation, daily household, agricultural, and industrial activities, are estimated to be around 2×10^{15} g per annum, have increased the demand for finding effective methods to reduce its concentration. That is also the reason why the conversion of CO_2 into more valuable gases is becoming a challenge now (Yamaji 1997).

The main problem to reduce the concentration of CO_2 from industrial gas waste is the bond energy of CO_2 which is chemically strongly–bounded. The thermodynamic calculation of CO_2 decomposition resulted that the homolytic-cracking of C–O bond starts at 1500 °C. The proposed way to avoid the above mentioned problem is by introducing ionic system which allows ionic dissociation mechanism that has lower decomposition energy that is hemolytic-cracking. Plasma which is populated by ionic species could be a good solution.

In recent years, some studies have been carried out on the application of new technologies to reduce the emission of CO_2. Plasma-assisted method, such as RF plasma (Savinov et al. 1999), corona (Wen and Jiang 2001; Maezono and Chang 1990), dielectric barrier discharge (Li et al. 2004), glow discharge (Wang et al. 1999; Buser and Sullovan 1970), and thermal plasma (Kobayashi et al. 2002), have also been developed. Currently, Indarto et al. (2006g, 2007c; Indarto 2007) tried to convert CO_2 into CO and O_2. Wen and Jiang (2001) showed that CO_2 could be destroyed using corona discharge which known as the lowest electrons density of non-thermal plasmas. At 24 ml/min, the conversion of CO_2 was below 10% and significantly increased up to 16% when the reactor was packed with Al_2O_3. The yield of CO was between 15 and 23%. Very low conversion of CO_2 was due to the lack of electron and energy to enhance the conversion of CO_2 (Maezono and Chang 1990). From this point, some process modification should be done to improve the conversion rate of CO_2. The presence of Al_2O_3, for example, could help to increase the conversion of CO_2 by adsorbing CO_2 on the surface of solid material which this phenomenon was exactly similar to the thermal-adsorption process. Instead of CO and O_2 as the main products, ozone (O_3) was also found in few concentrations. Another experiment by Maezono & Chang (1990) on CO_2 diluted in dry air using another type of corona discharge, so-called corona torch, showed that the conversion rate could be increased significantly by addition of noble gases, such as argon (Wen and Jiang 2001), helium (Wang et al. 1999). Light and lower excitation energy of noble gases will enable plasma to produce numerous amounts of active species which are useful to break the C–O bond. N_2, ca. 80% of atmospheric air fraction, actually acted the same as Ar and He; however, the presence of oxygen will result side products, such as NO_2, NO, or N_2O (Indarto et al. 2006g, 2007c). Bi-functional behavior of O_2 was detected as oxygen can abstract O from CO_2 in the beginning of the reaction

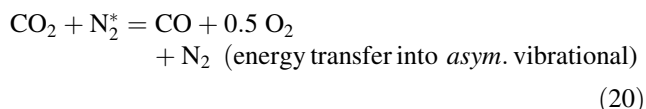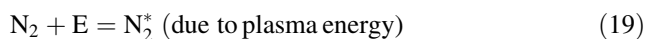$$CO_2 + \langle O \rangle \rightarrow CO + O_2 \qquad (15)$$

$$CO_2 + \langle O_2 \rangle \rightarrow CO + O_3 \qquad (16)$$
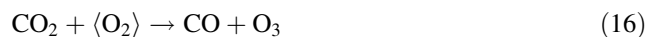
and later on it can oxidize C and CO back to CO_2

$$C + \langle O_2 \rangle \rightarrow CO_2 \qquad (17)$$

$$CO + O \rightarrow CO_2. \qquad (18)$$

Li et al. (2004) investigated the effect of dielectric materials of dielectric barrier discharge on the conversion of CO_2 to CO and O_2. They mentioned that choosing the correct dielectric material was very important to increase the conversion of CO_2. A comprehensive experimental to study the plasma parameters for CO_2 conversion by using dielectric barrier discharge was done by Wang et al. (1999). The conversion of CO_2 will increase by increment of frequency, residence time, supplied voltages, and the amounts of noble gases. In the absence of the catalyst, the process was far from efficient. Not all additive gases work well to enhance the better conversion of CO_2. Buser and Sullovan (1970) found that H_2 reduced the dissociation of CO_2 in the dielectric barrier discharge.

By thoroughly investigating on the different rates of two isotopic carbon ($^{12}C^{16}O_2$ and $^{13}C^{16}O_2$) diluted in nitrogen (N_2), Savinov et al. (2002) concluded that the decomposition of CO_2 was due to the vv-transfer of energy (transfer of vibrational energy between molecules) within the asymmetric mode of CO_2 vibration.

$$N_2 + E = N_2^* \text{ (due to plasma energy)} \quad (19)$$

$$CO_2 + N_2^* = CO + 0.5\,O_2 \\ \qquad + N_2 \text{ (energy transfer into } asym. \text{ vibrational)} \quad (20)$$

As the energy difference caused by first excitation of N_2 due to plasma was almost similar to asymmetric vibrational mode of CO_2, the C–O breaking occurred naturally. In the absence of nitrogen, Indarto et al. (2006g; 2007c) successfully decomposed CO_2 into O_2 and CO in relatively high conversion rate. Later on by simulating the kinetic model, they mentioned the importance of fast electron in collision with CO_2 (Indarto et al. 2007d).

$$CO_2 + e \rightarrow CO + O + e \quad (21)$$

$$CO_2 + e \rightarrow C^+ + O_2 + 2e \quad (22)$$

Once the population of radical oxygen (^1O), ionic oxygen (O_2^+), and excited oxygen increased, these species could significantly fasten the decomposition rate of CO_2 by recombination reaction

$$O_2^+ + CO_2 + e \rightarrow CO_2 + O_2 \quad (23)$$
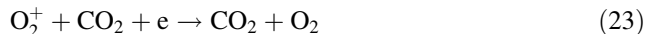
Furthermore, by variation of the O_2 to N_2 ratios of the input, they showed that the effect of N_2 to the CO_2 conversion is less than that by electron. Moreover, the behavior of N_2 itself is almost similar to noble gases. The application of thermal plasma is initiated by Kobayashi et al. (2002). High thermal efficiency was achieved above 80% by using high-energy torch. In very strong supplied power, the decomposition of CO_2 could break the two C–O bonds and produce solid carbon and oxygen.

$$CO_2 + E \rightarrow C + O_2 \quad (24)$$

Some researchers took advantage of this process to produce nano-sized carbon or black carbon. However, the energy efficiency of thermal plasma was usually very low compared to non-thermal plasma (Indarto et al. 2007c).

Conclusion

The application of plasma to decompose toxic compounds has just been studied for a few years. This area is attracting more and more researchers' attention and is flourishing. However, there are still a lot of problems needed to be solved. The low conversion of reactant and the utilization

cost which are usually very expensive have to be overcome. Most of the experiments on plasma conversion of gaseous emissions are still based on trial and error method in which the detailed mechanism on the global reaction has not been significantly addressed. Only a few mechanisms were assumed in the experiments, but they are still needed to be improved. However, it is shown that the plasma application is a visible method to be used for reducing the green house emissions and such combination, e.g., with appropriate catalyst, may be a good choice to increase the performance.

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