A Kinetic Study on the Oxidation of Volatile Organic Compounds

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Master of Engineering Thesis in Chemical Engineering

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ชื่อวิทยานิพนธ์ การศึกษาจลนพลศาสตร์ปฏิกิริยาออกซิเดชันของสารอินทรีย์ระเหย
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บทคัดย่อ

สารอินทรีย์ระเหย (Volatile Organic Compounds, VOCs) ถูกนำมาใช้อยู่ทั่วไปในอุตสาหกรรมประเภทต่างๆ โดยการระเหยของ VOCs สู่ชั้นบรรยากาศ และการปนเปื้อนของ VOCs ในแหล่งน้ำต่างๆ เป็นปัญหาที่ทวีความรุนแรงมากขึ้น และได้รับความสนใจในการหาทางป้องกันและแก้ไข วิธีการหนึ่งที่สามารถใช้บำบัด VOCs ได้ก็คือการทำให้ VOCs เกิดปฏิกิริยาออกซิเดชันกลายเป็นสารที่ไม่เป็นพิษ หรือมีความเป็นพิษน้อยลง ปัญหาของการใช้วิธีนี้ก็คือการขาดแคลนข้อมูลทางด้านจลนพลศาสตร์ งานวิจัยนี้จึงมีวัตถุประสงค์เพื่อหาค่าตัวแปรทางด้านจลนพลศาสตร์สำหรับปฏิกิริยาออกซิเดชันของสารอินทรีย์ระเหยที่สนใจ งานวิจัยนี้จะทำการศึกษาจลนพลศาสตร์ของปฏิกิริยาออกซิเดชันของโทลูอีน เอทานอล และเมทิลเอทิลคีโตน (MEK) ด้วยโซเดียมไฮโปคลอไรด์ (NaOCl) และโพแทสเซียมเปอร์แมงกาเนต ($KMnO_4$) ในปฏิกรณ์แบบแบทช์ ภายใต้สภาวะที่มีการผสมกันอย่างสมบูรณ์ มีค่าพีเอช และอุณหภูมิคงตัว ในส่วนแรกของงานวิจัยจะทำการทดลองหาตัวออกซิไดซ์ที่เหมาะสมกับสารอินทรีย์ที่สนใจศึกษา ผลจากการทดลองพบว่าตัวออก- ซิไดซ์ที่เหมาะสมสำหรับโทลูอีน และเอทานอล คือ NaOCl และ $KMnO_4$ ตามลำดับ ส่วนกรณีของ MEK พบว่าทั้ง NaOCl และ $KMnO_4$ สามารถออกซิไดซ์ MEK ได้ และจากการศึกษาหาค่าตัวแปรทางด้านจลนพลศาสตร์พบว่าปฏิกิริยาออกซิเดชันระหว่างโทลูอีน-NaOCl มีค่าอันดับของปฏิกิริยาเมื่อเทียบกับโทลูอีนเป็นปฏิกิริยาอันดับหนึ่ง และมีค่าอันดับของปฏิกิริยาเมื่อเทียบกับ NaOCl เป็นปฏิกิริยาอันดับศูนย์ สำหรับปฏิกิริยาระหว่างออกซิเดชันระหว่างเอทานอล-$KMnO_4$ จะพบว่าค่าอันดับของปฏิกิริยาจะเป็นปฏิกิริยาอันดับหนึ่งเมื่อเทียบกับทั้งเอทานอล และ $KMnO_4$ ส่วนปฏิกิริยาออกซิเดชันระหว่างMEK-NaOCl จะมีค่าอันดับของปฏิกิริยาเมื่อเทียบกับ MEK เป็นปฏิกิริยาอันดับ 0.5 (half-order reaction) และมีค่าอันดับของปฏิกิริยาเมื่อเทียบกับ NaOCl เป็นปฏิกิริยาอันดับศูนย์ ปฏิกิริยาออกซิเดชันระหว่างMEK-$KMnO_4$ มีค่าอันดับของปฏิกิริยาเมื่อเทียบกับ MEK เป็นปฏิกิริยาอันดับหนึ่ง และมีค่าอันดับของปฏิกิริยาเมื่อเทียบกับ $KMnO_4$ เป็นปฏิกิริยาอันดับ 0.5 นอกจากนี้ในงานวิจัยยังพบว่าปฏิกิริยาออกซิเดชันที่ทำการศึกษาจะเป็นไปตามสมการของอาร์รีเนียส และสามารถหาค่าพลังงานกระตุ้น (E_a) สำหรับปฏิกิริยาออกซิเดชันระหว่าง

โทลูอีน-NaOCl เอทานอล-$KMnO_4$ MEK-NaOCl และMEK-$KMnO_4$ มีค่าเท่ากับ 31.908 37.190 33.430 และ25.393 กิโลจูลต่อโมล ตามลำดับ จากนั้นพัฒนากฎอัตรา และทำการตรวจสอบความถูกต้องของกฎอัตราโดยนำกฎอัตราที่ได้ไปทำนายอัตราการเกิดปฏิกิริยาออกซิเดชัน และเปรียบเทียบผลการทำนายกับค่าที่วัดได้โดยตรงจากการทดลองทั้งที่อุณหภูมิห้อง และอุณหภูมิอื่น พบว่ามีความสอดคล้องกันดี ดังนั้นจึงสรุปได้ว่ากฎอัตราที่ได้พัฒนาขึ้นนี้จะสามารถใช้ทำนายอัตราการออกซิเดชันของสารอินทรีย์ระเหยในช่วงอุณหภูมิที่ทำการศึกษาได้ ทั้งนี้ผลจากการศึกษาในข้างต้นแสดงว่า NaOCl เป็นตัวออกซิไดซ์ที่เหมาะกับสารกลุ่มอะโรมาติก และคีโตน ในขณะที่ $KMnO_4$ เป็นตัวออกซิไดซ์ที่เหมาะกับ VOCs ในกลุ่มแอลกอฮอล์ ในส่วนสุดท้ายของงานวิจัยจึงได้ยืนยันข้อสรุปดังกล่าวโดยทำการเลือกเบนซีน เมทานอล และอะซิโตน เป็นตัวแทนของสารที่อยู่ในกลุ่มอะโรมาติก แอลกอฮอล์ และคีโตน ตามลำดับ จากการออกซิไดซ์สารในกลุ่มนี้ด้วยตัวออกซิไดซ์ที่กำหนด พบว่า NaOCl และ$KMnO_4$ สามารถออกซิไดซ์สารดังกล่าวได้ดี

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ABSTRACT

Volatile Organic Compounds (VOCs) are commonly used in many industries. Emission of VOCs into the atmosphere and VOCs contaminated in water basin are among the most pollutants leading to various environmental hazards. In such circumstances, it becomes obligatory for each VOCs emitting industry to opt for proper VOCs treatment. Oxidation reactions represent an important option because the toxic VOCs can be transform to non-toxic or less toxic. The problem arises because the lack in knowledge of the oxidation processes of VOCs. Thus, this research was aimed to investigate the oxidation reaction kinetics of interesting VOCs include toluene, ethanol, and methyl ethyl ketone (MEK) using sodium hypochlorite (NaOCl) or potassium permanganate ($KMnO_4$) in a homogeneous batch reactor under constant pH, isothermal, and completely mixed conditions. Experimental results indicated that the suitable oxidant for toluene and ethanol were NaOCl and $KMnO_4$, respectively while MEK can oxidized by both NaOCl and $KMnO_4$. In the study of the kinetics parameters, the reaction order for the oxidation reaction of toluene-NaOCl has been found to be one with respect to toluene and zero with respect to NaOCl. The oxidation reaction between ethanol and $KMnO_4$ was determined to be first-order with respect to both ethanol and $KMnO_4$. For MEK-NaOCl oxidation reaction, the reaction order was half-order with respect to MEK and zero-order with respect to NaOCl. MEK-$KMnO_4$ oxidation reaction was reported to be first-order with respect to MEK and half-order with respect to $KMnO_4$. The oxidation reactions follow an Arrhenius behavior with an activation energy of 31.908, 37.190, 33.430, and 25.393 kJ mol^{-1} for toluene-NaOCl, ethanol-$KMnO_4$, MEK-NaOCl, and MEK-$KMnO_4$, respectively. The rate law was determined and verified against experimental data. The results between

the experimental and the predicted oxidation rate were in good agreement. This supported the use of the rate law to predict the oxidation rate of toluene, ethanol, and MEK in the range of investigated temperature. From the study above, we can conclude that NaOCl was suitable for oxidizing an aromatic compound and ketone while $KMnO_4$ was suitable for oxidizing alcohol. In order to verify this, benzene, methanol, and acetone have been chosen as a representative of aromatic, alcohol, and ketone, respectively. These VOCs were then oxidized with specific oxidant as mentioned earlier. The results showed that NaOCl and $KMnO_4$ can also oxidize these substances as expected.

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Abbreviations and Symbols

Abbreviations

A = pre-exponential factor or frequency factor

a_1 = empirical fitting parameters

B = empirical fitting parameters

$C_{oxidant}$ = concentration of oxidants (mol L^{-1})

C_{VOC} = concentration of VOCs (mol L^{-1})

$C_{oxidant,0}$ = initial concentration of oxidants (mol L^{-1})

$C_{VOC,0}$ = initial concentration of VOCs (mol L^{-1})

E_a = activation energy (J mol^{-1})

k = rate constant

R = gas constant (J mol^{-1} K^{-1})

r_{VOC} = reaction rate of VOCs (mol L^{-1} min^{-1})

$r_{VOC,0}$ = initial reaction rate of VOCs (mol L^{-1} min^{-1})

T = absolute temperature (K)

t = time (minute)

VOCs = Volatile Organic Compounds

Symbols

α = order of the reaction with respect to the VOCs

β = order of the reaction with respect to the oxidants

Chapter 1

INTRODUCTION

1.1 Introduction

Over the last decade, there has been increased the serious environmental problems due to the emission of toxic substance into the atmosphere. Some of the most common toxic substances are volatile organic compounds (VOCs). The VOCs are used widely in industry as solvents and as starting compounds for producing other chemicals including pharmaceutical, plastics, paints, refrigerators and lubricants (Shineldecker, 1992; Leach *et al.*, 1999). The VOCs that are used in the industries depend upon the types of industries such as solvent which are used widely in furniture industries, for example, toluene, butyl acetate, and alcohol, while the VOCs that are used in fabric industries consists of acetone, benzene, ethanol, buthanol, toluene, xylene, and chloroform. Besides the industries mentioned above, VOCs are used in other industries such as hexane, methylethylketone, ethanol, and phenol, these all have high toxic and easy to volatile to the atmosphere. In addition to affecting the health of human being and all animals, some VOCs have been implicated in the problem of the depletion of the stratospheric ozone layer. Although many of the VOCs do not react in the photochemical oxidant cycles, the Environmental Protection Agency (EPA) recommends that emissions of these compounds would be reduced because of their possible toxic effects. From an environmental point of view, it is necessary to limit and control vapor emissions. Traditional treatment techniques available for reducing VOCs emissions such as thermal oxidation, catalytic oxidation, carbon adsorption, incineration, condensation, and bioreactors have proven to be effective for many pollutants (Grega *et at.*, 1994; Khan and Aloke, 2000). However, these techniques require high initial investment, as well as difficulty in design. One of the techniques is to use an oxidation reaction in which the toxic VOCs were oxidized to be non toxic or less harmful than the parent compounds, the generally reaction can be shown as Eq. (1)

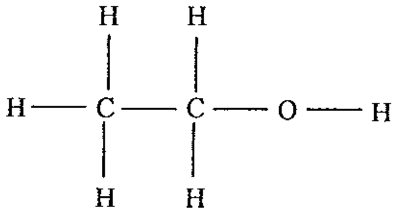
$$VOCs + Oxidant \rightarrow Main\ \ product\ \ (non\ \ or\, less\ \ toxic) + By\ \ product\ \ (non\ \ toxic) \qquad (1)$$

Main product and by product that occur in Eq. (1) depend on the kind of VOCs and oxidant. Although the treatment of VOCs by the oxidation had been investigated by a number of researchers (Damm *et al.*, 2002; Hood *et al.*, 2000; Huang *et al.*, 2001; Yan and Schwartz, 1999) but the reports seem to be specific only some group of VOCs. In this study the oxidation of various VOCs; ethanol, methylethylketone, and toluene using a number of oxidant has been investigated. Our investigations provide a detailed process-level understanding of the oxidation reactions of VOCs. The specific objectives are to examine kinetic parameters (i.e., rate constant, reaction order, and activation parameters) and obtained the rate law to predict the oxidation rate.

1.2 Chemicals and Oxidants

1.2.1 Chemical and Physical properties of VOCs

- **Ethanol**

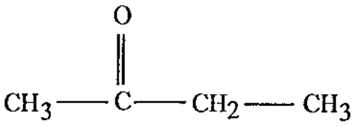


$$H-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-O-H$$

Ethanol (C_2H_5OH; CAS No. 64-17-5) is also known as ethyl alcohol or gain alcohol. Ethanol is an aliphatic alcohol; it contains hydrogen, carbon, and oxygen in its chemical structure. The oxygen makes ethanol a clean burning fuel. It can be produced chemically from ethylene or biologically from gains, agricultural wastes, or any material containing starch of sugar. The physical properties of ethanol are flammable, clear colorless liquid with a characteristic, agreeable odor. In dilute aqueous solution, it has a somewhat sweet flavor, but in more concentrated solutions it has a burning taste. It is miscible in all proportions with water and with most organic solvents. The molecular weight of ethanol is 46.07 g/mol with a vapor pressure of 44.6 mmHg at 20°C. Ethanol melts at –114.1°C, boils at 78.5°C, and has a density of 0.789 g/ml at 20°C. Its low freezing point has mad it useful as the fluid in thermometers for temperatures below -40°C, the freezing point of mercury, and for other low-temperature purposes, such as for antifreeze in automobile radiators.

Ethanol is useful as a solvent and is widely used in the cosmetic industry. Many cosmetics consist mainly of alcohol, such as aftershave lotion and some cologne, as well as many deodorants and mouth washes. It is also used in some shaving creams, shampoos and other skin lotions. Ethanol can be oxidized to form first acetaldehyde and then acetic acid. It can be dehydrate to form ether. Exposure to ethanol may happen from many sources, it is a direct central nervous system depressant that causes decreased motor function and decreased consciousness level. At high concentrations, ethanol is an anesthetic and can cause autonomic dysfunction, coma, and death from respiratory depression and cardiovascular collapse. However, the Occupational Safety and Health Administration (OSHA) and the International Agency for Research on Cancer (IARC) have not classified ethanol as to human carcinogenicity.

- **Methyl Ethyl Ketone**



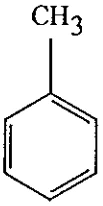
$$CH_3 - \overset{\overset{\displaystyle O}{\|}}{C} - CH_2 - CH_3$$

Methyl Ethyl Ketone (C_4H_8O; CAS No. 78-93-3) is also referred to as 2-butanone, or MEK. It is a colorless volatile liquid that is soluble in water. The odor threshold for MEK is 5.4 parts per million (ppm) with an acetone-like odor reported. It has a molecular weight of 72.11 g/mol with a boiling point of 79.6°C. The density of MEK is 0.8054 g/ml at 20°C and the vapor pressure is 90.6 mmHg at 25°C.

The primary use of MEK is as a solvent often found in mixtures with acetone, ethyl acetate, n-hexane, toluene or alcohols. It is also used in the synthetic rubber industry, in the production of paraffin wax, and in household products such as lacquer and varnishes, paint remover, and glues. MEK occurs as a natural product. It is made by some trees and found in some fruits and vegetables in small amounts.

It is also released to the air from car and truck exhausts as well as from oil refineries. People may be exposed to MEK in the environment by breathing, eating, or drinking substances containing the chemical or from the skin contact with it. The known health effects are irritation of the nose, throat, skin, and eyes. Other effects reported from acute inhalation exposure in humans include central nervous system depression, headache, and nausea. However, EPA has classified MEK as a Group D, not classifiable as to human carcinogenicity.

- **Toluene**



Toluene ($C_6H_5CH_3$; CAS No. 108-88-3), also known as methylbenzene, toluol, methylbenzol, phenylmethane, is occurs naturally in crude oil and in the tolu tree. At room temperature, it is a volatile, colorless liquid with a benzene-like odor that is slightly soluble in water. It has a molecular weight of 92.14 g/mol with a boiling point of 111°C. The density and vapor pressure of toluene at 20°C is 0.8669 g/ml and 22 mmHg, respectively.

Toluene is used in such industries as raw material in the production of organic compounds, and widely used as an industrial solvent for the manufacturing of paints, chemicals, pharmaceuticals, and rubber. It is also produced in the process of making gasoline and other fuels from crude oil and making coke from coal, and as a by product in the manufacture of styrene. From the uses of toluene from many sources, so toluene can enter the environment in a number of different ways. It can enter the air or water from the waste of manufacturing plants but for the human it can enter the body mainly by breathing its vapors. After being taken into the body, major acute effects in human are central nervous system dysfunction and neurological impairment. Inhaling high levels in a short term can feel light-headed, dizzy, or sleepy. It can also cause unconsciousness, and even death. Studies review by ATSDR (ATSDR, 2001) showed that studies in workers and animals exposed to toluene generally indicate that toluene does not cause cancer. The International Agency for Research on Cancer (IARC) and the Department of Health and Human Services (DHHS) has not classified toluene for carcinogenic effects. The EPA has determined that toluene is not classifiable as to its human carcinogenicity.

1.2.2 Chemical and Physical properties of Oxidizing Agent

- **Potassium Permanganate**

Potassium permanganate ($KMnO_4$; CAS No. 7722-64-7) is a purple crystalline compound with a metallic sheen. It is widely used as a powerful oxidizing agent, as a disinfectant in a variety of applications, and as an analytical oxidant reagent. As an oxidizing agent it has the ability to add oxygen, remove hydrogen or remove electrons from compound. It is recognized by its characteristic purple to pink color when made into a solution. In high concentrations it is a dark purple color. The molecular weight of permanganate is 158.04 g/mol with a density of 2.7 g/ml.

$KMnO_4$ is an oxidizing agent that has been used for many years in aquaculture. It is used primarily to control taste and odors, remove color, control biological growth in treatment plants, and remove iron and manganese. As an oxidizer, it is able to chemically burn up organic material. Although it has many potential uses as an oxidant, it is a poor disinfectant. The efficiency of the uses depends upon the permanganate concentration, contact time, temperature, pH, and presence of other oxidizable material. When $KMnO_4$ is contact with body, it can cause serious eye injury, is a skin and inhalation irritant, and can be fatal if swallowed. But it is not a known carcinogen.

- **Sodium Hypochlorite**

Sodium Hypochlorite (NaOCl; CAS No. 7681-52-9) is a green to yellow, watery liquid with a chlorine-like odor. Solutions containing sodium hypochlorite in water are known as bleach, or hypochlorous acid. The hypochlorite ion in aqueous solution is very stable and is a strong chemical oxidant. It is also soluble in water. The molecular weight of NaOCl is 74.44 g/mole with a boiling point of 40°C (decomposes). The density is 1.07-1.14 g/ml and the vapor pressure is 17.5 mmHg at 20°C. The pH is 9-10 (neutral solution-no excess sodium hydroxide). NaOCl is prepared by reacting dilute caustic soda solution with liquid or gaseous chlorine accompanied by cooling.

Chemical Reactions: $Cl_2 + 2NaOH --> NaOCl + H_2O + Heat$ (2)

The uses in laboratory, bleach has been used in the research laboratory for decontaminating surfaces that have come into contact with strong organophosphate compounds, such as nerve agents, that are easily hydrolyzed by NaOCl to nontoxic breakdown products. In industries, solutions up to 40% NaOCl are available. They are used as disinfectants and sanitizers in swimming pools, food processing plants, dairies, and hospitals. They are also used as bleach for textiles, paper and wood pulp, and in effluent treatment. When the spilled or uncontrolled release of NaOCl solution occurs, the worker is at risk for inhalation of mist, splashing of liquid into the eyes, and contact with the skin. NaOCl solutions may release small amounts of hypochlorous acid and chlorine gas, but usually in very low concentrations at room temperature. Chlorine gas can produce acute adult respiratory distress syndrome, characterized by nausea, vomiting, cough, dyspnea, and generalized weakness. The primary toxic effect from inhalation of high concentrations is severe respiratory irritation that can progress to pulmonary edema. From the toxic of NaOCl, there is inadequate evidence for carcinogenicity of hypochlorite salts in experimental animals and there are no studies in humans. Therefore, NaOCl cannot be classified as a carcinogen in humans.

1.3 Theory: Basic Concepts of Kinetics

1.3.1 Studying Kinetics

The subject of chemical kinetics is concerned with the rates of chemi reactions, and with the factors upon which the rates depend. The most important these factors are concentration, temperature, and hydrostatic pressure.

The study of kinetics can be undertaken for many reasons. Reaction rate is great practical interest in both laboratory and industrial practices. It is clea necessary to understand the factors controlling the rate at least to some extent befor reaction becomes useful on almost any scale. Besides that, the understanding t dependence of the various rates on the reaction variables (concentration, temperatu solvent, etc.) that one can predict the conditions required for favoring the desir product. Also, the study of equilibrium does not give any information about the ste involved in the reaction, for it is only concerned with the energies of the reactants a of the products. Finally, the selection of a reaction system that operates in the saf and most efficient manner can be the key to the economic success or failure of chemical plant.

A number of variables are recognized to influence the rate of a reaction. T major factors are the following: (1) concentrations of reactants, products, and possib catalysts, (2) physical conditions such as temperature and pressure, (3) the intensity absorbed radiation, and, for reactions in solution, (4) properties of the solvent such viscosity, dielectric constant, and ionic strength (Espenson, 1981).

1.3.2 Definition of the Rate of Reaction, r_A

A reaction occurring in a single phase is usually referred to as *homogeneous reaction*, while a reaction that takes place at or very near the interfa between the phases is known as a *heterogeneous reaction* (Flogler, 1999). The mo important data about any reaction that is to be studied kinetically is its stoichiometr For the general chemical reaction equation, the following rate laws can be written Eq. (3)

$$aA + bB \leftrightarrow cC + dD \qquad ($$

where a and b denote the number of moles of reactant A and B that react to yield c and d moles of products C and D.

Guldberg and Waage defined the rate of reaction as proportional to the concentration of each substance participating in the reaction raised to the power of its stoichiometric coefficients (Schnoor, 1996). For reaction (3), the rate of consumption of reactants is

$$r_A = -\frac{1}{a}\frac{dC_A}{dt} = -\frac{1}{b}\frac{dC_B}{dt} \tag{4}$$

where r_A denote the rate of reaction and Ci denote the concentration of species i. The negative signs in Eq. (4) indicate that during the course of the reaction the concentration of reactants decreases as the reactants are consumed. Conversely, a positive sign indicates that the concentration of products increases as those species are formed. Consequently, the rate of formation of products C and D can be written as Eq. (5)

$$r_C = +\frac{1}{c}\frac{dC_C}{dt} \quad \text{or} \quad r_D = +\frac{1}{d}\frac{dC_D}{dt} \tag{5}$$

The factor a, b, c, and d in Eq. (4) and (5) are referred to as the stoichiometric coefficients for the chemical entities taking part in the reaction. Since the concentrations of reactants and products are related by Eq. (3), measurement of the rate of change of any one of the reactants of products would suffice to determine r_A.

A number of different units have been used for the reaction rate. The dimensionality of r_A is

$$[concentration][time]^{-1} \tag{6}$$

The standard SI unit of concentration is moles per cubic decimeter, abbreviated mol dm^{-3}.

The rate of a chemical reaction may be expressed in various ways. In some investigations it is convenient to measure the concentration of a product of a reaction at various times, and curve a in Figure 1-1 shows schematically how such a concentration may vary with the time. The slope of such a curve at any time then provides a measure of the rate at that time. Alternatively, one may measure the concentration of a reactant, and curve b of Figure 1-1. shows how such a concentration may vary with time. (Laidler, 1963)

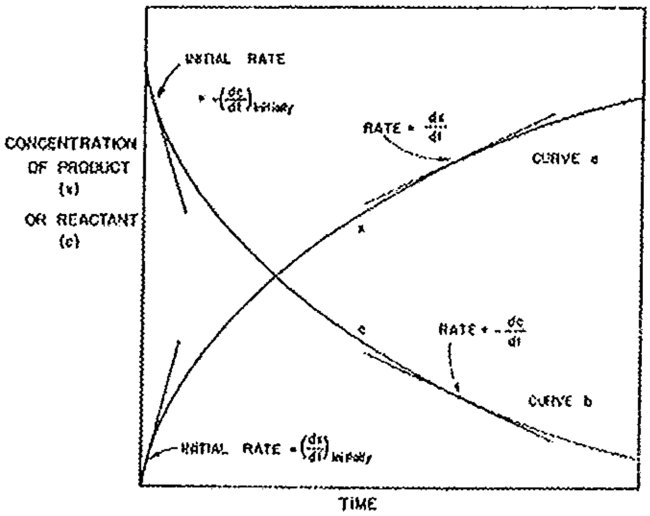


Figure 1-1 Schematic curves showing the concentration of a product, and the concentration of a reactant, as function of time

1.3.3 Reaction Order

The reaction rate of all chemical reactions depends on the concentration of one or more of the reactants. In general, the rate may be expressed as a function of these concentrations,

$$-r_A = fn\left(C_A, C_B\right) \tag{7}$$

In some cases the reaction rate also depends on the concentration of one or more intermediate species, e.g., in enzymatic reactions. In other cases the rate law may involve the concentration of some species, which do not appear in the stoichiometric Eq. (3); such species are known as catalyst. In still other cases, the concentration of product molecules may appear in the rate law.

The most frequently encountered functional dependence given by Eq. (7) is the rate's being proportional to a product of algebraic powers of the individual concentrations, i.e.,

$$-r_A \propto \mathrm{C_A}^{\alpha}\mathrm{C_B}^{\beta} \tag{8}$$

The exponents α and β may be integer, fractional, or negative. This proportionality can be converted to an equation by inserting a proportionality constant k, thus

$$-r_A = k\,\mathrm{C_A}^{\alpha}\mathrm{C_B}^{\beta} \tag{9}$$

This equation is called a *rate equation* or *rate law*. The exponent α is the *order* of the reaction with respect to reactant A, and β is the order with respect to reactant B. The proportionality constant k is called the *rate constant*. The overall order of the reaction is defined as the sum of the exponents in the rate law, $n = \alpha + \beta$.

Elementary reactions may be described by their molecularity, which specifies the number of reactants that are involved in the reaction step. If a reactant spontaneously decomposes to yield products in a single reaction step, the reaction is termed *unimolecular*, given by the Eq. (10).

$$A \rightarrow products \tag{10}$$

If two reactants A and B react with each other to give products, the reaction is termed *bimolecular*.

$$A + B \rightarrow products \tag{11}$$

Three reactants that come together to form products constitute a *termolecular* reaction. In principle, one could go on to specify the molecularity of four, five, etc., reactant involved in an elementary reaction, but such reactions have not been encountered in nature.

1.3.4 Elementary Reaction Rate Law

- **Zero-Order Reactions**

The rate law for a reaction that is zero order is

$$-r_A = \frac{dC_A}{dt} = kC_A^0 = k_0 \tag{12}$$

Zero-order reactions are most often encountered in heterogeneous reactions on surfaces. The rate of reaction for this case is independent of the concentration of the reacting substance. To find the time behavior of the reaction, Eq. (12) is put into the differential form

$$dC_A = -k\,dt \tag{13}$$

and then integrated over the boundary limits t_1 and t_2. Assuming that the concentration of A at $t_1 = 0$ is C_{A0}, and at $t_2 = t$ is C_{At}, Eq. (13) becomes

$$\int_{C_{A0}}^{C_{At}} dC_A = -k \int_{t_1=0}^{t_2=t} dt \tag{14}$$

Hence,

$$C_{At} - C_{A0} = -k(t-0) \tag{15}$$

Consequently, the integrated form of the rate law for the zero-order reaction is

$$C_{At} = C_{A0} - kt \tag{16}$$

A plot of C_A versus time should yield a straight line with intercept C_{A0} and slope $-k$.

- **First-Order Reactions**

A first-order reaction is one in which the reaction rate is proportional to the concentration of the reactant to the first power

$$A \xrightarrow{k_1} B \tag{17}$$

and the rate of disappearance of A can be written as

$$-r_A = -\frac{1}{a}\frac{dC_A}{dt} = kC_A^1 \tag{18}$$

Note that the reaction is of order one in the reactant A. Thus, since only one A molecule disappears to produce one product B molecule, $a = 1$ and Eq. (18) becomes

$$-\frac{dC_A}{dt} = kC_A \tag{19}$$

Integration of Eq. (19) leads to

$$-\int \frac{dC_A}{C_A} = k\int dt$$

$$-\ln C_A = kt + cons\tan t \tag{20}$$

If the boundary conditions are such that at $t = 0$ the initial value of A is C_{A0}, the constant of integration in Eq. (20) can be eliminated if we integrate over the boundary limits as follows

$$-\int_{C_{A0}}^{C_{At}} \frac{dC_A}{C_A} = k\int_0^t dt \tag{21}$$

This gives,

$$-(\ln C_{At} - \ln C_{A0}) = kt \tag{22}$$

and hence,

$$-\ln C_{At} = kt - \ln C_{A0} \tag{23}$$

Thus, the constant in Eq. (20) is just

$$cons\tan t = -\ln C_{A0} \tag{24}$$

Eq. (23) can be written in various forms. Some that are commonly used are

$$\ln\left(\frac{C_{At}}{C_{A0}}\right) = -kt \tag{25a}$$

$$C_{At} = C_{A0}\, e^{-kt} \tag{25b}$$

and

$$\frac{C_{At}}{C_{A0}} = e^{-kt} \tag{25c}$$

From the exponential form of Eq. (25b) and (25c), one can determined *time constant* τ which is called the decay time of the reaction. This quantity is defined as the time required for the concentration to decrease to $1/e$ of its initial value C_{A0}, where $e \approx 2.7183$ is the base of the natural logarithm. The time τ is given by

$$\tau = \frac{1}{k} \tag{26}$$

In experimental determinations of the rate constant k, the integral form of the rate law is often written in decimal logarithms as

$$\log_{10} C_{At} = \log_{10} C_{A0} - \frac{kt}{2.303} \tag{27}$$

and a semi-log plot of C_{At} versus t will yield a straight line with $k/2.303$ as slope and C_{A0} as intercept.

- **Second-Order Reactions**

There are two cases of second-order kinetics. The first is a reaction between two identical species, viz.,

$$A + A \rightarrow products \tag{28}$$

The rate law for this case is

$$-r_A = -\frac{1}{2}\frac{dC_A}{dt} = kC_A^2 \tag{29}$$

The second case is an overall second-order reaction between two unlike species, given by

$$A + B \rightarrow products \tag{30}$$

In this case, the reaction is first order in each of the reactants A and B and the rate law is

$$-r_A = -\frac{dC_A}{dt} = kC_A C_B \tag{31}$$

Note the appearance of the stoichiometric coefficient $\frac{1}{2}$ in Eq. (29), but not in Eq. (31).

Integrate the rate law, Eq. (29), to obtain

$$-\int_{C_{A0}}^{C_{At}} \frac{dC_A}{C_A^2} = 2k\int_0^t dt \tag{32}$$

which gives

$$\frac{1}{C_{At}}=\frac{1}{C_{A0}}+2kt \tag{33}$$

A plot of the inverse concentration of A $\left(C_A^{-1}\right)$ versus time should yield a straight line with slope equal to *2k* and intercept $1/C_{A0}$

To integrate the rate law for the second case, Eq. (30) and (31), it is convenient to define a progress variable *x* which measures the progress of the reaction to products as

$$x=\left(C_{A0}-C_{At}\right)=\left(C_{B0}-C_{Bt}\right) \tag{34}$$

where C_{A0} and C_{B0} are the initial concentrations. The rate law given by Eq. (31) can be rewritten in terms of *x* as

$$\frac{dx}{dt}=k\left(C_{A0}-x\right)\left(C_{B0}-x\right) \tag{35}$$

To find the time behavior, we integrate Eq. (35) thus

$$\int_{x_0}^{x_t}\frac{dx}{\left(A_{A0}-x\right)\left(C_{B0}-x\right)}=k\int_0^t dt \tag{36}$$

To solve the integral on the left-hand side of Eq. (36), we separate the variables and use the method of partial fractions

$$\int\frac{dx}{\left(C_{A0}-x\right)\left(C_{B0}-x\right)}=\int\frac{dx}{\left(C_{A0}-C_{B0}\right)\left(C_{B0}-x\right)}-\int\frac{dx}{\left(C_{A0}-C_{B0}\right)\left(C_{A0}-x\right)} \tag{37}$$

Solving the right-hand side of Eq. (37) and equating it to the left-hand side of Eq. (36), we obtain, as the solution to the rate law for the second case,

$$\frac{1}{\left(C_{A0}-C_{B0}\right)}\ln\left(\frac{C_{B0}C_{At}}{C_{A0}C_{Bt}}\right)=kt \tag{38}$$

In this case the experimental data may be plotted in the form of the left-hand side of the equation against *t*.

- **Reactions of General Order**

Many times a reaction is not elementary, and the rate law is not simply zero, first, or second order. The rate law for such reaction is

$$-r_A = -\frac{dC_A}{dt} = kC_A^n \tag{39}$$

A simple integration of this expression yields the result

$$\frac{1}{(n-1)}\left(\frac{1}{C_{At}^{n-1}} - \frac{1}{C_{A0}^{n-1}}\right) = kt \tag{40}$$

which can be rewritten as

$$\frac{1}{C_{At}^{n-1}} - \frac{1}{C_{A0}^{n-1}} = (n-1)kt \tag{41}$$

Eq. (41) is valid for any value of n except $n = 1$, in which case it is undefined and Eq. (25) must be used instead. Figure 1-2 shows several plots of concentration versus time for various values of n (Steinfeld *et al.*, 1989).

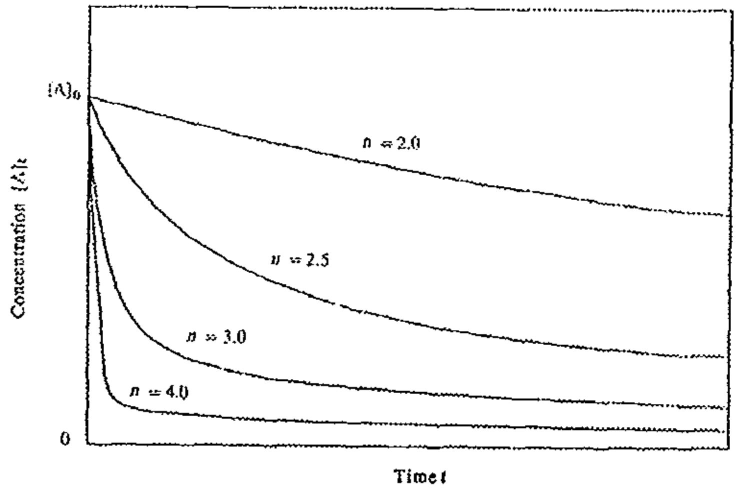


Figure 1-2 Plot of C_{At} versus time for reaction of general order. The plot shows various functional behaviors for n = *2, 2.5, 3, 3.5, and 4*. Concentration and time are in arbitrary units

1.3.5 Determination of Reaction Order : Initial Rate Method

In a kinetic investigation, batch reactors are used primarily to determine rate law parameters for homogeneous reactions. This determination is usually achieved by measuring, in some direct or indirect fashion, concentrations at various times. The problem is then to express the rate in terms of an equation that relates the rate to the concentrations of reactants, and sometimes of products or other substances present (e.g. of catalysts). If the reaction has a simple order one must determine what the order is, and also the rate constant. If it does not, the form of the rate equation and the magnitude of the constants must be determined.

There are several methods for dealing with such problems. The major methods are the following

(1) Differential Method
(2) Integral Method
(3) Initial Rates Method
(4) Half-Lives Method

Selection of the kinetic methods to abstract rate parameters essentially depends on the characteristics of reactions (Levenspiel, 1972; Flogler, 1999). In this study, we will focus on the use of Initial Rates Method.

Initial Rates Method

By using the initial rates method, the rate law in Eq. (9) can be rewritten as Eq. (42)

$$-r_{A0} = k\,\mathrm{C}_{\mathrm{A0}}^{\ \alpha}\,\mathrm{C}_{\mathrm{B0}}^{\ \beta} \tag{42}$$

where $-r_{A0}$ is the initial reaction rate of A (mol/L/min), C_{A0} is the initial concentration of A (mol/L), C_{B0} is the initial concentration of B (mol/L).

The initial reaction rate of A can be found by differentiating the experimental data and extrapolating to zero time. For constant-volume batch reactor, the initial rates can be express as Eq (43)

$$-r_{A0} = \left(\frac{dC_A}{dt}\right)_{t=0} \tag{43}$$

1.3.6 Temperature Dependence of Rate Constant

Rate laws are sometimes referred to as separable forms because they can be written as the product of two factors, one dependent on temperature and the other not. This can be illustrated by Eq. (44)

$$-r_A = k(T)\, C_A^{\alpha}\, C_B^{\beta} \ldots \tag{44}$$

where the rate constant $k(T)$ is indicated to be a function of temperature, and the concentration terms are independent of that variable. The possible dependence of α and β on temperature is small and normally arises from factors associated with the fitting of rate forms to kinetic data.

The first quantitative, experimental formulation of the dependence of reaction rates on temperature was made by Hood and later extended by Arrhenius. It should be expressed by an equation of form

$$k(T) = Ae^{-E/RT} \tag{45}$$

In Eq. (47), which is known as the *Arrhenius equation*, k is the specific rate constant at some temperature, R is the gas constant ($R = 8.314\ J\ mol^{-1}\ K^{-1}$), T is the absolute temperature (K), A is preexponential factor or frequency factor, and E is activation energy ($J\ mol^{-1}$).

The activation energy is determined by carrying out the reaction at several different temperatures. After taking the natural logarithm of Eq. (45),

$$\ln k = \ln A - \frac{E}{R}\left(\frac{1}{T}\right) \tag{46}$$

From the logarithmic form, it is apparent that the activation energy (E) and the preexponential factor (A) are determined from an *Arrhenius plot* of the reaction rate constant versus $1/T$. It can be seen that an Arrhenius plot should be a straight line whose slope is proportional to the activation energy and the intercept is proportional to the preexponential factor, as shown in Figure 1-3 (Schnoor, 1996).

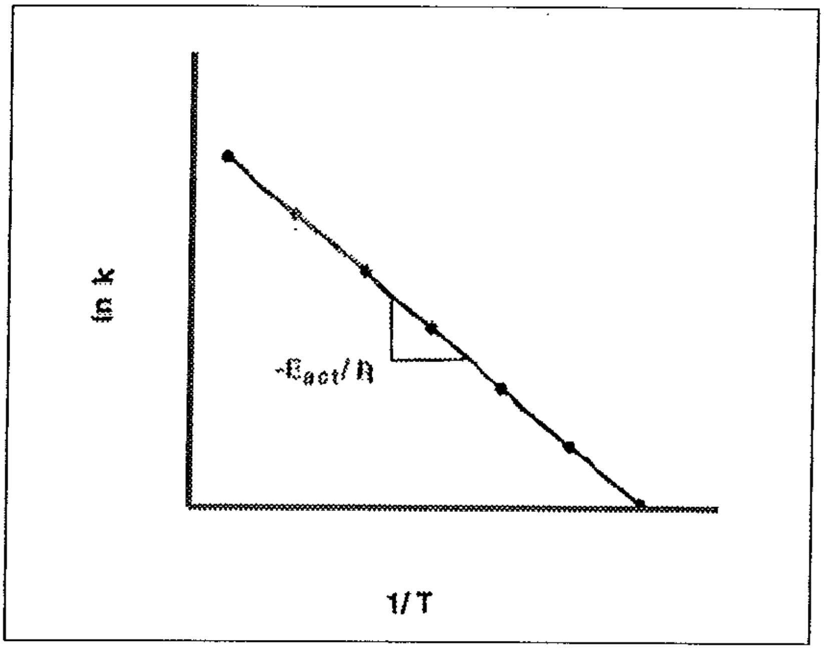


Figure 1-3 Arrhenius plot of reaction rate constant at any temperature. Activation energy and preexponential factor for the reaction can be obtained from the slope and the intercept of the line, respectively

In some cases the linear correlation may not be obtained. This may be due to several factors (Amundson, 1980), the most frequent of which are:

(1) The mechanism of the reaction changes over the temperature range studied.

(2) The form of rate expression employed does not correspond to the reaction occurring.

(3) Other rate processes, such as mass diffusion, are sufficiently slow to obscure the reaction rates.

(4) The temperature dependence of the preexponential factor becomes important.

1.4 Review of Literatures

Damm *et al.* (2002) determined the kinetics of the oxidation of methyl tert-butyl ether (MTBE) by potassium permanganate ($KMnO_4$) in a homogeneous aqueous batch system. The result shows that the oxidation of MTBE by $KMnO_4$ was second order overall and first order individually with respect to $KMnO_4$ and MTBE. The second- order rate constant was 1.426×10^{-6} L/mg/h. The half-life ranges from 55 to 495 h and is significantly higher compared to that reported for other oxidants. Moreover, the influence of pH on $KMnO_4$ oxidation of MTBE was demonstrated to have no significant effect on the reaction rate.

Hood *et al.* (2000) educated the kinetic rate law for the oxidation of percholroethylene (PCE) by potassium permanganate ($KMnO_4$). The objective of the study was to quantify the rate at which $KMnO_4$ oxidizes aqueous solutions of PCE over a range of concentration. In a series of homogeneous, observed and fitted data of nine experimental trials with excess oxidant concentrations ranging from 5 to 30 g/l was used to determine the reaction rate constant and the reaction order with respect to PCE and $KMnO_4$. The results indicate that the reaction is first-order with respect to both PCE and $KMnO_4$ with an overall specific reaction rate coefficient of 2.45 ± 0.65 M^{-1} min^{-1}.

Huang *et al.* (2001) studied the kinetics of oxidation of chlorinated ethenes (CEs) by potassium permanganate ($KMnO_4$). The CEs included perchloroethylene (PCE), tricholroethylene (TCE), three isomers of dichloroethylene (DCE) and vinyl chloride (VC). The experiments were investigated in phosphate-buffered solutions of pH 7 and ionic strength ~0.05 M under isothermal, completely mixed and zero headspace conditions. The results have shown that both $KMnO_4$ and all CEs (except VC) were fit with a first order decay model and the reaction appears to be second order overall. The second order rate constants at 20°C are 0.035 ± 0.004 M^{-1} s^{-1} (PCE), 0.80 ± 0.12 M^{-1} s^{-1} (TCE), 1.52 ± 0.05 M^{-1} s^{-1} (*cis*-DCE), 2.1 ± 0.2 M^{-1} s^{-1} (1,1-DCE), and 48.6 ± 0.9 M^{-1} s^{-1} (*trans*-DCE). Unlike other CEs, the degradation of VC by $KMnO_4$ appears to be a two-consecutive-step process. The second step, being the rate-limiting step, is of first order in VC and has E_a of 7.9 ± 1 kcal mol^{-1}. The E_a and entropy (ΔS^*) of the reaction between $KMnO_4$ and CEs (except VC) are in the range of 5.8-9.3 kcal mol^{-1} and -33 to –36 kcal mol^{-1} K^{-1}, respectively. Moreover, $KMnO_4$ is able to completely dechlorinate CEs, and the increase with number of chlorine substituents on the ethylene is directly proportional to the acidity of the solution but inversely proportional to the rate of reactions.

Huang *et al.* (2002) investigated the kinetics and mechanism of oxidation of tetrachloroethylene (PCE) by permanganate ($KMnO_4$) in aqueous solutions under constant pH, isothermal and zero headspace conditions. Experimental results have shown that the reaction, with an activation energy of 9.3±0.9 kcal/mol, is first-order in both PCE and $KMnO_4$ and appears to be independent of pH and ionic strength (I) over the range of pH 3-10 and I~0-0.2 M, respectively. The second-order rate constant at 20°C is 0.035±0.004 M^{-1} s^{-1}. However, the PCE degradation rates can be accelerated by increasing reaction temperature and oxidant concentration. The reaction may proceed through reaction pathways, greatly influenced by the acidity of the solution, to yield $CO_{2(g)}$, oxalic acid, formic acid and glycolic acid. Under acidic conditions (e.g., pH 3), the further oxidation pathway will dominate and PCE tends to be directly mineralized into CO_2 and chloride. Under neutral (e.g., pH 7) and alkaline conditions (e.g., pH 10), the hydroxylation pathway dominates the reaction and PCE is primary transformed into oxalic acid prior to complete PCE mineralization. In each case, all chlorine atoms in PCE can be rapidly and completely liberated during the reaction, as shown by the rate of chloride production nearly equal to the rate of PCE degradation.

Lesclaux *et al.* investigated the kinetic and mechanism for two types of reaction system. First type of reaction studied rate constants for $RO_2^{\bullet}+HO_2^{\bullet}$ reactions using laser-flash photolysis in which HO_2 radicals were in large excess compared to the RO_2 radical. The results indicated that rate constants increase with the number of carbon atoms of the RO_2 radical. Interestingly, for RO_2 radicals resulting from OH + terpene reactions react with HO_2 with rate equal to an upper limit ((2-2.2) x 10^{-11} cm^3 molecule^{-1} s^{-1}). The second type of reaction was studied the primary steps of the benzene oxidation. The study was focus on the thermodynamics of the reaction by adding the OH radical to the aromatic ring using both experimental and theoretical approaches. The results demonstrated that calculated thermochemical parameters are in good agreement with experimental data, thus adding to the reliability of results.

Li (2004) evaluated the enhancement of trichloroethylene (TCE) degradation by permanganate in the presence of surfactant. The surfactants used were hexadecyltrimethylammonium (HDTMA) bromide, a cationic surfactant, sodium dodecyl sulfate (SDS), a nonionic surfactant, an anionic surfactant and octylphenol ethylene oxide condensate. All experiments were performed in a continuous stir batch reactor system. The TCE degradation was determined by continuous monitoring the amount of chloride produced, which was then reverted to the rate of permanganate consumption. When no surfactants were present, it was found that the observed pseudo-first-order rate constant (k_{obs}) was 0.08-0.19 min^{-1} and the half-life ($t_{1/2}$) was 4-9 min for MnO_4^-. When the surfactant concentration was less than its critical micelle concentration (CMC), the k_{obs} values increased to 0.42-0.46 min^{-1} and the $t_{1/2}$ reduced to 1.5-1.7 min for MnO_4^-. As the surfactant concentration was greater than the CMC, the k_{obs} values increased to 0.56-0.58 min^{-1} and the $t_{1/2}$ reduced to 1.2-1.3 min. These results showed that combination of permanganate with a proper type of surfactant could speed up contaminant removal.

Liaw *et al.* (2001) proposed the behavior prediction of multiple runaway reaction of MEK oxidation reactions. In order to predict the runaway behavior of this process, it was necessary to determine the thermodynamic and kinetic parameters of individual reactions and a kinetic model. Then a model of the prediction curves was compared with experimental data. The results demonstrated that the behavior of multiple runaway reactions is more complex and difficult to predict compare with of a single runaway reaction and the model for the multiple runaway-reaction system can be used to predict both the time-temperature profile precisely, and the temperature-self heat rate curve approximately.

Saraswat *et al.* (2003) stated that quinolinium bromochromate (QBC) has been used as oxidizing agent for studying the oxidation of nine aliphatic primary alcohols in dimethylsulphoxide (DMSO). The oxidation reaction leads to the formation of the corresponding aldehyde and the reaction is first order with respect to both QBC and the alcohol. To determine the importance of cleavage of α-C-H bond in the rate-determining step, oxidation of [1,1-H_2]ethanol was studied. The results showed a substantial primary kinetic isotope effect in nineteen different organic solvents. Hydrogen ions has been used as catalyst with the form $k_{obs} = a + b[H]$ (a and b, for ethanol are $1.70 \pm 0.02 \times 10^{-3}$ s^{-1} and $1.71 \pm 0.03 \times 10^{-3}$ mol^{-1} dm^3 s^{-1} respectively). The observed hydrogen-ion dependence suggests that the reaction follows two mechanistic pathways, one is acid-independent and the other is acid dependent. The solvent effect was analyzed using Taft's and Swain's multiparametric equations. The results indicated that the rate of oxidation is susceptible to both polar and steric effects of the substituents. In the last section, the mechanism has been reported.

Sinbuathong *et al.* (2000) studied the removal of cyanide (CN^-) from laboratory wastewater using either sodium hypochlorite (NaOCl) and calcium hypochlorite ($Ca(OCl)_2$). The wastewaters with CN- concentrations ranging from 1-100 mg/l were prepared in NaOH solutions (pH 12.3). The product of chlorination was CNO^- which could be oxidized further to N_2. The residual CN^- left at any dose was determined by colorimetric method. The graphs were plotted to show the relationship of residual cyanide and the amount of NaOCl and $Ca(OCl)_2$ added to determine the optimum doses for each initial CN^- concentration. The chemical costs were calculated from the optimum doses. The results gave that; the optimum doses of NaOCl and $Ca(OCl)_2$ were Y = 17.3X and Y = 3.32X, respectively (where X = initial CN^- concentration in mg/l, and Y = chemical dose in mg/l). The chemical costs of NaOCl and ($Ca(OCl)_2$) were Y = 0.69X and Y = 0.50X, respectively (where X = initial CN^- concentration in mg/l, and Y = cost in bath/m^3 of wastewater). For the optimum doses of chemicals study found that 100% removal of this contaminant could be achieved. In the conclusion by considering the cost and dosage, $Ca(OCl)_2$ was more effective than NaOCl.

Yan and Schwartz (1999) investigated oxidative degradation and kinetics of chlorinated ethylenes (CE) by using potassium permanganate (MnO_4^-). Five chlorinated ethylenes including tetrachloroethylene (PCE), trichloroethylene (TCE), and three isomers of dichloroethylenes (DCEs) were performed in a series of batch kinetic tests. Experimental results have shown that the reaction was rapid decreased with pseudo-first-order rate constants ranging from 4.5 × 10^{-5} to 0.03 s^{-1} at MnO_4 = 1 mM. TCE oxidation has been used to confirm that it is independent of pH over the range of 4-8. The experiments also found that rate increased with a decreasing number of chlorine substituents on the ethylene. The higher reactivity of *trans*-DCE as compared to *cis*-DCE might caused by a significant steric effect due to the formation of a large cyclic activated complex. Furthermore, the activity of both Cl^- and hydrogen ions was monitored over time and suggests that the degradation products are much less harmful than the parent compounds. In TCE oxidation, spectrophotometric proved that MnO_4^- is reduced to form soluble colloidal manganese dioxide (MnO_2). However, the modeling results presented that the effect of MnO_2 on TCE degradation is significant when the system contains high concentration of MnO_4^- and total organic carbon (TOC).

1.5 Objectives

- To perform laboratory studies in order to determine the kinetic parameter for the oxidation of the selected VOCs; toluene, ethanol, and MEK.
- To determine the oxidation rate of various VOCs-oxidant system.
- To determine and verify the rate law for various VOCs-oxidant system.

1.6 Possible Achievement

- Obtain the rate law of VOCs-oxidant reaction that can be used to design VOCs treatment system using oxidation approach.

Chapter 2

EXPERIMENTAL

2.1 Chemicals

2.1.1 Volatile Organic Compounds, VOCs

- Acetone (99.5%, AR grade, Lab Scan)
- Benzene (99.7%, Merck, Germany)
- Ethanol (95%, AR grade, Lab Scan)
- Methanol (99.8%, Merck, Germany)
- Methyl Ethyl Ketone, MEK (99.5%, Merck)
- Toluene (99.5%, Merck, Germany)

2.1.2 Oxidizing chemicals

- Potassium permanganate, $KMnO_4$ (99%, Univar)
- Sodium hypochlorite solution in water, NaOCl (7±2%, Carlo Erba)

2.1.3 General chemicals

- Acetic acid (100%, AR grade, BDH)
- Potassium iodide, KI (99.7%, Carlo Erba)
- Sodium hydroxide, NaOH (99%, Lab Scan)
- Sodium thiosulfate, $Na_2S_2O_3$ (99.5-100.5%, Merck)
- Starch indicator solutions (Starch soluble, AR grade, BDH)

2.2 Instruments and Apparatus

2.2.1 Batch reactor system

- Reactor 2000 ml
- Agitator
- pH meter
- Speed control
- Temperature control

2.2.2 Gas Chromatography-Flame Ionization Detector (GC-FID)

- Gas Chromatography (model 5790A, Hewlett Packard), equipped with a flame ionization detector (detector: 300°C, injector: 250°C)
- Packed column: 10% OV-1 on Chromosorb WHP
- Carrier Gas: High Purity Nitrogen

2.2.3 Spectrophotometer

- Spectrophotometer (UV-120-01, Shimadzu)
- Wavelength: 525 nm
- Photometric range: Absorbance ranges "ABS 0-2"
- Sens: Low

2.2.4 Syringe 10 µl (Hewlett Packard)

2.2.5 Syringe filter 0.45 µm

2.2.6 Parafilm

2.2.7 Dropper

2.2.8 Spatula

2.2.9 Stop-watch

2.2.10 Microliter pipette and Tips

2.2.11 Magnetic stirrer and Magnetic bar

2.2.12 Mortar

2.2.13 Balances

2.2.14 Desiccator

2.2.15 Oven

2.3 Glassware

2.3.1 Beaker
2.3.2 Buret
2.3.3 Pipette
2.3.4 Flask
2.3.5 Volumetric pipette
2.3.6 Volumetric flask
2.3.7 Vial with screw cap and septa

2.4 Methodology

2.4.1 Preparation of VOCs solutions

The solution of VOCs for each experiment was prepared separately by adding predetermined amount of VOCs, using a micropipette, into a 2000 ml volumetric flask. The deionized water was then added to the volumetric flask to make a final volume of 2000 ml. The solution was then agitated using a magnetic stirrer and the homogeneous solution was obtained.

2.4.2 Preparation of Oxidizing solutions

Solutions of $KMnO_4$ and NaOCl of the required concentrations were prepared by dissolving the oxidizing chemicals (2.1.2) with deionized water. Then, the solutions were agitated using a magnetic stirrer. The stock solution was stored in flask and used freshly. For $KMnO_4$ solution, it was evaporated in the oven and stored in desiccator before using while NaOCl solution was kept in the dark and cool place.

2.4.3 Samples collecting

During the experiment, samples of 10 ml were collected at a fixed time interval from the batch reactor then sealed with parafilm and screw cap. Following, the sample was analyzed for VOCs and oxidant concentration immediately.

2.4.4 Analyzing of VOCs solutions

2.4.4.1 *Calibration curve of VOCs*

A series of VOCs standard solutions of known concentration were prepared by diluting the VOCs standard chemicals (2.1.1) with deionized water. Each of these standard solutions, 2.0 μl, were analyzed by using a gas chromatography at optimum conditions. A calibration curve was obtained by plotting the peak area versus the VOCs concentrations.

2.4.4.2 *Concentrations of VOCs in sample*

Samples concentrations were analyzed by using a gas chromatography in the same conditions of the calibration curve. From the knowledge of the peak area in samples, the VOCs concentrations in the samples can be determined from the calibration curve.

2.4.5 Analyzing of Oxidizing solutions

2.4.5.1 Calibration curve of $KMnO_4$

A series of $KMnO_4$ solutions of known concentrations were prepared by diluting $KMnO_4$ (2.1.2) with deionized water. The amount of light absorbed by each sample was measured by UV spectrophotometer and plotted against the concentration.

2.4.5.2 Concentrations of $KMnO_4$ in sample

Samples from the experiment were pre-filtered at 0.45 μm with syringe filler to remove manganese dioxide (MnO_2). The sample concentrations were diluted as necessary with deionized water to the value with in a range of spectrophotometer. The absorbances of unknown samples were measured at the same conditions of calibration curve. Finally, the concentrations of these unknown solutions were then determined from the calibration curve.

2.4.5.3 Calibration curve of NaOCl

The concentration of NaOCl can be determined by titration technique according to the following step. First, a series of standard solutions of known NaOCl concentrations was prepared by diluting NaOCl (2.1.2) in deionized water. Secondly, 2 ml of acetic acid and 1 g of KI were added in the solutions and it was titrated with standardized 0.025N of $Na_2S_2O_3$ until the yellow iodine color is almost disappear. A 1 ml of starch indicator solutions was then added and the titration was continued until the disappearance of the blue color. The amount of chlorine used was calculated and the calibration curve was then constructed by plotting the amount of chlorine usage versus concentration of NaOCl in standard sample.

2.4.5.4 Concentrations of NaOCl in sample

The 10 ml of samples was collected and titrated with 0.025N of $Na_2S_2O_3$ in the same method of preparing calibration curve. The amount of chlorine used was determined and the NaOCl concentration was determined from the calibration curve.

2.4.6 VOCs oxidation experiment

The VOCs oxidation experiments were conducted in a batch system that comprised of a reactor 2000 ml connected to the agitator, speed control, pH meter, and temperature control as diagrammatically shown in Figure 2-1.

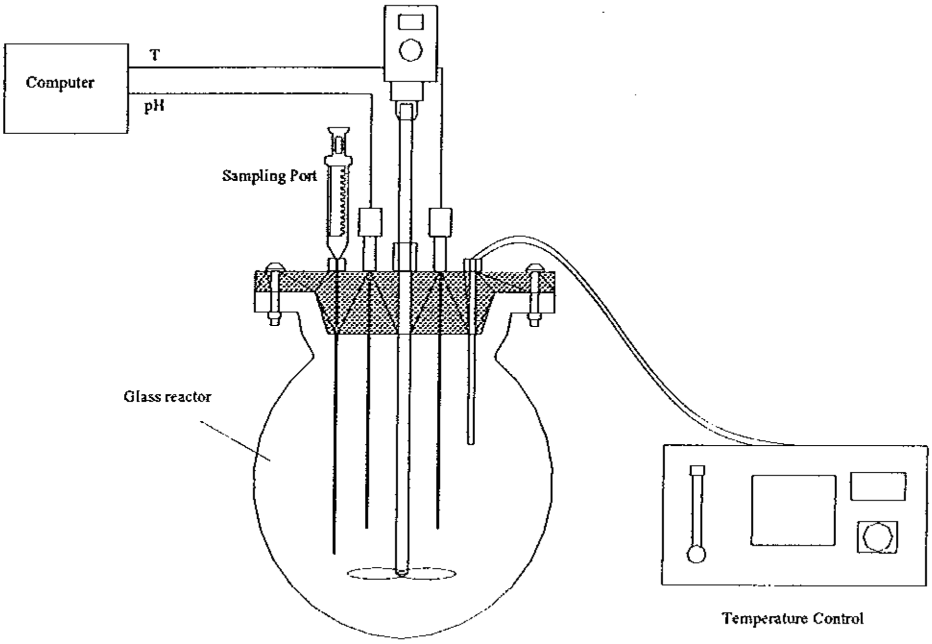


Figure 2-1 Schematic diagram of a batch reactor system.

The oxidation reactions were performed at a constant pH under completely mixed and isothermal conditions. In a typical experimental run, the VOCs solution was prepared, according to the procedure as mentioned above. The VOCs solution was then filled into the reactor and agitated with an agitator at 250 rpm for 10 minutes. A sample of 10 ml was then drawn from the reactor to determine the initial VOCs concentration $(C_{VOCs,0})$. Following the initial sampling, the reaction was initiated by filling predetermined concentration of the oxidant solution into the reactor and the initial oxidant concentration $(C_{oxidant,0})$ was determined. In case of using $KMnO_4$ as an oxidant, adjusted pH by adding NaOH and control at pH 11±1. During the oxidation reaction, several samples of 10 ml were drawn periodically during the experimental run and were analyzed for both VOCs concentration and oxidant concentration. Additional parameters including pH and temperatures were also measured over the reaction period. Several experiments were run in duplicate to ascertain the repeatability of the experimental procedures. The initial experimental conditions for all runs are listed in Table 2-1 to Table 2-16.

Table 2-1 Initial experimental conditions for study the suitable oxidant for selected VOCs at 29±1°C

Run No.	Initial Concentration x 10^5 (mol L^{-1})		T (°C)	pH
	VOCs	Oxidant		
T.5	Toluene 338 311 ppm	NaOCl 2830	29	11.6
T.14	Toluene 332	$KMnO_4$ 2596	30	11.5
E.14	Ethanol 492 229 ppm	NaOCl 278	30	11.9
E.2	Ethanol 498	$KMnO_4$ 258	30	11.7
M.5	MEK 511 368 ppm	NaOCl 921	29	11.4
M.11	MEK 516	$KMnO_4$ 921	29	11.5

Ethanol = 46.07
MEK = 72.11
Toluene = 92.14
$KMnO_4$ = 158.04
$NaOCl_4$ = 74.44

Table 2-2 Initial experimental conditions for the order of reaction determination from the oxidation reaction of toluene and NaOCl at 29±1°C

Run No.	Initial Concentration x 10^5 (mol L^{-1})		T (°C)	pH
	Toluene	NaOCl		
T.1	128	669	30	11.3
T.2	161	1636	29	11.4
T.3	185	4073	29	11.3
T.4	263	5407	29	11.8
T.5	338	2830	29	11.6
T.6	415	2962	30	11.3
T.7	489	2723	29	11.8
T.8	679	2917	30	11.5
T.9	1027	1108	29	11.5

Table 2-3 Initial experimental conditions for the order of reaction determination from the oxidation reaction of ethanol and $KMnO_4$ at 29±1°C

Run No.	Initial Concentration x 10^5 (mol L^{-1})		T (°C)	pH
	Ethanol	$KMnO_4$		
E.1	454	654	29	11.9
E.2	498	258	30	11.8
E.3	892	310	29	11.7
E.4	961	114	30	11.7
E.5	1044	377	29	11.7
E.6	1303	512	30	11.7
E.7	1627	279	30	11.8
E.8	2060	192	30	11.7
E.9	2790	321	30	11.8

Table 2-4 Initial experimental conditions for the order of reaction determination from the oxidation reaction of MEK and NaOCl at 29±1°C

Run No.	Initial Concentration x 10^5 (mol L^{-1})		T (°C)	pH
	MEK	NaOCl		
M.1	217	2380	29	11.8
M.2	226	3675	30	11.7
M.3	242	672	30	10.9
M.4	282	1458	30	11.3
M.5	511	921	29	11.4
M.6	773	1343	30	11.3
M.7	1024	1343	30	11.3
M.8	1055	1151	29	11.3
M.9	1422	1785	30	11.4

Table 2-5 Initial experimental conditions for the order of reaction determination from the oxidation reaction of MEK and $KMnO_4$ at 29±1°C

Run No.	Initial Concentration x 10^5 (mol L^{-1})		T (°C)	pH
	MEK	$KMnO_4$		
M.10	341	724	29	11.6
M.11	516	921	29	11.5
M.12	607	275	29	11.5
M.13	697	278	30	11.4
M.14	784	196	29	11.6
M.15	879	773	29	11.6
M.16	1312	285	30	11.6
M.17	1898	139	29	11.5
M.18	2997	146	29	11.6

Table 2-6 Initial experimental conditions for the rate constant determination from the oxidation reaction of toluene and NaOCl

Run No.	Initial Concentration x 10^5 (mol L^{-1})		T (°C)	pH
	Toluene	NaOCl		
T.8	679	2917	30	11.5
T.10	658	2917	35	11.5
T.11	727	2955	40	11.4
T.12	711	2994	45	11.4
T.13	719	2998	50	11.9

Table 2-7 Initial experimental conditions for the rate constant determination from the oxidation reaction of ethanol and $KMnO_4$

Run No.	Initial Concentration x 10^5 (mol L^{-1})		T (°C)	pH
	Ethanol	$KMnO_4$		
E.2	498	258	30	11.8
E.10	495	261	35	11.9
E.11	493	264	40	11.8
E.12	499	262	45	11.8
E.13	505	253	50	11.8

Table 2-8 Initial experimental conditions for the rate constant determination from the oxidation reaction of MEK and NaOCl

Run No.	Initial Concentration x 10^5 (mol L^{-1})		T (°C)	pH
	MEK	NaOCl		
M.9	1422	1785	30	11.4
M.19	1481	1767	35	11.2
M.20	1392	1759	40	11.2
M.21	1460	1762	45	11.1
M.22	1429	1766	50	11.1

Table 2-9 Initial experimental conditions for the rate constant determination from the oxidation reaction of MEK and $KMnO_4$

Run No.	Initial Concentration x 10^5 (mol L^{-1})		T (°C)	pH
	MEK	$KMnO_4$		
M.13	697	278	30	11.4
M.23	730	299	35	11.4
M.24	664	306	40	11.4
M.25	725	286	45	11.4
M.26	653	300	50	11.4

Table 2-10 Initial experimental conditions for the oxidation of toluene by NaOCl used for verifying the rate law at various conditions

Run No.	Initial Concentration x 10^5 (mol L^{-1})		T (°C)	pH
	Toluene	NaOCl		
T.15	164	2917	30	11.7
T.16	492	1382	37	11.3
T.17	797	2955	48	11.4

Table 2-11 Initial experimental conditions for the oxidation of ethanol by $KMnO_4$ used for verifying the rate law at various conditions

Run No.	Initial Concentration x 10^5 (mol L^{-1})		T (°C)	pH
	Ethanol	$KMnO_4$		
E.15	1977	577	30	11.9
E.16	869	510	37	11.8
E.17	468	278	48	11.9

Table 2-12 Initial experimental conditions for the oxidation of MEK by NaOCl used for verifying the rate law at various conditions

Run No.	Initial Concentration x 10^5 (mol L^{-1})		T (°C)	pH
	MEK	NaOCl		
M.27	592	652	31	11.6
M.28	943	921	36	11.3
M.29	2685	1343	47	11.1

Table 2-13 Initial experimental conditions for the oxidation of MEK by $KMnO_4$ used for verifying the rate law at various conditions

Run No.	Initial Concentration x 10^5 (mol L^{-1})		T (°C)	pH
	MEK	$KMnO_4$		
M.30	3022	674	30	11.6
M.31	695	1308	38	11.5
M.32	1123	238	48	11.3

Table 2-14 Initial experimental conditions for the oxidation reaction of benzene and NaOCl at 29±1°C

Run No.	Initial Concentration x 10^5 (mol L^{-1})		T (°C)	pH
	Benzene	NaOCl		
B.18	265	5548	30	11.8
B.19	334	2801	29	11.4
B.20	412	2942	29	11.7
B.21	683	2821	30	11.9

Table 2-15 Initial experimental conditions for the oxidation reaction of methanol and $KMnO_4$ at 29±1°C

Run No.	Initial Concentration x 10^5 (mol L^{-1})		T (°C)	pH
	Methanol	$KMnO_4$		
Me.18	453	691	30	12.1
Me.19	1039	382	29	12.1
Me.20	1308	519	30	12.1
Me.21	2775	330	29	12.1

Table 2-16 Initial experimental conditions for the oxidation reaction of acetone and NaOCl at 29±1°C

Run No.	Initial Concentration x 10^5 (mol L^{-1})		T (°C)	pH
	Acetone	NaOCl		
A.33	228	3675	29	11.8
A.34	284	1478	29	11.4
A.35	514	922	30	11.2
A.36	1020	1170	29	11.2

Chapter 3

RESULTS AND DISCUSSION

3.1 Suitable Oxidant for selected VOCs

Toluene, ethanol, and MEK had been chosen because these were representative for three groups of VOCs including aromatic, alcohol, and ketone, respectively, which are commonly used in many industries. As mentioned in Chapter1, these VOCs were used in the industries as solvent, raw materials, and intermediates for the manufacture of several types of products therefore they had good commercial value, on the other hand, they may cause the adverse health effects that may be cause cancer producing and their emission also cause photochemical pollution (Chang *et al.*, 2002; Decottignies and Gasnot, 2002; Guo and Murray, 2000 and Hernandez *et al.*, 2002).

For the oxidant used in the study, NaOCl and $KMnO_4$ were selected since they have been commonly used in water and wastewater treatment process (Benefield *et al.*, 1982 and Robert *et al.*, 2002).

3.1.1 Suitable Oxidant for Toluene

To determine the suitable oxidants for toluene, the oxidation reaction between toluene and selected oxidant, NaOCl and $KMnO_4$, was performed as detailed in Chapter 2. The concentrations of toluene were measured as a function of time. The toluene concentration-time data for investigated oxidant are compared in Table 3-1. The comparison results are also shown in Figure 3-1. From Figure 3-1 it clearly shown that the concentration of toluene, when NaOCl was used as an oxidant, was significantly decreased with increasing time. On the contrary, when $KMnO_4$ was used as an oxidant, the concentration of toluene was not decreased over a similar time period. This implies that under the same condition toluene can be oxidized by NaOCl faster than $KMnO_4$. Thus NaOCl is a suitable oxidant for toluene.

Table 3-1 The concentration of toluene as a function of time for the comparison of toluene oxidized with NaOCl and $KMnO_4$ at 29±1°C

Time (minutes)	Toluene-Concentration x 10^5 (mol L^{-1})	
	oxidized with NaOCl *	oxidized with $KMnO_4$ **
0	338	332
5	270	331
15	246	329
30	238	330
60	227	332
90	202	329
120	181	329

* Data from Run No. T.5 in Appendix B ** Data from Run No. T.14 in Appendix B

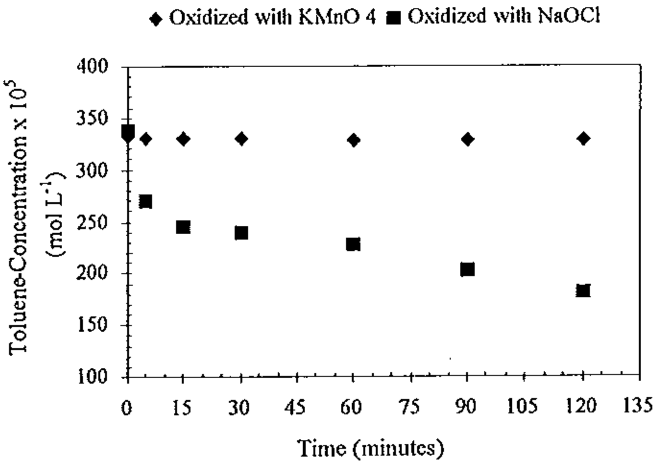


Figure 3-1 The comparison of the degradation curve of toluene oxidized with NaOCl and $KMnO_4$

3.1.2 Suitable Oxidant for Ethanol

The oxidation of ethanol by using NaOCl and $KMnO_4$ was performed at condition listed in Table 2-1. The concentration-time data for the oxidation of ethanol were measured and illustrated in Table 3-2 and Figure 3-2. It can be observed from Figure 3-2 that the oxidation rate of ethanol by using NaOCl and $KMnO_4$ in the first 30 minutes were approximated, but after 30 minutes it clearly shown that the oxidation rate of ethanol by using $KMnO_4$ were higher than of NaOCl. Hence, $KMnO_4$ is a suitable oxidant for ethanol.

Table 3-2 The concentration of ethanol as a function of time for the comparison of ethanol oxidized with NaOCl and $KMnO_4$ at 29±1°C

Time (minutes)	Ethanol-Concentration x 10^5 (mol L^{-1})	
	oxidized with NaOCl*	oxidized with $KMnO_4$**
0	492	498
5	489	493
15	485	483
30	481	469
60	478	440
90	478	409
120	474	400

* Data from Run No. E.14 in Appendix B ** Data from Run No. E.2 in Appendix B

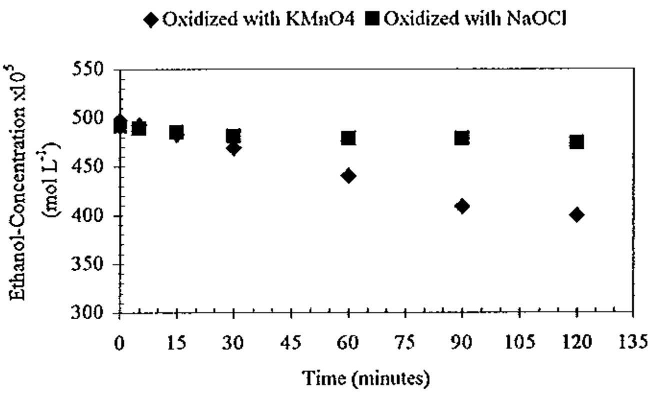


Figure 3-2 The comparison of the degradation curve of ethanol oxidized with NaOCl and $KMnO_4$

3.1.3 Suitable Oxidant for MEK

NaOCl and $KMnO_4$ were also used to oxidize MEK. The oxidation conditions for MEK oxidation reaction studied are listed in Table 2-1. The oxidation results of MEK using different oxidant are compared in Table 3-3 and Figure 3-3. From such figure, we can see that MEK was oxidized well by both NaOCl and $KMnO_4$. However, the initial oxidation rate by using $KMnO_4$ was significantly higher than that of NaOCl. This may be attributed to the forming of brown precipitate of manganese dioxide (MnO_2) which can be performed as a catalyst and thus enhances the oxidation rate. From this investigation, we can say that both NaOCl and $KMnO_4$ are suitable for MEK oxidation.

Table 3-3 The concentration of MEK as a function of time for the comparison of MEK oxidized with NaOCl and $KMnO_4$ at 29±1°C

Time (minutes)	MEK-Concentration x 10^5 (mol L^{-1})	
	oxidized with NaOCl*	oxidized with $KMnO_4$**
0	511	516
5	461	447
15	440	369
30	408	283
60	344	172
90	277	171
120	230	169

* Data from Run No. M.5 in Appendix B ** Data from Run No. M.11 in Appendix B

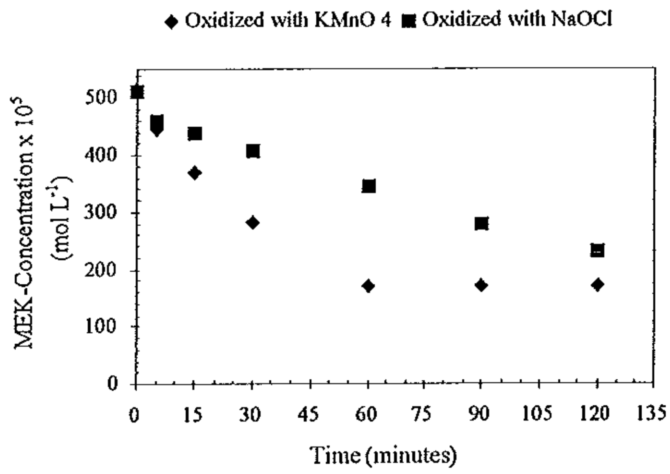


Figure 3-3 The comparison of the degradation curve of MEK oxidized with NaOCl and $KMnO_4$

From the experimental result for all cases investigated, we can conclude that the appropriated oxidant that suite for the oxidation of toluene is NaOCl, for ethanol is $KMnO_4$, and for MEK are NaOCl and $KMnO_4$. In later section, the determination of using these oxidant are discussed to modify the rate law for the oxidation of toluene, ethanol, and MEK.

3.2 Rate Law Determination

3.2.1 Order of Reaction

In this section, the rate laws for the oxidation of toluene, ethanol and MEK by using suitable oxidant found in previous section were investigated. For each VOCs, two sets of oxidation reaction were perform. The first set of reaction was conducted at room temperature with various VOCs and oxidant concentrations as detail in Table 2-2, Table 2-3, Table 2-4 and Table 2-5 for toluene, ethanol, and MEK, respectively. During the experimental runs the temperatures and the pH were monitored through out the experiment. The temperature was constant over the reaction period while the pH was slightly varied within ± 0.5. This, however, has no significant effect on the reaction rate. (Damm *et al.*, 2002; Huang *et al.*, 2002 and Yan and Schwartz, 1999).

From results of each experimental run, the plots of reactant concentrations versus times were made (see Appendix B). Such a plot also called a *concentration-time curve*. The resulting from concentration-time curve will be suggested that how the concentration of the reactants varies with time and how the rate was expressed mathematically.

A typical graph showing the degradation of toluene, ethanol and MEK are presented in Figure 3-4, Figure 3-5, Figure 3-6, and Figure 3-7, respectively. The results in Figure 3-4 to Figure 3-7 depicted the degradation behavior. Apparently, they were indicated that the concentration of toluene, ethanol and MEK were decreased with increasing time.

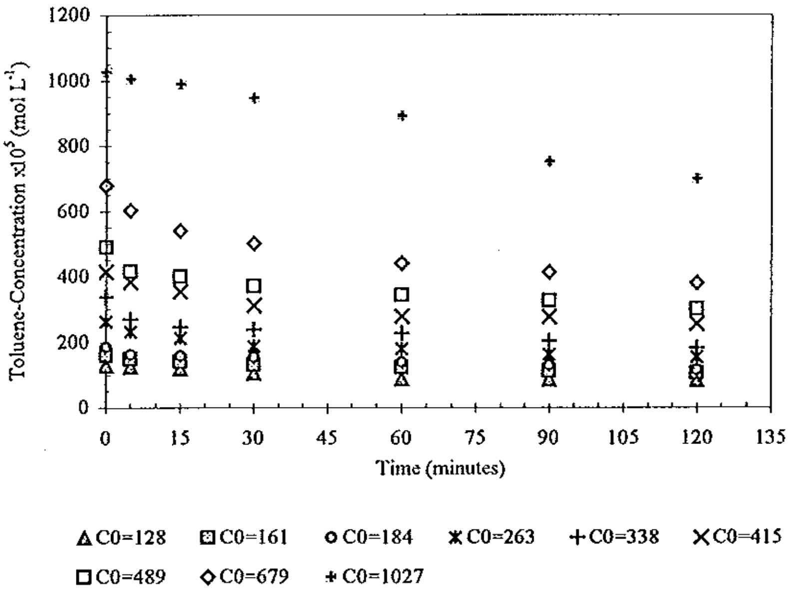


Figure 3-4 Toluene concentration-time curve for the oxidation of toluene by NaOCl at various initial toluene concentrations

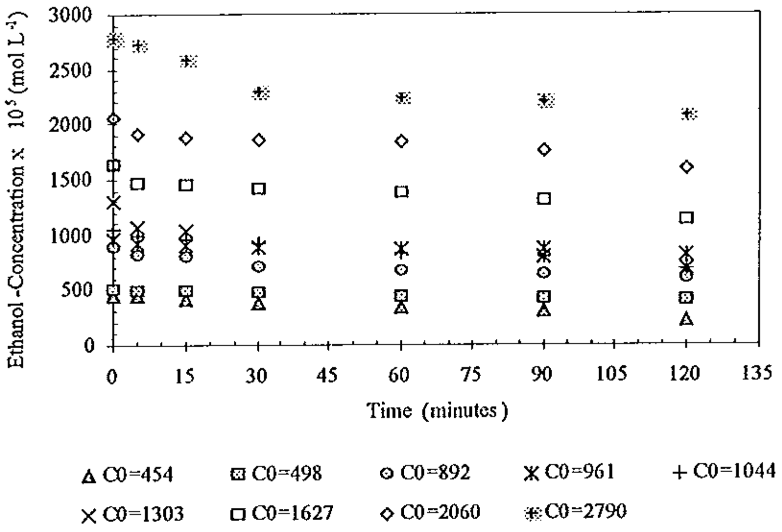


Figure 3-5 Ethanol concentration-time curve for the oxidation of ethanol by $KMnO_4$ at various initial ethanol concentrations

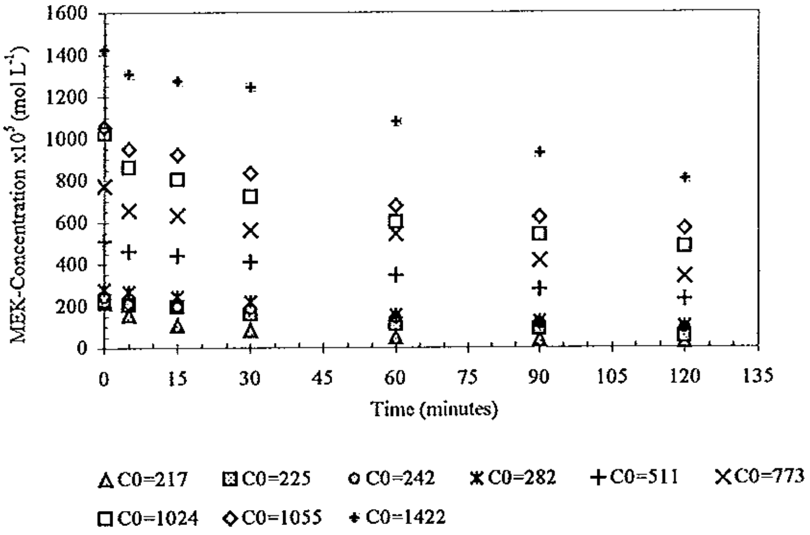


Figure 3-6 MEK concentration-time curve for the oxidation of MEK by NaOCl at various initial MEK concentrations

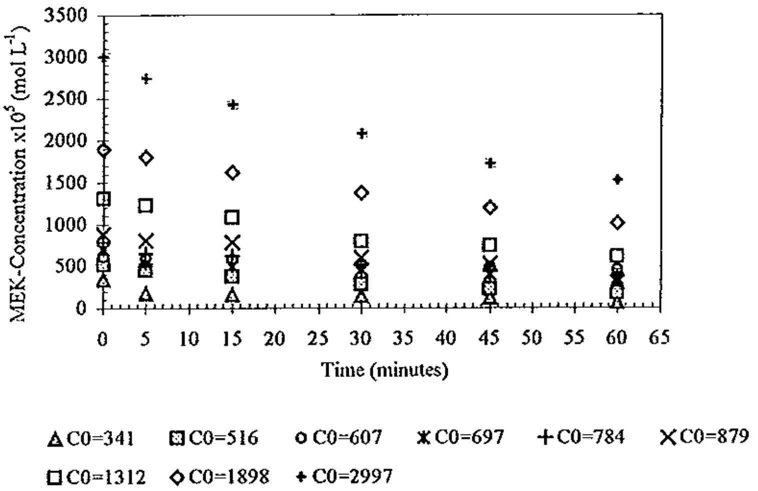


Figure 3-7 MEK concentration-time curve for the oxidation of MEK by $KMnO_4$ at various initial MEK concentrations

To avoid the errors from the occurrence of other effects such as the presence of a significant reverse reaction by using the differential method or the decomposition of reagent by using the integral method. Thus the initial rate method was employed to determine the kinetic parameters. At the beginning of the reaction, the concentrations of VOCs, as well as the concentrations of oxidants, are known. The rate law for the degradation, Eq. (42), could be rewritten as Eq. (47)

$$-r_{vocs,0} = kC^{\alpha}_{vocs,0}C^{\beta}_{oxidant,0} \qquad (47)$$

where $-r_{vocs,0}$ is the initial reaction rate for VOCs (i.e., toluene, ethanol and MEK) (mol L^{-1}min^{-1}), $C_{vocs,0}$ is the initial concentration of VOCs (mol L^{-1}), $C_{oxidant,0}$ is the initial concentration of oxidants (i.e., NaOCl and $KMnO_4$) (mol L^{-1}), k is rate constant, α is the order of the reaction with respect to the VOCs, and β is the order with respect to the oxidant.

The initial rate of VOCs could be found from the tangent of the concentration-time curves (by differentiating the experimental data) and extrapolating to zero time. Thus, for constant-volume batch reactor, the initial rates could be express as Eq (48):

$$-r_{VOCs,0}=\left(\frac{dC_{VOCs}}{dt}\right)_{t=0} \tag{48}$$

Using curve fitting fit data from each experimental run. As expected, the concentration-time profile in all runs were fit well with an exponential curve, of the form;

$$C_{VOCs}(t)=Be^{a_1 t} \tag{49}$$

where C_{VOCs} is the concentration of VOCs (mol L^{-1}), B and a_1 are empirical fitting parameters.

Substrate Eq. (49) into Eq. (48), one obtains;

$$-r_{VOCs,0}=\left(\frac{d\left(Be^{a_1 t}\right)}{dt}\right)_{t=0} \tag{50}$$

The values of B, a_1 and $-r_{vocs,o}$ for each run for the oxidation of toluene, ethanol, and MEK are summarized in Table 3-4 to 3-7.

Table 3-4 The values of B, a_1 and $-r_{Toluene,0}$ for the oxidation of toluene by NaOCl at 29±1°C

Run No.	$B\,x10^3$	$a_1\,x\,10^3$	$-r_{Toluene,0}\,x\,10^6$ (mol L^{-1} min^{-1})	r^2
T.1	1.20	-3.80	4.56	0.90
T.2	1.50	-3.30	4.95	0.95
T.3	1.70	-3.30	5.71	0.95
T.4	2.30	-4.00	9.20	0.87
T.5	2.90	-4.00	11.47	0.83
T.6	3.80	-3.70	13.97	0.87
T.7	4.40	-3.40	14.93	0.87
T.8	6.10	-4.30	26.14	0.90
T.9	10.40	-3.30	34.32	0.98

Table 3-5 The values of B, a_1 and $-r_{Ethanol,0}$ for the oxidation of ethanol by $KMnO_4$ at 29±1°C

Run No.	$B \times 10^3$	$a_1 \times 10^3$	$-r_{Ethanol,0} \times 10^6$ (mol L^{-1} min^{-1})	r^2
E.1	4.60	-5.50	25.30	0.97
E.2	5.00	-1.90	9.50	0.98
E.3	8.30	-2.90	24.07	0.90
E.4	9.30	-1.20	11.16	0.89
E.5	10.20	-3.10	31.62	0.98
E.6	11.30	-4.30	48.59	0.86
E.7	15.40	-2.30	35.42	0.89
E.8	19.80	-1.60	31.68	0.87
E.9	26.70	-2.30	61.41	0.85

Table 3-6 The values of B, a_1 and $-r_{MEK,0}$ for the oxidation of MEK by NaOCl at 29±1°C

Run No.	$B \times 10^3$	$a_1 \times 10^3$	$-r_{MEK,0} \times 10^6$ (mol L^{-1} min^{-1})	r^2
M.1	1.60	-16.10	25.76	0.94
M.2	2.30	-11.50	26.45	0.99
M.3	2.30	-7.80	17.94	0.99
M.4	2.80	-8.80	24.64	0.99
M.5	4.90	-6.30	30.87	0.99
M.6	7.10	-6.00	42.60	0.95
M.7	9.00	-5.70	51.30	0.94
M.8	9.90	-5.00	49.50	0.95
M.9	13.90	-4.50	62.55	0.99

Table 3-7 The values of B, a_1 and $-r_{MEK,0}$ for the oxidation of MEK by $KMnO_4$ at 29±1°C

Run No.	$B \times 10^3$	$a_1 \times 10^3$	$-r_{MEK,0} \times 10^6$ (mol L^{-1} min^{-1})	r^2
M.10	2.60	-20.30	52.78	0.84
M.11	5.00	-18.00	90.00	0.99
M.12	6.10	-5.00	30.50	0.98
M.13	6.10	-9.70	59.17	0.90
M.14	7.30	-11.60	84.68	0.98
M.15	9.30	-16.20	150.66	0.93
M.16	12.90	-13.00	167.70	0.98
M.17	19.00	-10.40	197.60	0.99
M.18	29.20	-11.30	329.96	0.99

The reaction orders (α and β) can be achieved by fitting $-r_{VOCs,0}$, $C_{VOCs,0}$, and $C_{oxidant,0}$ onto Eq. (47), then non-linear regression techniques was used to determine the constant in rate law equation. (see the detail in Appendix C). The result is given in Table 3-8.

Table 3-8 Summary of the reaction orders of the oxidation reaction of toluene, ethanol, and MEK at the temperature of 29±1°C

VOCs-Oxidant	α	β	r^2
Toluene-NaOCl	1.10	0.11	0.99
Ethanol-$KMnO_4$	0.83	0.84	0.99
MEK-NaOCl	0.55	0.23	0.99
MEK-$KMnO_4$	1.25	0.45	0.98

3.2.2 Reaction Rate Constant and Activation Energy

To determine the rate constant, k, the oxidation reactions of interested VOCs and specific oxidant were performed the same as previous section but the initial VOCs and oxidant concentration were fixed while the reaction temperatures were varied in the range of 30 to 50°C. The summarized of experimental conditions are shown in Table 2-6 to Table 2-9. The concentration-time data were measured and detailed in Appendix B. For each run, the values of B, a_1 and $-r_{vocs,o}$ were determined from concentration-time data and are summarized in Table 3-9 to 3-12.

Table 3-9 The values of B, a_1 and r^2 for the oxidation of toluene by NaOCl at various temperatures (30, 35, 40, 45 and 50°C)

Run No.	T (°C)	$B \times 10^3$	$a_1 \times 10^3$	r^2
T.8	30	6.10	-4.30	0.90
T.10	35	6.50	-4.90	0.99
T.11	40	7.30	-6.00	0.99
T.12	45	7.60	-6.70	0.96
T.13	50	6.20	-9.90	0.98

Table 3-10 The values of B, a_1 and r^2 for the oxidation of ethanol by $KMnO_4$ at various temperatures (30, 35, 40, 45 and 50°C)

Run No.	T (°C)	$B \times 10^3$	$a_1 \times 10^3$	r^2
E.2	30	5.00	-1.90	0.98
E.10	35	4.90	-2.80	0.99
E.11	40	4.90	-3.40	0.99
E.12	45	4.50	-4.50	0.94
E.13	50	4.30	-5.70	0.90

Table 3-11 The values of B, a_l and r^2 for the oxidation of MEK by NaOCl at various temperatures (30, 35, 40, 45 and 50°C)

Run No.	T (°C)	$B \times 10^3$	$a_l \times 10^3$	r^2
M.9	30	13.90	-4.50	0.99
M.19	35	14.30	-5.30	0.99
M.20	40	12.30	-7.10	0.96
M.21	45	14.50	-8.00	0.99
M.22	50	13.40	-10.50	0.95

Table 3-12 The values of B, a_l and r^2 for the oxidation of MEK by $KMnO_4$ at various temperatures (30, 35, 40, 45 and 50°C)

Run No.	T (°C)	$B \times 10^3$	$a_l \times 10^3$	r^2
M.13	30	6.10	-9.70	0.90
M.23	35	6.40	-11.90	0.92
M.24	40	5.50	-14.00	0.88
M.25	45	7.30	-13.50	0.98
M.26	50	5.90	-18.10	0.96

In order to determine the activation parameters (i.e., activation energy and frequency factor), the rate constant (k) at temperatures of 30, 35, 40, 45 and 50°C were determined by substituting initial VOCs concentration, initial oxidant concentration and the predetermined order of reaction (α and β) into Eq. (47). Once the rate constant at specific is known, the activation energy can then be determined using the linearized Arrhenius equation as expressed by Eq. (51)

$$\ln k = \ln A - \left(\frac{E_a}{R}\right)\frac{1}{T} \tag{51}$$

This equation applied to all rate constants, regardless of the order of reaction. The summarized of values of $-r_{vocs,o}$, *ln k*, and *1/T* for the oxidation at various temperatures are listed in Table 3-13 to 3-16.

Table 3-13 The values of $-r_{Toluene,0}$, *ln k*, and *1/T* for the oxidation of toluene by NaOCl used for calculating activation energy and frequency factor

Run No.	$-r_{Toluene,0} \times 10^6$ (mol L^{-1} min^{-1})	$k \times 10^3$	$ln\ k$	$T (K)$	$1/T \times 10^5$ (K^{-1})
T.8	26.23	9.39	-4.67	303.15	329.87
T.10	31.85	12.00	-4.42	308.15	324.52
T.11	43.80	14.84	-4.23	313.15	319.34
T.12	50.92	17.28	-4.04	318.15	314.32
T.13	61.38	20.58	-3.88	323.15	309.45

Table 3-14 The values of $-r_{Ethanol,0}$, *ln k*, and *1/T* for the oxidation of ethanol by $KMnO_4$ used for calculating activation energy and frequency factor

Run No.	$-r_{Ethanol,0} \times 10^6$ (mol L^{-1} min^{-1})	$k \times 10^3$	$ln\ k$	$T (K)$	$1/T \times 10^5$ (K^{-1})
E.2	9.50	116.91	-2.15	303.15	329.87
E.10	13.72	167.93	-1.78	308.15	324.52
E.11	16.17	196.85	-1.63	313.15	319.34
E.12	20.25	245.12	-1.41	318.15	314.32
E.13	24.51	302.52	-1.20	323.15	309.45

Table 3-15 The values of $-r_{MEK,0}$, $\ln k$, and $1/T$ for the oxidation of MEK by NaOCl used for calculating activation energy and frequency factor

Run No.	$-r_{MEK,0} \times 10^6$ (mol L^{-1} min^{-1})	$k \times 10^3$	$\ln k$	T (K)	$1/T \times 10^5$ (K^{-1})
M.9	62.55	1.63	-6.42	303.15	329.87
M.19	75.79	1.94	-6.25	308.15	324.52
M.20	87.33	2.31	-6.07	313.15	319.34
M.21	116.00	2.99	-5.81	318.15	314.32
M.22	140.70	3.67	-5.61	323.15	309.45

Table 3-16 The values of $-r_{MEK,0}$, $\ln k$, and $1/T$ for the oxidation of MEK by $KMnO_4$ used for calculating activation energy and frequency factor

Run No.	$-r_{MEK,0} \times 10^6$ (mol L^{-1} min^{-1})	$k \times 10^3$	$\ln k$	T (K)	$1/T \times 10^5$ (K^{-1})
M.13	59.17	401.13	-0.91	303.15	329.87
M.23	76.16	471.69	-0.75	308.15	324.52
M.24	77.00	532.02	-0.63	313.15	319.34
M.25	98.55	628.03	-0.47	318.15	314.32
M.26	106.79	758.63	-0.28	323.15	309.45

Table 3-13 to 3-16 were represented that the rate of reaction increased with increasing temperature. This result was in agreed with at higher temperatures, a greater fraction of the reactants posses the necessary energy and the reaction proceeds faster.

The Arrhenius plot of toluene, ethanol and MEK at various temperatures was shown in Figure 3-8. The *lnk* versus *1/T* curve was highly linear as indicated by r^2 value of 0.98-1.00. This implies that the rate expression employed in previous section corresponds to the reaction occurring and the reaction mechanism is consistent over the investigated temperature range. The activation energy, E_a, and frequency factor can then be determined from the slope of Arrhenius plot according to Eq. (51). The E_a for different reaction systems including toluene-NaOCl, ethanol- $KMnO_4$, MEK-NaOCl, and MEK-$KMnO_4$ were 31.908, 37.190, 33.430, and 25.393 kJ mol^{-1}, respectively. These activation energy presented that there must be a minimum energy possessed by colliding molecules in order for a reaction to take place.

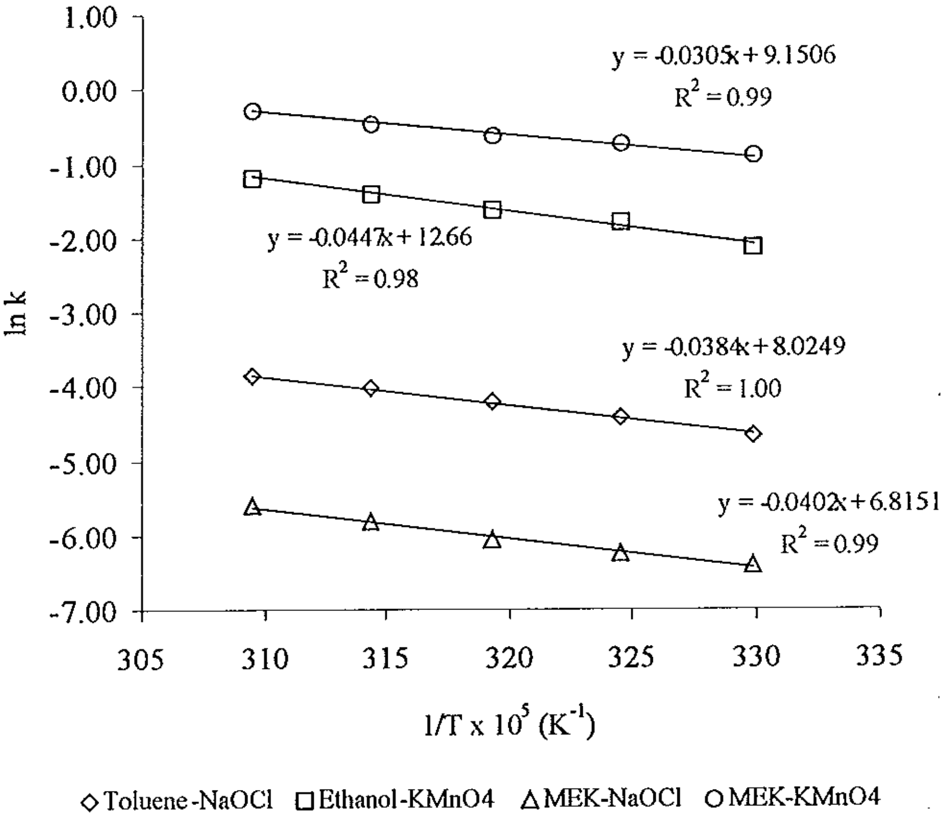


Figure 3-8 Plot of *lnk* versus *1/T* for determining the activation energy and frequency factor for the oxidation of toluene, ethanol, and MEK

Substitute the value of activation energy and the frequency factor into Eq. (45). the rate constants as function of temperature for the oxidation of toluene, ethanol, and MEK can be expressed as Eq. (52), (53), (54), and (55)

$$k(T) = 3{,}056e^{\frac{-31{,}908}{RT}} \tag{52}$$

$$k(T) = 314{,}897e^{\frac{-37{,}190}{RT}} \tag{53}$$

$$k(T) = 912e^{\frac{-33{,}430}{RT}} \tag{54}$$

$$k(T) = 9{,}420e^{\frac{-25{,}393}{RT}} \tag{55}$$

3.2.3 Rate Law

By combining the rate constant and the order of reaction obtained previously, we can expresses the rate law for the oxidation of toluene, ethanol, and MEK as a function of the reaction temperature as shown in Eq. (56), (57), (58), and (59), respectively.

$$-r_{Toluene} = 3{,}056e^{\frac{-31{,}908}{RT}} C_{Toluene}^{1.10} C_{NaOCl}^{0.11} \qquad mol\, L^{-1} \min^{-1} \tag{56}$$

$$-r_{Ethanol} = 314{,}897e^{\frac{-37{,}190}{RT}} C_{Ethanol}^{0.83} C_{KMnO_4}^{0.84} \qquad mol\, L^{-1} \min^{-1} \tag{57}$$

$$-r_{MEK} = 912e^{\frac{-33{,}430}{RT}} C_{MEK}^{0.55} C_{NaOCl}^{0.22} \qquad mol\, L^{-1} \min^{-1} \tag{58}$$

$$-r_{MEK} = 9{,}420e^{\frac{-25{,}393}{RT}} C_{MEK}^{1.25} C_{KMnO_4}^{0.45} \qquad mol\, L^{-1} \min^{-1} \tag{59}$$

The rate law for toluene-NaOCl oxidation can be estimated the reaction order to be first-order with respect to toluene and zero-order with respect to NaOCl, this implied that the oxidation reaction of toluene strongly depend with the concentration of toluene and independent with the concentration of NaOCl. Similar with the rate law for MEK-NaOCl oxidation, except that the reaction order with respect to MEK was half-order. The oxidation reaction between ethanol and $KMnO_4$ was determined to be first-order with respect to both ethanol and $KMnO_4$. This signified that the oxidation reaction of ethanol depend with both the concentration of ethanol and $KMnO_4$. For MEK-$KMnO_4$ oxidation, the reaction order with respect to MEK and $KMnO_4$ were estimated to be first-order and half-order, respectively. The oxidation reaction of MEK and $KMnO_4$ seem to depend with the concentration of MEK and slightly depend with the concentration of $KMnO_4$.

3.3 Rate law verification

To cover the verification of the rate law obtained from this study, another set of experiments using various initial concentrations of toluene, ethanol, MEK, NaOCl, and $KMnO_4$ at various temperatures were performed in random conditions. The initial conditions of these experiments are listed in Table 2-10 to 2-13. The concentrations of VOCs were analyzed as function of time. The values of B, a_l and r^2 were determined and listed in Table 3-17 to 3-20, respectively.

Table 3-17 The values of B, a_l and r^2 from the experimental data for the oxidation of toluene by NaOCl used for verifying the rate law at various conditions

Run No.	T (°C)	$B \times 10^3$	$a_l \times 10^3$	r^2
T.15	30	0.0016	-0.0033	0.93
T.16	37	0.0048	-0.0047	0.98
T.17	48	0.0076	-0.0083	0.99

Table 3-18 The values of B, a_1 and r^2 from the experimental data for the oxidation of ethanol by $KMnO_4$ used for verifying the rate law at various conditions

Run No.	T (°C)	$B x10^3$	$a_1 x 10^3$	r^2
E.15	30	0.0197	-0.0031	0.99
E.16	37	0.0087	-0.0046	0.99
E.17	48	0.0042	-0.0055	0.95

Table 3-19 The values of B, a_1 and r^2 from the experimental data for the oxidation of MEK by NaOCl used for verifying the rate law at various conditions

Run No.	T (°C)	$B x10^3$	$a_1 x 10^3$	r^2
M.27	31	0.0055	-0.0064	0.98
M.28	36	0.0088	-0.0076	0.96
M.29	47	0.0239	-0.0076	0.93

Table 3-20 The values of B, a_1 and r^2 from the experimental data for the oxidation of MEK by $KMnO_4$ used for verifying the rate law at various condition

Run No.	T (°C)	$B x10^3$	$a_1 x 10^3$	r^2
M.30	30	0.0263	-0.0121	0.92
M.31	38	0.0069	-0.0179	0.97
M.32	48	0.0111	-0.0140	0.98

From the concentration profile and temperature, the measured oxidation rates were obtained. The measured oxidation rate of toluene, ethanol, and MEK were then compared with the predicted value for various conditions, obtained from Eq. (56), (57), (58), and (59) as shown in Figure 3-9, Figure 3-10, Figure 3-11, and Figure 3-12, respectively.

As seen in Figure 3-9 to Figure 3-12 that the predicted value and the experimental value coincided very well over the oxidizing time. This confirms that the rate law of VOCs oxidation determined from this work can be used to satisfactorily predict the oxidation rate of VOCs at various concentrations of VOCs and oxidant over investigated range of reaction temperatures.

Table 3-21 The values of the measured oxidation rates compared with the predicted values at various temperatures for the oxidation of toluene by NaOCl

Time (minutes)	Reaction rate of toluene x 10^6 (mol L^{-1} min^{-1})								
	T = 30°C *			T = 37°C **			T = 48°C ***		
	Measure	Predict	|%Error|	Measure	Predict	|%Error|	Measure	Predict	|%Error|
0	5.28	5.69	7.25	22.56	23.30	3.18	63.08	65.85	4.21
5	5.19	5.58	6.86	22.04	22.90	3.76	60.52	60.42	0.15
15	5.03	4.91	2.34	21.02	20.53	2.40	55.70	51.82	7.49
30	4.78	4.60	4.07	19.59	19.56	0.19	49.18	45.85	7.26
60	4.33	4.20	3.11	17.02	15.94	6.74	38.34	38.50	0.41
90	3.92	3.83	2.35	14.78	13.98	5.73	29.89	27.47	8.79
120	3.55	3.63	2.23	12.84	12.81	0.19	23.30	20.92	11.38

* Run No. T.15 in Appendix B ** Run No. T.16 in Appendix B *** Run No. T.17 in Appendix B

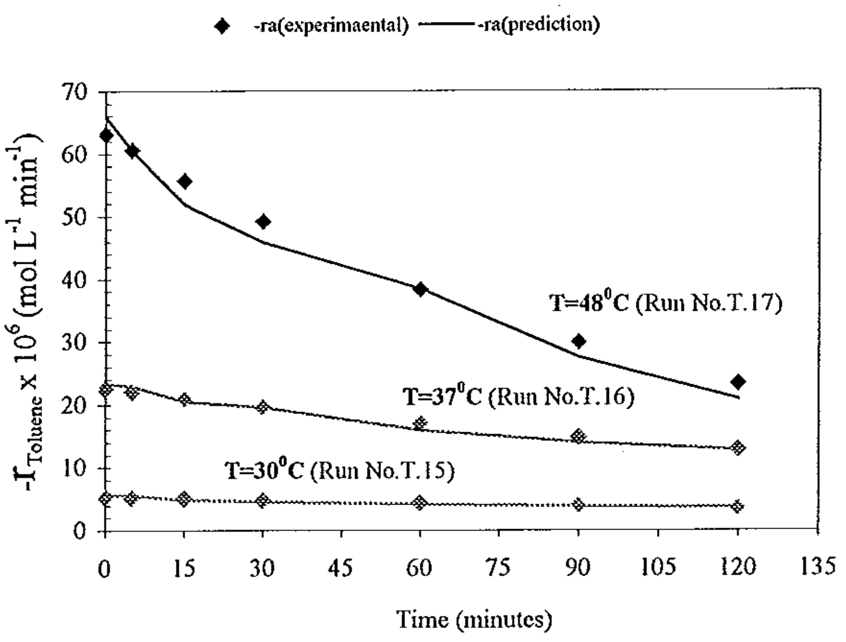


Figure 3-9 Comparison for the oxidation rate of toluene by NaOCl between the experimental values and the prediction values at temperatures of 30, 37, and 48°C

Table 3-22 The values of the measured oxidation rates compared with the predicted values at various temperatures for the oxidation of ethanol by $KMnO_4$

Time (minutes)	Reaction rate of ethanol x 10^6 (mol L^{-1} min^{-1})								
	T = 30°C *			T = 37°C **			T = 48°C ***		
	Measure	Predict	|%Error|	Measure	Predict	|%Error|	Measure	Predict	|%Error|
0	61.07	62.07	2.09	40.02	39.62	1.00	23.10	23.38	1.18
5	60.13	60.99	1.42	39.11	38.70	1.05	22.47	20.26	10.92
15	58.30	56.83	2.57	37.35	37.66	0.82	21.27	18.99	12.00
30	55.65	54.31	2.45	34.86	36.84	5.37	19.59	16.99	15.29
60	50.70	49.93	1.54	30.37	34.27	11.40	16.61	15.52	7.02
90	46.20	45.68	1.14	26.45	28.70	7.82	14.08	13.98	0.72
120	42.10	42.28	0.43	23.04	25.54	9.79	11.94	11.77	1.45

* Run No. E.15 in Appendix B ** Run No. E.16 in Appendix B *** Run No. E.17 in Appendix B

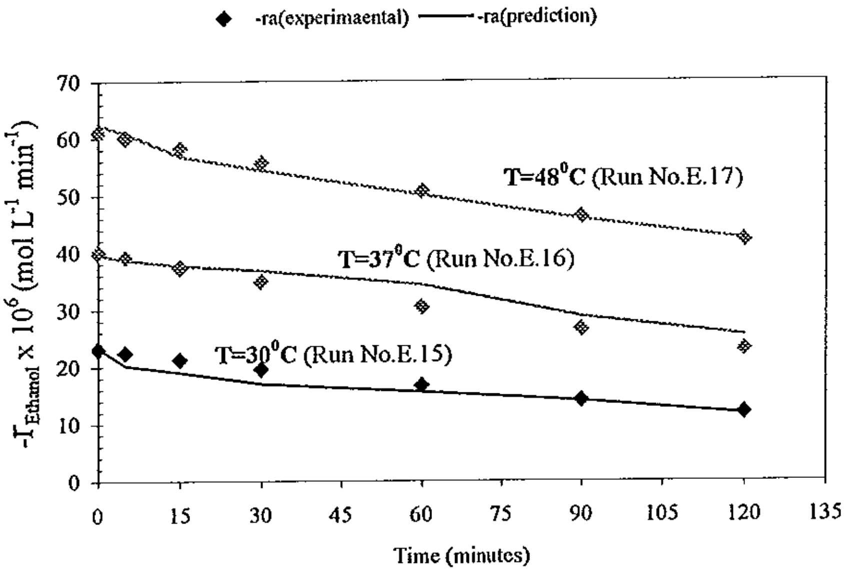


Figure 3-10 Comparison for the oxidation rate of ethanol by $KMnO_4$ between the experimental values and the prediction values at temperatures of 30, 37, and 48°C

Table 3-23 The values of the measured oxidation rates compared with the predicted values at various temperatures for the oxidation of MEK by NaOCl

Time (minutes)	Reaction rate of MEK x 10^6 (mol L^{-1} min^{-1})								
	T = 31°C *			T = 36°C **			T = 47°C ***		
	Measure	Predict	|%Error|	Measure	Predict	|%Error|	Measure	Predict	|%Error|
0	35.20	32.55	8.14	63.36	56.17	12.79	181.64	170.71	6.40
5	34.09	30.68	11.13	61.12	53.62	13.98	174.87	161.06	8.57
15	31.98	29.07	10.01	56.87	51.09	11.33	162.07	144.66	12.04
30	29.05	27.00	7.59	51.05	49.81	2.49	144.61	134.40	7.59
60	23.98	24.71	2.98	41.13	42.91	4.14	115.13	114.36	0.67
90	19.79	22.05	10.24	33.14	38.70	14.35	91.65	107.11	14.43
120	16.33	20.32	19.63	26.70	35.46	24.70	72.97	98.37	25.82

* Run No. M.27 in Appendix B ** Run No. M.28 in Appendix B *** Run No. M.29 in Appendix B

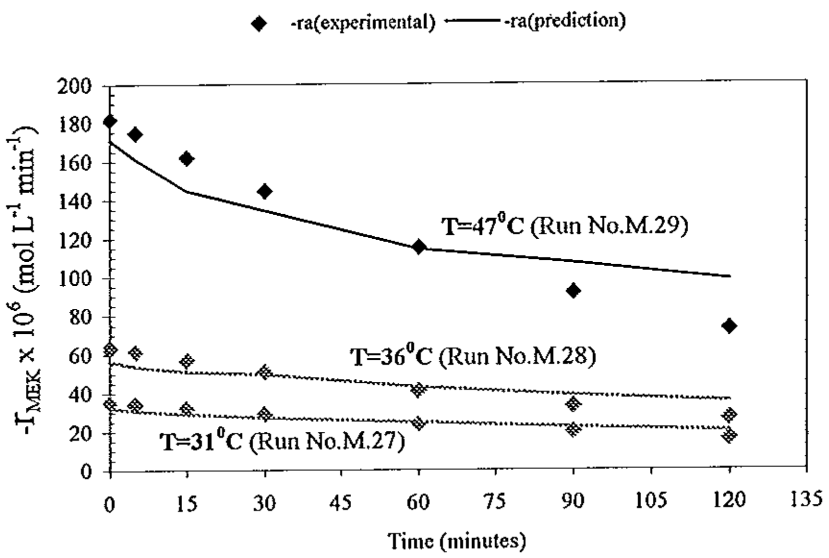


Figure 3-11 Comparison for the oxidation rate of MEK by NaOCl between the experimental values and the prediction values at temperatures of 31, 36, and 47°C

Table 3-24 The values of the measured oxidation rates compared with the predicted values at various temperatures for the oxidation of MEK by $KMnO_4$

Time (minutes)	Reaction rate of MEK x 10^6 (mol L^{-1} min^{-1})								
	T = 30°C *			T = 38°C **			T = 48°C ***		
	Measure	Predict	|%Error|	Measure	Predict	|%Error|	Measure	Predict	|%Error|
0	31.82	37.68	15.55	12.35	1464	15.66	15.54	16.81	7.56
5	29.95	26.87	11.47	11.29	12.99	13.04	14.49	14.68	1.32
15	26.54	24.12	10.02	9.44	9.58	1.43	12.60	12.32	2.25
30	22.14	21.48	3.05	7.22	7.46	3.20	10.21	8.76	16.62
45	18.46	16.82	9.73	5.52	6.17	10.53	8.28	8.22	0.66
60	15.40	13.26	16.10	4.22	3.41	23.83	6.71	5.20	28.89

* Run No. M.30 in Appendix B ** Run No. M.31 in Appendix B *** Run No. M.32 in Appendix B

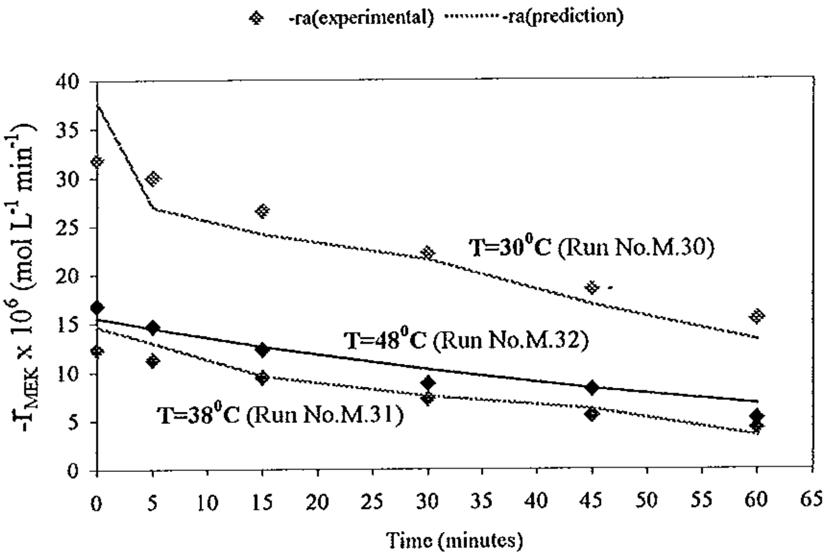


Figure 3-12 Comparison for the oxidation rate of MEK by $KMnO_4$ between the experimental values and the prediction values at temperatures of 30, 38, and 48°C

3.4 Oxidation of others VOCs using suitable oxidant used in this study

In previous section, we found that NaOCl, $KMnO_4$ and NaOCl, were the suitable oxidant for oxidation of toluene, ethanol and MEK, respectively. Thus NaOCl, $KMnO_4$ and NaOCl are then recommended for the oxidation of aromatic, alcohol and ketone. Three other organics compounds including benzene, methanol and acetone were selected and oxidized using NaOCl, $KMnO_4$ and NaOCl, respectively.

The oxidation of benzene using NaOCl as a oxidant was performed. The concentration of benzene was measured as function of time. The concentration profile can be explained by Eq. (49). The oxidation rates of benzene by using NaOCl were compared with that of toluene in Figure 3-13 and Table 3-25. It confirmed that benzene could be oxidized by NaOCl as expected. However the oxidation rate of benzene using NaOCl was lower than that of toluene throughout the reaction period as illustrated in Figure 3-13.

Table 3-25 The reaction rate of toluene and benzene as a function of time used for verifying the oxidation with NaOCl at 29±1°C

Time (minutes)	Reaction rate of VOCs x 10^6 (mol L^{-1} min^{-1})							
	T.4	B.18	T.5	B.19	T.6	B.20	T.8	B.21
	Toluene	Benzene	Toluene	Benzene	Toluene	Benzene	Toluene	Benzene
0	9.20	5.20	11.60	7.13	14.06	8.20	26.23	15.18
5	9.02	5.15	11.37	7.05	13.80	8.12	25.67	15.01
15	8.66	5.05	10.92	6.89	13.30	7.96	24.59	14.69
30	8.16	4.90	10.29	6.65	12.58	7.72	23.06	14.21
60	7.24	4.61	9.12	6.21	11.26	7.27	20.27	13.30
90	6.42	4.34	8.09	5.80	10.08	6.85	17.81	12.45
120	5.69	4.09	7.18	5.41	9.02	6.45	15.66	11.66

Table 3-26 The values of B, a_l for the oxidation of toluene and benzene used for verifying the oxidation with NaOCl at 29±1°C

Run No.	$B x10^3$	$a_l x 10^3$	r^2	Run No.	$B x10^3$	$a_l x 10^3$	r^2
T.4	2.30	-4.00	0.87	B.18	2.60	-2.00	0.95
T.5	2.90	-4.00	0.83	B.19	3.10	-2.30	0.86
T.6	3.80	-3.70	0.87	B.20	4.10	-2.00	0.99
T.8	6.10	-4.30	0.90	B.21	6.90	-2.20	0.97

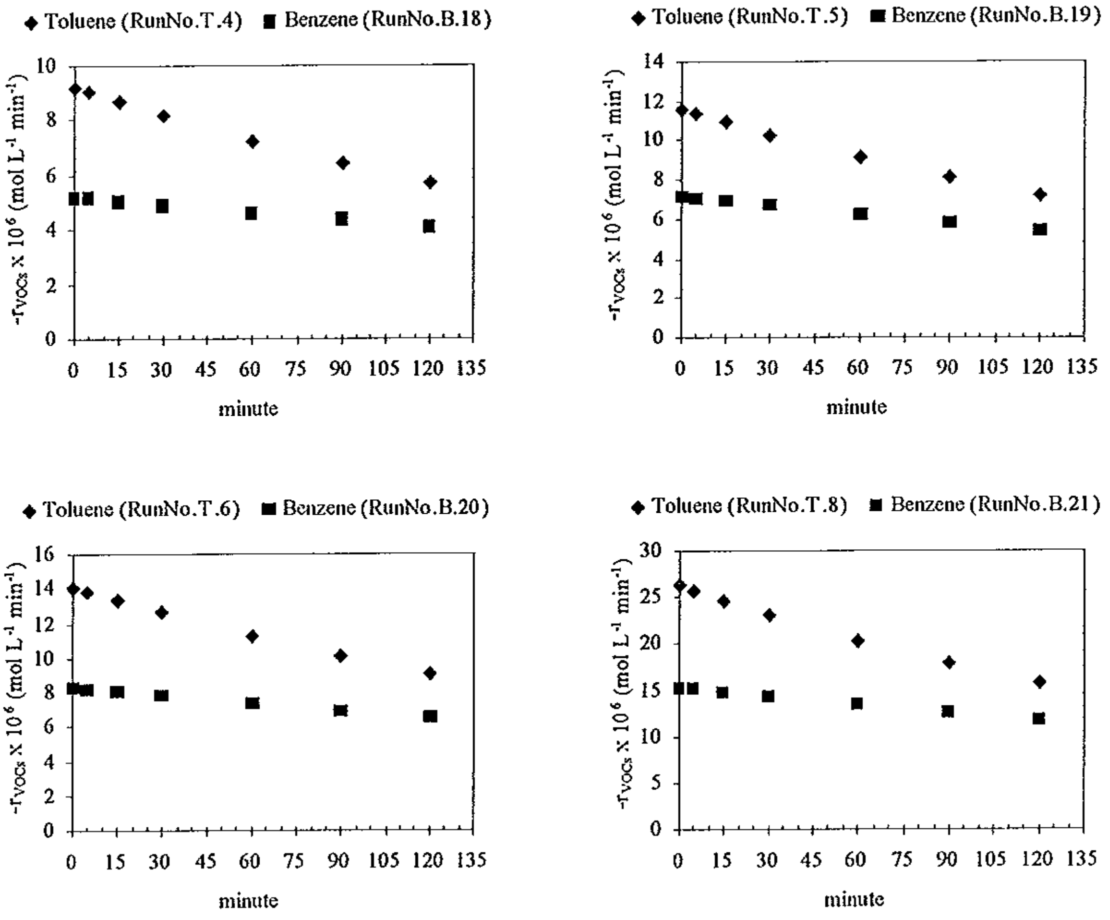


Figure 3-13 The comparison of the oxidation reaction rate of toluene and benzene by using NaOCl as an oxidant

With in the same method, the oxidation of methanol by using $KMnO_4$ was performed. The values of the *B* and a_l were summarized in Table 3-28. The oxidation rates were measured and compared with those of ethanol as shown in Figure 3-14. From Figure 3-14, it was clearly shown that methanol can be sufficiently oxidized using $KMnO_4$ and the oxidation rates of methanol were slightly higher than those of ethanol over the investigated concentration and reaction time. This is due to its smaller molecular size (methanol: CH_3OH, ethanol: C_2H_5OH) and its lower boiling point (methanol: 64.6°C, ethanol: 78.5°C).

Table 3-27 The reaction rate of ethanol and methanol as a function of time used for verifying the oxidation with $KMnO_4$ at 29±1°C

Time (minutes)	Reaction rate of VOCs x 10^6 (mol L^{-1} min^{-1})							
	E.1	Me.18	E.5	Me.19	E.6	Me.20	E.9	Me.21
	Ethanol	Methanol	Ethanol	Methanol	Ethanol	Methanol	Ethanol	Methanol
0	25.30	35.55	31.62	48.45	48.59	75.52	61.41	94.86
5	24.61	34.17	31.13	47.23	47.56	73.32	60.71	93.26
15	23.30	31.58	30.18	44.88	45.55	69.12	59.33	90.14
30	21.45	28.05	28.81	41.58	42.71	63.27	57.32	85.66
60	18.19	22.13	26.25	35.68	37.54	53.01	53.49	77.35
90	15.42	17.46	23.92	30.62	33.00	44.41	49.93	69.85
120	13.08	13.78	21.80	26.27	29.00	37.20	46.60	63.08

Table 3-28 The values of B, a_1 for the oxidation of ethanol and methanol used for verifying the oxidation with $KMnO_4$

Run No.	$B \times 10^3$	$a_1 \times 10^3$	r^2	Run No.	$B \times 10^3$	$a_1 \times 10^3$	r^2
E.1	4.60	-5.50	0.97	Me.18	4.50	-7.90	0.99
E.5	10.20	-3.10	0.98	Me.19	9.50	-5.10	0.92
E.6	11.30	-4.30	0.86	Me.20	12.80	-5.90	0.99
E.9	26.70	-2.30	0.85	Me.21	27.90	-3.40	0.99

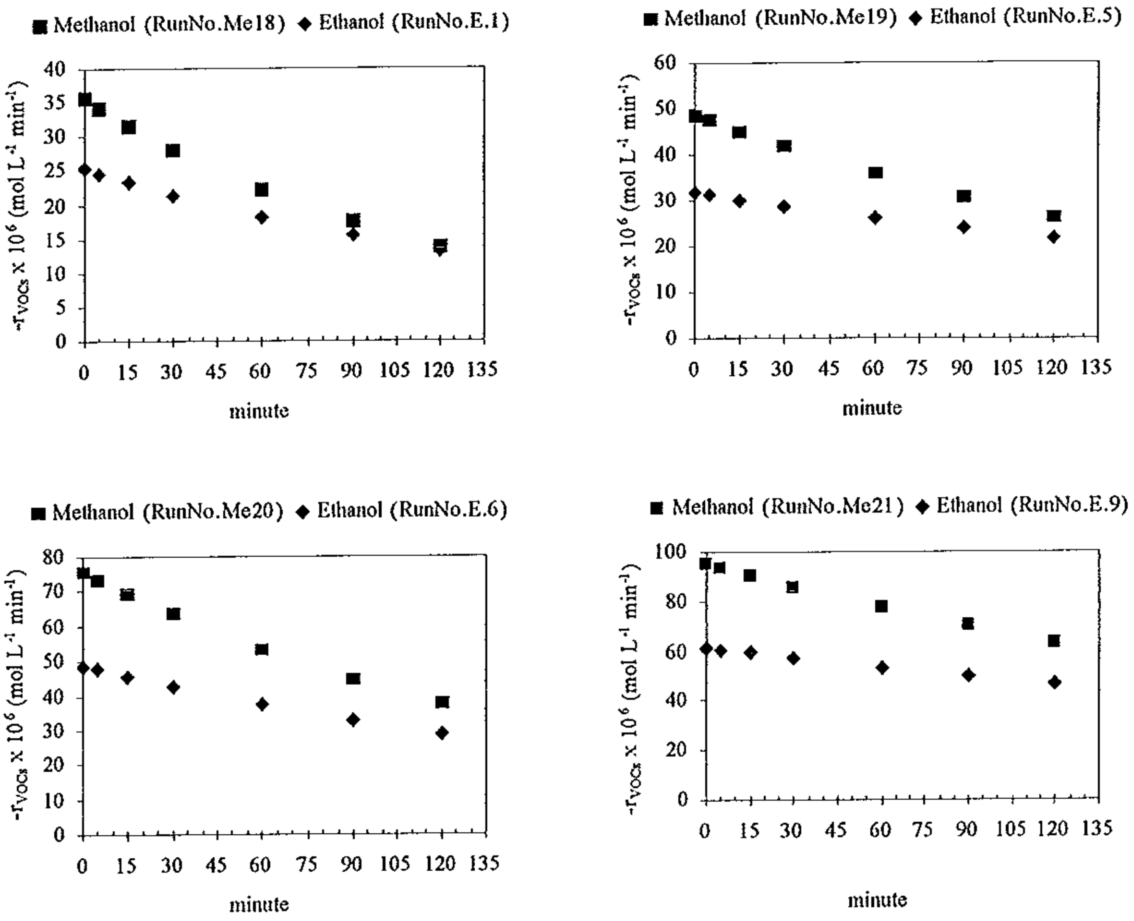


Figure 3-14 The comparison of the reaction rate between ethanol and methanol by using $KMnO_4$ as an oxidant

Finally, the oxidation of acetone by using NaOCl as an oxidant was performed. The concentrations profile of acetone were measured and the value *B* and a_j were summarized in Table 3-29. The reaction rates of acetone were measured and compared to that of MEK as illustrated in Figure 3-15. It again, as expected, NaOCl oxidized acetone well with the oxidation rate were very much similar to that of MEK as depicted in Figure 3-15. The higher oxidation rates of acetone are due to the smaller molecular structure (acetone: C_3H_6O, MEK: C_4H_8O) and the lower boiling point (acetone: 56.2°C, MEK: 79.6°C) effecting to the higher rate of evaporation.

From these set of oxidation reaction, we have proved that the oxidant suitable for one VOCs can be applied to others VOCs that are listed in the same group.

Table 3-29 The reaction rate of MEK and acetone as a function of time used for verifying the oxidation with NaOCl at 29±1°C

Time (minutes)	Reaction rate of VOCs x 10^6 (mol L^{-1} min^{-1})							
	M.2	A.33	M.4	A.34	M.5	A.35	M.7	A.36
	MEK	Acetone	MEK	Acetone	MEK	Acetone	MEK	Acetone
0	24.64	33.48	26.45	35.64	30.87	44.18	51.30	61.10
5	23.58	31.47	24.97	32.87	29.91	42.15	49.86	59.15
15	21.59	27.80	22.26	27.95	28.09	38.37	47.10	55.42
30	18.92	23.08	18.73	21.92	25.55	33.32	43.24	50.28
60	14.53	15.91	13.27	13.48	21.15	25.14	36.44	41.37
90	11.16	10.97	9.40	8.29	17.51	18.96	30.71	34.04
120	8.57	7.56	6.65	5.10	14.49	14.30	25.89	28.01

Table 3-30 The values of B, a_1 for the oxidation of MEK and acetone used for verifying the oxidation with NaOCl

Run No.	$B x10^3$	$a_1 x 10^3$	r^2	Run No.	$B x10^3$	$a_1 x 10^3$	r^2
M.2	2.30	-11.50	0.99	A.33	2.20	-16.20	0.97
M.4	2.80	-8.80	0.99	A.34	2.70	-12.40	0.99
M.5	4.90	-6.30	0.99	A.35	4.70	-9.40	0.97
M.7	9.00	-5.70	0.94	A.36	9.40	-6.50	0.97

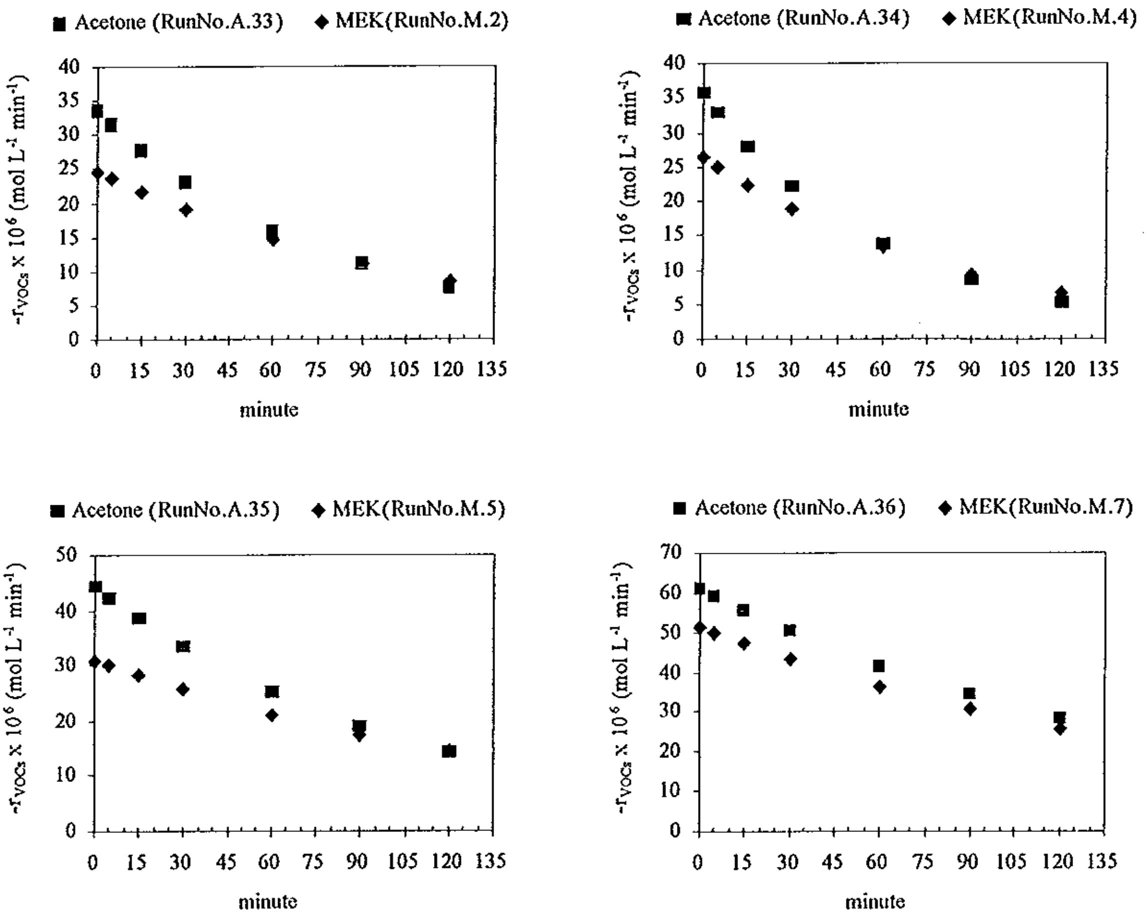


Figure 3-15 The comparison of the reaction rate between MEK and acetone by using NaOCl as an oxidant

Chapter 4

CONCLUSIONS

The kinetics studies of the oxidation of volatile organic compounds in a homogeneous aqueous batch system were investigated in this research. First part of the work was aimed to determine the suitable oxidant for interesting VOCs. The conclusions from the study are:

1. The oxidant suited for toluene is NaOCl.
2. The oxidant suited for ethanol is $KMnO_4$.
3. The oxidants suited for MEK are NaOCl and $KMnO_4$.

Second part of the research was aimed to determine the kinetic parameter for toluene-NaOCl, ethanol-$KMnO_4$, MEK-NaOCl, and MEK-$KMnO_4$ oxidation reaction. The conclusion for this part are listed below:

1. Toluene-NaOCl oxidation was first-order with respect to toluene and zero-order with respect to $KMnO_4$.
2. The oxidation of ethanol by $KMnO_4$ was second-order overall and first-order individually with respect to ethanol and $KMnO_4$.
3. MEK-NaOCl oxidation was half-order with respect to MEK and zero-order with respect to NaOCl.
4. MEK-$KMnO_4$ oxidation was first-order with respect to MEK and half-order with respect to $KMnO_4$.
5. The activation energy (E_a) for the oxidation of toluene-NaOCl, ethanol-$KMnO_4$, MEK-NaOCl, and MEK-$KMnO_4$ were determined from the Arrhenius plot with the values of 31.908, 37.190, 33.430, and 25.393 kJ mol^{-1}, respectively.

The third part of experimental was aimed to verify the rate law. It can be concluded that the rate law developed from this study can be used to predict the oxidation rate of invested VOCs over the range of investigated reaction temperature.

Finally, the oxidant suitable for toluene, ethanol, and MEK can be applied to other VOCs which are classified as aromatic, alcohol, and ketone, respectively.

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Appendix A

Calibration Curve of VOCs and Oxidizing agents

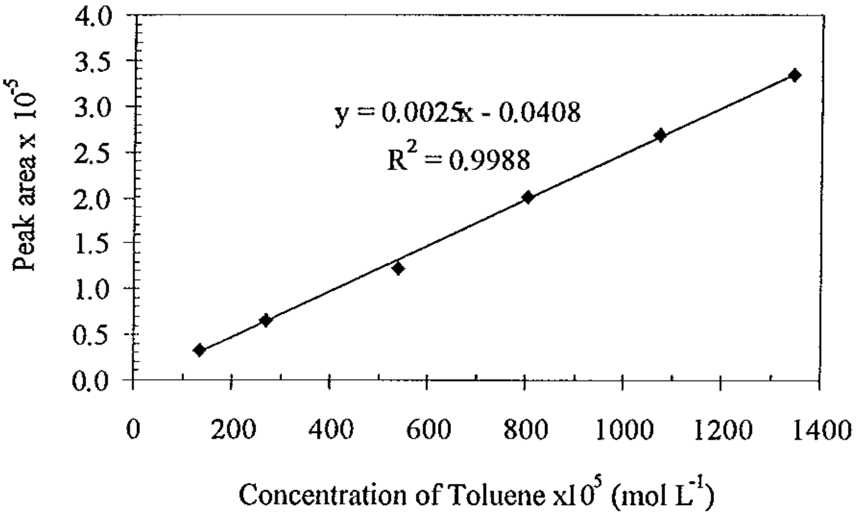


Figure A-1 Calibration curve of toluene-water solution

Conditions : Oven temperature 100°C

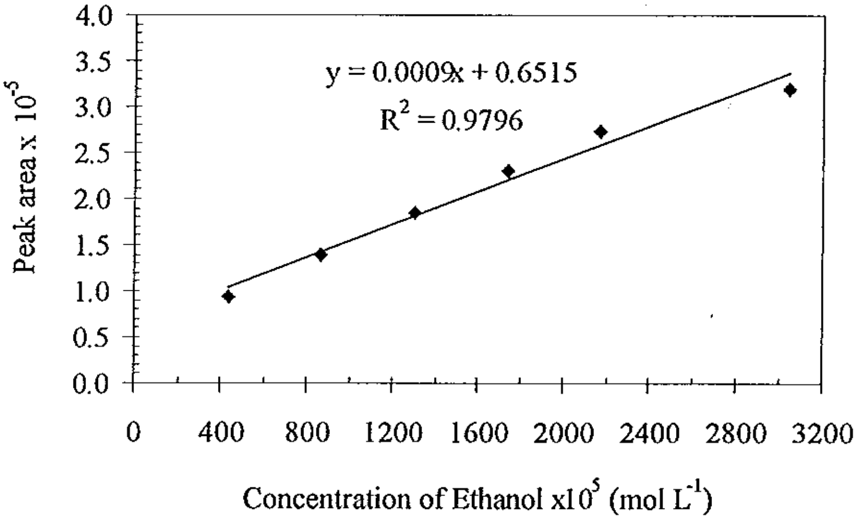


Figure A-2 Calibration curve of ethanol-water solution

Conditions : Oven temperature 60°C

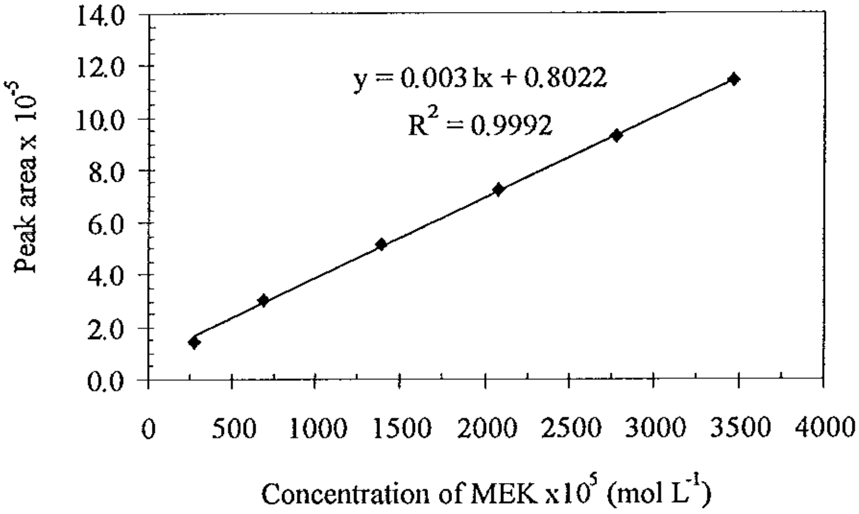


Figure A-3 Calibration curve of MEK-water solution

Conditions : Oven temperature 60°C

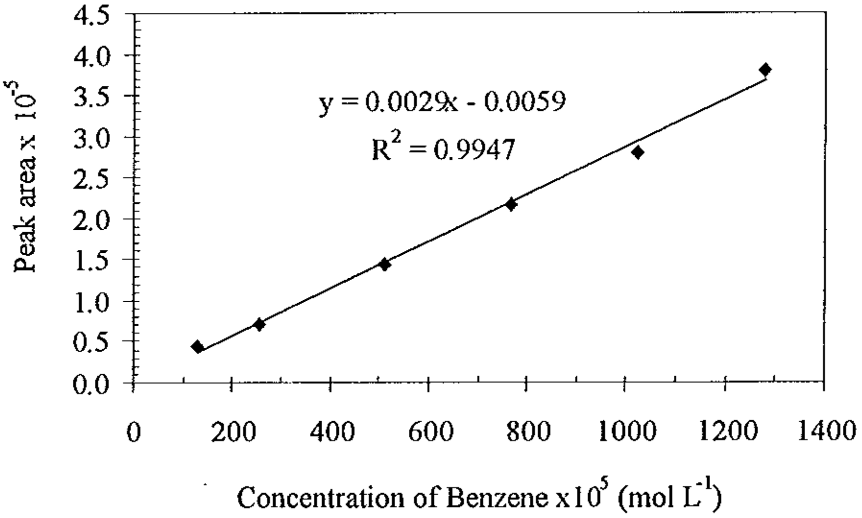


Figure A-4 Calibration curve of benzene-water solution

Conditions : Oven temperature 80°C

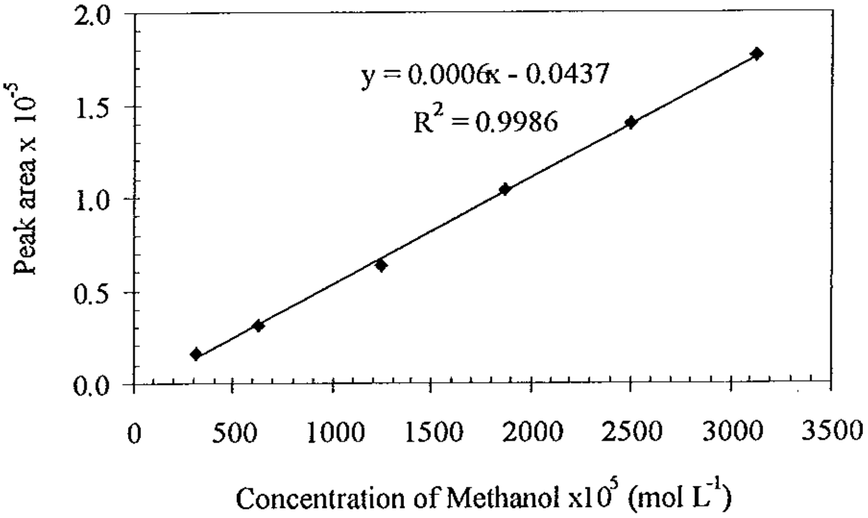


Figure A-5 Calibration curve of methanol-water solution

Conditions : Oven temperature 60°C

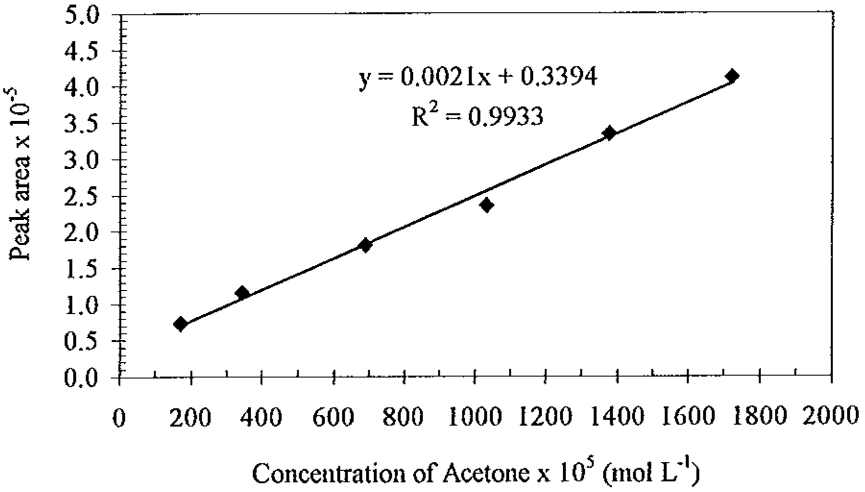


Figure A-6 Calibration curve of acetone-water solution

Conditions : Oven temperature 60°C

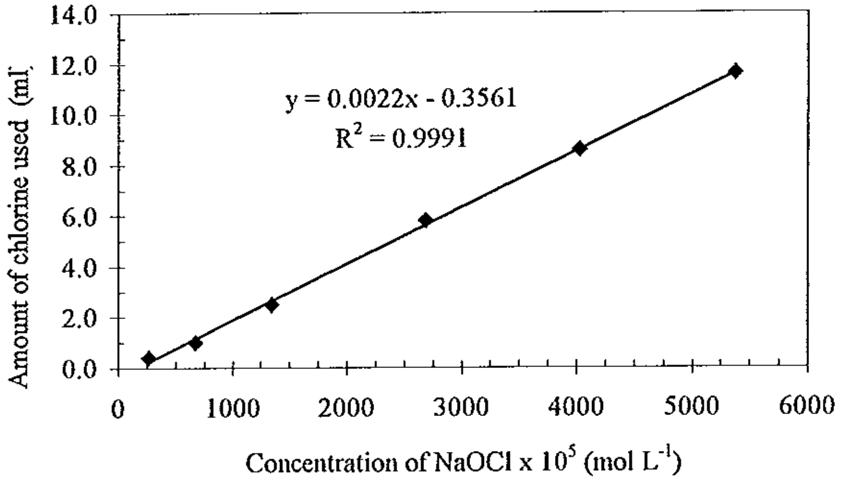


Figure A-7 Calibration curve of NaOCl-water solution

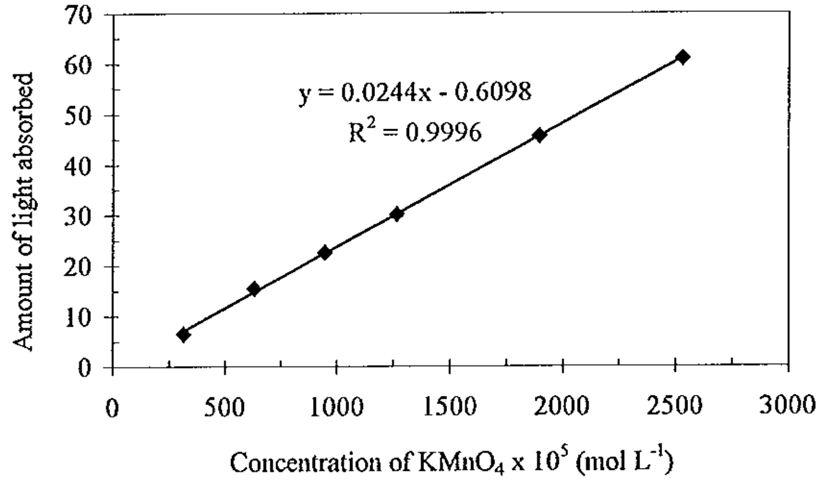


Figure A-8 Calibration curve of $KMnO_4$-water solution

Conditions : Wavelength 525 nm.

Appendix B

Concentrations of VOCs and Oxidizing agents as a function of time

Table B-1 Toluene concentration-time for the oxidation of toluene by NaOCl for Run No. T.1: T = 30°C, pH = 11.37

Time (minutes)	Concentration of Toluene x 10^5 (mol L^{-1})				
	Point 1	Point 2	Point 3	Average	SD
0	127	129	128	128	0.58
5	126	125	124	125	0.67
15	117	120	121	119	1.86
30	105	105	105	105	0.28
60	87	89	90	89	1.44
90	87	86	86	86	0.76
120	83	83	84	84	0.56

Table B-2 Toluene concentration-time for the oxidation of toluene by NaOCl for Run No. T.2: T = 29°C, pH = 11.44

Time (minutes)	Concentration of Toluene x 10^5 (mol L^{-1})				
	Point 1	Point 2	Point 3	Average	SD
0	162	160	161	161	0.77
5	148	151	148	149	1.69
15	143	141	140	141	1.77
30	130	133	132	132	1.11
60	123	122	125	123	1.41
90	111	109	111	111	0.95
120	104	105	105	105	0.14

Table B-3 Toluene concentration-time for the oxidation of toluene by NaOCl for Run No. T.3: T = 29°C, pH = 11.35

Time (minutes)	Concentration of Toluene x 10^5 (mol L^{-1})				
	Point 1	Point 2	Point 3	Average	SD
0	185	183	185	185	1.03
5	164	163	161	163	1.43
15	158	158	159	158	0.30
30	153	154	153	153	0.54
60	140	140	137	139	1.62
90	127	128	129	128	1.39
120	118	118	113	116	2.79

Table B-4 Toluene concentration-time for the oxidation of toluene by NaOCl for Run No. T.4: T = 29°C, pH = 11.87

Time (minutes)	Concentration of Toluene x 10^5 (mol L^{-1})				
	Point 1	Point 2	Point 3	Average	SD
0	262	264	264	263	1.13
5	233	234	232	233	1.09
15	213	214	213	213	0.41
30	186	190	188	188	2.35
60	178	177	181	179	1.92
90	162	159	162	161	1.57
120	152	153	155	153	1.57

Table B-5 Toluene concentration-time for the oxidation of toluene by NaOCl for Run No. T.5: T = 29°C, pH = 11.66

Time (minutes)	Concentration of Toluene x 10^5 (mol L^{-1})				
	Point 1	Point 2	Point 3	Average	SD
0	338	339	337	338	0.83
5	270	270	270	270	0.38
15	245	247	245	246	1.30
30	239	238	238	238	0.80
60	227	227	227	227	0.25
90	202	202	202	202	0.11
120	181	181	182	181	0.42

Table B-6 Toluene concentration-time for the oxidation of toluene by NaOCl for Run No. T.6: T = 30°C, pH = 11.28

Time (minutes)	Concentration of Toluene x 10^5 (mol L^{-1})				
	Point 1	Point 2	Point 3	Average	SD
0	417	414	415	415	1.56
5	387	380	388	385	4.25
15	360	355	350	355	5.22
30	313	315	306	311	5.01
60	283	277	275	278	4.34
90	273	274	282	276	4.76
120	254	259	256	256	2.47

Table B-7 Toluene concentration-time for the oxidation of toluene by NaOCl for Run No. T.7: T = 29°C, pH = 11.79

Time (minutes)	Concentration of Toluene x 10^5 (mol L^{-1})				
	Point 1	Point 2	Point 3	Average	SD
0	489	489	491	489	1.32
5	417	417	414	416	1.73
15	400	400	401	400	0.51
30	367	374	370	370	3.53
60	346	337	345	343	4.76
90	326	326	323	325	1.65
120	300	302	298	300	1.96

Table B-8 Toluene concentration-time for the oxidation of toluene by NaOCl for Run No. T.8: T = 30°C, pH = 11.53

Time (minutes)	Concentration of Toluene x 10^5 (mol L^{-1})				
	Point 1	Point 2	Point 3	Average	SD
0	679	677	680	679	1.86
5	605	597	607	603	5.13
15	539	542	540	540	1.64
30	510	498	495	501	7.78
60	451	437	434	441	8.89
90	403	416	420	413	9.33
120	376	374	388	380	7.38

Table B-9 Toluene concentration-time for the oxidation of toluene by NaOCl for Run No. T.9: T = 29°C, pH = 11.54

Time (minutes)	Concentration of Toluene x 10^5 (mol L^{-1})				
	Point 1	Point 2	Point 3	Average	SD
0	1036	1017	1026	1027	9.46
5	1002	1004	1006	1004	2.32
15	987	983	997	989	7.18
30	940	945	952	945	6.09
60	898	892	882	891	8.46
90	749	754	749	751	2.86
120	696	702	696	698	3.39

Table B-10 Toluene concentration-time for the oxidation of toluene by NaOCl for Run No. T.10: T = 35°C, pH = 11.49

Time (minutes)	Concentration of Toluene x 10^5 (mol L^{-1})				
	Point 1	Point 2	Point 3	Average	SD
0	653	657	664	658	5.62
5	636	638	637	637	1.15
15	596	596	597	596	0.40
30	567	565	567	567	1.03
60	487	495	489	490	4.13
90	419	419	419	419	0.27
120	361	361	371	364	5.77

Table B-11 Toluene concentration-time for the oxidation of toluene by NaOCl for Run No. T.11: T = 40°C, pH = 11.45

Time (minutes)	Concentration of Toluene x 10^5 (mol L^{-1})				
	Point 1	Point 2	Point 3	Average	SD
0	727	728	727	727	0.46
5	703	707	705	705	2.03
15	681	676	678	679	2.45
30	606	609	605	607	1.81
60	511	508	511	510	1.77
90	458	461	457	459	1.95
120	425	423	427	425	2.23

Table B-12 Toluene concentration-time for the oxidation of toluene by NaOCl for Run No. T.12: T = 45°C, pH = 11.42

Time (minutes)	Concentration of Toluene x 10^5 (mol L^{-1})				
	Point 1	Point 2	Point 3	Average	SD
0	693	722	718	711	15.76
5	669	675	674	673	3.05
15	652	651	652	652	0.71
30	623	618	623	621	2.94
60	511	541	509	521	18.14
90	417	415	415	415	1.14
120	345	348	328	340	10.68

Table B-13 Toluene concentration-time for the oxidation of toluene by NaOCl for Run No. T.13: T = 50°C, pH = 11.87

Time (minutes)	Concentration of Toluene x 10^5 (mol L^{-1})				
	Point 1	Point 2	Point 3	Average	SD
0	744	683	729	719	31.81
5	595	595	590	593	2.76
15	533	528	541	534	6.91
30	470	468	463	467	3.49
60	347	345	355	349	5.34
90	264	259	251	258	6.38
120	204	204	205	204	0.54

Table B-14 Toluene concentration-time for the oxidation of toluene by $KMnO_4$ Run No. T.14: T = 30°C, pH = 11.50

Time (minutes)	Concentration of Toluene x 10^5 (mol L^{-1})				
	Point 1	Point 2	Point 3	Average	SD
0	334	332	329	332	2.47
5	330	330	332	331	1.23
15	328	331	328	329	1.21
30	328	331	332	330	2.09
60	329	330	336	332	4.18
90	328	331	328	329	1.56
120	329	328	328	329	0.67

Table B-15 Toluene concentration-time for the oxidation of toluene by NaOCl for Run No. T.15: T = 30°C, pH = 11.66

Time (minutes)	Concentration of Toluene x 10^5 (mol L^{-1})				
	Point 1	Point 2	Point 3	Average	SD
0	164	164	164	164	0.34
5	162	162	161	161	0.47
15	144	142	145	144	1.39
30	134	133	139	135	3.30
60	129	121	125	125	3.59
90	114	115	116	115	1.01
120	109	109	109	109	0.18

Table B-16 NaOCl concentration-time for the oxidation of toluene by NaOCl for Run No. T.15: T = 30°C, pH = 11.66

Time (minutes)	Concentration of NaOCl x 10^5 (mol L^{-1})				
	Point 1	Point 2	Point 3	Average	SD
0	2924	2911	2915	2917	6.84
5	2870	2888	2879	2879	8.96
15	2884	2875	2879	2879	4.48
30	2920	2920	2911	2917	5.17
60	2808	2803	2794	2802	6.84
90	2839	2834	2848	2840	6.84
120	2924	2920	2906	2917	9.32

Table B-17 Toluene concentration-time for the oxidation of toluene by NaOCl for Run No. T.16: T = 37°C, pH = 11.25

Time (minutes)	Concentration of Toluene x 10^5 (mol L^{-1})				
	Point 1	Point 2	Point 3	Average	SD
0	493	491	491	492	1.29
5	481	484	487	484	3.06
15	441	438	432	437	4.49
30	422	416	420	419	3.32
60	349	344	346	346	2.56
90	305	309	308	307	2.13
120	285	285	284	285	0.64

Table B-18 NaOCl concentration-time for the oxidation of toluene by NaOCl for Run No. T.16: T = 37°C, pH = 11.25

Time (minutes)	Concentration of NaOCl x 10^5 (mol L^{-1})				
	Point 1	Point 2	Point 3	Average	SD
0	1384	1388	1375	1382	6.84
5	1375	1379	1393	1382	9.32
15	1424	1419	1415	1419	4.48
30	1393	1375	1379	1382	9.32
60	1464	1460	1455	1460	4.48
90	1473	1455	1451	1460	11.85
120	1428	1415	1415	1419	7.76

Table B-19 Toluene concentration-time for the oxidation of toluene by NaOCl for Run No. T.17: T = 48°C, pH = 11.44

Time (minutes)	Concentration of Toluene x 10^5 (mol L^{-1})				
	Point 1	Point 2	Point 3	Average	SD
0	788	798	805	797	8.34
5	740	728	735	734	5.90
15	639	640	642	640	1.61
30	578	570	571	573	4.49
60	481	492	490	488	5.97
90	352	353	360	355	4.33
120	288	284	280	284	3.82

Table B-20 NaOCl concentration-time for the oxidation of toluene by NaOCl for Run No. T.17: T = 48°C, pH = 11.44

Time (minutes)	Concentration of NaOCl x 10^5 (mol L^{-1})				
	Point 1	Point 2	Point 3	Average	SD
0	2951	2960	2955	2955	4.48
5	3076	3072	3065	3071	5.63
15	3000	2987	2996	2994	6.84
30	2996	2996	2991	2994	2.59
60	3027	3036	3032	3032	4.48
90	3040	3027	3027	3032	7.76
120	3067	3072	3072	3070	2.59

Table B-21 Benzene concentration-time for the oxidation of benzene by NaOCl
Run No. B.18: T = 30°C, pH = 11.80

Time (minutes)	Concentration of Benzene x 10^5 (mol L^{-1})				
	Point 1	Point 2	Point 3	Average	SD
0	265	270	260	265	4.55
5	255	254	254	254	0.92
15	250	253	248	250	2.48
30	241	236	230	236	5.43
60	221	226	225	224	2.38
90	215	218	216	216	1.30
120	206	206	206	206	0.36

Table B-22 Benzene concentration-time for the oxidation of benzene by NaOCl
Run No. B.19: T = 29°C, pH = 11.36

Time (minutes)	Concentration of Benzene x 10^5 (mol L^{-1})				
	Point 1	Point 2	Point 3	Average	SD
0	334	332	335	334	1.43
5	298	298	297	297	0.60
15	285	285	287	286	1.03
30	277	276	277	277	0.51
60	266	268	270	268	2.15
90	250	249	245	248	2.87
120	239	240	236	238	1.85

Table B-23 Benzene concentration-time for the oxidation of benzene by NaOCl
Run No. B.20: T = 29°C, pH = 11.66

Time (minutes)	Concentration of Benzene x 10^5 (mol L^{-1})				
	Point 1	Point 2	Point 3	Average	SD
0	411	411	413	412	1.30
5	410	410	410	410	0.18
15	402	404	402	402	1.02
30	389	388	388	388	0.80
60	365	368	371	368	3.30
90	335	340	342	339	3.89
120	328	326	325	327	1.62

Table B-24 Benzene concentration-time for the oxidation of benzene by NaOCl
Run No. B.21: T = 30°C, pH = 11.87

Time (minutes)	Concentration of Benzene x 10^5 (mol L^{-1})				
	Point 1	Point 2	Point 3	Average	SD
0	685	682	681	683	2.39
5	673	675	672	673	1.21
15	659	659	659	659	0.49
30	644	643	641	643	1.15
60	606	604	608	606	1.93
90	576	576	577	576	0.82
120	510	513	509	511	1.98

Table B-25 Ethanol concentration-time for the oxidation of ethanol by $KMnO_4$ for Run No. E.1: T = 59°C, pH = 11.99

Time (minutes)	Concentration of Ethanol x 10^5 (mol L^{-1})				
	Point 1	Point 2	Point 3	Average	SD
0	454	452	457	454	2.68
5	443	444	444	444	0.71
15	423	419	410	417	6.64
30	385	388	383	385	2.69
60	341	343	338	341	2.77
90	304	302	302	303	1.56
120	216	226	217	220	5.28

Table B-26 Ethanol concentration-time for the oxidation of ethanol by $KMnO_4$ for Run No. E.2: T = 30°C, pH = 11.76

Time (minutes)	Concentration of Ethanol x 10^5 (mol L^{-1})				
	Point 1	Point 2	Point 3	Average	SD
0	502	499	492	498	5.13
5	492	492	495	493	1.92
15	478	483	487	483	4.40
30	469	465	475	469	4.89
60	440	446	435	440	5.93
90	422	399	406	409	11.78
120	392	404	404	400	7.10

Table B-27 Ethanol concentration-time for the oxidation of ethanol by $KMnO_4$ for Run No. E.3: T = 29°C, pH = 11.67

Time (minutes)	Concentration of Ethanol x 10^5 (mol L^{-1})				
	Point 1	Point 2	Point 3	Average	SD
0	895	901	880	892	10.54
5	804	811	802	806	4.81
15	782	778	787	788	6.29
30	712	698	730	713	16.13
60	668	694	662	675	17.13
90	635	639	622	632	9.18
120	604	605	605	604	0.77

Table B-28 Ethanol concentration-time for the oxidation of ethanol by $KMnO_4$ for Run No. E.4: T = 30°C, pH = 11.68

Time (minutes)	Concentration of Ethanol x 10^5 (mol L^{-1})				
	Point 1	Point 2	Point 3	Average	SD
0	966	955	962	961	5.76
5	926	928	921	925	3.62
15	906	907	913	909	3.62
30	887	878	877	881	5.63
60	870	862	860	864	5.30
90	858	864	855	859	4.41
120	812	823	793	809	15.15

Table B-29 Ethanol concentration-time for the oxidation of ethanol by $KMnO_4$ for Run No. E.5: T = 29°C, pH = 11.66

Time (minutes)	Concentration of Ethanol x 10^5 (mol L^{-1})				
	Point 1	Point 2	Point 3	Average	SD
0	1042	1059	1031	1044	13.82
5	991	1005	985	994	10.33
15	962	969	956	963	6.78
30	924	930	917	924	6.67
60	829	824	844	832	10.42
90	792	801	782	792	9.20
120	695	715	675	695	20.02

Table B-30 Ethanol concentration-time for the oxidation of ethanol by $KMnO_4$ for Run No. E.6: T = 30°C, pH = 11.65

Time (minutes)	Concentration of Ethanol x 10^5 (mol L^{-1})				
	Point 1	Point 2	Point 3	Average	SD
0	1314	1273	1322	1303	26.41
5	1073	1066	1072	1070	3.55
15	1031	1047	1014	1030	16.46
30	887	905	874	889	15.11
60	868	892	848	869	21.96
90	807	817	783	802	17.42
120	683	666	708	685	21.20

Table B-31 Ethanol concentration-time for the oxidation of ethanol by $KMnO_4$ for Run No. E.7: T = 30°C, pH = 11.79

Time (minutes)	Concentration of Ethanol x 10^5 (mol L^{-1})				
	Point 1	Point 2	Point 3	Average	SD
0	1704	1551	1626	1627	76.76
5	1445	1472	1473	1463	15.71
15	1424	1464	1452	1447	20.86
30	1408	1427	1397	1411	15.33
60	1371	1379	1354	1368	13.20
90	1301	1312	1291	1301	10.47
120	1015	1256	1111	1127	121.08

Table B-32 Ethanol concentration-time for the oxidation of ethanol by $KMnO_4$ for Run No. E.8: T = 30°C, pH = 11.69

Time (minutes)	Concentration of Ethanol x 10^5 (mol L^{-1})				
	Point 1	Point 2	Point 3	Average	SD
0	2030	2100	2049	2060	36.07
5	1913	1911	1899	1907	7.72
15	1885	1900	1877	1887	11.69
30	1855	1865	1848	1856	8.77
60	1844	1848	1841	1844	3.42
90	1738	1781	1742	1754	23.83
120	1612	1594	1592	1599	11.04

Table B-33 Ethanol concentration-time for the oxidation of ethanol by $KMnO_4$ for Run No. E.9: T = 30°C, pH = 11.77

Time (minutes)	Concentration of Ethanol x 10^5 (mol L^{-1})				
	Point 1	Point 2	Point 3	Average	SD
0	2786	2808	2777	2790	15.83
5	2738	2727	2733	2733	5.54
15	2579	2590	2568	2579	10.92
30	2275	2331	2270	2292	33.71
60	2233	2241	2238	2237	3.79
90	2195	2202	2195	2197	4.01
120	2049	2098	2074	2074	24.31

Table B-34 Ethanol concentration-time for the oxidation of ethanol by $KMnO_4$ for Run No. E.10: T = 35°C, pH = 11.89

Time (minutes)	Concentration of Ethanol x 10^5 (mol L^{-1})				
	Point 1	Point 2	Point 3	Average	SD
0	495	502	489	495	6.63
5	473	474	472	473	1.23
15	468	466	465	466	1.64
30	452	448	445	449	3.51
60	414	415	415	415	0.52
90	375	388	366	376	11.11
120	345	360	347	351	7.66

Table B-35 Ethanol concentration-time for the oxidation of ethanol by $KMnO_4$ for Run No. E.11: T = 40°C, pH = 11.81

Time (minutes)	Concentration of Ethanol x 10^5 (mol L^{-1})				
	Point 1	Point 2	Point 3	Average	SD
0	491	494	494	493	1.80
5	472	475	474	474	1.28
15	459	462	458	460	2.38
30	438	448	436	441	6.17
60	396	391	400	396	4.44
90	358	348	350	352	4.93
120	348	329	319	332	14.31

Table B-36 Ethanol concentration-time for the oxidation of ethanol by $KMnO_4$ for Run No. E.12: T = 45°C, pH = 11.85

Time (minutes)	Concentration of Ethanol x 10^5 (mol L^{-1})				
	Point 1	Point 2	Point 3	Average	SD
0	501	497	498	499	2.28
5	422	431	417	423	6.95
15	411	408	410	410	1.41
30	379	395	364	379	15.97
60	340	353	340	345	7.53
90	310	313	318	314	3.97
120	256	264	259	260	4.09

Table B-37 Ethanol concentration-time for the oxidation of ethanol by $KMnO_4$ for Run No. E.13: T = 50°C, pH = 11.80

Time (minutes)	Concentration of Ethanol x 10^5 (mol L^{-1})				
	Point 1	Point 2	Point 3	Average	SD
0	504	487	523	505	18.36
5	403	420	392	405	14.11
15	379	378	372	376	3.47
30	327	322	323	324	2.83
60	305	319	295	306	12.19
90	260	264	257	260	3.52
120	228	228	221	226	3.86

Table B-38 Ethanol concentration-time for the oxidation of ethanol by NaOCl for Run No. E.14: T = 30°C, pH = 11.90

Time (minutes)	Concentration of Ethanol x 10^5 (mol L^{-1})				
	Point 1	Point 2	Point 3	Average	SD
0	486	504	485	492	10.89
5	488	496	483	489	6.20
15	471	502	483	485	15.47
30	485	486	473	481	7.19
60	474	489	472	478	9.40
90	476	480	479	478	2.30
120	479	467	476	474	6.76

Table B-39 Ethanol concentration-time for the oxidation of ethanol by $KMnO_4$ for Run No. E.15: T = 30°C, pH = 11.89

Time (minutes)	Concentration of Ethanol x 10^5 (mol L^{-1})				
	Point 1	Point 2	Point 3	Average	SD
0	1975	1967	1988	1977	10.52
5	1957	1939	1940	1945	10.22
15	1875	1878	1876	1876	1.44
30	1801	1804	1785	1797	10.28
60	1626	1642	1641	1636	8.92
90	1491	1471	1500	1488	14.70
120	1356	1359	1357	1357	1.44

Table B-40 $KMnO_4$ concentration-time for the oxidation of ethanol by $KMnO_4$ for Run No. E.15: T = 30°C, pH = 11.89

Time (minutes)	Concentration of $KMnO_4$ x 10^5 (mol L^{-1})				
	Point 1	Point 2	Point 3	Average	SD
0	578	577	577	577	0.41
5	571	572	570	571	0.86
15	545	544	545	544	0.63
30	538	539	537	538	0.86
60	533	534	535	534	1.03
90	527	529	528	528	0.86
120	528	525	528	527	1.56

Table B-41 Ethanol concentration-time for the oxidation of ethanol by $KMnO_4$ for Run No. E.16: T = 37°C, pH = 11.81

Time (minutes)	Concentration of Ethanol x 10^5 (mol L^{-1})				
	Point 1	Point 2	Point 3	Average	SD
0	866	871	870	869	2.32
5	846	849	838	844	5.67
15	804	805	802	803	1.39
30	765	764	769	766	2.62
60	669	668	673	670	2.62
90	570	568	571	570	1.51
120	505	505	499	503	3.56

Table B-42 $KMnO_4$ concentration-time for the oxidation of ethanol by $KMnO_4$ for Run No. E.16: T = 37°C, pH = 11.81

Time (minutes)	Concentration of $KMnO_4$ x 10^5 (mol L^{-1})				
	Point 1	Point 2	Point 3	Average	SD
0	511	510	510	510	0.63
5	510	509	511	510	1.03
15	519	518	518	518	0.86
30	529	530	529	529	0.63
60	554	555	554	554	0.63
90	526	528	528	527	0.86
120	519	520	519	519	0.41

Table B-43 Ethanol concentration-time for the oxidation of ethanol by $KMnO_4$ for Run No. E.17: T = 48°C, pH = 11.85

Time (minutes)	Concentration of Ethanol x 10^5 (mol L^{-1})				
	Point 1	Point 2	Point 3	Average	SD
0	464	470	470	468	3.41
5	418	413	404	412	7.32
15	368	377	365	370	6.15
30	343	336	338	339	3.40
60	302	303	300	302	1.76
90	270	270	278	273	4.85
120	222	222	215	220	4.41

Table B-44 $KMnO_4$ concentration-time for the oxidation of ethanol by $KMnO_4$ for Run No. E.17: T = 48°C, pH = 11.85

Time (minutes)	Concentration of $KMnO_4$ x 10^5 (mol L^{-1})				
	Point 1	Point 2	Point 3	Average	SD
0	279	279	278	278	0.47
5	267	266	266	266	0.63
15	274	274	275	274	0.47
30	262	263	263	262	0.63
60	265	264	264	264	0.63
90	257	257	258	257	0.24
120	259	259	261	259	1.03

Table B-45 Methanol concentration-time for the oxidation of methanol by $KMnO_4$
Run No. Me.18: T = 30°C, pH = 12.09

Time (minutes)	Concentration of Methanol x 10^5 (mol L^{-1})				
	Point 1	Point 2	Point 3	Average	SD
0	461	448	449	453	7.45
5	431	434	429	431	2.76
15	400	397	394	397	2.91
30	354	367	357	360	6.86
60	288	280	296	288	8.44
90	209	208	211	210	1.27
120	180	180	180	180	0.19

Table B-46 Methanol concentration-time for the oxidation of methanol by $KMnO_4$
Run No. Me.19: T = 29°C, pH = 12.06

Time (minutes)	Concentration of Methanol x 10^5 (mol L^{-1})				
	Point 1	Point 2	Point 3	Average	SD
0	1033	1048	1036	1039	7.99
5	976	972	965	971	5.59
15	807	806	838	817	17.92
30	734	734	720	729	7.94
60	671	713	685	690	21.14
90	621	601	581	601	20.06
120	528	533	533	531	3.05

Table B-47 Methanol concentration-time for the oxidation of methanol by $KMnO_4$
Run No. Me.20: T = 30°C, pH = 12.06

Time (minutes)	Concentration of Methanol x 10^5 (mol L^{-1})				
	Point 1	Point 2	Point 3	Average	SD
0	1304	1297	1323	1308	13.58
5	1237	1240	1233	1237	3.16
15	1163	1174	1153	1163	10.33
30	1063	1046	1060	1056	9.03
60	891	904	896	897	6.74
90	776	780	771	775	4.34
120	626	617	618	620	4.70

Table B-48 Methanol concentration-time for the oxidation of methanol by $KMnO_4$
Run No. Me.21: T = 29°C, pH = 12.08

Time (minutes)	Concentration of Methanol x 10^5 (mol L^{-1})				
	Point 1	Point 2	Point 3	Average	SD
0	2786	2763	2778	2775	11.38
5	2734	2737	2745	2738	5.58
15	2644	2660	2650	2651	7.81
30	2521	2523	2530	2525	4.84
60	2295	2280	2273	2282	11.17
90	2063	2082	2073	2072	9.52
120	1849	1831	1812	1831	18.48

Table B-49 MEK concentration-time for the oxidation of MEK by NaOCl for Run No. M.1: T = 29°C, pH = 11.81

Time (minutes)	Concentration of MEK x 10^5 (mol L^{-1})				
	Point 1	Point 2	Point 3	Average	SD
0	214	217	219	217	2.50
5	155	159	157	157	1.79
15	107	106	107	107	0.23
30	85	80	81	82	2.68
60	46	52	51	50	3.02
90	37	37	37	37	0.25
120	27	25	30	27	2.46

Table B-50 MEK concentration-time for the oxidation of MEK by NaOCl for Run No. M.2: T = 30°C, pH = 11.68

Time (minutes)	Concentration of MEK x 10^5 (mol L^{-1})				
	Point 1	Point 2	Point 3	Average	SD
0	221	226	229	226	3.87
5	204	205	206	205	1.12
15	195	197	196	196	1.00
30	160	143	169	158	13.26
60	114	112	108	111	3.27
90	88	89	88	89	0.87
120	54	50	54	53	2.29

Table B-51 MEK concentration-time for the oxidation of MEK by NaOCl for Run No. M.3: T = 30°C, pH = 10.95

Time (minutes)	Concentration of MEK x 10^5 (mol L^{-1})				
	Point 1	Point 2	Point 3	Average	SD
0	245	226	255	242	14.74
5	210	213	213	212	1.79
15	199	197	195	197	1.98
30	182	192	177	184	7.76
60	140	138	142	140	2.16
90	114	114	114	114	0.44
120	90	91	91	90	0.82

Table B-52 MEK concentration-time for the oxidation of MEK by NaOCl for Run No. M.4: T = 30°C, pH = 11.32

Time (minutes)	Concentration of MEK x 10^5 (mol L^{-1})				
	Point 1	Point 2	Point 3	Average	SD
0	281	280	285	282	2.87
5	268	271	270	270	1.53
15	245	246	241	244	2.82
30	220	217	220	219	1.93
60	155	155	154	155	0.45
90	126	128	126	127	1.06
120	99	101	98	99	1.24

Table B-53 MEK concentration-time for the oxidation of MEK by NaOCl for Run No. M.5: T = 29°C, pH = 11.36

Time (minutes)	Concentration of MEK x 10^5 (mol L^{-1})				
	Point 1	Point 2	Point 3	Average	SD
0	514	509	509	511	2.56
5	463	462	457	461	3.07
15	441	440	438	440	1.30
30	411	406	408	408	2.40
60	345	344	344	344	0.81
90	280	280	272	277	4.65
120	231	229	232	231	1.60

Table B-54 MEK concentration-time for the oxidation of MEK by NaOCl for Run No. M.6: T = 30°C, pH = 11.29

Time (minutes)	Concentration of MEK x 10^5 (mol L^{-1})				
	Point 1	Point 2	Point 3	Average	SD
0	782	790	749	773	21.65
5	656	639	674	656	17.40
15	634	651	608	631	21.78
30	560	555	567	561	5.70
60	541	547	538	542	4.70
90	382	425	435	414	28.26
120	338	333	349	340	8.09

Table B-55 MEK concentration-time for the oxidation of MEK by NaOCl for Run No. M.7: T = 30°C, pH = 11.29

Time (minutes)	Concentration of MEK x 10^5 (mol L^{-1})				
	Point 1	Point 2	Point 3	Average	SD
0	1020	996	1055	1024	29.33
5	855	884	848	862	18.72
15	806	804	802	804	1.78
30	730	712	717	720	8.93
60	574	582	642	599	36.95
90	529	556	532	539	14.82
120	473	493	473	480	11.43

Table B-56 MEK concentration-time for the oxidation of MEK by NaOCl for Run No. M.8: T = 29°C, pH = 11.34

Time (minutes)	Concentration of MEK x 10^5 (mol L^{-1})				
	Point 1	Point 2	Point 3	Average	SD
0	1054	1065	1046	1055	9.42
5	947	939	965	950	13.51
15	923	962	877	921	42.45
30	837	807	859	834	26.22
60	679	697	653	677	22.24
90	638	615	615	623	13.59
120	565	542	594	567	25.67

Table B-57 MEK concentration-time for the oxidation of MEK by NaOCl for Run No. M.9: T = 30°C, pH = 11.38

Time (minutes)	Concentration of MEK x 10^5 (mol L^{-1})				
	Point 1	Point 2	Point 3	Average	SD
0	1424	1442	1400	1422	20.89
5	1307	1289	1326	1308	18.39
15	1265	1271	1281	1272	8.18
30	1249	1243	1233	1242	7.98
60	1063	1112	1062	1079	28.40
90	931	908	942	927	17.38
120	805	789	819	804	15.41

Table B-58 MEK concentration-time for the oxidation of MEK by NaOCl for Run No. M.19: T = 35°C, pH = 11.24

Time (minutes)	Concentration of MEK x 10^5 (mol L^{-1})				
	Point 1	Point 2	Point 3	Average	SD
0	1462	1487	1494	1481	16.74
5	1376	1368	1352	1365	11.90
15	1307	1311	1301	1307	4.94
30	1212	1189	1231	1211	20.77
60	1048	1067	1026	1047	20.27
90	894	902	867	887	18.44
120	754	769	761	761	7.29

Table B-59 MEK concentration-time for the oxidation of MEK by NaOCl for Run No. M.20: T = 40°C, pH = 11.18

Time (minutes)	Concentration of MEK x 10^5 (mol L^{-1})				
	Point 1	Point 2	Point 3	Average	SD
0	1391	1386	1399	1392	6.73
5	1138	1101	1150	1130	25.41
15	1052	1068	1045	1055	11.43
30	953	980	926	953	27.04
60	775	781	787	781	6.18
90	654	626	673	651	23.57
120	538	556	515	536	20.48

Table B-60 MEK concentration-time for the oxidation of MEK by NaOCl for Run No. M.21: T = 45°C, pH = 11.13

Time (minutes)	Concentration of MEK x 10^5 (mol L^{-1})				
	Point 1	Point 2	Point 3	Average	SD
0	1470	1438	1472	1460	18.85
5	1384	1401	1360	1382	21.03
15	1246	1216	1239	1233	15.69
30	1190	1190	1124	1168	37.93
60	969	967	926	954	24.16
90	703	659	735	699	37.79
120	539	568	526	544	21.82

Table B-61 MEK concentration-time for the oxidation of MEK by NaOCl for Run No. M.22: T = 50°C, pH = 11.10

Time (minutes)	Concentration of MEK x 10^5 (mol L^{-1})				
	Point 1	Point 2	Point 3	Average	SD
0	1405	1450	1432	1429	22.35
5	1299	1265	1325	1296	30.01
15	1290	1287	1289	1289	1.60
30	819	804	825	816	10.70
60	633	637	640	637	3.53
90	545	520	505	523	20.46
120	437	412	390	413	23.32

Table B-62 MEK concentration-time for the oxidation of MEK by NaOCl for Run No. M.27: T = 31°C, pH = 11.65

Time (minutes)	Concentration of MEK x 10^5 (mol L^{-1})				
	Point 1	Point 2	Point 3	Average	SD
0	591	605	580	592	12.64
5	537	536	533	535	2.00
15	489	505	470	488	17.25
30	440	436	420	432	10.23
60	370	348	399	372	25.69
90	307	301	312	307	5.70
120	265	262	269	266	3.59

Table B-63 NaOCl concentration-time for the oxidation of MEK by NaOCl for Run No. M.27: T = 31°C, pH = 11.65

Time (minutes)	Concentration of NaOCl x 10^5 (mol L^{-1})				
	Point 1	Point 2	Point 3	Average	SD
0	645	658	654	652	6.84
5	647	636	640	641	5.63
15	636	627	636	633	5.17
30	618	613	611	614	3.42
60	598	591	596	595	3.42
90	582	569	578	576	6.84
120	569	573	562	568	5.63

Table B-64 MEK concentration-time for the oxidation of MEK by NaOCl for Run No. M.28: T = 36°C, pH = 11.25

Time (minutes)	Concentration of MEK x 10^5 (mol L^{-1})				
	Point 1	Point 2	Point 3	Average	SD
0	923	951	955	943	17.29
5	874	867	863	868	5.18
15	797	817	808	807	9.72
30	620	636	609	622	13.64
60	509	503	536	516	17.78
90	444	466	422	444	22.42
120	375	342	408	375	33.14

Table B-65 NaOCl concentration-time for the oxidation of MEK by NaOCl for Run No. M.28: T = 36°C, pH = 11.25

Time (minutes)	Concentration of NaOCl x 10^5 (mol L^{-1})				
	Point 1	Point 2	Point 3	Average	SD
0	918	922	922	921	2.59
5	911	913	927	917	8.48
15	891	876	882	883	7.44
30	775	788	797	787	11.27
60	769	770	766	768	2.30
90	761	766	766	764	2.59
120	743	752	748	748	4.48

Table B-66 MEK concentration-time for the oxidation of MEK by NaOCl for Run No. M.29: T = 47°C, pH = 11.10

Time (minutes)	Concentration of MEK x 10^5 (mol L^{-1})				
	Point 1	Point 2	Point 3	Average	SD
0	2658	2693	2703	2685	23.50
5	2427	2433	2419	2426	7.08
15	1993	1970	2030	1998	30.34
30	1751	1826	1758	1778	41.30
60	1360	1318	1348	1342	21.83
90	1202	1171	1245	1206	37.32
120	1059	1050	1002	1037	30.86

Table B-67 NaOCl concentration-time for the oxidation of MEK by NaOCl for Run No. M.29: T = 47°C, pH = 11.10

Time (minutes)	Concentration of NaOCl x 10^5 (mol L^{-1})				
	Point 1	Point 2	Point 3	Average	SD
0	1388	1384	1375	1382	6.84
5	1361	1366	1370	1366	4.48
15	1357	1366	1366	1363	5.17
30	1312	1299	1303	1305	6.84
60	1263	1272	1267	1267	4.48
90	1214	1231	1240	1228	13.68
120	1214	1220	1218	1217	3.42

Table B-68 Acetone concentration-time for the oxidation of acetone by NaOCl
Run No. A.33: T = 29°C, pH = 11.85

Time (minutes)	Concentration of Acetone x 10^5 (mol L^{-1})				
	Point 1	Point 2	Point 3	Average	SD
0	220	236	228	228	7.83
5	192	203	192	196	6.26
15	177	175	174	175	1.58
30	120	129	144	131	11.95
60	90	86	84	87	3.07
90	38	51	52	47	7.70
120	33	26	41	33	7.40

Table B-69 Acetone concentration-time for the oxidation of acetone by NaOCl
Run No. A.34: T = 29°C, pH = 11.38

Time (minutes)	Concentration of Acetone x 10^5 (mol L^{-1})				
	Point 1	Point 2	Point 3	Average	SD
0	284	282	287	284	2.08
5	242	243	245	243	1.57
15	218	217	218	218	0.68
30	196	201	203	200	3.69
60	121	129	131	127	5.17
90	75	74	77	75	1.15
120	70	70	66	68	2.25

Table B-70 Acetone concentration-time for the oxidation of acetone by NaOCl
Run No. A.35: T = 30°C, pH = 11.16

Time (minutes)	Concentration of Acetone x 10^5 (mol L^{-1})				
	Point 1	Point 2	Point 3	Average	SD
0	510	510	523	514	7.40
5	463	485	415	454	35.89
15	384	384	392	387	4.36
30	348	357	346	350	5.94
60	240	236	230	235	5.07
90	197	194	186	192	5.31
120	169	165	165	166	2.58

Table B-71 Acetone concentration-time for the oxidation of acetone by NaOCl
Run No. A.36: T = 29°C, pH = 11.15

Time (minutes)	Concentration of Acetone x 10^5 (mol L^{-1})				
	Point 1	Point 2	Point 3	Average	SD
0	1041	988	1030	1020	27.99
5	916	935	935	929	10.73
15	865	773	806	815	46.79
30	719	691	763	724	36.18
60	629	610	618	619	9.52
90	544	559	518	540	20.68
120	417	444	458	439	21.02

Table B-72 MEK concentration-time for the oxidation of MEK by $KMnO_4$ for Run No. M.10: T = 29°C, pH = 11.57

Time (minutes)	Concentration of MEK x 10^5 (mol L^{-1})				
	Point 1	Point 2	Point 3	Average	SD
0	326	339	358	341	16.12
5	184	177	175	179	4.60
15	164	159	165	162	3.23
30	142	151	144	146	4.62
45	127	122	115	121	6.37
60	70	81	57	69	12.17

Table B-73 MEK concentration-time for the oxidation of MEK by $KMnO_4$ for Run No. M.11: T = 29°C, pH = 11.50

Time (minutes)	Concentration of MEK x 10^5 (mol L^{-1})				
	Point 1	Point 2	Point 3	Average	SD
0	504	520	524	516	10.68
5	439	428	474	447	24.05
15	379	361	367	369	9.37
30	301	281	267	283	17.01
45	235	217	202	218	16.59
60	171	162	183	172	10.69

Table B-74 MEK concentration-time for the oxidation of MEK by $KMnO_4$ for Run No. M.12: T = 29°C, pH = 11.47

Time (minutes)	Concentration of MEK x 10^5 (mol L^{-1})				
	Point 1	Point 2	Point 3	Average	SD
0	610	607	605	607	2.21
5	596	592	599	596	3.76
15	574	583	580	579	4.65
30	508	513	520	514	6.31
45	485	490	495	490	4.91
60	455	458	451	455	3.33

Table B-75 MEK concentration-time for the oxidation of MEK by $KMnO_4$ for Run No. M.13: T = 30°C, pH = 11.44

Time (minutes)	Concentration of MEK x 10^5 (mol L^{-1})				
	Point 1	Point 2	Point 3	Average	SD
0	695	666	728	697	30.70
5	536	532	538	536	2.88
15	491	494	489	492	2.21
30	458	465	450	458	7.81
45	395	388	407	396	9.41
60	348	349	349	349	0.35

Table B-76 MEK concentration-time for the oxidation of MEK by $KMnO_4$ for Run No. M.14: T = 29°C, pH = 11.58

Time (minutes)	Concentration of MEK x 10^5 (mol L^{-1})				
	Point 1	Point 2	Point 3	Average	SD
0	727	772	852	784	62.94
5	639	629	682	650	28.31
15	620	598	620	613	12.72
30	474	519	545	513	35.66
45	424	415	451	430	18.90
60	365	381	373	373	7.74

Table B-77 MEK concentration-time for the oxidation of MEK by $KMnO_4$ for Run No. M.15: T = 29°C, pH = 11.58

Time (minutes)	Concentration of MEK x 10^5 (mol L^{-1})				
	Point 1	Point 2	Point 3	Average	SD
0	876	890	871	879	9.86
5	827	788	808	808	19.50
15	781	785	783	783	1.66
30	596	587	610	597	11.39
45	532	473	561	522	44.94
60	289	305	315	303	13.19

Table B-78 MEK concentration-time for the oxidation of MEK by $KMnO_4$ for Run No. M.16: T = 30°C, pH = 11.58

Time (minutes)	Concentration of MEK x 10^5 (mol L^{-1})				
	Point 1	Point 2	Point 3	Average	SD
0	1291	1210	1435	1312	113.95
5	1269	1230	1187	1229	41.28
15	1027	1077	1140	1081	56.61
30	813	825	744	794	43.41
45	748	735	725	736	11.61
60	614	562	647	608	43.08

Table B-79 MEK concentration-time for the oxidation of MEK by $KMnO_4$ for Run No. M.17: T = 29°C, pH = 11.50

Time (minutes)	Concentration of MEK x 10^5 (mol L^{-1})				
	Point 1	Point 2	Point 3	Average	SD
0	1934	1872	1887	1898	32.08
5	1806	1787	1814	1802	13.71
15	1617	1627	1628	1624	6.31
30	1365	1380	1384	1376	10.39
45	1155	1180	1238	1191	42.85
60	970	995	1074	1013	54.45

Table B-80 MEK concentration-time for the oxidation of MEK by $KMnO_4$ for Run No. M.18: T = 29°C, pH = 11.60

Time (minutes)	Concentration of MEK x 10^5 (mol L^{-1})				
	Point 1	Point 2	Point 3	Average	SD
0	2918	3018	3057	2997	71.76
5	2694	2766	2758	2739	39.28
15	2396	2416	2470	2427	38.28
30	2138	2087	2016	2080	61.37
45	1693	1770	1699	1720	42.78
60	1541	1520	1500	1521	20.37

Table B-81 MEK concentration-time for the oxidation of MEK by $KMnO_4$ for Run No. M.23: T = 35°C, pH = 11.41

Time (minutes)	Concentration of MEK x 10^5 (mol L^{-1})				
	Point 1	Point 2	Point 3	Average	SD
0	727	776	687	730	44.48
5	579	555	587	574	16.53
15	485	470	498	484	13.95
30	419	431	414	421	8.58
45	380	391	379	383	6.48
60	325	321	327	324	2.68

Table B-82 MEK concentration-time for the oxidation of MEK by $KMnO_4$ for Run No. M.24: T = 40°C, pH = 11.35

Time (minutes)	Concentration of MEK x 10^5 (mol L^{-1})				
	Point 1	Point 2	Point 3	Average	SD
0	661	655	675	664	10.23
5	439	431	446	438	7.19
15	404	383	428	405	22.54
30	360	371	369	367	5.96
45	307	301	321	310	10.31
60	233	235	232	233	1.27

Table B-83 MEK concentration-time for the oxidation of MEK by $KMnO_4$ for Run No. M.25: T = 45°C, pH = 11.38

Time (minutes)	Concentration of MEK x 10^5 (mol L^{-1})				
	Point 1	Point 2	Point 3	Average	SD
0	692	730	752	725	29.89
5	651	663	669	661	9.24
15	600	610	604	605	4.79
30	463	484	506	484	21.70
45	425	416	435	425	9.29
60	301	310	306	306	4.18

Table B-84 MEK concentration-time for the oxidation of MEK by $KMnO_4$ for Run No. M.26: T = 50°C, pH = 11.36

Time (minutes)	Concentration of MEK x 10^5 (mol L^{-1})				
	Point 1	Point 2	Point 3	Average	SD
0	646	653	660	653	6.73
5	512	578	489	526	46.60
15	428	433	415	425	9.37
30	309	306	320	312	7.10
45	248	252	240	247	6.23
60	218	224	213	218	5.91

Table B-85 MEK concentration-time for the oxidation of MEK by $KMnO_4$ for Run No. M.30: T = 30°C, pH = 11.57

Time (minutes)	Concentration of MEK x 10^5 (mol L^{-1})				
	Point 1	Point 2	Point 3	Average	SD
0	2926	3219	2920	3022	171.24
5	2254	2196	2182	2211	38.22
15	1997	2078	2099	2058	54.04
30	1976	1896	1796	1890	90.31
45	1553	1577	1447	1526	69.05
60	1307	1213	1335	1285	64.04

Table B-86 $KMnO_4$ concentration-time for the oxidation of MEK by $KMnO_4$ for Run No. M.30: T = 30°C, pH = 11.57

Time (minutes)	Concentration of $KMnO_4$ x 10^5 (mol L^{-1})				
	Point 1	Point 2	Point 3	Average	SD
0	321	320	321	320	0.63
5	360	360	359	360	0.63
15	346	345	345	345	0.41
30	338	338	339	338	0.41
45	357	355	356	356	1.03
60	339	337	337	338	0.95

Table B-87 MEK concentration-time for the oxidation of MEK by $KMnO_4$ for Run No. M.31: T = 38°C, pH = 11.53

Time	Concentration of MEK x 10^5 (mol L^{-1})				
(minutes)	Point 1	Point 2	Point 3	Average	SD
0	703	669	682	695	11.00
5	616	561	720	632	81.04
15	488	495	504	496	7.64
30	404	410	402	406	4.21
45	347	354	344	348	5.21
60	222	209	219	217	6.74

Table B-88 $KMnO_4$ concentration-time for the oxidation of MEK by $KMnO_4$ for Run No. M.31: T = 38°C, pH = 11.53

Time	Concentration of $KMnO_4$ x 10^5 (mol L^{-1})				
(minutes)	Point 1	Point 2	Point 3	Average	SD
0	1308	1309	1308	1308	0.41
5	1301	1301	1300	1301	0.63
15	1301	1302	1301	1301	0.41
30	1303	1303	1300	1302	1.71
45	1301	1301	1302	1301	0.41
60	1303	1302	1303	1302	0.63

Table B-89 MEK concentration-time for the oxidation of MEK by $KMnO_4$ for Run No. M.32: T = 48°C, pH = 11.32

Time (minutes)	Concentration of MEK x 10^5 (mol L^{-1})				
	Point 1	Point 2	Point 3	Average	SD
0	1101	1115	1152	1123	26.14
5	1017	1007	1019	1014	6.57
15	905	896	905	902	5.06
30	716	700	667	694	24.95
45	604	648	673	641	35.25
60	462	452	459	458	5.14

Table B-90 $KMnO_4$ concentration-time for the oxidation of MEK by $KMnO_4$ for Run No. M.32: T = 48°C, pH = 11.32

Time (minutes)	Concentration of $KMnO_4$ x 10^5 (mol L^{-1})				
	Point 1	Point 2	Point 3	Average	SD
0	237	238	239	238	0.82
5	232	233	233	233	0.41
15	219	219	219	219	0.41
30	213	213	211	212	0.86
45	228	229	229	229	0.63
60	212	213	213	212	0.24

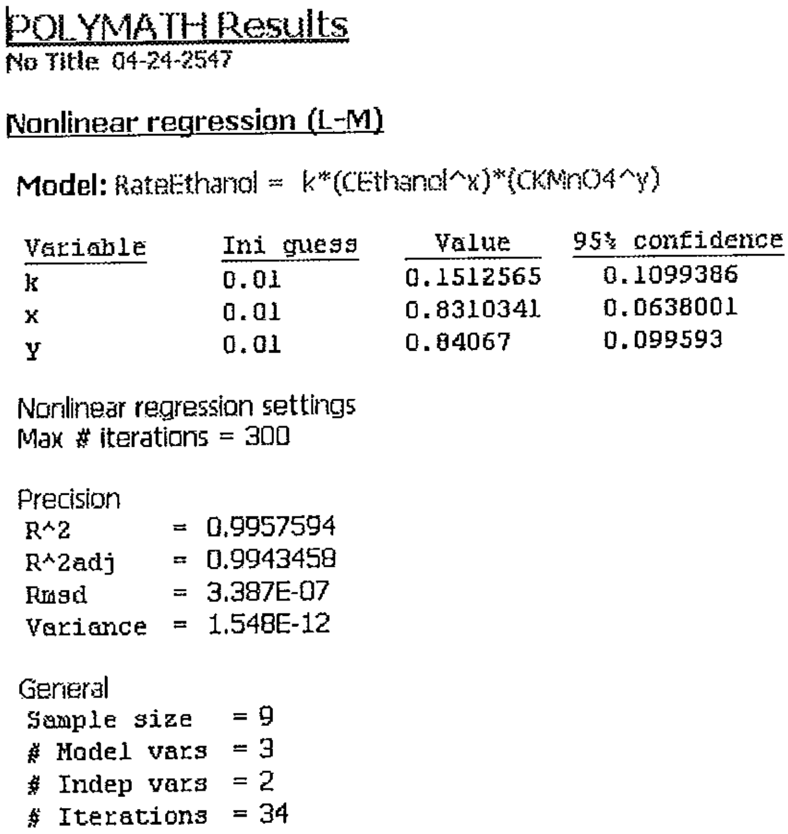
Appendix C

Reaction rate constant and Reaction order given by Program Polymath 5.1

Figure C-1 Maththematic analysis by program Polymath 5.1 using non-linear regression for the oxidation of toluene by NaOCl

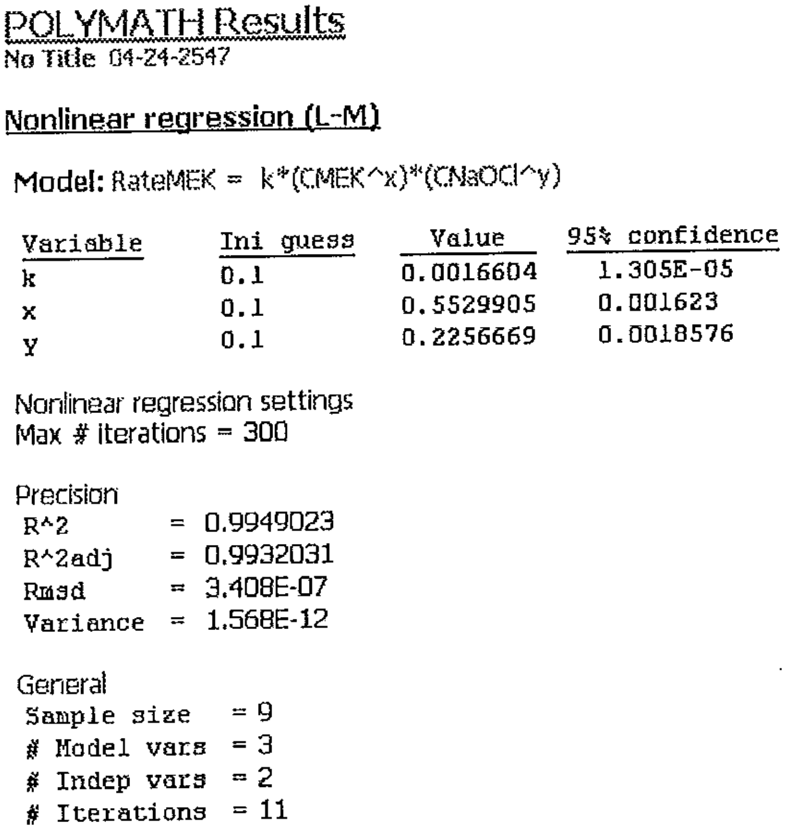
```
POLYMATH Results
POLYMATH Report 04-24-2547

Nonlinear regression (L-M)

 Model: RateToluene =  k*(CToluene^x)*(CNaOCl^y)

 Variable      Ini guess    Value       95% confidence
 k             0.001        0.008905      1.602E-04
 x             0.001        1.1009987     0.0035941
 y             0.001        0.1132557     0.0044758

 Nonlinear regression settings
 Max # iterations = 300

 Precision
 R^2         =  0.9891508
 R^2adj      =  0.9855344
 Rmsd        =  3.334E-07
 Variance    =  1.501E-12

 General
 Sample size    = 9
 # Model vars   = 3
 # Indep vars   = 2
 # Iterations   = 51
```

Figure C-2 Maththematic analysis by program Polymath 5.1 using non-linear regression for the oxidation of ethanol by $KMnO_4$



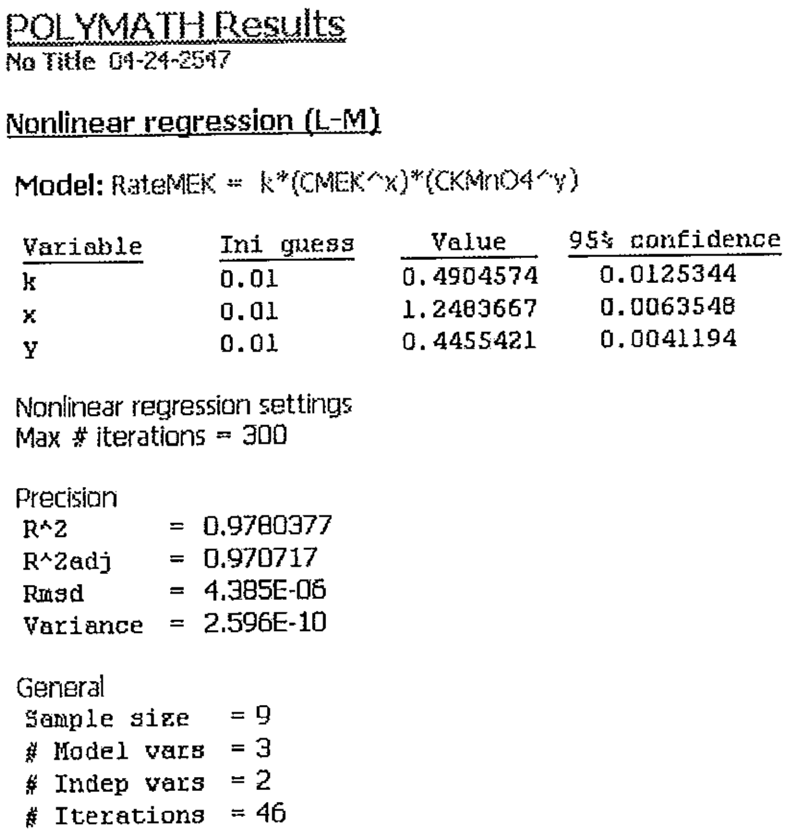
```
POLYMATH Results
No Title 04-24-2547

Nonlinear regression (L-M)

 Model: RateEthanol =  k*(CEthanol^x)*(CKMnO4^y)

 Variable          Ini guess        Value       95% confidence
 k                 0.01             0.1512565    0.1099386
 x                 0.01             0.8310341    0.0638001
 y                 0.01             0.84067      0.099593

 Nonlinear regression settings
 Max # iterations = 300

 Precision
 R^2          =  0.9957594
 R^2adj       =  0.9943458
 Rmsd         =  3.387E-07
 Variance     =  1.548E-12

 General
 Sample size    = 9
 # Model vars   = 3
 # Indep vars   = 2
 # Iterations   = 34
```

Figure C-3 Maththematic analysis by program Polymath 5.1 using non-linear regression for the oxidation of MEK by NaOCl



```
POLYMATH Results
No Title 04-24-2547

Nonlinear regression (L-M)

 Model: RateMEK =  k*(CMEK^x)*(CNaOCl^y)

 Variable      Ini guess     Value       95% confidence
 k             0.1           0.0016604     1.305E-05
 x             0.1           0.5529905     0.001623
 y             0.1           0.2256669     0.0018576

 Nonlinear regression settings
 Max # iterations = 300

 Precision
 R^2        =  0.9949023
 R^2adj     =  0.9932031
 Rmsd       =  3.408E-07
 Variance   =  1.568E-12

 General
 Sample size    = 9
 # Model vars   = 3
 # Indep vars   = 2
 # Iterations   = 11
```

Figure C-4 Maththematic analysis by program Polymath 5.1 using non-linear regression for the oxidation of MEK by $KMnO_4$



```
POLYMATH Results
No Title 04-24-2547

Nonlinear regression (L-M)

Model: RateMEK = k*(CMEK^x)*(CKMnO4^y)

Variable      Ini guess     Value       95% confidence
k             0.01          0.4904574     0.0125344
x             0.01          1.2483667     0.0063548
y             0.01          0.4455421     0.0041194

Nonlinear regression settings
Max # iterations = 300

Precision
R^2         = 0.9780377
R^2adj      = 0.970717
Rmsd        = 4.385E-06
Variance    = 2.596E-10

General
Sample size    = 9
# Model vars   = 3
# Indep vars   = 2
# Iterations   = 46
```

Appendix D

Standard chemical preparations and Physical properties of VOCs and Oxidizing agent

Standard sodium thiosulfate titrant, 0.1*N*:

Dissolve 25 g $Na_2S_2O_3{\bullet}5H_2O$ in 1 liter freshly boiled distilled water and standardize the solution against potassium biniodate or potassium dichromate after at least 2 weeks' storage. Use boiled distilled water and add a few milliliters of chloroform to minimize bacterial decomposition of the thiosulfate solution.

Standard sodium thiosulfate titrant, 0.025*N*:

Improve the stability of 0.025*N* $Na_2S_2O_3$ by diluting an aged 0.1*N* solution, made as directed above, with freshly boiled distilled water. Avoid trouble by adding a few milliliters of chloroform of 0.4 g sodium borate and 10 mg mercuric iodide per liter of solution. For accurate work, standardize this solution daily in accordance with the directions given above, using 0.025*N* $KH(IO_3)_2$ or $K_2Cr_2O_7$. Use an automatic buret of a type in which rubber does not come in contact with the solution, to speed up operations where many samples must be titrated. Standard sodium thiosulfate titrants, exactly 0.0250*N*, are equivalent, respectively, to 354.5 µg and 886.3 µg available Cl per 1.00 ml.

Starch indicator solution

To 5 g starch, add a little cold water and grind in a mortar to a thin paste. Pour into 1 liter of boiling distilled water, stir, and allow to settle overnight. Use the clear supernate. Preserve with 1.25 g salicyclic acid, 4 g zinc chloride, of a combination of 4 g sodium propionate and 2 g sodium azide added to 1 liter of starch solution.

Physical properties of VOCs

VOCs	Molecular Weight ($g\ mol^{-1}$)	Density ($g\ ml^{-1}$)	Boiling Point (°C)
Acetone	58.08	0.7899	56.2
Benzene	78.11	0.8765	80.1
Ethanol	46.07	0.7890	78.5
MEK	72.11	0.8054	79.6
Methanol	32.04	0.7900	64.6
Toluene	92.14	0.8669	111

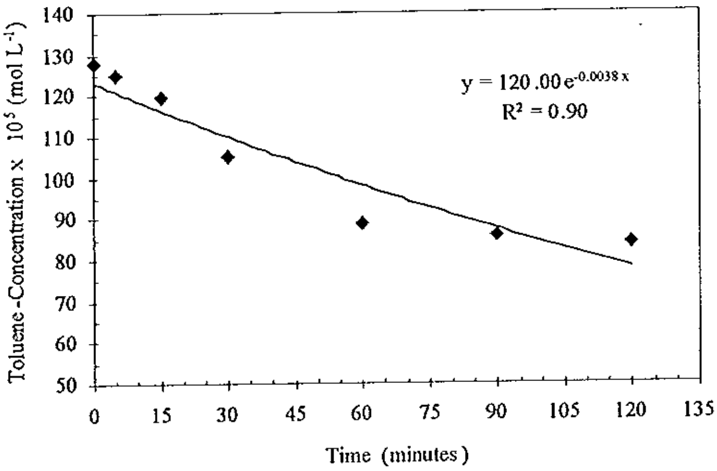
Physical properties of Oxidizing agent

Oxidizing agent	Molecular Weight ($g\ mol^{-1}$)	Density ($g\ ml^{-1}$)
Potassium Permanganate	158.04	2.7
Sodium Hypochlorite	74.44	1.07-1.14

Appendix E

Example of the Calculations

- ***Calculation of initial reaction rate ($-r_{Toluene,0}$) for the oxidation of toluene by NaOCl***



Concentration-time curve of toluene by NaOCl (Run No.T.1)

By curve fitting data from the concentration-time curves, the data were fit well with an exponential curve. Then empirical fitting parameters (B and a_I) are known. The initial rate of reaction were determined from:

$$-r_{Toluene,0} = \left(\frac{d\left(Be^{a_I t}\right)}{dt}\right)_{t=0} = -Ba_I(e^{a_I t_0}) = -Ba_I$$

Run No. T.1 $B = 0.0012$ and $a_I = -0.0038$

$$-r_{Toluene,0} = -(0.0012)(-0.0038)$$
$$= 0.00000456$$

So that; $-r_{Toluene,0}$ for Run No. T.1 $= 0.00000456 \ mol \ L^{-1} \ min^{-1}$

- Calculation of kinetic rate constant (k) for the oxidation of toluene by NaOCl

$$k = \frac{-r_{Toluene,0}}{(C^{\alpha}_{Toluene,0})(C^{\beta}_{NaOCl,0})}$$

Run No. T.8 $C_{Toluene,0} = 0.00679\ mol\,L^{-1}$, $C_{NaOCl,0} = 0.02917\ mol\,L^{-1}$

$-r_{Toluene,0} = 0.00002623$, $\alpha = 1.10$ and $\beta = 0.11$

$$k = \frac{(0.00002623)}{(0.00679^{1.10})(0.02917^{0.11})}$$

$$= 0.00939$$

So that; k for Run No. T.8 $= 0.00939$

- Calculation of activation energy (E_a) and frequency factor (A) for the oxidation of toluene by NaOCl

$$ln\,k = ln\,A - \left(\frac{E_a}{R}\right)\frac{1}{T}$$

From the plotted of linearized Arrhenius, the interception of the graph will give A and the slope of the graph will give E_a (where $R = 8.314\ J\,mol^{-1}\,K^{-1}$)

$$ln\,k = 8.0249 - 3{,}838\frac{1}{T}$$

$ln\,A = 8.0249$ $\therefore$ $A = e^{8.0249} = 3{,}056$

$\frac{E_a}{8.314} = 3{,}838$ $\therefore$ $E_a = 31{,}908$

So that; The oxidation of toluene by NaOCl $A = 3{,}056$ and $E_a = 31{,}908\ J\,mol^{-1}$

- Calculation of the measured oxidation rate $(-r_{measured})$ and the predicted oxidation rate $(-r_{predicted})$ for the oxidation of toluene by NaOCl

$$-r_{measured} = \left(\frac{d\left(Be^{a_1 t}\right)}{dt}\right)_{t=t} = -Ba_1(e^{a_1 t})$$

$$-r_{predicted} = 3{,}056e^{\frac{-31{,}908}{RT}} C_{Toluene,t}^{1.10} C_{NaOCl,t}^{0.11}$$

Run No. T.15 at 30°C $\quad B = 0.0012, \;\; a_1 = -0.0038$

$R = 8.314 \; J\,mol^{-1}\,K^{-1}$ and $T = 303.15\,K$

t=0 min ;

$$-r_{measured} = -(0.0016)(-0.0033)(e^{(-0.0033)(0)})$$

$$= 0.000005280 \quad mol\,L^{-1}\,min^{-1}$$

$$-r_{predicted} = 3{,}056e^{\frac{(-31{,}908)}{(8.314)(303.15)}}(0.00164)^{1.10}(0.02917)^{0.11}$$

$$= 0.000005693 \quad mol\,L^{-1}\,min^{-1}$$

$$\%error = \left|\left(\frac{(-r_{measured}) - (-r_{predicted})}{(-r_{predicted})}\right)\right| \times 100$$

$$= \left|\left(\frac{(0.000005280) - (0.000005693)}{(0.000005693)}\right)\right| \times 100$$

$$= 7.25\%$$

t=60 min ;

$$-r_{measured} = -(0.0016)(-0.0033)(e^{(-0.0033)(60)})$$

$$= 0.000004331 \quad mol\,L^{-1}\,min^{-1}$$

$$-r_{predicted} = 3{,}056e^{\frac{(-31{,}908)}{(8.314)(303.15)}}(0.00125)^{1.10}(0.02802)^{0.11}$$

$$= 0.000004200 \quad mol\,L^{-1}\,min^{-1}$$

$$\%error = \left|\left(\frac{(0.000004331) - (0.000004200)}{(0.000004200)}\right)\right| \times 100$$

$$= 3.11\%$$

VITAE

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