SUPERCRITICAL WATER OXIDATION OF NITROGEN-CONTAINING ORGANIC COMPOUNDS: PROCESS ENHANCEMENT USING PROPYLENE GLYCOL

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ABSTRACT

This research aims to investigate the feasibility and efficiency of the supercritical water oxidation treatment method in destroying two diluted hazardous nitrogen-containing hydrocarbons. Monoethanolamine (MEA) and 3-methylpyridine (3MP) are selected due to their resistant nature under supercritical conditions and they are found in the effluent of different industries.

A continuous plug flow reactor (laboratory-scale system) was used to investigate the destruction of MEA and 3MP at different operating conditions. The ranges of temperature were from 400 to 525 °C for MEA and 425 to 525 °C for 3MP at pressure of 250 bar. Propylene glycol (PG) was used as a co-fuel to enhance SCWO performance. PG could be considered as a novel approach for improving the destruction of two compounds. Also, isopropyl alcohol (IPA) was used as co-fuel to compare between the effect of PG and IPA on efficiency of SCWO at different operating conditions. The effect of co-fuel on by-products of MEA and 3MP was investigated. The results were employed to determine the kinetic parameters in the absence and presence of co-fuel.

The effect of operating conditions such as temperature, residence time, oxidant ratio, initial concentration and co-fuel ratio on the destruction of MEA and 3MP was investigated. The results illustrated the positive effect of temperature on the destruction of two nitrogen-containing compounds. The complete removal efficiency of chemical oxygen demand (COD) of MEA was achieved at 525 °C and the maximum removal efficiency of total organic carbon (TOC) of 3MP was also achieved at 525 °C. The yield of NH_4-N increased with operating temperature in the MEA and 3MP systems.

The initial concentration of MEA and 3MP, oxidant ratio and residence time positively enhanced the COD removal and TOC removal efficiencies respectively. Although these effects were significant, the effect of operating temperature was influential on the destruction of two compounds in the absence and presence of co-fuel.

PG has a significant effect on the destruction of MEA and 3MP at different operating conditions. The results of the removal efficiency in the presence of PG were more remarkable than IPA. For example, COD removal efficiency of MEA increased from 61.0 % (fuel-free system) to 80.0 % (PG system) at the temperature of 400 °C and residence time of 14 s. The efficiency of TOC removal of 3MP increased from 69.9 % (fuel-free system) to 84.8 % (PG system) at the temperature of 425 °C and residence time of 14 s. In the presence of PG, the removal efficiency of nitrogen of MEA was 85.0 % at the ratio of (2.5 PG: 1 MEA) and the temperature of 400°C, the removal efficiency of nitrogen of 3MP was 88.0 % at the ratio of (3 PG:1 3MP) and the temperature of 425°C. The enhancement of the SCWO performance in the presence of PG was due to the activity of two hydroxyl groups.

The effect of PG occurred significantly on activation energy of two compounds. For instance, the activation energy of MEA decreased from 79.746 kJ.mol^{-1} (fuel-free system) to 46.807 kJ.mol^{-1} and 47.497 kJ.mol^{-1} in the presence of IPA and PG respectively. In the case of 3MP, the activation energy decreased from 31.85 kJ.mol^{-1} (fuel-free system) to 31.2 kJ.mol^{-1} and 28.4 kJ.mol^{-1} in the presence of IPA and PG respectively. Consequently, the number of reactant molecules increases at lower activation energy in the presence of co-fuel and the rate of reaction will be fast.

Finally, the destruction of MEA at 400 °C and 3MP at 425 °C in the presence of PG considers an essential goal to avoid using high temperature.

To my big family

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LIST OF ABBREVIATIONS AND SYMBOLS

Abbreviations

3MP	3-Methylpyridine
COD	Chemical Oxygen Demand
GC/TCD	Gas Chromatography / Thermal Conductivity Detector
HPLC	High-Performance Liquid Chromatography
HO•	Hydroxyl radical
HO_2•	Hydroperoxyl radical
MEA	Monoethanolamine
NIST	National Institute for Standards and Technology
NO_x	Nitrous oxides
SCWO	Supercritical Critical Water Oxidation
SR	Stoichiometric Ratio
SO_x	Sulphur oxides
SS	Stainless Steel
TN	Total Nitrogen
TOC	Total Organic Carbon
TWR	Transpiring Wall Reactor
WAO	Wet Air Oxidation

Alphabetical Symbols

[Organic]	the organics initial concentration in mol.L^{-1}
[Oxidant]	the oxidant initial concentration in mol.L^{-1}.
[Water]	Water concentration (mol.L^{-1})
A	the pre-exponential factor in $M^{1-a-b-c}$ s^{-1}
a	the reaction order relating to an organic compound
b	the reaction order relating to oxidant.
c	the reaction order relating to water.
E_a	the activation energy in J.mol^{-1}
k	Reaction rate constant (s^{-1})
K_w	Ion Product of water
L	Reactor length
r	Rate of reaction
R	Constant of universal gas (8.314 J.mol^{-1}.K^{-1}).
Re	Reynolds Number
T	Reaction temperature (K)
T,P	Temperature and pressure
Sc	Supercritical
X_{COD}, X_{MEA}, $X_{MEA+IPA}$, X_{MEA+PG}	Conversion of COD
X_{TOC}, X_{3MP}, $X_{3MP+IPA}$, X_{3MP+PG}	Conversion of TOC

Greek Symbols

ε	Static dielectric constant
μ	Dynamic viscosity
ρ	Fluid density
τ	Reactor residence time

CHAPTER ONE: INTRODUCTION

1.1 Background and Motivation

Numerous daily activities, such as industry and municipal services, contribute to the generation of large amounts of waste. These wastes are divided into hazardous and non-hazardous. Hazardous waste is a real problem if disposed of in the environment without treatment. Hazardous waste can be defined as substances with the ability to harm the environment and human health, which are either toxic, reactive, ignitable or corrosive. By 2025, the world will be producing more than 2.2 billion tonnes of waste every year, according to a report for the United Nations Environmental Programme (UNEP, 2018). These vast quantities will necessitate strict management and careful handling. The impacts of hazardous waste on human health are harmful due to high toxicity, poor biodegradability and bioaccumulation. Environmental guidelines applied by governments or environmental agencies must focus on the enhancement of treatment methods for wastewater before disposal into the environment. For example, the council of European communities issued the directive (91/271/EEC) that provided a standard for wastewater disposal into the environment.

There are two ways to dispose of hazardous waste: directly through incineration (without recovery of energy), or via landfill. Both options have disadvantages. The cost of landfill disposal has increased due to increased taxes for hazardous wastes in accordance with the EU landfill directive 1999/31/EC. In addition, impacts of hazardous wastes on the surface environment and groundwater may make landfill risky. Incineration is a common method of dealing with a wide range of hazardous wastes. Like landfill disposal, incineration is an expensive technology, and risks emitting dangerous gases such as nitrogen oxide (NO_x). Also, produced ash must be disposed of in landfill because it contains highly toxic materials, and this is another added cost. Consequently, alternative treatment methods must be developed. Several technologies have potential and may have economic advantages over incineration and landfill.

The wide range of organic wastewaters leads to many challenges and necessitates the development of treatment techniques, including biological, physical and chemical. One of these technologies is supercritical water oxidation (SCWO). SCWO operates above 374℃ and 22.1MPa; these conditions promote essential changes in the thermodynamic properties of water. Lowering the density of water in the supercritical phase will lead to improved mass and heat transfer properties. The produced medium is a suitable solvent for organic matter and gases for example, a wide range of hydrocarbons, biopolymers and biomass due to the weakness of hydrogen bonds under supercritical temperature and pressure. This technology can efficiently complete the destruction of organic hazardous waste in a short time, mineralising it to produce carbon dioxide and water. In addition, it has other advantages such as a removal efficiency of more than 99% and high miscibility between organic wastes and gases; there are also no toxic gas emissions (e.g. fly ash, NO_x, metal vapours, dioxins, SO_x). Also, the reaction under supercritical conditions is exothermic, and this contributes to energy recovery in large-scale SCWO to produce electric power or elevate the temperature of the pumped solution. Consequently, this process is economically and environmentally competitive with incineration and landfill. On the other hand, SCWO suffers from two problems: corrosion and generation of non-dissolved salts. These pose technical challenges that may limit the spread of SCWO commercially worldwide.

Nitrogen-containing compounds constitute one of the essential classes of hydrocarbons found in hazardous waste effluents. The main properties of nitrogen-containing hydrocarbons are poor biodegradability, toxicity and abundance in the effluent of numerous industries, such as chemical, pharmaceutical, petrochemical and domestic wastewater. The chemical behaviour of nitrogen is complex, and the main SCWO by-products of nitrogen-containing wastes are resistant. For example, ammonia causes harm to aquatic life until concentration is reduced to moderate. For complete destruction of such by-products, high temperatures of more than 600℃ must be used. Other by-products are nitrate and nitrite, which can cause illnesses such as *blue baby disease*;

nitrite may also react chemically or enzymatically with an amine group to form *nitrosamines*, which cause cancer. A primary gaseous emission is nitrogen oxide, which is generated through incineration under high temperature (>850℃). Therefore, the destruction of nitrogen-containing hydrocarbons by suitable treatment methods is an essential problem for environmental and public health.

Therefore, the evaluation of the performance of SCWO technology is the main motivation in this study which was chosen two models of nitrogen-containing contaminates with different structures. In this work, two chemical models were observed in the effluent of petrochemical and pharmaceutical industries. Monoethanolamine (MEA) (C_2H_7NO) is a primary amine. MEA is considered an essential compound in various industries. It contains an amino group and an alcohol group. It is used to reduce the concentration of CO_2 in natural gas and used in other industries. The second compound was 3-methylpyridine (3MP) (C_6H_7N); it is a heterocyclic compound that is used as a solvent in pharmaceutical and agriculture applications.

Enhancement of the SCWO performance has taken various forms, one of them is applying co-oxidation by using different types of alcohols which were observed the rate of reaction increasing with adding co-fuel more than the rate of reaction of a single compound under supercritical conditions. Many researchers have demonstrated the positive effect of co-fuel on removal efficiency and by-products. For instance, methanol, ethanol and isopropyl alcohols (monohydric alcohols) are applied to enhance the conversion of ammonia and organic wastes, and several examples have shown the use of co-fuel to enhance the removal efficiency of organic waste (Al-Duri et al., 2016; Marrone et al., 2005; Yang et al., 2018; Bermejo et al., 2008; Ploeger et al., 2007; Savage et al., 2000). In this study, propylene glycol ($C_3H_8O_2$) was selected to evaluate the effect of co-fuel on improving SCWO performance. The studies in this field are rare if compared with monohydric alcohols studies such as methanol, ethanol and isopropyl alcohol. Using a new co-fuel may give this work a high novelty.

1.2 Aims and Objectives

The main aim of this study is to investigate the effect of propylene glycol on the enhancement of the removal efficiency of two nitrogen-containing compounds at various supercritical conditions in the tubular reactor. An examination of the influence of co-fuel is on intermediate compounds, especially ammonia that needs a high temperature to be destroyed. Also, the evaluation of the kinetic parameters is for different reactions. The results of this study will provide significant guidance about the role of propylene glycol and play an essential role in the feasibility of SCWO. Development of this technology as a competitive and alternative wastewater treatment method is via enhancement of the system design, performance, cost of large scale and diagnosis and elimination of obstacles.

The objectives of this study are:

1- Selection two nitrogen-containing compounds was to study treatability under various supercritical water conditions by using a continuous flow reactor. Study MEA and 3MP will provide valuable information that would generally play a significant role in understanding the SCWO process as an efficient treatment method. Treatment two compounds by SCWO may help to apply the same study with the same compounds or with their groups because two compounds found as real wastewater in the environment.

2- Examination of the effect of co-fuel on the destruction of two organic compounds at various conditions. Then, it must prepare a plan that explains the possible conditions to reach the standard removal of MEA and 3MP. In addition, investigation of the effect of PG on by-products such as ammonia that is considered a real problem in the environment and it is a primary by-product of amines.

3- Examination of the effect of isopropyl alcohol (IPA) on the destruction of two organic compounds at various operating conditions and compare its result with the result of PG.

4- Study the kinetics reaction of MEA and 3MP. Determination of the kinetic parameters and oxygen order are for each case. In addition, evaluation of the effect of co-fuel on activation energy is to know the appropriate temperature for the reaction and reduce the cost of external energy.

1.3 Structure of the Thesis

This study includes eight chapters:

Chapter one discusses the background, motivation, aims and objectives as well as the structure of the thesis.

Chapter two covers the literature review on the conventional and current technologies that used in treatment of wastewater, thermodynamic properties of supercritical water (SCW), description the SCWO process and explains advantages and disadvantages, types of reactor, presents the previous SCWO works with model compounds and real wastes, kinetic studies and shows the commercial SCWO scales and their challengers.

Chapter three presents units of the rig, materials, procedure and analytical methods that applied in the laboratory work.

Chapter four presents the results and discussion of SCWO MEA system and MEA and IPA system at different conditions as well as the kinetic studies with using IPA.

Chapter five presents the results and discussion of SCWO MEA and PG system at different conditions as well as the kinetic study with using PG and comparison is between the effect of co-fuels.

Chapter six covers the results and discussion of SCWO 3MP system and 3MP and IPA system at different conditions as well as the kinetic studies with using IPA.

Chapter seven covers the results and discussion of SCWO 3MP and PG system at different conditions as well as the kinetic study with using PG and comparison is between the effect of two co-fuels.

Chapter eight is the final part of this thesis that explains the conclusion of this study and recommendations for future work.

CHAPTER TWO: LITERATURE SURVEY

This chapter displays the current state of wastewater treatment technologies, supercritical wastewater oxidation technology and other technologies in this field as well as the latest SCWO research that has been applied to a wide range of different wastewaters.

2.1 Introduction

Hazardous waste is a substance that has a harmful effect on human health or/and the environment, produced during different activities from generation to disposal. A waste will be regarded as hazardous if this substance has one or more of these properties: flammable, corrosive, reactive or toxic. Hazardous waste can be liquid, solid or gaseous. There are various sources of hazardous wastes, for instance, industrial sources and municipal sources. Hazardous wastes include medical, pesticides, petroleum, chemical manufacturing, household, mining and sludge. The components of organic wastes are various if compared with the inorganic wastes for example, PCBs, phenols, halogens, cutting oils solvent, chlorinated organic, polyaromatics compounds and carboxylic acids. The main characterises of organic wastes are poor-biodegradable and chemical inertness (Harrison, 2014; Fang & Xu., 2014).

By 2025, the world will produce more than 2.2 billion tonnes of waste every year in a report by the United Nations Environmental Programme (UNEP) (UNEP, 2018) and these wastes require special methods to disposal without any pollution during the treatment to protect the environment and human health. The world counts is a website that illustrates the average generation of hazardous wastes reaches to 13 ton.s^{-1} and this amount may consider a real threat to the public health and the environment. In addition, the amount of hazardous wastes is increasing each day and needs to strict management.

Currently, the prevalent techniques for non-recyclable waste disposal are incineration (see later) and landfill. The destruction of organic wastes by landfill is not complete because microorganism would be killed by dioxins and furans that would be generated from the decomposition of wastes in a landfill. The complex solution is produced from metabolized organic wastes in the landfill called leachate. Landfill needs strict management to avoid leakage to the surrounding. Also, landfill leachate has required treatment in order to destroy toxic effluent (Fang & Xu, 2014; Fodor and Klemeš, 2012; Harrison, 2015). Incineration can destroy a wide range of organic wastes; however, it is highly energy-intensive, releases toxic gas and particle emissions thus it is facing increasing bans by environment directives. Most advanced destruction processes would be developed to apply strict environmental criteria in order to increase the destruction efficiency of hazardous wastes and/or convert these wastes to non-harmful and biodegradable products. EPA (Environmental Protection Agency) recommends destruction levels up to 99.999 % and enclosed treatment systems for some wastes while the European Environmental Agency (EEA) has issued new disposal rules to control environment pollution. Also, the urban wastewater directive (Directive 91/271/EEC) aims to protect the environment from the adverse effect of domestic and industrial wastewater. They limited the chemical oxygen demand (COD) and biological oxygen demand (BOD) to the values of 125 mg.L^{-1} and 25 mg.L^{-1}, respectively. Consequently, conventional treatment methods like biological, physical and chemical processes may not satisfy environmental standards (Li et al., 1991; Zou et al., 2013).

2.2 Treatment Methods

This section shows an overview of the main current treatment methods. In general, wastewater treatment processes can be classified into biological, chemical and physical methods.

2.2.1 Physical and Biological Methods

An example of physical treatment methods is adsorption by activated carbon that depends on the porous structure and surface area of carbon particles, to remove organic molecules from wastewater. Adsorption is suitable for treatment very diluted hazardous waste stream with less than 1 wt.% organic content and will not be feasible for high concentrations (Anikeev & Fan, 2013; Veriansyah & Kim, 2007).

Biological treatment is effective for very diluted organic wastes with organic content less than 1wt. %. It is based on using microorganisms to digest the organic matter and convert it to carbon dioxide and water. Biological treatment has the ability to destroy biodegradable organic matter with very low toxic level to avoid killing microorganisms; otherwise chemical treatment becomes more favourable (Cocero, 2001). Also, temperature, pH, moisture, nutrients of a medium are important factors to obtain a high growth rate thus efficient waste treatment. The operation cost for biological treatment is relatively low and deals with large volumes of wastewater stream, but it needs prolonged residence times (days to weeks) to destroy the organic matter to the target level of removal efficiency, provided that the medium is suitable for microorganisms (Fang and Xu, 2014; Fang et al., 1993).

2.2.2 Chemical Oxidation Methods

Chemical treatment methods are based on using chemical agents to remove organic wastes and remove the contaminants in various industrial effluent streams, and/or raw waters, such as alum and ferric chloride. The flocculation method is a good example where chemical agents have played a significant role in increased chemical precipitation. Consequently, the chemical methods could have higher removal efficiency if compared with physical treatment.

More effective processes include various chemical oxidation techniques such as hydrothermal oxidations, advanced oxidation processes and incineration.

2.2.2.1 Incineration

Incineration is a thermal process commonly used to destroy hazardous, commercial and municipal wastes, and due to the Industrial Revolution, the first incinerator was developed and applied in the UK in 1874, before it spread to Europe and US. The primary part of an incinerator is the furnace where organic and inorganic wastes are burnt and converted to ash, gases, and generated thermal energy that could be recovered for other uses. Design of an incinerator unit in Europe must follow regulations of the European Waste Directive with regard to furnace temperature (850 °C as minimum level during 2 sec for non-hazardous waste and 1150 °C for hazardous waste), excess air (100-200 %) for effective destruction of polluted wastes and converted to ash, gases and heat. The thermal content of gases can be recovered and used in other applications; consequently, a filtration system must be provided to purify the gaseous flow (Fang & Xu, 2014; Fodor & Klemeš, 2012).

Incineration is a waste disposal method and is capable of treating a wide range of hazardous and non-hazardous wastes in which the ratio of reduction is 95% by volume and 80% by mass before disposal to landfill (DEFRA, 2013)**.** Incineration may be regarded as an appropriate method to destroy medical wastes because the high temperature will kill pathogens and destroys organics. In addition, because of its rich organic content, the calorific value of medical waste is high, and the heat of incineration can be recovered from the gaseous stream using this energy for power generation. Also, incineration is suitable for small areas because landfill needs large area (Alsoqyani, 2017).

On the other hand, incineration has several disadvantages; the main drawback is gaseous emissions and fly ash. Incineration generates toxic gaseous emissions such as dioxins, furans, sulfur oxides (SO_x), nitrous oxides (NO_x), carbon oxides, metal vapours and ash that contains heavy metals and solid particles. These products cause harm to the environment and human health. The problem of emissions during incineration treatment may be solved in modern incinerators by using advanced cleaning systems to reduce the concentration of hazardous emissions while this problem still exists in old incinerators. However, the released pollutants must be destroyed to reduce their effects before final disposal, where different pollutants lead to various problems, for example, dioxins and furans cause serious illnesses. In addition, the capital and operating cost of incineration are high. Consequently, the cost of other technologies may be less than the incineration technology.

Another challenge for incineration is where some industries produce toxic non-biodegradable organic wastes with a low concentration (less than 20% wt.). Incineration would be highly energy-intensive due to the significant drying requirement; therefore, the process cost and energy requirement become prohibitively high. In other words, the organic content is advised to be more than 30 % wt. to secure performance within recommended limits (Fang and Xu, 2014).

The challenges that incineration has suffered necessitate the search for alternative technologies, which will be discussed in the following sections.

2.2.2.2 Advanced Oxidation Processes (AOPs)

Advanced Oxidation Processes are a group of chemical processes that depend on generation of free radicals such as hydroxyl radicals ($HO\bullet$, $HO_2\bullet$). Hydroxyl is a powerful radical with a good potential oxidation if compared with other free radicals. Table 2.1 shows the types of free radicals and their oxidation ability. Strongly, rapidly and non-selectively, once produced, hydroxyl radicals attack the molecules of organic compounds. Three necessary steps represent the mechanism of AOPs including (i) generation of the free radicals [$HO\bullet$, $HO_2\bullet$,…] (initiation), (ii) serial attack on organic molecules via a series of reactions (propagation), (iii) reactions continue until the organic molecules converted to water and CO_2 (termination). There are two main ways that are used in AOPs to oxidise organic wastes, firstly, using oxygen as an oxidant in incineration or using ozone, hydrogen peroxide and/or photons as high powerful oxidants to produce free reactive radicals.

Table 2.1: Relative oxidation power of some radicals (Munter, 2001).

Oxidising species	*Relative oxidation power*
Chlorine	*1.00*
Hypochlorous acid	*1.10*
Permanganate	*1.24*
Hydrogen peroxide	*1.31*
Ozone	*1.52*
Atomic oxygen	*1.78*
Hydroxyl radical	*2.05*
Positively charged hole on titanium dioxide, TiO_2^+	*2.35*

Below two lists which show several AOPs treatment methods and are classified as photochemical or non-photochemical methods depending on using light as well as generated free radicals (Legrini et al., 1993).

- Photochemical methods list

Ozone O_3/UV

hydrogen peroxide H_2O_2/UV

Ozone (O_3)/ hydrogen peroxide (H_2O_2)/UV

Photo-Fenton(H_2O_2/Fe^{2+})/Fenton-like systems

Photocatalytic oxidation (UV/TiO_2)

- Non-Photochemical methods list

Ozonation(O_3) at elevated pH (> 8.5)

Ozone(O_3) + hydrogen peroxide (H_2O_2)

Ozone (O_3) + catalyst

Fenton system (H_2O_2/Fe^{2+})

Mineralisation of organic compounds in the presence of oxygen as oxidant leads to create a series of complex reactions. For example, the intermediate compounds of oxidised chlorinate compounds are carboxylic acids and aldehydes. Then, final products are CO_2, H_2O and chloride ions while nitrate or N_2 are produced from oxidant organic nitrogen compounds. There are different dissolved organic compounds that are treated by AOPs for instance aromatics, halogenated compounds, detergents, pesticides.

There are large scale applications of advanced oxidation processes in Europe and the USA that have been applied to treat wastewater, groundwater and drinking water. The main processes that are used in these plants are UV/O_3, UV/H_2O_2, or O_3/H_2O_2. There is a drinking water plant containing O_3/H_2O_2 system to remove atrazine at a scale of 5000 $m^3.h^{-1}$. In Los Angeles at a scale of 450 $m^3.h^{-1}$, O_3/H_2O_2 is used to remove trichloroethylene (TCE) from water wells. Also, there are UV plants in USA and Europe to disinfect the drinking water.

Advantages of AOPs

- The rate of reaction is rapid.
- AOPs are used for destruction a wide range of hazardous compounds and $HO^{\bullet}$ radicals have non-selectivity and high reactivity with different organic molecules.
- The destruction efficiency of AOPs may be considered of more interest in aqueous streams when the products of free radical reactions with organic wastes are water and non-risky level concentration of organic waste.
- AOPs do not form sludge (Sharma et al., 2011).

Disadvantages of AOPs

- In continuous systems, AOPs are costly because of the high cost of chemical reagents.
- Some scrubbers in wastewater contribute to the reducing of the activity of hydroxyl radical.

- The full understanding of the mechanism of AOPs reactions seems limited.
- Using AOPs as one unit to treat a large amount of organic waste is not enough to obtain an effective removal efficiency and must use a primary and secondary treatment.

For these reasons, it is necessary to investigate hydrothermal processes to apply high temperature and high pressure and to obtain a high-performance treatment method.

2.3 The Chemistry of Water

The elevated temperature and pressure of water above ambient conditions is the main principle of hydrothermal oxidation processes, and the physicochemical properties of water will be converted to create a medium reaction which becomes more suitable to dissolve the organic materials and gases. There are two types of hydrothermal oxidation process based on the range of temperature and pressure as sub-critical and supercritical water oxidation. The range of temperatures and pressures for sub-critical water is 150 ℃ to 350 ℃ and 2 MPa to 20 MPa respectively, while supercritical water conditions are above the critical point of 374℃ temperature and 22.1 MPa pressure (Miguélez et al., 1997). Along the vapor-pressure curve and as increasing temperature, the liquid water and gaseous water coexist in equilibrium. The properties of liquid water and gaseous water are equating at the end of this curve (critical point). The supercritical phase is not liquid water or vapour water, it is homogenous mono-phase. In other words, the boundary of water for two phases would not appear (Brunner, 2014). According to Williams and Onwudili (2006) the boundary of liquid water and vapour water was not clear above or near the critical point. The phase diagram of pure water is shown in Figure 2.1. Supercritical water conditions influence on hydrogen bonds. Seward and Driesner (2004) found the effect of supercritical temperature and pressure on hydrogen bonds to be significant as the percent of hydrogen bonds decreased to 29% at 40 MPa and 400 ℃ and decreased to 13% at temperature 500℃ and pressure 43 MPa. Galkin and Lunin (2005) reported hydrogen bonds to be broken by 50 % at density of 850 kg.m^{-3} and temperature 400℃. Consequently, the weakening of hydrogen bonds is regarded as a key to understanding the changes in the thermophysical properties of water, for example, the dielectric constant decreases due to rupture of hydrogen bonds (García et al., 2003; Brunner, 2014).

Static dielectric constant (Ɛ) is another indicator that is used to measure the polarity of the solvent. For instance, static dielectric constant at ambient conditions is 78.2 As/Vm, and this value decreases to 21 As/Vm at 300 ℃ while at 500 ℃ and pressure 27.5 MPa the static dielectric constant lowers to become 1.59 As/Vm (Brunner, 2014; Fang and Xu, 2014). Decreased the static dielectric constant is a consequence of the weakening of hydrogen bonds at supercritical conditions, converts the behaviour of water from polar to non-polar solvent. This leads to enhance the miscibility of organic substances and gases with water. In addition, increased pressure at constant temperature raises the static dielectric constant (Akiya and Savage, 2002; Brunner, 2014, 2009a). Williams and Onwudili (2006) reported the decreased dielectric constant would enhance the solubility of organic compounds under supercritical water conditions if compared with water at ambient conditions as well as the rate of reaction is rapid.

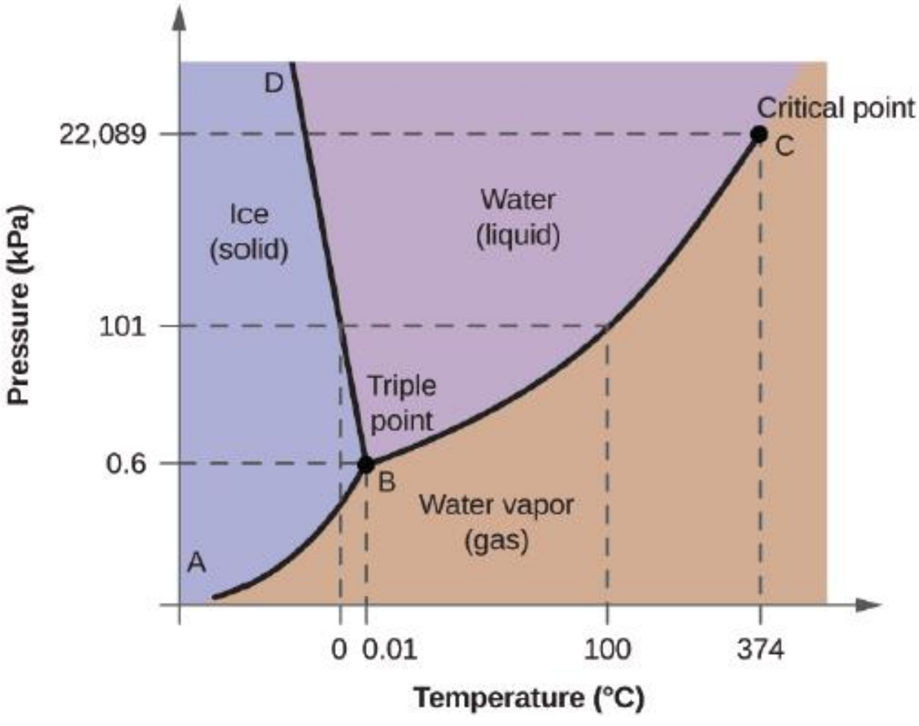


Figure 2.1: Phase diagram of pure water

Water dissociates to negative and positive ions and the reaction of dissociation can be written:

$$2H_2O \leftrightarrow \ H_3O^+ + HO^- \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots . \dots\dots\dots\dots\dots\dots\dots\dots\dots . (2.1)$$

Ion water product (K_w) is another indicator to measure the concentration of ions. Molarity units are used to measure the ion concentration. The value of K_w is very close to 10^{-14} at ambient temperature. Supercritical temperature and pressure conditions have a significant effect on ion water product. Ion product of water increases with increasing the temperature if compared with its value at ambient environment then, this value decreases under supercritical conditions. For example, the value of ion product liquid water around the critical point is 3 orders more than at ambient conditions (García et al., 2003; Akiya and Savage, 2002). Increased ion product of water leads to generate a high concentration of hydrogen and hydroxide ions, and these ions favour organic reactions. According to Brunner (2009), at a supercritical point, the reactivity of free radicals becomes predominant, and the oxidation reaction takes place by radicals. Figure 2.2 illustrates the properties of water at high temperature and dielectric constants of common organic solvent.

In summary, the supercritical water conditions have influenced the physicochemical properties and contributed to prepare a unique medium that consists of one homogenous phase and has the ability to completely dissolve the organic compounds and gases without mass transfer processes, as well as a rapid rate of reaction.

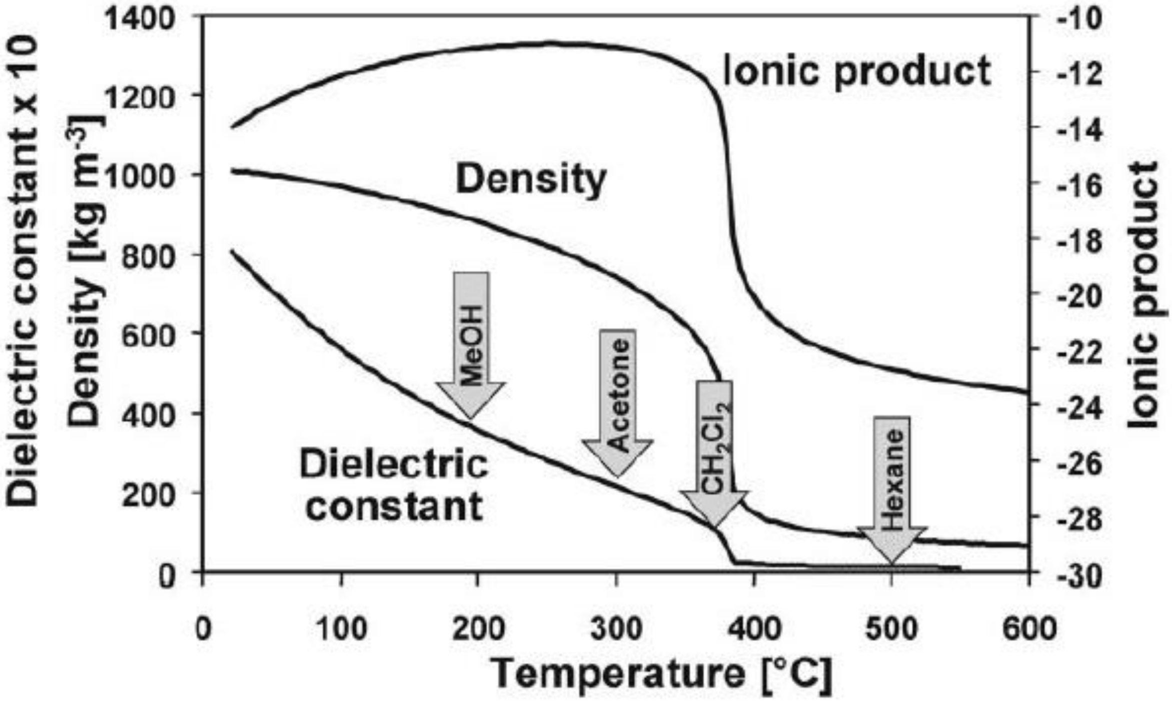


Figure 2.2: Physical properties of pure water against various temperature at 24 MPa, and a dielectric constant of common organic solvents (Kritzer and Dinjus, 2001).

2.4 Hydrothermal Treatment Methods

The utilisation of water under high temperature and pressure to create a unique medium in order to oxidise organic compounds and gases is regarded as the main concept of hydrothermal treatment methods. In late 70s of the past century, the pressurised hot water and supercritical water applications became of interest as a result of several factors including the oil crisis, the strict environmental legislations and the spread of supercritical fluids investigations (Brunner, 2009a). Supercritical carbon dioxide was the common supercritical fluid technology in 80s that developed and used to become as an alternative method to toxic organic solvents and for reducing the cost of separation and applied in synthesis and extraction materials. In the last four decades (since 1980) supercritical water oxidation received a significant consideration for utilisation as alternative incineration to oxidise organic wastes as well as increased interest in wet air oxidation (WAO), to destroy organic wastes. In addition to treatment of waste, pressurised hot water has been used as a good process to generate biogas from biomass (Kritzer and Dinjus, 2001; Brunner, 2009a).

2.4.1 Wet Air Oxidation

Wet air oxidation (WAO) can convert aqueous organic waste to non-hazardous products under a range of temperatures from 150 to 350 ℃ and a range of pressures from 2 to 20 MPa (Fang and Xu, 2014). In the presence of oxygen, WAO provides a suitable reaction medium by improving the efficiency of gas-liquid contact under pressure and temperature and then increase the solubility of organic wastes throughout two phases. It has the ability to deal with low concentration organics (compared with incineration for concentrations less than 20% wt.), in an enclosed system. Also, it is possible to recover heat and inorganics. WAO may be regarded as alternative method to incineration, but the efficiency of waste destruction unless with a catalyst is not complete, especially if the waste contains recalcitrant compounds such as ammonia and acetic acid. Despite the limited efficiency, there are 200 plants around the world. This technology, as a treatment method of organic waste has some disadvantages. WAO needs further treatment before disposal of effluent to the environment because the residual organic carbon is 20 to 50 % as well as, residence time is more than one hour (National Research Council,1994; Kritzer and Dinjus, 2001). Loppinet-Serani et al. (2010) reported that the residence time was several hours to achieve the removal of organic carbon (70-80) % and this indicates the need to enlarge the volume of reactor. The lower removal efficiency is because of the relatively low solubility of organic compounds under sub-critical conditions.

The disadvantages of conventional oxidation treatment methods like the WAO process and incineration, as well as the strict environmental legislations for waste disposal, have encouraged the development of advanced oxidation technologies. Supercritical water oxidation is suggested to become the alternative method to obtain on wanted products. Also, the SCWO unit is sufficient to achieve a high removal efficiency.

2.4.2 Supercritical Water Oxidation (SCWO)

2.4.2.1 Introduction

The properties of medium reaction in supercritical water (above 374.1 ºC and 22.1 MPa) are unique due to the complete miscibility of organic compounds and gases such as CO_2, CO, N_2 and O_2 at near or above the critical point. SCWO is a green process because organic compounds are converted to non-toxic products and, benign gaseous stream. In addition, the enhanced mass and heat transfer in the one-phase SCWO medium lead to very high reaction rates; consequently, short residence time is the main character in SCWO where it ranges from seconds to minutes. Several research groups reported the removal efficiency to increase rapidly to reach to full oxidation in less than one minute (Bermejo & Cocero, 2006; Hodes et al., 2004) and the products of reaction are biodegradable, simple and fewer compared with the products of conventional treatment methods. The final products of oxidation under supercritical water are carbon dioxide, water and nitrogen gas if an organic compound contains nitrogen. On the other hand, the by-products of incineration are NO_x and SO_x gases while these gases would not appear in emissions of the SCWO process because the maximum critical temperature in SCWO is less than the minimum temperature required to generate NO_x, which appears in incineration (> 1000 °C). The advantage of SCWO technology is safe final products of the liquid phase and non-harm gaseous emissions, with no need for further treatment (Loppinet-Serani et al., 2010).

The range of organic concentration is from 1 wt.% to 20 wt.%, and this concentration is a suitable amount to be treated by SCWO technology. Incineration needs to the organic content more than 30 wt. %, and if the organic content less than this percentage, the amount of fuel must be increased (Fang and Xu, 2014). Toxic by-products such as halogenated volatile or polyaromatic hydrocarbons, dibenzo furan, carbon monoxide, dioxins, oxides of sulphur, oxides of nitrogen, and solid particles would be generated from incineration if the removal efficiency of organic is not complete. Also, if compared between the range of SCWO temperature and incineration temperature, SCWO needs to energy less than incineration. The removal efficiency of SCWO is complete with safe final products. At the same time, recovery of excess heat in the SCWO system may significantly make this technology economically viable. In addition, an injected high heating value stream would be interested, and the SCWO system becomes self-sufficient because the excess heat would use in elevated temperature of the preheated solution before injection into the reactor. Consequently, these points will promote the feasibility of the SCWO technology (Cocero et al., 2002). The advantages of SCWO prepare the environment to apply this technology as an alternative treatment method to incineration.

Generally, the features of SCWO can be summarised as below:

- The reaction medium (water) can dissolve all organics and gases, providing a suitable environment for highly efficient conversion of complex harmful organics.
- SCW is a green solvent and needs no further separation or removal from the process afterwards.
- SCWO has the high efficiency to destroy the organic wastes rapidly in short residence time and convert the wastes to non-harmful by-products and benign gases. Toxic emissions like NO_x, SO_x, dioxins, furans, metal vapours, fly ash, etc. are not detected in the gas product, yet are problematic emissions of incinerations.
- SCWO has the ability to deal with low concentrations unlike incineration, which is highly energy intensive for concentrations less 20 % wt. due to the need for drying.
- Thermal energy produced by SCWO can be recovered, reused within the process as well as converted to electricity. This is an important feature, which makes SCWO economically feasible.

2.4.2.2 SCWO Technology Description

Figure 2.3 is a conceptual block diagram of the main stages required in a typical SCWO process. They include feed preparation and pressurisation, reaction, cooling (energy recovery), depressurisation then gas/liquid separation. The apparatus built in this work will be explained in Chapter 3.

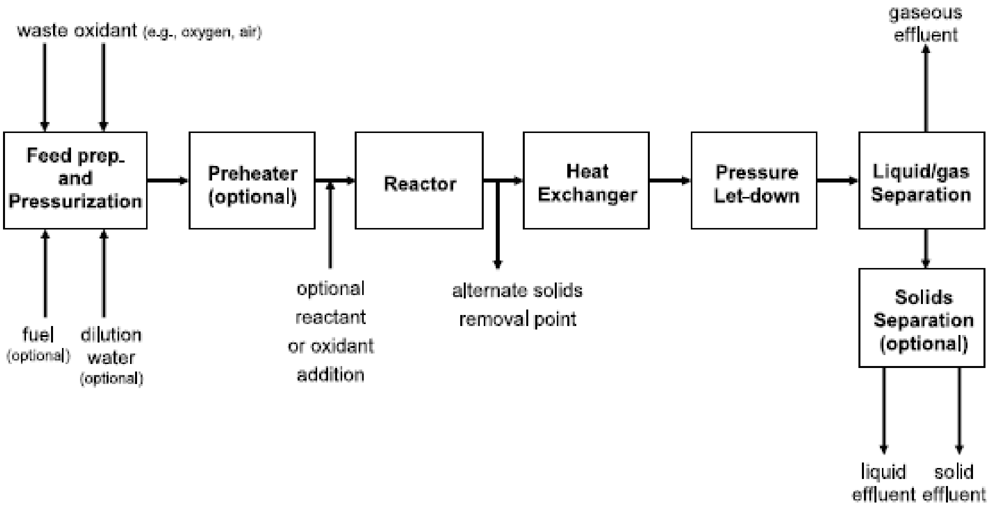


Figure 2.3: Basic SCWO process (Marrone et al., 2004)

Feed Preparation and Pressurisation

It is the first section of the SCWO process where organics and compressed oxidant solution are delivered via two lines to be pressurised and heated in separate preheaters, to acquire the reaction conditions (above 374.1°C, 22.1MPa). Source of oxygen can be hydrogen peroxide, liquid oxygen or air (Bermejo & Cocero, 2006).

Reaction

Under supercritical conditions, the delivered organics solution and oxidant are mixed at the reactor inlet where the reaction starts. As oxidation is exothermic, it releases considerable thermal energy which contributes to raising the temperature along the reactor and enhances the reaction rate (Bermejo & Cocero, 2006).

Cooling and Depressurization

The high-pressure effluent stream leaves the reactor with a temperature significantly higher that the input temperature where it enters the cooling section. Temperature is reduced to around 25 °C via a heat exchanger, before being de-pressurised by the back-pressure regulation system. The exit 3-phase stream enters a gas/liquid separator where gases leave at the top, and the liquid stream (containing some particulate matter) leaves at the bottom to a solid/liquid separator. The main products of SCWO are water, gases (CO_2, N_2, unreacted O_2, N_2O…), some salts, metal oxides depending on the composition of feedstock. Heat exchanger recovers the heat of reaction to be utilised for preheating the reactor input streams, and the excess heat is usable for external applications like hot water and generation of steam for electric power (Bermejo et al., 2004; Kritzer and Dinjus, 2001; Bermejo & Cocero, 2006).

2.4.2.3 SCWO Operating Conditions

Temperature, pressure, initial concentration of organics, oxidant ratio and residence time are the main process parameters, which influence the SCWO process. The selected degree of removal and feedstock composition play a major role in deciding the optimum operating conditions and the design of process. The influences of these parameters will be discussed in more details in Chapters 4, 5, 6 and 7 in this work.

2.4.2.3.1 Temperature and Pressure

As a thermal process, the temperature has a significant role in enhancing SCWO of organic waste, and the range of operating temperatures is around 400-650°C (Brunner, 2009b). Cocero (2001) reported the products of oxidation reaction at temperature above 650 °C to be non-harmful with no intermediates. Kritzer and Dinjus (2001) tested a range of operating pressures between 24 and 50 MPa and found the effect of pressure on the removal efficiency above 22.1MPa to be negligible. Some researchers have reported the increased pressure would not enhance the conversion of organics, while lower pressure with increased temperature was favourable (Bermejo and Cocero, 2006).

2.4.2.3.2 Oxidant

In SCWO, several oxidants are used such as hydrogen peroxide, oxygen and air. Selection the oxidant depends on the scale of the SCWO process and the cost of oxidant. In laboratory-scale hydrogen peroxide is preferred as it is safe to handle and keep, while on a larger scale, using hydrogen peroxide becomes too expensive if compared with the cost of air or pure oxygen. In addition, selection of pure oxygen seems more efficient than air. Also, air contains a high percentage of nitrogen thus requires larger compressors (Bermejo & Cocero, 2006). Several studies referred to the efficiency of hydrogen peroxide in a laboratory scale. Svishchev and Plugatyr (2006) pointed out that hydrogen peroxide was more efficient than pure oxygen in the laboratory-scale because hydrogen peroxide decomposed to generate strong free radicals ($HO^{\bullet}$) while pure oxygen needed several steps to generate free radicals. Another research reported that hydrogen peroxide had suitable characteristics to be delivered via a pump and easy to mix with organic substance (Pinto, 2004).

2.4.2.3.3 Residence Time

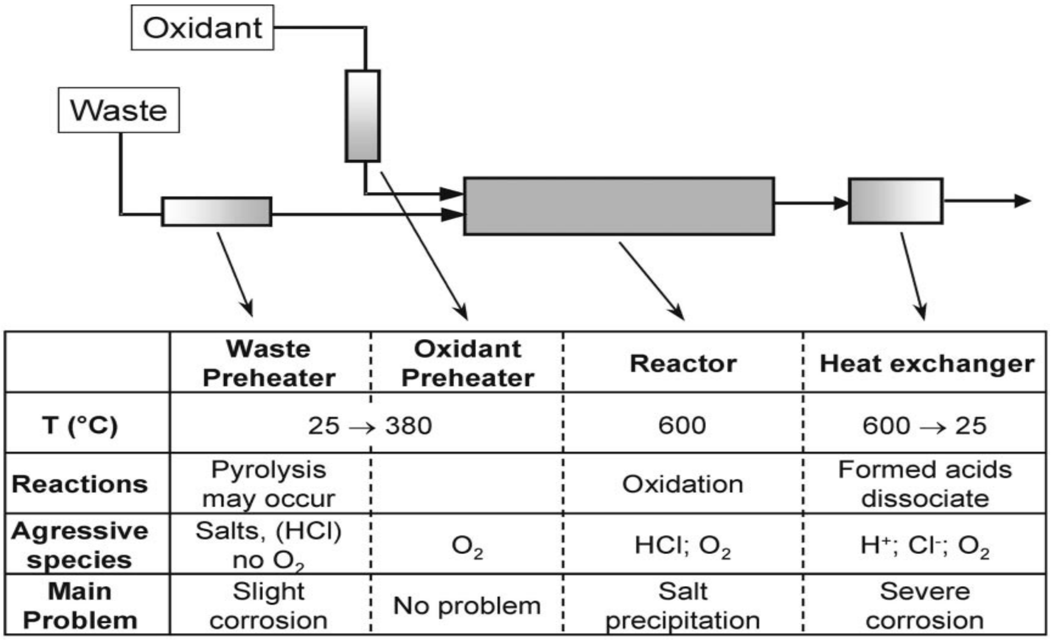
The selection of residence time is based on the volume of the reactor and the range volumetric flow rate, in other words, the capacity of pumps to deliver the organic and oxidant streams in SCWO system as well as keeping the turbulent flow at different temperatures.

2.4.2.4 Process Design Considerations

To avoid technical problems and enhance the performance of the SCWO process, there are essential considerations that must be taken an account. M^{c}Ketta Jr (2017) summarised the essential aspects to maximise the performance of SCWO. These included construction materials, influent pre-treatment, heat integration, monitoring, system integration, handling of effluent and ash disposal. Selection of construction materials depends on the concentration of waste, composition, the efficiency of treatment and process configuration. For example, to obtain a high destruction of organic waste, the important key of design depends on the selection of suitable residence time. In addition, some applications of SCW are a synthesis of chemicals or handling waste to produce some substances by using hydrolysis or recovery by-products. As such, the design considerations of the SCWO process might be operating conditions, selective or partial oxidation, providing professional staff and availability of raw materials as water and fuel.

2.4.2.5 SCWO Engineering Challenges

As the technology for the treatment of complex and non-biodegradable organic wastes, SCWO has suffered some challenges that hampered this technology from wide scale commercialisation. The two main issues that have been highlighted in many studies are corrosion and salt precipitation, which ultimately caused the shutdown of several commercial plants worldwide. Corrosion occurs because the heteroatoms in waste organic compounds decompose to corresponding acids under high temperatures and pressure. Generally, the change in density of water due to a variation in temperature and using oxidant will prepare a suitable environment for aggressive compounds. The second challenge is salt precipitation. While water is a good solvent for ionic compounds (including salts) under ambient conditions, they are insoluble in SCW. If the waste contains inorganic salts, they will precipitate on the inner wall of the reactor. The source of inorganic salts may be present in waste streams or generated during treatment. According to Kritzer and Dinjus (2001), using reactor concepts and innovative construction materials will contribute to avoid these challenges. Figure 2.4 illustrates the components of the SCWO process that suffer from corrosion and salt precipitation as well as causes. These challenges generally appear in the heat exchanger and the reactor respectively.



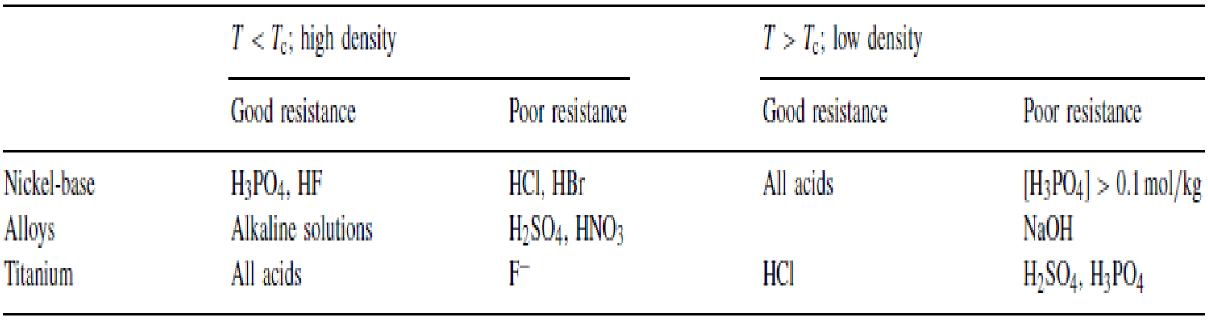
	Waste Preheater	**Oxidant Preheater**	**Reactor**	**Heat exchanger**
T (°C)	25 → 380		600	600 → 25
Reactions	Pyrolysis may occur		Oxidation	Formed acids dissociate
Agressive species	Salts, (HCl) no O_2	O_2	HCl; O_2	H^+; Cl^-; O_2
Main Problem	Slight corrosion	No problem	Salt precipitation	Severe corrosion

Figure. 2.4: Conventional SCWO process and reactions leading to problems in the particular parts of the plant (Kritzer and Dinjus, 2001).

2.4.2.5.1 Materials of Construction

Several essential factors are adopted to select suitable materials of construction that withstand the reactor’s operating conditions, show high resistance to corrosion in the presence of oxidant and some elements that aid corrosion such as phosphorus and sulphur and halogens (Fang and Xu, 2014). According to Kritzer (2004), common construction materials for SCWO systems are nickel-based alloys, stainless steel (as SS 316), ceramic materials and titanium alloys. Stainless steel could be a suitable selection to resist corrosion at a temperature range of 300°C to 500°C with non-heteroatom waste feeding; otherwise, the acidic medium will attack the stainless-steel pipes and cause corrosion. Table 2.2 illustrates some construction materials that face corrosion at different temperatures and densities with various corrosion substances. This table shows the possibility to select the waste stream with the suitable construction material at operating temperatures and densities. In general, and in the supercritical phase, chromium-based alloys and nickel such as Inconel 625 and Hastelloy C-276 have demonstrated the acidic medium does not highly affect the SCW system. According to Foy et al. (1996), titanium has a high resistance to corrosion, and another researcher has reported ceramic materials have the resistance to corrosion at pH equal 7 or less (acidic environment) (Cocero, 2001).

Table 2.2: Materials of corrosion resistance at different temperatures and densities (Kritzer and Dinjus, 2001).



	$T < T_c$; high density		$T > T_c$; low density	
	Good resistance	Poor resistance	Good resistance	Poor resistance
Nickel-base Alloys	H_3PO_4, HF	HCl, HBr	All acids	$[H_3PO_4] > 0.1$ mol/kg
	Alkaline solutions	H_2SO_4, HNO_3		NaOH
Titanium	All acids	F^-	HCl	H_2SO_4, H_3PO_4

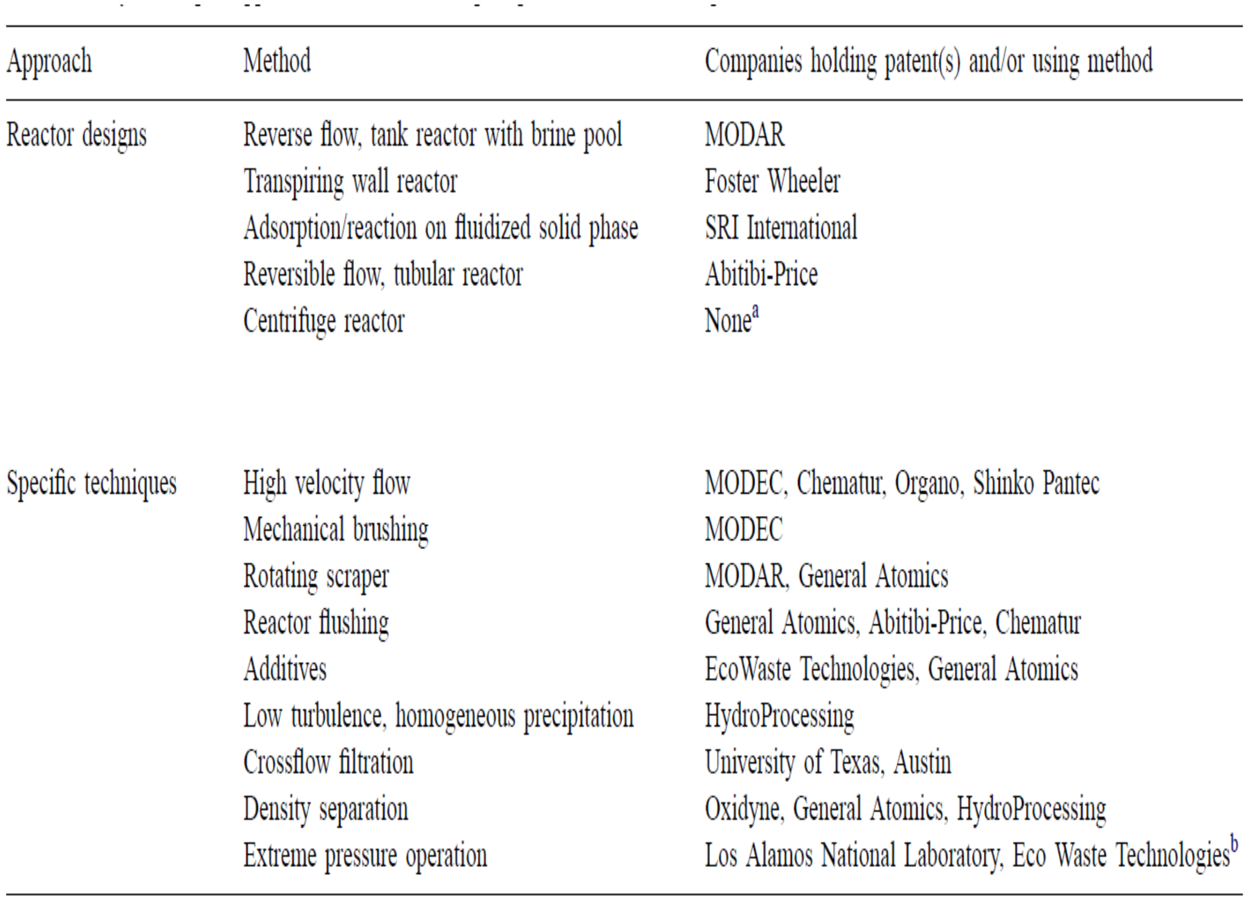
2.4.2.5.2 Salt Precipitation

Salt precipitation is a second challenge for SCWO that affected the commercialisation despite it has unmatched advantages include a high removal efficiency in a short residence time if compared with other treatment methods. Inorganic salts can be generated during the reaction or the stream of waste contains a high concentration of salt. Salt precipitation appears because inorganic salt does not dissolve at supercritical conditions. Consequently, salt accumulates on an inner wall that causes limitation heat transfer, pressure build-up and eventually the system may be plugging. However, it must improve the design of system or reduce the salty content to avoid the challenges of SCWO (Bermejo and Cocero, 2006; Hodes et al., 2004).

Marrone et al. (2004) reviewed commercial SCWO approaches undertaken by commercial companies to control solid build-up and salt precipitation as Table 2.3 shows. Special management techniques and reactor designs are the main approaches as well as some approaches that focus on corrosion like the Transpiring wall reactor.

Finally, it is possible to control the behaviour of water under supercritical conditions by controlling the temperature-pressure combination, which subsequently determines the density and other thermophysical properties, and helps in the management of the challenges of the SCWO process environment. For instance, using high pressure and low temperature in supercritical phase will manage the problem of salt deposition, and high temperature and low pressure will keep the system from corrosion. Kritzer and Dinjus (2001) pointed out the density of solution in the reactor must be less than 200 kg.m^{-3} that would help to reduce the corrosion.

Table 2.3: Commercially developed reactor designs and specific techniques to SCWO solids deposition control and salt precipitation (Marrone et al., 2004)



Approach	Method	Companies holding patent(s) and/or using method
Reactor designs	Reverse flow, tank reactor with brine pool	MODAR
	Transpiring wall reactor	Foster Wheeler
	Adsorption/reaction on fluidized solid phase	SRI International
	Reversible flow, tubular reactor	Abitibi-Price
	Centrifuge reactor	None[a]
Specific techniques	High velocity flow	MODEC, Chematur, Organo, Shinko Pantec
	Mechanical brushing	MODEC
	Rotating scraper	MODAR, General Atomics
	Reactor flushing	General Atomics, Abitibi-Price, Chematur
	Additives	EcoWaste Technologies, General Atomics
	Low turbulence, homogeneous precipitation	HydroProcessing
	Crossflow filtration	University of Texas, Austin
	Density separation	Oxidyne, General Atomics, HydroProcessing
	Extreme pressure operation	Los Alamos National Laboratory, Eco Waste Technologies[b]

2.4.2.6 SCWO Reactor Configuration

The development design of the reactor and optimisation of operating conditions significantly contribute to improve the SCWO process. There are several reactor designs including tank, tubular, transpiring wall and cooled wall reactors, which are designed to overcome SCWO challenges (Schmieder and Abeln, 1999, Cocero, 2001, Marrone et al., 2004, Bermejo and Cocero, 2006, Queiroz et al., 2015). The tank reactor was developed by MODAR to solve the problem of inorganic salt precipitation. This reactor consists of two zones at supercritical pressure: the upper supercritical zone (600 °C) and the bottom subcritical zone (300 °C). Reactants are injected from the top via a nozzle into the supercritical zone, and the products leave from the supercritical region via a nozzle. Formed salt will fall by its weight to dissolve in the subcritical temperature zone or accumulate on the inner wall of the bottom zone, and after that cold water is pumped to dissolve salts in order to dispose from the nozzle at the end of the bottom part. Figure 2.5 shows the basic diagram of the tank reactor.

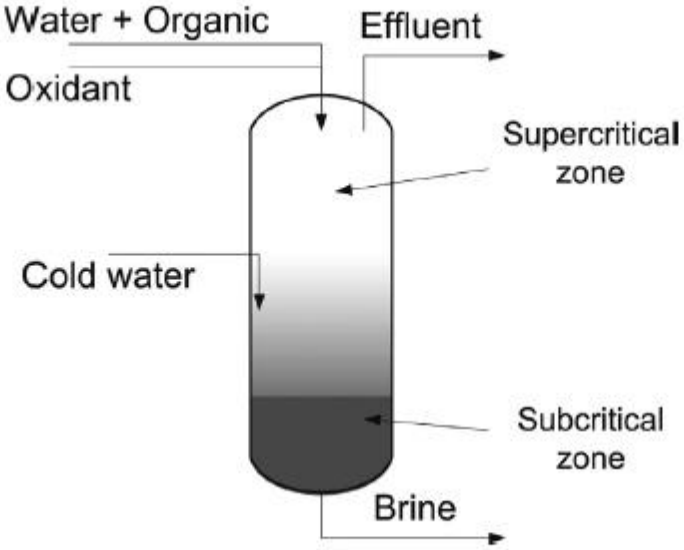


Figure 2.5: Basic diagram of reverse flow tank reactor (Queiroz et al., 2015)

Transpiring wall reactor

Transpiring wall reactor is another reactor that was developed to keep the pressure wall from corrosive reagents and salt precipitation. It consists of a duel shell; the outer shell is a resistant pressure wall, and the inner shell is a porous wall that surrounds the reaction zone. Clean water circulates through the porous wall to form a thin and cold cover in order to protect the reactor wall. The effluent of the reactor would be used as a clean fluid at the end of the operation to remove the salt. The main disadvantage of this reactor is using a large volume of water, thus increased the cost of treatment (Bermejo and Cocero, 2006). Figure 2.6 shows the schematic diagram of TWR.

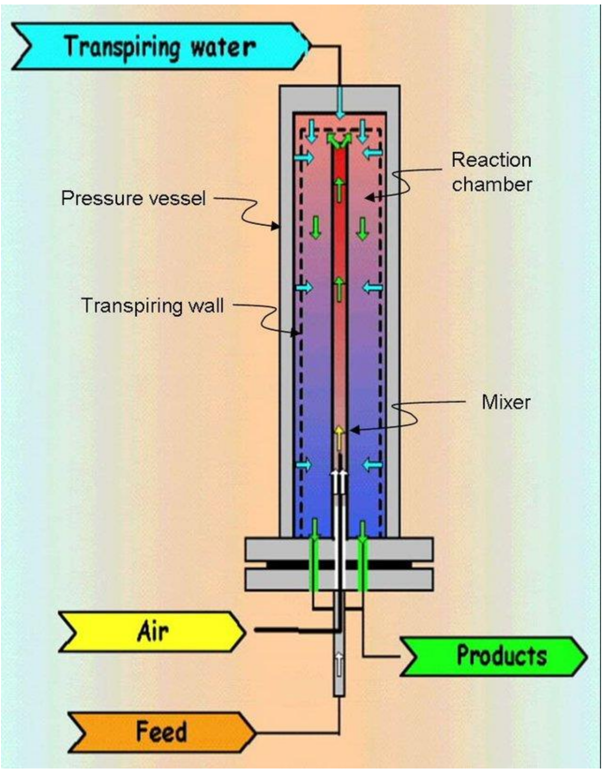


Figure 2.6: Schematic diagram of transpiring wall reactor (TWR) (Martín et al., 2011)

Another simple design is a tubular reactor that is commonly used in SCWO studies in order to investigate the fundamentals of SCWO such as reaction kinetics, process parameters and energies of reaction. A plug flow reactor is a good example of the tubular reactor that has the efficiency to destroy the organic substances at short residence time, and a Pseudo first order is regarded the kinetics of the SCWO process with respect to an organic concentration. (Bermejo and Cocero, 2006). This reactor is appropriate for organic wastes treatment, and these wastes contain a low solid concentration to avoid plugging. The small diameter of the tube would play a good role to generate a high velocity. Thus, the high velocity contributes to reduce the salt precipitation. The treatment of the high concentration wastes needs to the multi-injection reactor. Currently, the tubular reactor is widely used in several industrial applications, for example, the AquaCritox® process. Figure 2.7 displays this application in the UK.

Figure 2.7: View of the tubular reactor of the AquaCat® Process (Bermejo and Cocero, 2006)

The cooled-wall reactor was developed at the University of Valladolid (by the High-Pressure Process Group) in Spain. The cooled-wall reactor is characterised by isolating the effects of temperature from pressure, and cooled wall vessel is utilised to achieve this case and preserve the temperature of the wall near 400 °C. Reactions start in the reaction chamber where the reactants are mixed. The maximum temperature and pressure of the reaction chamber that made of a special material are 800°C and 25 MPa respectively. The reaction chamber is placed inside the pressure vessel that is made of a low thickness of stainless steel and is not in contact with the reactants. The reaction chamber is cooled and pressurised by the feed streams. In addition, the advantage of the cooled-wall reactor is a possibility to preheat the pumped feed streams, and part from effluent can be collected from the upper zone without any mixing between the cold water and effluent products. Consequently, this advantage will help to build a compact unit that may become a suitable mobile unit for treatment wastewater (Bermejo and Cocero, 2006; Queiroz et al., 2015). Figure 2.8 shows the cooled-wall reactor.

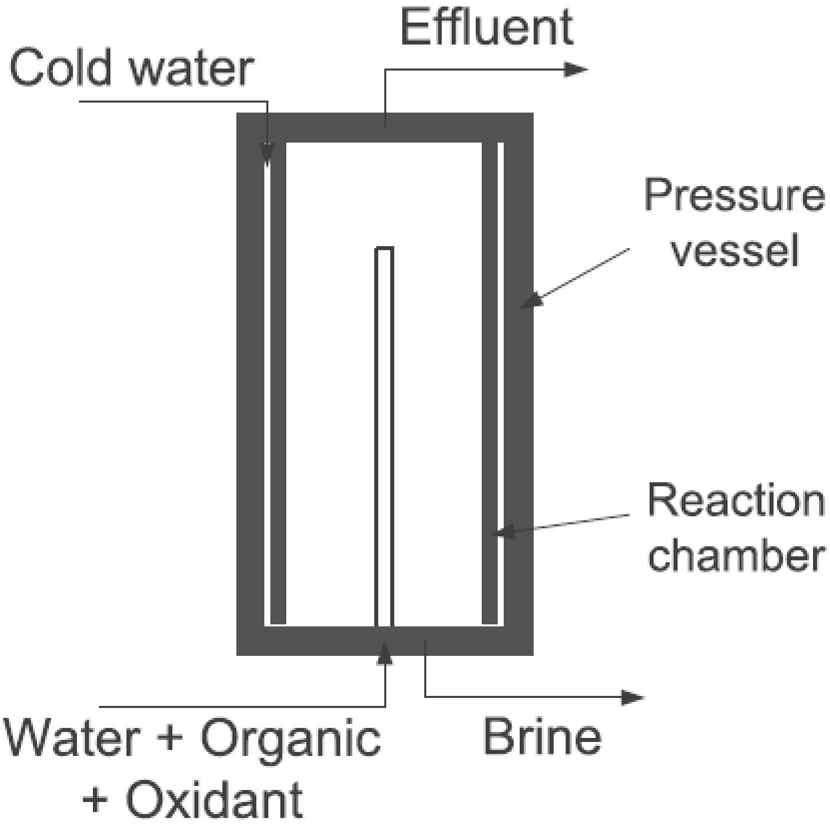


Figure 2.8: Scheme of cooled wall reactor (Queiroz et al., 2015)

As well as these designs, there are several designs that applied to reduce the challenges of the SCWO process such as reversible flow tubular, centrifuge, fluidised bed reactor and double wall stirred reactor (Bermejo and Cocero, 2006).

2.5 Overview of SCWO Research Development

2.5.1 Introduction

Different earlier surveys of SCWO research focused on new characteristics and their reactions while other authors have reviewed the treatability and fundamentals of SCWO. Some authors have focused on the development of SCWO to deal with solid separation and salt solubility. Other researchers have reviewed the engineering problems of SCWO that influenced the commercialisation such as salt scaling, process integration and corrosion. Also, others discussed the kinetics and reaction pathways for a wide range of chemical wastes either a single compound or real waste. Some studies investigated the recovery of excess heat and how can benefit from this energy in other applications (Savage, 1999; Kritzer and Dinjus, 2001; Marrone et al., 2004; Bermejo and Cocero, 2006).

In general, the efficiency of SCWO and reliability occurred clear in numerous studies, and various examples have been confirmed the ability of this technology in the treatment of hazardous wastes if compared with several technologies that were applied in laboratory and industrial scales. The next sections will explain the efficiency of SCWO to treat a wide range of organic wastes. Beside using SCWO to treat organic waste, it is applied for the synthesis of different chemical substances.

2.5.2 SCWO of Nitrogen-Containing Hydrocarbons

Numerous studies have been carried out on the destruction of nitrogen-containing hydrocarbons present in wastewater such as ammonia, pyridine, aniline, p-nitroaniline and real waste (as sewage). The main reasons to select this group are (1) the decomposition of nitrogen-containing hydrocarbons in water would produce ammonia that would be considered toxic to aqueous life such as fish; (2) the chemistry of nitrogen is complex: the incomplete destruction of these wastes by incineration would generate unwanted substances as NO_x; and (3) nitrogen-containing hydrocarbons are used in various industries (Martín et al., 2011; Segond et al., 2002; Qi et al., 2002; Lee et al., 1997). Most of these studies examined the effects of SCWO operating conditions on the removal efficiency of nitrogen-containing hydrocarbons and their intermediates, TOC removal % and COD removal %. In addition, some studies focused on the mechanisms of the reaction to determine the behaviour of nitrogenous hydrocarbons under various operating conditions. The main investigated by-products of this group are molecular nitrogen, ammonia, nitrate and nitrite. Other studies determined kinetic parameters to study the rate of reaction.

Ammonia is the primary intermediate that is produced from the destruction of N-containing hydrocarbons and has therefore been examined by several researchers. It is a recalcitrant compound and thus needs high temperatures, even under supercritical water conditions.

Conventional treatment methods have been applied to treat N-containing hydrocarbons including biological and physical-chemical treatments. Biological treatment destroyed ammonia-nitrogen at a low concentration range (20–80 mg.L^{-1}) with over 90% conversion to nitrites during a retention period of 7–14 days. These products would need further treatment to convert nitrite to nitrate. Also, residence time is extensive if compared with residence time of SCWO (Fang et al., 1993). SCWO has shown more positive outcomes.

According to Helling and Tester (1988), ammonia was oxidised above 600 °C and pressure of 24.6 MPa due to ammonia's refractory nature. The ammonia conversion did not occur below temperatures of 525°C, and at 540 °C the ammonia conversion was 5% with a residence time of 6–13 s in a tubular reactor. They suggested using high temperature and prolonging the residence time would destroy ammonia. Webley et al. (1991) oxidised ammonia in the absence and presence of methanol under supercritical conditions and used a tubular reactor (Inconel 625). In the fuel-free system and unpacked reactor, the activation energy reached to 38 kcal.mol^{-1} when the operating temperature ranged from 640 to 700 °C, while in the packed reactor, the activation energy reached 7.1 kcal.mol^{-1} when the operating temperature ranged from 530 to 680 °C. In the presence of methanol, the results were not remarkable due to the adsorption methanol and ammonia that lowered the rate of oxidation. Ding et al. (1998) studied the oxidation of ammonia in the presence of MnO_2/CeO_2 in a packed-bed reactor using a continuous system. The operating temperature ranged from 410 to 470 °C. The residence time was less than 1 s. The conversion of ammonia was enhanced to reach 40% at 450 °C and 0.8 s and was converted predominantly into N_2. In the absence of MnO_2/CeO_2, the ammonia conversion was not enhanced at below 525°C. The positive effect of the catalyst was significant under supercritical oxidation. Cocero et al. (2000) studied the effect of excess oxygen on the ammonia conversion in the presence of 2-

propanol at 650°C, and the residence time ranged from 36 to 50 s. The TOC removal efficiency was improved to reach more than 99.95% at varying amounts of oxygen. Ammonia did not occur effluent when oxygen was increased, while nitrate increased to reach 85 ppm when in the presence of excess oxygen of more than 35.5 %. Excess oxygen of 30% led NO_x to occur in gaseous effluent to reach 40 ppm, while at low oxygen the concentration was less than 10 ppm. The selection of a suitable percentage of excess oxygen influenced the result of nitrogen products. Bermejo et al. (2008) used a cooling wall reactor (a pilot plant) to oxidise various ammonia concentrations ranged from 1 wt.% to 7 wt.%. Operation temperatures ranged from 710 to 780 °C and the range of residence times was 35-45 s. Also, air was used as the oxidant and IPA as co-fuel in this study. The removal of ammonia was increased with increasing temperature and concentration. Low concentrations of acetic acid and nitrate were also observed at these temperatures. NO_x did not occur in the stream of effluent. In addition, the increased removal of ammonia was possible at high concentrations, and 40 s and the oxidant ratio. Segond et al. (2002) investigated the oxidation of ammonia in the sub and supercritical environment with operating temperatures ranging from 803 to 903 K, pressure ranging from 14 to 28 MPa, and various surfaces to volume ratios at a residence time of 1 min. Ammonia was oxidised into molecular nitrogen and a low concentration of nitrous oxide and nitrate ion. The main generated products depended on the catalysis of the reactor wall. The high ammonia conversion was recorded at 30 s, 873 K, 24.5 MPa and with a high surface to volume ratio.

Nitromethane, nitroethane, and 1-nitropropane were oxidised in a tubular reactor in supercritical water. It was found that the effect of the increased number of carbon atoms negatively influenced the rate of decomposition of these compounds and positively influenced the rate of oxidation (Anikeev et al., 2004).

Lee et al. (1997) investigated p-nitroaniline decomposition in a tubular reactor in the absence of oxygen at the temperature range 385--440°C and in the presence of oxygen at the range of 380--420°C. The results of decomposition in the absence of the oxidant were significant, while the destruction of p-nitroaniline improved in the presence of oxygen. Furthermore, the amount of ammonia produced was exceptionally low due to the co-oxidation of ammonia by a nitro group in supercritical water oxidation.

Another study investigated nitrobenzene in the absence and the presence of oxygen (Lee and Park, 1996). The results showed the rate of decomposition was slower in the absence of oxygen, with main by-products of benzene and nitrite, while the rate of decomposition significantly improved in the presence of oxygen, with main by-products of aniline, phenol, dibenzofuran and 2-(2-pyridinyl)-benzonitrile. Nitrogen in the compound was mainly converted to N_2. Chen et al. (2001) oxidised nitrobenzene, aniline and phenol in the tubular reactor and under supercritical conditions. The results showed the effect of increased temperature and residence time on the COD removal efficiency was significantly more than increased pressure. The COD removal efficiency for nitrobenzene and aniline reached 90% in a short residence time at temperatures above 650 °C and 600 °C respectively. The rate of conversion was low for nitrobenzene and aniline when compared with phenol.

Perez et al. (2004) oxidised high concentrations of phenol and 2,4-dinitrophenol at high temperature, pressure, various oxidant ratios and residence time in a tubular reactor (pilot plant). For phenol, the operating temperature ranged from 393 to 505 °C. The range of residence time was varied with the operating temperature from 30 to 60 s. Results showed the TOC removal efficiency of phenol ranged from 75% to 99.77% and the phenol removal efficiency ranged from 94% to 99.98%. The second compound was 2,4-dinitrophenol that was premixed with ammonia or ammonium sulphate. Although the removal efficiency was high, the tubing was alloy 625 which corroded with the sulphate in the heat exchanger tubing and preheaters. TOC removal of 2,4-dinitophenol, ammonia and 2,4-dinitophenol, ammonium sulphate solutions ranged 98.98-99.98% and 99.92 % respectively. The range of residence time was 20-25 s. The ammonia conversion was ranged from 37 to 50%.

Fenuron was oxidised under various sub and supercritical conditions in a tubular reactor where the temperatures ranged 200-540°C and pressure was 25 MPa. The range of residence time was 20–410 s. The results showed the complete mineralisation of fenuron to CO_2 and N_2 at high temperatures of 540 °C and 39 s. At 200°C the COD removal was 70% and nitrogen in fenuron was converted to nitrate ions, ammoniacal nitrogen and nitro groups of nitrobenzene. The study also showed the decomposition of ammonia to N_2 was due to the redox reaction between nitrate ions and ammoniacal nitrogen (Aymonier et al., 2000).

Gong et al. (2014) studied the destruction of wastewater produced from manufacturing acrylic acid plant. Experiments were carried out in a continuous flow system and the reactor was the Hastelloy C-276. Various ranges of operating conditions were applied. The temperature ranged from 673 to 773 K, the residence time ranged from 72.7 to 339 s, and constant oxidant ratio and constant pressure of 25 MPa was applied. The results showed the positive effect of temperature and residence time on the removal efficiency. The COD conversion enhanced with increasing residence time and temperature to reach 98.73% at 180.1s and 773 K. The reduction NH_3-N reached 43.71%.

Aniline was studied under supercritical water oxidation and the effect of various parameters were investigated, such as operating temperature, pressure, hydrogen peroxide doses, residence time, the concentration of organic substance and even pH on the destruction efficiency. In addition, the study investigated the effect of manganous sulphate and ferrous sulphate on the destruction of aniline. The results showed the TOC removal was positively affected by temperature, initial concertation of aniline and residence time. The influence of various pressures on the TOC removal efficiency was limited. Catalysts enhanced the removal efficiency but increased manganous sulphate and ferrous sulphate concentrations had little effect on the enhancement of the aniline destruction. pH also had a limited effect on TOC removal. High removal efficiency reached 100 % at 450 °C, 45 s and 28 MPa (Qi et al., 2002).

Shin et al. (2009) used the tubular reactor on a laboratory scale to treat acrylonitrile under subcritical and supercritical conditions by carrying out a set of experiments at temperatures ranging 299–552 °C, 25 MPa and residence time was of 3 to 30 s. The manufacturing plant of acrylonitrile was the primary source of wastewater. Acrylonitrile is poorly biodegradable in the natural environment. This study investigated various operating conditions. The results illustrated the total organic carbon removal efficiency was enhanced at increased operating temperatures and residence time, while the organic concentration and oxidant ratio had no influence on the removal efficiency. The highest removal efficiency achieved was 97 % at 552 °C, with an oxidant ratio of 2.5, resident time of 15 s and an initial TOC concentration of 0.45 $mol.L^{-1}$. The destruction of acrylonitrile under supercritical conditions promotes applying this technology.

2.5.3 SCWO of Non-Heteroatom Organic Compounds

Numerous SCWO studies have been carried out into the destruction of aliphatic or aromatic non-heteroatom compounds. These compounds are produced as wastewater by various industries. Wastewater effluents need to be investigated by SCWO in order to assess their treatability. The previous SCWO studies have concentrated on various organic compounds, including methane, acetic acid and phenol.

Savage et al. (1998) oxidised methane in a tubular reactor under supercritical water conditions, the reaction temperature ranging from 525 to 587 °C, pressure 250 atm. The main product at a low conversion was CO while CO_2 was the main product at the high conversion of methane. Another team, Aki and Abraham (1994) employed a catalyst, using Cr_2O_3 and MnO_2 to partially oxidise methane and produce methanol. All experiments were carried out in the tubular reactor under a supercritical environment, the operating temperature ranging from 400 to 475 °C at a constant reaction time. The main products were methanol and formic acid. Other methane conversion products were acetic acid, acetone and ethyl alcohol.

Another resistant organic compound, acetic acid, has been investigated by several researchers. Lee et al. (1990) examined the effect of hydrogen peroxide and oxygen on the conversion of acetic acid in a batch reactor; the reaction temperatures were 400, 450 and 500 °C. They found the acetic acid conversion to be significantly improved by using H_2O_2 to reach 97.7% at 500°C and 10 min more than O_2 to reach 64.3% at 500 °C and 30 min. The oxidant ratio was also examined; the effect of an increased oxidant ratio was significant, and the TOC removal efficiency improved at 5 SR and 450 °C to reach 97.8% in the presence of H_2O_2 and 63.9% in the presence of O_2. Another study investigated acetic acid at 250 bar and an initial reaction temperature of 400 °C in an adiabatic tubular reactor, with residence time of 34.2, 26.4 and 24.6 s. The concentrations of acetic acid were 3.35%, 3.92% and 4.9%. The flow rate of oxidant was replaced with changing the residence time. The results of the conversion of acetic acid were 30.5%, 98.4%, and 96.6% at the high temperatures of 438, 558, and 568 °C, respectively. The increment in temperature was from oxidation acetic acid, and the major by-products of acetic acid were carbon dioxide and water (Aymonier et al., 2001).

Phenol is a resistant organic compound that has been produced by various industries as wastewater and been found to be an intermediate during the destruction of complex compounds. This compound has therefore been studied by several researchers. Thornton and Savage (1990) oxidised phenol under sub-supercritical conditions. Reaction temperatures ranged from 300 to 420 °C, pressure from 188 to 278 atm, residence time from 4 to 111 s. Their results showed the effect of residence time on the conversion of phenol. The conversion of phenol was 46.2% at 15.75 s and 99.8% at 66.75 s. Operating pressure showed a positive effect on improvement of the removal efficiency; for example, the removal efficiency was enhanced from 2.2% at 188 atm to 72.9% at 278 atm and 32 s. The main products of the phenol conversion were monocarboxylic acid, dicarboxylic acid, dihydroxybenzenes, dibenzofuran and phenoxyphenols. In addition, corrosion (reactor metals in effluent) was not observed at a high concentration of phenol.

Oshima et al. (1998) studied the kinetics of phenol in a continuous flow reactor. Many data were collected to find the kinetic parameters of reaction under different conditions. The operating temperature ranged from 370 to 430 °C. They found that the rate of reaction did not depend on the pressure and density of water. The concentration of phenol and oxygen influenced on the rate of reaction. Thornton and Savage (1990) had pointed out that the rate of reaction depended on the pressure and concentration of oxygen.

2.5.4 SCWO of Heteroatom Organic Compounds

Numerous researchers have demonstrated the ability of this technology to destroy organic compounds containing hydrogen, oxygen and carbon. SCWO has converted organic compounds to carbon dioxide and water, but when the organic compound contains heteroatoms such as chloride and sulfate, the destruction of these organic compounds will generate acids that attack the system at the temperature range 250 to 350 °C. The organic compound will influence the performance of the SCWO process. To control this problem, the solution would be neutralised with alkaline to produce salt. This step may produce dissolved salt, but if this salt does not dissolve in water under supercritical conditions, salt precipitation will occur in SCWO system because the SCWO medium is not a suitable solvent for some salts. Consequently, salt will accumulate on the wall and plug the tubing. Both domestic and industrial wastewater streams have contained on these heteroatoms organic compounds that were treated by SCWO to assess the performance and capability of this technology at different conditions, to deal with corrosion and salt precipitation and enhance the efficiency of SCWO. Also, the products of the conversion of these compounds might be considered dangerous if compared to the products of other organic compounds and must be treated before disposal to the environment (Fang and Xu, 2014).

Lee et al. (1990) showed the effect of hydrogen peroxide and oxygen on the enhancement of the removal efficiency of 2,4-dichlorophenol at 450 °C and 2 min. The removal efficiency in the presence of hydrogen peroxide increased to 99.99% whereas the effect of oxygen occurred less than the effect of hydrogen peroxide; for example, the removal efficiency of 2,4-dichlorophenol was 87% at 500 ℃ and 10 min. Also, at 400 ℃ they found the effect of water density at reaction conditions on the conversion of this compound to be low.

Marrone et al. (1998) studied the destruction of methylene chloride in a tubular reactor under sub and supercritical conditions. The experimental pressure was 246 bar, the operating temperature ranged from 25 to 600 ℃ and the residence time ranged from 7 to 23 s. The major products of the methylene chloride conversion were hydrochloric acid, formaldehyde, carbon monoxide, carbon dioxide, methanol and hydrogen, while the minor products were a low concentration of methane, chloromethane and chlorinated hydrocarbons. The major compounds under sub-critical conditions were formaldehyde and hydrochloric acid. Formaldehyde converted into carbon monoxide and hydrogen. While the oxidation of this compound could generate CO, hydrogen, methanol and HCOH, but CH_2Cl_2 and chlorinated hydrocarbons were still not oxidised at 550 ℃. The oxidation of methylene chloride was high at 600 ℃ and the main products were CO_2 and HCl.

Hatakeda et al. (1999) studied the effects of hydrogen peroxide and oxygen under supercritical water oxidation on the conversion of 3-chlorobiphenyl, with operating temperatures ranging from 473 to 723 K in a batch reactor. They also studied the effect of temperature and oxidant concentration. The efficient hydrogen peroxide significantly enhanced the 3-chlorobiphenyl conversion to reach 99.99% at 30 min and 0.36 g/ml, while the oxygen effect at the same conditions increased the conversion to 14%; the researchers referred to the role of free radicals to improve the TOC conversion. In addition, they used a flow system to destroy polychlorinated biphenyls and kanechlor at 30 MPa, 673 K; residence times ranged from 10.7 to 101.7 s, using hydrogen peroxide, and the findings showed the conversion to be 99% in all runs. 22 intermediate compounds were produced at oxidant ratio 56%, organic concentration 21 mM and the conversion 63.5%, including m-chlorophenol, biphenyl, dibenzofuran, 3-chlorobiphenyl, dichlorobiphenyl, 2-monochlorodibenzofuran, and 4-monochlorodibenzofuran. The team observed a low concentration of nickel, iron, molybdenum, chromium and cobalt occurred in the results of Hastelloy C-276 analysis.

Ma et al. (2014) treated o-chlorophenol in SCW and studied the effect of sodium hydroxide and potassium hydroxide on the removal efficiency, and the yield of Cl^- with the temperature range of 380−420 °C. Their results showed the effect of potassium hydroxide on removal efficiency to be better than that of sodium hydroxide, and the effect of potassium hydroxide on the yield of Cl^- to be significantly more than that of sodium hydroxide, due to the fact that potassium hydroxide would generate free ions in SCW more readily than sodium hydroxide.

2.5.5 Co-Oxidation in SCWO

This section discusses the use of co-fuel in SCWO, focusing on the role of co-fuel in improving the destruction of resistant compounds. There are numerous examples illustrating the role of co-oxidation in SCWO. For instance, ammonia has been oxidised by various co-fuels because it needs high temperature, long residence time, and/or the addition of a catalyst, to complete the destruction. Various co-oxidation fuels have been used in SCWO to improve the conversion of organic compounds. In general, the reaction co-fuel and the oxidant is faster. Thus, this reaction would accelerate the oxidation process of other compounds in the reactor. (Helling and Tester, 1988; Ploeger et al., 2007; Yang et al., 2018). Co-fuels could be considered as a second-generation source for free radicals when the reaction takes place; then the free radicals contribute to an increase in the conversion of organic waste (Helling and Tester, 1988; Yang et al., 2018; Oe et al., 2007). The excess heat that is released from the oxidation of co-fuels could add some heat to the reaction. Then, the conversion of organic waste would increase (Bermejo et al., 2008; Yang et al., 2018). Yang et al. (2018) demonstrated the hydroxyl group in IPA, ethanol and methanol was to be active under supercritical conditions, contributing to an acceleration in the decomposition rate.

Numerous studies have shown that using co-fuels such as methanol, ethanol and IPA in SCWO improve the rate of oxidation. Ploeger et al. (2007) used the plug flow reactor to destroy ammonia by using ethanol as a co-oxidiser. The operating temperature ranged from 655 to 705 °C. They found the rate of conversion improved from 20% to 65% at residence time 2.5 s, 1 mM as an initial concentration of ammonia and 1 mM of ethanol and 700 °C, pressure of 246 bar. The findings showed the yield of nitrous oxide to increase from 40% to 75% with the addition of ethanol at 680°C, while the yield of nitrous oxide under the same conditions increased from 4% to 13% in the absence of ethanol. Increased temperature also had a positive effect on the conversion of ammonia. The role of ethanol was remarkable in improving the conversion of ammonia at 1 mM.

Another group has investigated ammonia oxidation under supercritical conditions, Helling and Tester (1988) using a tubular reactor for treating ammonia, carbon monoxide and ethanol. They observed that the conversion of ethanol improved from 16% at 484°C to 99.5% at 541°C and that ammonia still needed a high temperature and long residence time to enhance the conversion. In addition, adding ethanol to ammonia did not affect its conversion; the conversion of ammonia was 5% at 540°C in the presence of ethanol. Yang et al. (2018) studied the effect of methanol, ethanol and isopropyl alcohol as co-fuels on the NO_3^-/NH_4^+ ratio as TN% and TOC% at 450°C. Their observations illustrated the positive effect of co-fuels on the removal TN. IPA would influence TN% more than ethanol and methanol. The excess heat would be added to the reaction that would be released from co-fuels. This heat may contribute to increasing the conversion NH_4^+, while the effect of methanol on TOC removal% was more than ethanol and IPA. Oe et al. (2007) investigated the effect of methanol as co-fuel on the conversion of ammonia in a system similar to commercial plant conditions. The temperature ranged from 560 to 620 °C. They observed that the rate of conversion was improved when the concentration of methanol was twice that of the ammonia concentration, and that the concentration of the nitrate ion increased on increasing the concentration of the co-fuel. In addition, nitrous oxide appeared in the results of gaseous samples.

Thus, to avoid forming N_2O and NO_3^-, post-treatment should be used to reduce N_2O in the gaseous stream. Nitrate should be reduced in the reactor to avoid corrosion.

Bermejo et al. (2008) applied a set of experiments in the presence of IPA as co-fuel to oxidise 7% wt. as a maximum concentration of ammonia by using the pilot scale and the cooling wall reactor. The results demonstrated the positive effect of co-fuel on the conversion of ammonia at 40 s and high temperature, in which the ammonia conversion was enhanced to be more than 99% at temperature above 780℃. In addition, they found the removal TOC to be increased by increasing the temperature. Nitrate ion and acetic acid showed a low concentration and the main products in the effluent of the reactor. Several studies have been made of the effect of IPA on ammonia oxidation. Cabeza et al. (2014) used a laboratory-scale reactor to investigate the effect of IPA as co-fuel on the destruction of ammonia at temperature of 400−525 ℃, 250 bar and residence time 2−10 s. The results showed the positive effect of IPA on the destruction of ammonia, its removal reaching 35% by increasing the IPA/ammonia ratio. They found the nitrate ion to be increased by increasing the IPA/ammonia ratio. Also, the conversion of ammonia was improved by increasing the temperature from 10% at 400 ℃ to 30% 525 ℃. The concentration of nitrate and nitrite was low. Webley et al. (1991) investigated the effect of methanol on the conversion of ammonia in a tubular reactor at 480−530℃ and 6.7 s, the mixture of methanol and ammonia being fed into the reactor. All experiments were carried out in a supercritical water environment. The results were insignificant, and the ammonia conversion was very low. The main product the oxidation of ammonia was N_2, while methanol produced carbon monoxide and hydrogen. Killilea et al. (1992) used ethanol as a co-fuel to destroy ammonia released from urea and carried out two groups of tests. The result of the destruction of ammonia in the absence of ethanol was 41% at 690 ℃ while the complete destruction of ammonia in the presence of ethanol at 690 ℃, the N_2O concentration occurred more than N_2 in the effluent at low temperature. Also, the concentration of nitrate and nitrite was less than 1 ppm, and NO_x was not observed in gaseous samples. In two systems, ammonia conversion was enhanced with increased temperature and favoured to convert into molecular nitrogen.

Other examples illustrate the use of co-fuels to destroy resistant compounds such as methylphosphonic acid and acetic acid. Ploeger et al. (2006) oxidised methylphosphonic acid (MPA) under supercritical water conditions in the plug flow reactor. They used 0.1 to 2.4 mM ethanol as co-fuel to improve the conversion of MPA and their findings showed enhanced conversion after increasing ethanol concentration from 1 mM to 2.4 mM. The destruction of MPA increased from 29% to 41% at 9 s, 473 °C and initial concentration MPA was 1 mM, while the conversion of MPA reached 14% in the absence of ethanol under the same conditions. On the other hand, the range of ethanol concentration from 0.1 to 0.3 mM did not affect the MPA conversion. Cabeza et al. (2011) studied the destruction of acetic acid in a tubular reactor in the presence of IPA. The removal efficiency increased to reach 99% at temperature 710 °C and 0.7 s, while the removal efficiency of acetic acid in the absence of IPA was 90% at the temperature range 400−600 °C in a tubular reactor (Meyer et al., 1995).

Cocero et al. (2000) studied the oxidation of nitrogenous compounds such as aniline, pyridine, acetonitrile and ammonia under supercritical conditions, in a pilot plant and in the presence of 2-propanol as co-fuel. Their results demonstrated the positive effect of co-fuel on TOC removal and nitrogen removal. The TOC removal efficiency enhanced to reach more than 99% and nitrogen removal efficiency more than 97% at 40 s and the range of temperature of 600−700 °C. In addition, they found the positive effect of co-fuel on the concentration of ammonia at above 650 °C.

Al-Duri et al. (2015, 2016) oxidised DMF and DBU in the presence of IPA under supercritical conditions. The range of temperature was 400−525 °C at constant pressure 250 bar. The residence time ranged from 2 to 10 s. The results showed the effects of temperature, oxidant ratio, initial concentration and IPA ratio to be positive on the TOC% and total nitrogen. The maximum removal efficiency of TOC for DMF and DBU was more than 99% at 525 °C and 10 s.

Their study referred to the excess heat of IPA, which had a positive effect on removal efficiency of nitrogen and IPA would contribute to providing a further source of free radicals as HO• and HO_2•.

Marrone and his group (2005) presented data from two tests. Two systems were used to investigate the performance of two different designs under different conditions. The duration of the test, carried out in 2000−2002, was 500 h. The sample of waste was the hydrolysis of chemical agents. Two groups performed two tests: General Atomics (GA) and Foster Wheeler. The Foster Wheeler group employed PG as a co-fuel to improve the SCWO performance and reduce unwanted gaseous emissions. The results from the two systems illustrated the ability of SCWO to destroy wastewater with high reliability and long-term operability.

In this work, PG was used as a co-fuel to study his effect on MEA and 3MP and by-products. These results will be compared with the results of IPA. In addition, most studies on co-oxidation depended on monohydric alcohol and PG contains two hydroxyl groups. Thus, this work has a high novelty.

2.5.6 Treatment of Specific Waste

Nuclear power plants have used organic ion exchange resins in water treatment systems to reduce corrosion, to remove radioactive contaminants and to control system chemistry. Organic resins are employed in cleaning processes for removing radionuclide and regeneration system water. The volume of organic ion exchange resins is large and spent organic resins are contaminated radioactive materials and need to an effective technology to protect the environment. Incineration is used to reduce the volume and destroy this waste, but unwanted radioactive materials (radionuclides) are released from an incinerator when the temperature is raised more than 800 °C and harmful emissions such as nitric oxides or sulphuric (IAEA, 2002; Leybros et al. 2010). Leybros and his team have oxidised organic resins under supercritical conditions. All experiments were carried out in a continuous supercritical system. The effluent was analysed by GC/MS and was found around 50 species that were classified to cationic and anionic resins. The results were illustrated the TOC degradation of organic rate resins was more than 95 %. However, this work did not refer to radionuclide contaminants in the effluent and their destiny. Also, the nitrogen compounds present in the effluent of the reactor without decomposition and sulphur was converted to sulphur ions. Lastly, the findings of SCWO have promised the ability of this technology in the destruction of organic resins and reducing unwanted emissions.

2.5.7 SCWO of Complex Wastes

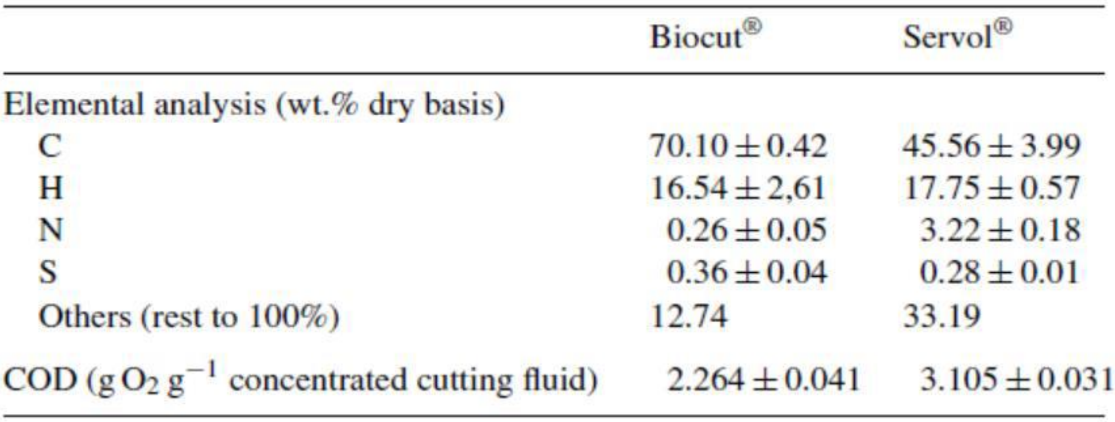
There are numerous examples that explain the efficiency of SCWO in the destruction of a single model in the absence or presence of co-fuel, but there are other examples which have demonstrated the ability of this technology in the removal of multi-compound wastes which have carried out by using a laboratory scale and a pilot-scale such as dyehouse waste. Dealing with complex wastes may be considered necessary to understand the feasibility of SCWO and provide a right guidance when using this technology on a large scale to treat complex industrial wastes. However, the assessment of the removal efficiency as TOC, COD or organic compound concentration is essential to examine the performance of SCWO. Furthermore, it will observe engineering obstacles of SCWO as corrosion and salt precipitation, then how these obstacles can be reduced in large applications in order to assess the reliability.

Söğüt and Akgün (2010) have used the tubular reactor (laboratory scale) to treat dyehouse waste under supercritical conditions. Set of experiments was carried out at a range of temperature 400-600 °C, 25 MPa and a range of residence time from 8 to 16 sec. The source of dyehouse was the textile plant and effluent of waste was contained various compounds such as dimethyl benzyl ammonium chloride and acetic acid, heavy metals as chromium, calcium, iron, and lead and solid materials. The TOC and total nitrogen concentrations were 860 ppm and 118 ppm respectively in the feed stock. The SCWO technology has achieved the high TOC removal efficiency to reach 100 % at 10 s and 550 °C.

Due to the results of conventional treatment methods such as filtration, evaporation or phase separation are not having the efficiency in dealing with and treating oils cutting. Sánchez-

Oneto et al. (2007) have applied SCWO to investigate the removal efficiency and studied the kinetic of reaction. All runs were carried out at a range of operating temperature from 400 to 500℃ using a continuous flow system and pure oxygen as a source of oxidant, pressure 25 MPa. The semi-synthetic cutting fluids emulsion (Biocut$^{®}$ and Servol$^{®}$) that contained a mixture of various oil compounds. The components of oils were synthetic oils, surfactant, water and some additives. Also, the concentration of different components in both fluids was various and depended on a metalworking operation. These oils were used to reduce the heat that was produced from the metalworking operation. Deionised water was added with these oils for diluting and preparing the solution that contributed to absorb the released heat. Then, a complex oily effluent will be produced at the end. Table 2.4 shows the components of cutting oils. The findings were a significant indicator that showed the efficiency of SCWO. TOC removal % and COD removal % were enhanced with increasing temperature, TOC, COD removal efficiencies for Biocut$^{®}$ were 97 %, 96 % respectively at 34 s while for Servol$^{®}$ TOC, COD removal efficiencies were 97.9 %, 97.5 % respectively at 9.7 s. Also, a Pseudo-first order model has been demonstrated as TOC and COD removals for both cutting oils. As a result, SCWO has the efficiency to treat a complex effluent.

Table 2.4: Elements of cutting oils (Sánchez-Oneto et al., 2007)



	Biocut$^{®}$	Servol$^{®}$
Elemental analysis (wt.% dry basis)		
C	70.10 ± 0.42	45.56 ± 3.99
H	16.54 ± 2,61	17.75 ± 0.57
N	0.26 ± 0.05	3.22 ± 0.18
S	0.36 ± 0.04	0.28 ± 0.01
Others (rest to 100%)	12.74	33.19
COD (g O_2 g^{-1} concentrated cutting fluid)	2.264 ± 0.041	3.105 ± 0.031

Another example from waste of petroleum industry is oily sludge that is treated by conventional methods as biological treatment, incineration and landfill. Selection treatment or disposal method depends on essential factors including simple operating, low cost and high removal efficiency. These technologies have suffered from several problems. Thus, oily sludge was oxidised under supercritical conditions. The operating temperature ranged from 663 to 723 K, the residence time ranged from 1 to 10 min and pressure ranged from 23 to 27 MPa. This study investigated the effect of temperature, pressure, excess oxygen, residence time and the concentration on the COD removal efficiency. The results showed the significant role of temperature, residence time and initial concentration in the COD removal efficiency while the effect of pressure and oxygen excess was not remarkable. The high COD removal efficiency was 92% at 10 min. The main by-product was carbon monoxide that increased with temperature while the minor by-product was acetic acid that decreased with temperature (Cui et al., 2009).

The main by-product of the landfill is leachate, which is considered as a complex aqueous solution. It requires an effective treatment method because it contains many organic compounds and inorganic salts, heavy metals and ammonia. Using biological treatment and chemical treatment would not be efficient to destroy leachate; thus, further treatment must be provided to protect the environment. Civan and his team investigated the SCWO of leachate by using Ni/Al_2O_3, the operating temperature ranged from 400 to 600 °C, residence time ranged from 30 to 150 s and pressure 25 MPa. This study examined the effect of the temperature, excess oxygen, concentration of Ni/Al_2O_3 on the total organic carbon and total nitrogen. The results showed the positive impact of catalyst on the TOC removal efficiency and total nitrogen to reach 98 % and 57 % respectively. Also, the effect of temperature on the TOC removal efficiency was more than the effect of excess oxygen (Civan et al., 2015).

Briefly, SCWO is a suitable technology to treat a wide range of organic wastes, either a single compound or mixture of compounds with a high removal efficiency and a short residence time.

2.6 Reaction Mechanisms and Basic Kinetics of Simple Organic Compounds

2.6.1 Mechanism of The SCWO Reaction

The development of kinetic models is important and rely on the full understanding of reaction pathways and mechanisms while the engineering design purposes are based on sufficient knowledge of the primary SCWO pathways. Also, the amount and type of generated recalcitrant intermediate compounds could affect the rate of reaction of organic waste. The formation of resistant compounds, such as ammonia and acetic acid, would represent the reaction rate-limiting step. In addition, the type of oxidant is another factor that influences the SCWO mechanism. For example, air, oxygen, and hydrogen peroxide are the primary sources of oxidants, and other types of oxidants are used as effective oxidants in SCWO, such as potassium persulphate (Kronholm et al., 2000) and nitrite-nitrate (Dellorco et al., 1995).

In the SCWO medium, the predominant mechanism is the mechanism of free radicals rather than the ionic mechanism. This mechanism is like the WAO mechanism. In the presence of an oxidant and when the density of the medium decreases as the operating temperature increases, according to Brunner (2009b), the free radical mechanism above the supercritical point overcomes the ionic mechanism. The free radical mechanism generates high reactive radicals that selectively attack the weakest C-H bond of organic molecules or water if oxygen is the main oxidant. Then, the radicals rapidly and unselectively attack the organic molecules or other species in the SCWO medium that contribute to the continuation of oxidation and produce other radicals as illustrated in the following steps.

The temperature of the hydrogen peroxide is increased in the preheater to decompose the oxygen and water as shown in this equation.

$H_2O_2 \rightarrow H_2O + 0.5O_2$ ………………………………………………………………… (2.1)

Produced oxygen from decomposed hydrogen peroxide reacts with molecules of organic at high temperature to produce organic free radical ($R^\bullet$) as in this equation:

$O_2 + RH \rightarrow R^\bullet + OOH^\bullet$ ……………………………………………………………….. (2.2)

Then, organic peroxyl radical will be produced from the reaction between oxygen and organic free radical as in this equation:

$O_2 + R^\bullet \rightarrow ROO^\bullet$ ……………………………………………………………………. (2.3)

Then, organic peroxyl radical reacts with organic to take a hydrogen atom and generate a new $R^\bullet$ and organic hydroperoxide (ROOH) as below:

$ROO^\bullet + RH \rightarrow ROOH + R^\bullet$…………………………………………………..……………. (2.4)

Finally, the organic hydroperoxides will decompose to form small carbon intermediates because these compounds are relatively unstable; thus, the decomposition will continue and convert these organics into CO_2.

2.6.2 SCWO Reaction Kinetics

Depending on numerous studies of various organics, most of the SCWO reaction rates are described by a global rate law expression, and equation 2.5 shows the SCWO rate reaction. The order of the reaction with respect to an organic substance is unity. There are several studies illustrated the order of the oxidant has value more than zero. The order of water is considered to be zero due to the percentage of water, forming more than 99 %. Thus, the water effect would not appear. Several studies explain that the value of oxidant order would be more than zero when the amount of oxidant is increased (Cocero, 2001; Pinto et al., 2006; Sánchez-Oneto et al., 2007).

$$\frac{-d[Organic]}{dt} = k[Organic]^a[Oxidant]^b[Water]^c = Ae^{\frac{-Ea}{RT}}[Organic]^a[Oxidant]^b[Water]^c \ldots (2.5)$$

Where

k is a constant of reaction rate in $M^{1\text{-}a\text{-}b\text{-}c}\ s^{-1}$

A is a pre-exponential factor in $M^{1\text{-}a\text{-}b\text{-}c}\ s^{-1}$

E_a is activation energy in $J.mol^{-1}$

R is a constant of universal gas (8.314 $J.mol^{-1}.K^{-1}$)

T is a reaction temperature in K

[Organic] is an initial organic concentration ($mol.L^{-1}$)

[Oxidant]is an initial oxidant concentration ($mol.L^{-1}$)

[Water] is a water concentration (mol.L^{-1})

a is a reaction order relation to an organic compound

b is a reaction order relation to oxidant

c is a reaction order relation to water

Controlled reaction conditions such as temperature, concentration, pressure and residence time have been applied in numerous kinetic studies. Some studies have focused on mixture wastes such as cutting oils, military wastes and sludge, while other studies have focused on the one substance or model of chemical substance and co-fuel under various controlled conditions. Consideration is given to reaction pathways and determines global rate laws. However, there are numerous research groups which have investigated the oxidation of various groups of organic substances and Table 2.5 shows the different examples of SCWO kinetic research.

Table 2.5: Different examples of SCWO kinetic research

Compound	Temperature (°C)	Pressure (bar)	Reactor Type	Kinetic parameters					Reference
				A (s^{-1})	Ea ($kJ.mol^{-1}$)	a	b	c	
Ethanol	400-540	246	Tubular	$10^{21.82}$	340	1	0	_	Helling and Tester, 1988
Ethanol	433-494	246	Tubular	$10^{13.4}$	180	1	0	0	Schanzenbacher et al., 2002
Ammonia	655-705	245	Tubular	10^{19}	347	1	0.44	0	Ploeger et al., 2006
Ammonia	530-630	140-280	Tubular	$4*10^{8}$	166	0.9	0.06	-0.14	Segond et al., 2002
Ammonia	410-470	276	Tubular	$1.14*10^{14}$	189	0.63	0.71	0	Ding et al., 1998
Ammonia	640- 700	246	Tubular	$3.16*10^{6}$	157	1	0	0	Webley et al., 1991
Quinoline	480-650	50-300	Tubular	$2.7 *10^{13}$	226	1	0	0	Pinto et al, (2004)
Pyridine	426-525	276	Tubular	$1.3*10^{13}$	209.5	1	0.2	_	Crain et al., 1993
p-Nitroaniline	380-420	250	Tubular	$1.3*10^{9}$	128	0.85	0	-0.91	Lee et al., 1997
Methanol	442-571	276	Tubular	1.67	85.9	1	0	_	Rice and Steeper, 1998
H_2O_2	450	50-340	Tubular	$10^{13.4}$	180	1	0	0	Croiset et al., 1997
Methane	560-650	245.8	Tubular	$10^{11.4}$	42.8	0.99	0.66	0	Webley & Tester, 1991
Sewage sludge	400-500	300	Batch	$1.08*10^{4}$	76.3	1	0	_	Goto et al., 1999
Alcohol distillery	400-500	300	Batch	$7.85*10^{2}$	64.7	1	0	_	Goto et al., 1999

Compound	Temperature (°C)	Pressure (bar)	Reactor Type	Kinetic parameters					Reference
				A	*Ea*	*a*	*b*	*c*	
Acetic acid	475-600	246	Tubular	$7.9*10^9$	168	1	_	_	Meyer et al., 1995
Phenol	300-500	250	Tubular	$10^{1.34}$	39	1	0	_	Portela et al., 2001
Acrylic acid	400-500	250	Tubular	345	52	1.98	0.17	0	Gong et al., 2014
Phenol	380-480	250	Tubular	$10^{2.34}$	12.4	0.8	0.5	0.42	Gopalan and Savage,1995
O-Cresol	350-500	250	Tubular	$10^{5.7}$	124.26	0.57	0.22	1.44	Martino & Kasiborski, 1995
Pyridine	426-525	276	Tubular	$1.3*10^{13}$	210	1	0.2	_	Crain et al., 1993
Semi-synthetic cutting fluid	400-500	250	Tubular	35	70	1	0.579	_	S´anchez-Oneto et al., 2007
Benzene	479-587	246	Tubular	$2.7*10^5$	204	0.4	0.17	1.4	DiNaro et al.,2000
Acrylonitrile wastewater	299-552	250	Tubular	$5.22*10^2$	53.48	1	0	0	Shin et al., 2009

2.7 Energy Recovery

Apart from the ability of SCWO to destroy various organic hydrocarbons, several works have focused on the recovery of excess heat that makes this treatment method feasible (Kritzer and Dinjus, 2001). The SCWO reaction is exothermic, and this reaction depends on the calorific value of the feeding stream. The excess energy can be used to preheat the feeding streams, raising the temperature of any fluid during heat exchange or using it to produce high-temperature steam to generate electric power. Bermejo and Cocero (2006) have referred to the role of the high energy of co-fuel that can be used to raise the feeding temperature. Consequently, SCWO could be a self-sufficient process. For example, if the heat content of the feeding waste is more than 930 $kJ.kg^{-1}$, it can be used to generate excess heat effluent that can be sufficient to raise the temperature of the feeding stream to 400 ℃.

Several studies were carried out by several companies to improve the heat recovery system and to support the economy of the SCWO process. For example, SuperWater Solutions constructed an SCWO plant in 2005 to treat sludge in Orlando, and the excess heat that was used to produce hot water and steam was subsequently used to produce electricity. Supercritical Fluids International (SCFI) operated an SCWO plant to treat waste and used the excess heat to raise the temperature of the aqueous feeding. The large plant scale contributes to the generation of excess heat. Consequently, the cost of SCWO technology would be reduced (Fang and Xu, 2014).

2.8 Current Status of Industrial SCWO Technology

Several reviews have summarised the status of commercial SCWO plants. They have reported that SCWO technology can treat wastewater despite the effect of the operational and technical obstacles that influenced the first SCWO commercialised application in 1980 by MODAR (Bermejo and Cocero, 2006). The main problems with SCWO technology are corrosion and plugging; further research could help to control and avoid these challenges. Several companies have worked to improve SCWO performance by using various designs, constructed materials, and operating conditions. Table 2.6 shows these companies and their approaches.

Several companies have built various SCWO plants around the world to treat dangerous waste. For example, GA has implemented several projects to destroy various organic waste for the US Army. In 1999, GA operated a large-scale SCWO plant to treat a hydrolysed VX nerve agent in Indiana. GA operated a pilot-scale plant in 2000 and 2001 to treat chemical agents for the US Army and to support the large-scale plant. In 1999, GA designed a compact SCWO plant to treat shipboard waste that contains hydraulic fluid, halogenated solvents, lube oil, and paint with a capacity of 45 kg.h^{-1}. GA used Hastelloy-lined reactors in the pilot plant to avoid corrosion. Another company that has worked with the US Army, Foster Wheeler, implemented a large SCWO system (full scale) to destroy wastewater for the US Army. Also, the same company operated a pilot-scale plant for testing shipboard waste in 1999. This plant was used to treat chemical agents such as HD, GB, and VX. Mitsubishi Heavy Industries (MHI) built the first SCWO plant (large scale) in 2005 in Japan after obtaining the required licences from SRI International to treat PCB waste with a high flowrate (6 tonne/day). Also, MHI investigated the destruction of PCB in a pilot plant in 1998. Hydro Processing (LLC) created the Harling wastewater treatment plant to treat municipal wastewater and sludge in 2001. This plant consisted of two units with a capacity of 47 L.min^{-1}. Hydro processing investigated the cost of treatment of waste, and they found the operating cost of an SCWO to be less than that of a landfill.

In 1994, Eco Waste Technologies implemented the first commercial SCWO plant to treat amines, glycols, and alcohols with a high flow rate of 1100 kg.h^{-1}. In 2002, Chematur Engineering achieved the first SCWO system in the UK, which was used to recover platinum and treat organic waste; this was a large-scale plant. Hanwha Chemical operated a large SCWO plant in Korea to destroy melamine and DNT/MNT wastewater in 2000. Also, the same company built another SCWO plant to treat toluene diisocyanate in 2008 (Marrone, 2013). Also, Innoveox built an

SCWO plant in 2011 to treat industrial waste in France. SCFI built an SCWO plant in 2012 to treat wastewater in Ireland. Lastly, SuperWater Solutions built an SCWO plant in 2013 to treat wastewater sludge in Florida.

Table 2.6: Commercial SCWO plants currently in existence (Marrone, 2013).

company	*Licensees*	*Full-scale plants*	*Application*
MODAR, Inc. (1980-1996)	*Organo*	*Nittetsu Semiconductor, Japan (1998-2002)* *moved to university of Tokyo (2002-2010)*	*Semiconductor manufacture wastes* *University waste (since 2002)*
MODEC (1986-1995)	*Organo, Hitachi, NGK*	*None (1991- 1996)*	*Pharmaceutical wastes, pulp and paper mill waste, sewage sludge*
General Atomics (1990-present)	*Komatsu, Kurita Water Industries*	*US Army Newport Chemical Depot, Newport, IN (1999-stopped)*	*Bulk VX nerve agent; other feeds treated in smaller-scale systems: chemical agents & explosives (US Army), shipboard wastes (US Navy), rocket propellant (US Air Force)*
Foster-Wheeler (1993-2004)	*Sandia National Laboratories*	*US Army Pine Bluff Arsenal, AR (1998-2002)*	*Smokes and dyes; other feeds treated in smaller-scale systems: chemical agents & explosives (US Army), shipboard wastes (US Navy)*
EcoWaste Technologies (1990-1999)	*Chematur*	*Huntsman Chemical, Austin, TX (1994-2000)*	*Oxygenated and nitrogen-containing hydrocarbons (e.g., alcohols, glycols, amines)*
Chematur (1995-2007)	*Shinko Pantec*	*Johnson Matthey, Brimsdown, UK (2002-2007)* *Japan (2000-2004)*	*Spent catalyst (recover platinum and destroy organic contaminants)* *Municipal sludge*
SRI International (1990-present)	*Mitsubishi Heavy Industries*	*JESCO, Japan (2005-present)*	*PCBs, chlorinated wastes*
Hydro-Processing 1996-2003)	–	*Harlingen Wastewater Treatment, Plant No. 2, Harlingen, TX (2001-2002)*	*Mixed municipal and industrial wastewater sludge*
Hanwha Chemical (1994-present)	–	*Namhae Chemical Corp., Korea (2000-2005)* *Fine Chemical Co., Korea (2008-present)*	*DNT/MNT and Melamine plant wastewaters* *Toluene diisocyanate (TDI)*
SuperWater Solutions (2006-present)	–	*Orlando, FL (2013-Present)*	*Wastewater sludge*
SuperCritical Fluids International (SCFI)	–	*Eras Eco, Ireland (2012-present)*	*Wastewater treatment*

(2007-present)			
Innoveox *(2008-present)*	–	*Arthez-de-Bearn, France* *(2011-present)*	*Hazardous industrial waste*

Table 2.6 illustrates some companies that are no longer in operation due to technical problems. Some active companies are still working on a large scale and a pilot scale. Some universities have supported the research by using the pilot-scale plant such as the universities of Cadiz, Valladolid and British Columbia.

CHAPTER THREE: EXPERIMENTAL EQUIPMENT, PROCEDURES AND ANALYTICAL TECHNIQUES

This chapter explains the laboratory work including description of all instruments and procedures that were used and applied to analyse the samples from SCWO of monoethanolamine (MEA) and 3-methylpyridine (3MP).

3.1 Description of SCWO Rig

The laboratory-scale SCWO rig is described in Figure 3.1. This rig was designed and built in the University of Birmingham. It comprises reactant feeds, reaction part, effluent cooling unit, back pressure regulator, liquid-gas separator and sample collection points. The tubular plug flow reactor was used to carry out all experiments and put inside an electric furnace (isothermally SCWO system).

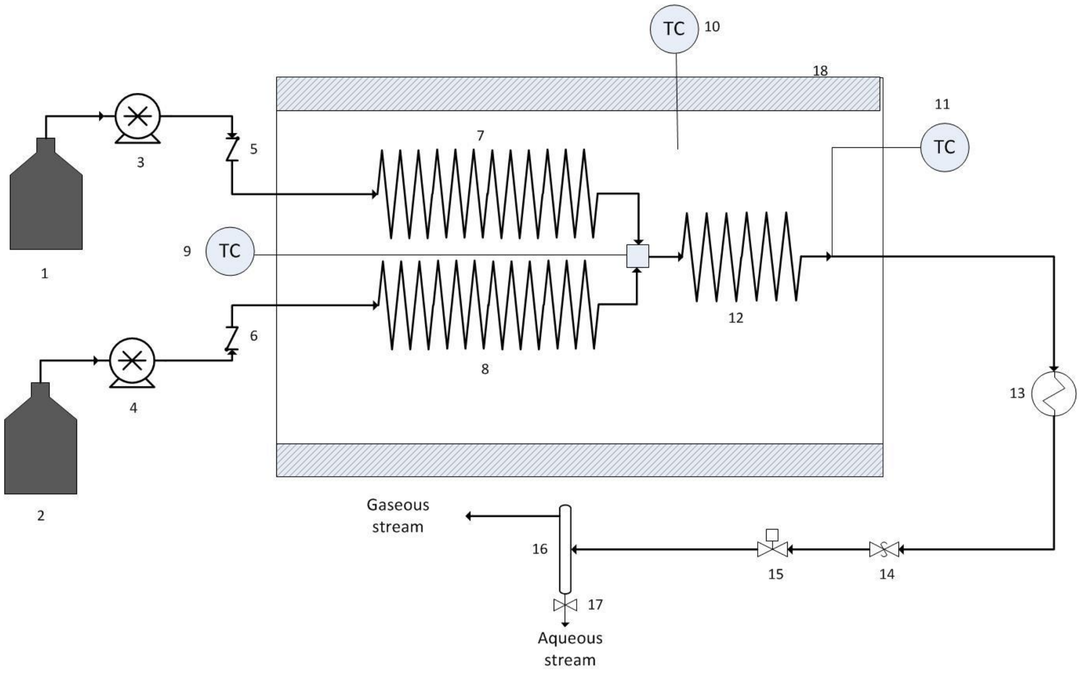


Figure 3.1: Process diagram of the SCWO apparatus

1-Oxidant tank, 2-Organic tank, 3,4- HPLC pumps, 5,6- Check Valves, 7- Pre-heater (oxidant) 8-Pre-heater (organic), 9,10,11- Thermocouples, 12-Reactor, 13-Cooler, 14-Relief Valve 15-Back Pressure Regulator, 16-Separator, 17- Check Valve, 18- Furnace

3.1.1 Reactant Feeds

The reactants were separately delivered to the reactor from the feed organic tank and the oxidant feed tank via two HPLC pumps (Model: Jasco PU-2086 Plus) that pressurise the two streams and inject them to the pre-heater section immediately prior to the reactor. The range of flow rates of the HPLC pump is 0.001 to 20 ml.min^{-1}. Teflon tubes are used to deliver reactants from the storage tanks to the pumps, and stainless steel tubes are used to deliver organic and oxidant streams from the pumps to preheaters.

3.1.2 Reactor Section

This part consists of the preheater and the reactor. In the preheaters, the temperature of the oxidant and the organic solutions was elevated from ambient temperature to the suitable reaction temperature before injection into the reactor. In general, the pre-heater has two main tasks: (1) to ensure the complete decomposition of the oxidant to generate oxygen and (2) elevate the temperature of oxidant and organic streams to the desired value (Croiset et al., 1997). The lengths of the pre-heater are 27 m and 21 m for the oxidant and organic preheaters respectively, and the outer diameter of pre-heater 1/8" (SS-316/316L). After elevation of the temperature of the reactant streams to the desired conditions, the organic and oxidant streams met at the reactor entrance and the oxidation process began. The length of the reactor is 9.0 m, and the outer diameter was 3.175 mm (SS-316/316L). The volume of the reactor was 13.795 ml (dimensions: L= 9 m, I.D =1.397 mm). The reactor and pre-heater tubes were supported on the stainless-steel frame inside the furnace. The reactor and preheater tubes and unions were purchased from Swagelok (stainless steel).

The mixing of organic and oxidant streams took place in the cross-union (1/8") at desired operating conditions. Two thermocouples (K-type, O.D =1/16") were located at inlet and outlet of the reactor to monitor the reaction temperature. The thermocouples were joined to the reactor using a reducer (SS-1/16" x 1/8").

3.1.2.1 Furnace

An electric, air-driven furnace (AEW, Andover-Hampshire, England) was used to raise the reaction temperature of the reactants to the required condition. The size of the furnace was medium (96, 77, 96) cm with a maximum temperature of the furnace was 600 °C. A small 10 cm diameter chimney at the top of the cavity was used to access the furnace through which all input lines, output lines and thermocouples were passed.

The temperature of the furnace was controlled via a PID controller (RKX 900) that regulates the set-point temperature with increment up to 1℃. The temperature of the reactants at the inlet and outlet of the reactor was measured via K-type thermocouple (TC Direct, UK) and recorded using a USB TC-08 (Pico) (Pico Technology, UK) datalogger connected to a laptop running Picolog temperature software. The reaction temperature was monitored to ensure the system of the reaction was isothermal thought out the always monitoring to the Picolog software to check the temperature of inlet and outlet the reactor, and the variation of the reaction temperature was ±3 ℃ as a maximum value.

3.1.3 Depressurisation Part and Separator Phase

To monitor and control the pressure in the SCWO rig, there are two instruments being used: a pressure transducer (Druck, Model PTX 521) and a back-pressure regulator (BP66, Go regulators, USA). The pressure transducer was joined to the line of product stream after the cooler via tee union to measure the pressure during all experiments, and the pressure reading was displayed on a digital indicator. The reading of the pressure transducer was similar to pressure reading on the display of the HPLC pump. The effluent continued to pass via a relief valve (Swagelok, UK) that was used for safety in case the pressure of system increased beyond design levels. The maximum pressure of the relief valve was 27.5 and its calibrated to 26.5 MPa. Then the effluent passed through the back-pressure regulator to leave with normal pressure, and the back-pressure was used to control and elevate the pressure to the required condition in all experiments. The maximum pressure allowed by this regulator 10000 psig (68.8 MPa). The always monitoring to the pressure display to ensure the system was isobaric status, which observed the variation of pressure was ±2.5 bars. The effect of this variation may consider minor if compared with the operating pressure 250 bars.

The temperature and pressure of effluent that left the back-pressure regulator were at ambient conditions. The reactor products were then passed to the top glass separator unit via a tube. This separator phase was closed two rubber bungs with one further tube at the top for collecting the sample of gas and one at the bottom for collecting the liquid sample. At the end of the gas line, there was a butterfly valve that could be closed to prevent atmosphere ingress when collected the sample of gas or measured a flowrate of gas. The gas flowrate was measured by using a glass graduated tube (50 ml), a stopwatch and a soap bubble flowmeter. Figure 3.2 shows the separator phase and gas graduated tube for measuring gas flowrate. The same valve allowed for gas to pass via a Teflon tube (left direction line) to collect by using a gas syringe that contains a PTFE valve. The volume of a gas syringe is 25 ml (Model:1025TLL/Hamilton, Sigma-Aldridge, UK). Then, the sample of gas was analysed using GC/TCD. After measuring and collecting the sample of gas, the sample of liquid was collected and analysed.

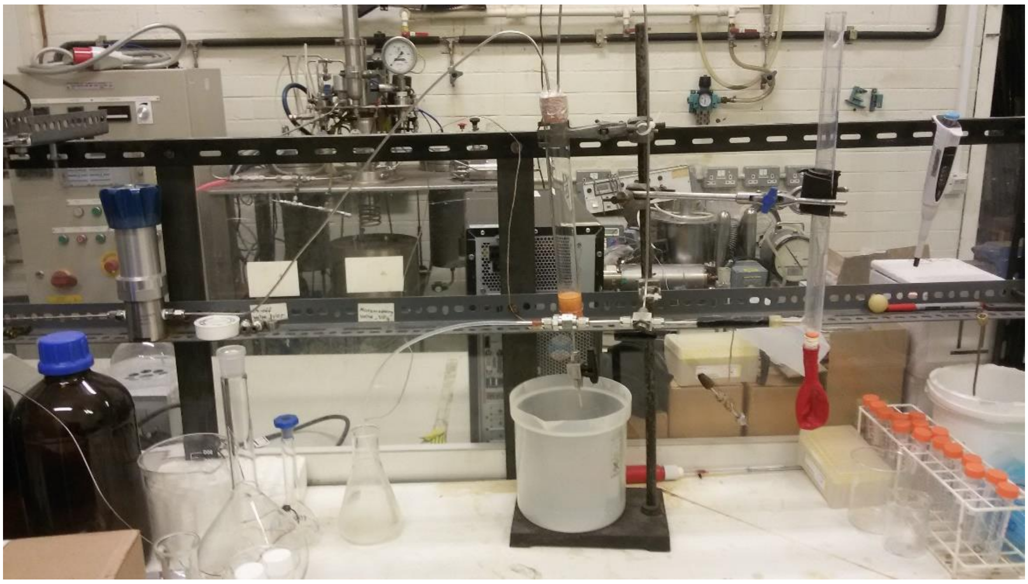


Figure 3.2: Separator phase and glass graduated tube for measuring gas flowrate

3.2 Experimental Procedure

3.2.1Preparation of Reactants

- *Organic Solutions*

In this work, MEA and 3MP organic model compounds were investigated. Various MEA (Sigma-Aldrich, ≥ 99 wt.%) concentrations were prepared by mixing a reagent of organic with distilled water in a volumetric flask. Then, the feedstock was stored in brown Winchester bottle in order to avoid organic reaction with the light. For 3MP (Sigma-Aldrich, 99 wt.%), Various concentrations were prepared by mixing a reagent of organic with distilled water in volumetric flask. Then, the feedstock was stored in brown Winchester bottle in order to avoid organic reaction with the light. Two organic compounds have a high solubility in distilled water. The reaction samples for each experiment were analysed using photometer (Spectroquant photometer *NOVA* 60) or TOC analyser (Model: TOC-L). Also, the initial concentration of the chemical oxygen demand (COD) for MEA, total organic carbon for 3MP and total nitrogen must be tested to calculate the removal efficiency.

- *Hydrogen Peroxide Solution*

The selection of oxidant depends on the scale of the SCWO process and the cost of oxidant. The source of oxygen in this work was hydrogen peroxide because hydrogen peroxide may be easy to apply and to avoid problems of the compression of air or pure oxygen. Svishchev and Plugatyr (2006) have pointed out that hydrogen hydroxide was more efficient than pure oxygen in the laboratory scale tests because hydrogen peroxide decomposed to generate strong free radicals ($HO^\bullet$) while pure oxygen needed to several steps to generate free radicals. Further researcher has reported that hydrogen peroxide had suitable mixing characteristics if compared to oxygen and solution of hydrogen peroxide is easy to deliver via the pump (Pinto, 2004). Lee et al. (1990) have found that the effect of hydrogen peroxide on the destruction of acetic acid was more efficient than that pure oxygen.

The required hydrogen peroxide concentration was prepared by mixing a reagent of H_2O_2 (Sigma-Aldrich, UK, 30 wt.%) with distilled water in a volumetric flask. 35 ml of 30 wt. % H_2O_2 was added to 2 litres of distilled water. H_2O_2 was calculated depending on the amount of O_2 that needed to oxidise the organic compound. In all experiments, hydrogen peroxide solution feedstock was stored in a brown Winchester bottle to avoid reactions with the light, and the bottle placed in a steel bath filled with ice to avoid any the decomposition before pumping.

3.2.2 Procedure of Experiment

The first step was to prime the HPLC pumps using distilled water. Streams of distilled water was separately fed via two pumps to elevate the pressure of the SCWO system to the supercritical reaction condition using a total flow rate of 5 $ml.min^{-1}$. The BPR was controlled manually and slowly to reach the required pressure of 250 bar. Then, the elevation of temperature was begun by changing the furnace set point to set up the desired reaction condition. The elevation time of pressure could take 20 to 30 min, and the elevation time of temperature could take 50 to 75 min by depending on the required temperature of the reaction. After the temperature and pressure of the system reached to a stable case, the flow rates of two pumps were adjusted from distilled water to the calculated oxidant and organic flow rates to apply the desired residence time, and once again the pressure and temperature were left to stabilise. At this point, the experimental runs began and 15 to 30 min was allowed to elapse at steady state depending on the residence time before samples of gas and liquid were collected and to ensure that enough time had passed to allow representative samples to reach the separator unit. During this time the flow rate and pressure were constantly checked to ensure the steady state was maintained, and the temperature at an input and output the reactor. It was necessary to ensure the state of flow rate must be the steady state, by testing flow rate was every 5 min via a catch and weight method. The flow rate of the sample gas was measured three times using soap-bubbles the flow meter then, collected the sample and injected into GC-TCD (model: 6890N, Agilent). The flow rate of liquid for each experiment was calculated by depending on the temperature and pressure and this flow rate was examined more than two times before collecting samples. Liquid samples were collected three times of analysis the COD or TOC content and nitrogen species. After collecting product samples and original organic sample for analysing, it could be changed the operating conditions to carry out a new experiment or the organic and oxidant streams could be replaced with distilled water in order to reduce the temperature and pressure of the rig and shut down. Gradually, reducing the temperature and pressure of the rig was important to avoid thermal stress (Al-Soqyani, 2017).

3.3 Analytical Techniques

The SCWO process is a technology to treat an aqueous organic stream and it has a high efficiency to destroy organic waste in short residence time. However, it is necessary to investigate products of reaction to assess the ability of this technology to treat waste and to follow the by-products in order to study reaction kinetics.

Liquid effluent of the reactor was examined to check the chemical oxygen demand (COD) or total organic carbon (TOC, Shimadzu, Japan). Nitrogen species in the liquid were quantified by photometric methods (Spectroquant *NOVA* 60). Methods of analysis will be explained in the next section. Gaseous effluent was examined by GC/TCD (Model: GC-6890N/Agilent).

3.3.1 Liquid Sample Analysis

The samples from oxidation MEA and 3MP were usually investigated using two techniques. A photometer was used to test COD of MEA oxidation derived samples and to quantify the nitrogen species in all samples, and TOC analyser was used to test total organic carbon content of effluent of the oxidation of 3MP. The main aim of this study was focused on the destruction of different organic compounds under various supercritical conditions and the effect of co-fuel on the efficiency of removal nitrogen and reduction of ammonia as well as the kinetics study. Two techniques were enough to determine the removal efficiency of COD, TN, TOC and investigate by-products of the reaction.

3.3.1.1 Total Organic Carbon (TOC) Analysis

To assess the efficiency of SCWO technology, TOC analysis was used to investigate the total organic carbon content in products of the reaction. All samples were tested in the School of Geography, Earth and Environmental Sciences. In this work, the total organic carbon was applied to check the efficiency of the destruction 3MP because the COD was not appropriate to oxidise pyridine and derivatives of pyridine. The method of test of TOC was NPOC (Non-purgeable organic carbon) that is the most widely used to determine TOC. The TOC analyser (Model: TOC-L, Shimadzu, Japan) is linked with auto-sampler (Model: ASI-L, Shimadzu, Japan) and PC that runs the software. The main operation in this analyser is combustion/non-dispersive infrared gas (NDIR) that considers a wide using in TOC (Shimadzu, 2016). The main principle to measure TOC depends on removing inorganic carbon from the sample by sparging, and the remained organic carbon will be investigated by the TOC analyser. The amount of carbon represents TOC in the sample.

The total organic carbon is investigated by acidifying organic sample to reduce the pH value to 2-3 and sparging with oxygen to remove inorganic carbon. The method of analysis is a combustion/ non-dispersive infrared gas (NDIR). Then, the organic sample is fed to the total carbon tube that contains on oxidation catalyst in order to elevate the temperature of the sample to 680°C. The investigated sample will be combusted to CO_2. CO_2 is transferred by carrier gas to inorganic tube to reduce the temperature and dehydrated. Then, the effluent is carried to the non-dispersive infrared gas analysis for measuring CO_2 by a carrier gas via a halogen scrubber to remove halogens. The software (TOC-Control L) is directly measuring the concentration of TOC from a detected signal that is generated by the NDIR.

3.3.1.2 Spectrophotometric Analysis

The two selected organic model compounds were nitrogen-containing compounds that are considered one of essential classes in hazardous wastes, and the by-products when oxidised may be regarded as a real problem in the environment such as ammonia, nitrite and nitrate. Therefore, it was necessary to assess the removal efficiency of total nitrogen and determine the reduction of nitrogen species at different conditions. The main principle to measure a concentration in sample by Spectrophotometry depends on measurement of the amount the light absorbed by a substance in the sample after treatment with a reagent. The reaction between the sample and reagent generates a specific colour that is measured by the spectrophotometer with a comparison made between the light intensity of the sample and the standard light intensity to find the concentration of substance either nitrogen species or COD, depending on the cell test employed. The chemistry of each cell test was different and is explained in the following sections.

Chemical Oxygen Demand (COD)

Chemical oxygen demand tests were used for each experiment to calculate the efficiency of the SCWO process and to study the effect of different operating conditions on the conversion of the COD. The COD content of each sample was examined using the spectrophotometer. This test method depends on the oxidation of the liquid sample with a hot sulfuric solution of potassium dichromate using silver sulfate as a catalyst. The remaining concentration of $Cr_2O_7^{2-}$ ions is measured photometrically. To find the COD concentration, the content of the cell test must be mixed before adding the sample. Then, 2 ml of the sample must be added to the COD cell test and mixed to prepare the sample for the digestion. The temperature of the cell test sample was elevated to 150 °C for 120 min using a thermoreactor. After the digestion time, the sample was mixed after 10 min and left to cool. Then, the COD was measured by the spectrophotometer (MERCK cell test manual, 2016).

Nitrogen species analysis

MEA and 3MP contain nitrogen, the analysis of the liquid sample is necessary to investigate the destination of their by-products. Different nitrogen species were generated when oxidised MEA and 3MP under supercritical conditions. The Spectroquant spectrophotometric cell test (*Merck*) was used to test nitrogen species and prepared a coloured liquid sample to be investigated the concentration of nitrogen species by Spectroquant *Nova* 60.

The tests included total nitrogen (TN), nitrite (NO_2^-), nitrate (NO_3^-) and ammonium nitrogen (NH_4-N). However, only one of each test was carried out for each experiment at 10 s due to the high cost of the cell tests and to avoid a laminar flow rate regime that probable at high residence time. A second test was accomplished only when the previous result test was erroneous. The photometer was calibrated and regularly checked. The following is procedure tests that were conducted for each experiment.

Ammonium Nitrogen

One of the main products of oxidation of the nitrogen-containing compounds is ammonia. Ammonia is known as a resistant by-product under supercritical conditions. This cell test estimating the concentration of ammonium nitrogen required taking 0.1 ml of liquid sample that was produced from the reactor at desired supercritical conditions and mixing it with the content of the test cell kit that contained an alkaline solution. Ammonium nitrogen in strongly alkaline solution is considered as ammonia. In the cell test, hypochlorite ions react with ammonia to make monochloramine. A blue indophenol derivative is produced from the reaction between monochorinamine and a substituted phenol. Consequently, the concentration of ammonium nitrogen in the liquid sample is depending on the intensity of this colour and is measured photometrically by Spectroquant *NOVA 60* (Merck cell test manual, 2016).

Nitrate Ion (NO_3^-)

Another nitrogen product was nitrate ion, by depending on the supercritical reaction conditions, nitrate ions may be formed as oxidation products. To find the concentration of this ion a 0.5 ml sample of the reactor effluent and added to the nitrate cell test that contains a mixture of phosphoric acid and sulphuric.

4-nitro-2, 6-dimethylphenol is a pink colour that is made due to the reaction between 1 ml of 2,6-dimethphenol with nitrate ions in an acidic medium. The concentration of nitrate ions was determined photometrically by depending on the intensity of the colour (Merck cell test manual, 2016).

Nitrite Ion (NO_2^-)

Depending on the supercritical conditions, nitrite ions could be made as oxidation products. To test the liquid sample, 5 ml of the effluent of the reactor was added to a nitrite cell test that contains a powder reagent. The test cell contains sulfanilic acid that reacts with nitrite ions to create a diazonium salt and this salt reacts with N-(1-naphth) ethylenediamine dihydrochloride to creat an azo-dye. The concentration of nitrite ions is measured photometrically by depending on the intensity of the red colour of azo dye (Merck cell test manual, 2016).

Total Nitrogen (TN)

To find the total nitrogen concentration in the effluent of the reactor, 1ml of the effluent of the reactor was taken and put in an empty cell. 9 ml of distilled water was added to the cell and mixed. Then, oxidising reagents were added and mixed to the empty cell to prepare the sample for the digestion and the solution was mixed before transferring to a thermoreactor (ECO8, VELP SCIENTIFICA). The thermoreactor was set to a temperature 120 °C and the sample was heated for 60 min. The digested sample will be mixed after 10 min of cooling. 1 ml was taken for analysing after cooling the digested solution. According to Koroleff's method, inorganic and organic nitrogen are converted to nitrate ions when the sample was put in the thermoreactor. The cell test solution was acidified with phosphoric and sulfuric acid, and the digested sample reacts with 1 ml of 2, 6-dimethylphenol (DMP) to produce 4-nitro-2, 6- dimethylphenol that is investigated by Spectroquant (Merck cell test manual, 2016).

3.3.2 Gas Sample Analysis

The gaseous samples were investigated by Gas Chromatography fitted with a Thermal Conductivity Detector (GC-TCD) (Agilent Model:6890N) to quantify the species of gases and their concentration. A 1.82 m concentric stainless steel CTR I-type column (3.175 mm i.d., 6.35 mm o.d., Alltech) was employed to detect several gases such as N_2, CO, CO_2, O_2, CH_4, with Helium used as a carrier gas. The gaseous sample was injected into GC-TCD and was taken through the column by the carrier gas, whereupon it entered a detector that generated a signal representing the quantity of different gases in sample. Before testing a sample by GC, it was necessary to calibrate the column so that it was possible to compare between the standard gases and products of gaseous effluent. The standard mixture gas consisted of a range of gases that could be detected by the column, and which could be generated from the oxidation of nitrogen-containing compounds under supercritical conditions. The standard gas contains 1% CO, 1% CO_2, 1% N_2, 1% O_2, 1% CH_4, 1% H_2 and He as a balance gas. After preparing the GC, 2 ml of the gaseous sample was injected. The conditions employed can be seen in Table 3.1. Each component in the sample corresponded to a retention time before it was eluted from the column. The typical chromatogram of gas sequence on the CTR I is shown in Figure 3.3, with the area under curve being proportional to the quantity for every gas in sample. To calculate the concentration of each component in sample of gas, equation 3.1 can be used:

$$Gas_x\, volume(\%) = \left(\frac{AUC_x \times 1\%}{AUC_{standard}}\right) \times 100. \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(3.1)$$

Although the collected and injected gaseous sample was investigated directly for each experiment, it was still likely that there was some small contamination by room air because the system of SCWO was not connected directly with GC-TCD. There were other challenges for example, the inlet of injection was non-secure, the inlet valve has a leak, as a result, the results of test sample of gas may be not precise. Thus, the balance of nitrogen in this work was not closed because organic nitrogen was not measured and CTRI column is not suitable for measuring nitrous oxide.

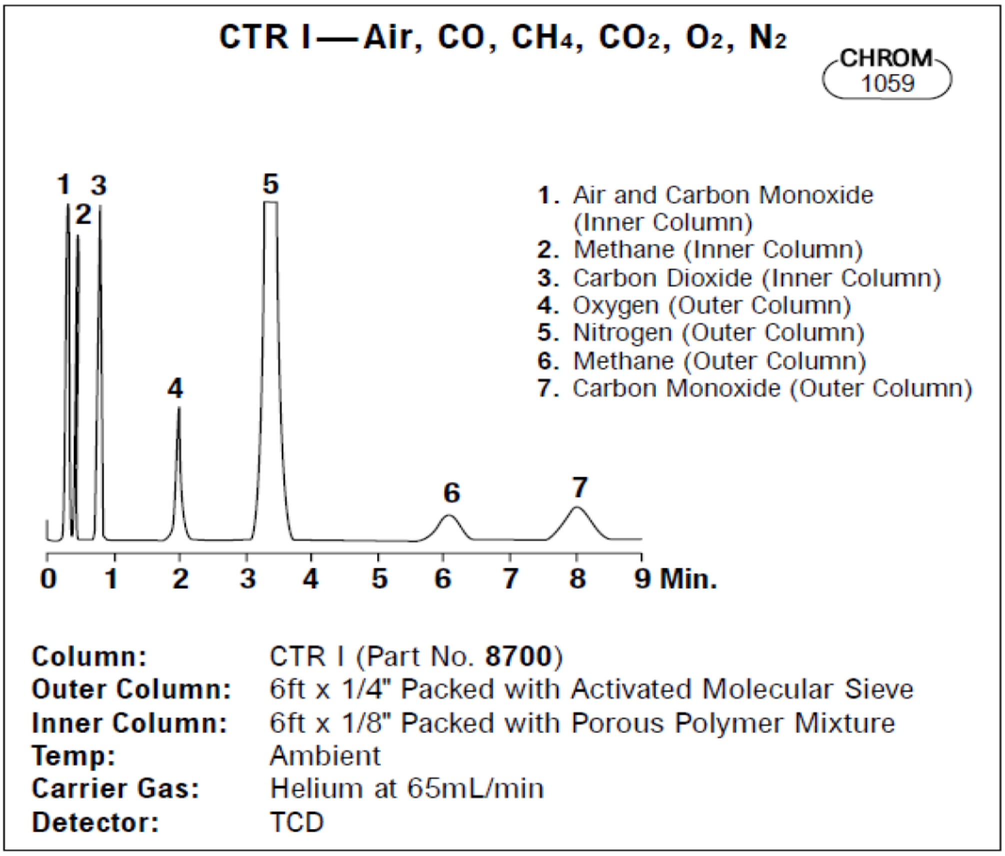


Figure 3.3: Typical Chromatogram of gas sequence on the CTR I (Alltech UK, 2012)

Table 3.1: GC-TCD operating conditions

Detector Conditions	
Detector Type	*TCD*
Detector Operating Temperature	*250℃*
Reference Gas	*Helium*
Reference Gas Flow rate	*65 ml/min*
Oven	
Equilibrium Time	*1 minute*
Oven Temperature	*33℃*
Carrier Gas	
Carrier Gas	*Pure Helium*
Flow rate (via column)	*65 ml/min*
Injection	
Injection (front inlet) Temperature	*50℃*
Loading Time	*0.5 min*
Run Time	*15 minutes*

3.4 Calculation Parameters

3.4.1 Flow Rate Delivery and Stoichiometric Ratio

The quantity of organic feeding affects the amount of oxidant. The molar and volumetric flow rates of required oxidant at various desired conditions were calculated by depending on the molar and the volumetric flow rates of organic substance and the stoichiometric ratio that was reached the reaction to the desired oxidation state.

In this system, the oxidation ratio represents the quantity of oxidant that was delivered in order to obtain on suitable oxidation. If the SR >1, the amount oxidant is more than a stoichiometric amount and SR<1, the amount oxidant was less than the stoichiometric amount.

$$SR = \frac{(\frac{[oxidant]}{[organic]})actual}{(\frac{[oxidant]}{[organic]})stoichiometric} \quad (3.2)$$

3.4.2 Concentration of Reactants

The concentration of the reaction medium under supercritical conditions are different to that at ambient conditions, where temperature has influenced the density of reactants at desired reaction conditions. Therefore, a series of calculations were applied that were based on a ratio density to calculate the concentrations of reactants at ambient conditions to ensure the correct concentrations at supercritical conditions. However, the organic, co-fuel and oxidant solutions were quite dilute (more than 99 % water). Consequently, the properties of these solutions are taken to be approximately similar to the properties of water, which were used to calculate the concentration of organic, co-fuel and oxygen at the inlet of the reactor. This assumption was also necessary given that there is not a reference that provides a thermophysical properties of the reaction mixtures, therefore the NIST database was used as the reference of thermophysical properties of water such as density, viscosity, etc, under different conditions (webbook.nist.gov/chemistry/fluid**)**.

3.4.3 Volumetric Flow Rate

There were two HPLC pumps at ambient conditions (25°C) delivering a constant volumetric flow rate of organic and oxidant solutions. By considering the density, the volumetric flow rate was converted to mass flow rate that remains constant throughout the system. The volumetric flow rate changes with varying temperature and so to maintain the mass flow rate constant, the following relationship between volumetric flow rates between two points, F_1 and F_2 is employed.

$$F_2 = F_1 \frac{\rho(T_1,P_1)}{\rho(T_2,P_2)} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(3.3)}$$

3.4.4 Reynolds Number (Re)

Reynolds Number is an essential parameter to assess a turbulent flow of fluid at a supercritical temperature, which it was calculated for each experiment, and viscosity, velocity and density were changed with the difference of reaction conditions. This relationship was used for calculating Reynolds Number:

$$\text{Re (T, P)} = \frac{\rho(T,P)u(T,P)D}{\mu(T,P)} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(3.4)}$$

The minimum Reynolds number was 2380 at 525 °C.

3.4.5 Residence Time

Residence time was a required period for completing the reactants pass via the reactor at reaction conditions. In other words, the residence time was calculated from the volume of the reactor and the volumetric flow rate at supercritical conditions. Equation 3.5 was used to obtain the residence time:

$$\text{Residence time (t)} = \frac{volume\ of\ reactor}{volumetric\ flow\ rate_{sc}} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(3.5)}$$

To calculate the removal efficiency of organic compounds and to assess the SCWO technology, the initial organic concentrations (COD_o or TOC_o) the effluent concentrations (COD_f or TOC_f) of each experiment were measured. The COD and TOC removal efficiencies according to these equations have been calculated by equations 3.6 and 3.7:

$$COD\ Removal\ (\%) = \left(\frac{COD_o - COD_f}{COD_o}\right) \times 100 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(3.6)}$$

$$TOC\ Removal\ (\%) = \left(\frac{TOC_o - TOC_f}{TOC_o}\right) \times 100 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(3.7)}$$

Similarly, to, to calculate the removal efficiency of total nitrogen at different conditions, the concentration of total nitrogen for the original organic solution (TN$_o$) and the effluent (TN$_f$) were measured. The TN removal efficiency has been calculated according to equation:

$$TN\ Removal\ (\%) = \left(\frac{TN_o - TN_f}{TN_o}\right) \times 100 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (3.8)$$

To determine the yield of nitrogen products, the following form was applied:

$$Nitrogen\ yield(\%) = \frac{moles\ N_{effluent}}{moles\ N_{initial}} \times 100 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (3.9)$$

Moles N effluent are moles of each nitrogen component in the effluent and moles N initial are moles of nitrogen in initial stream.

3.5 Risk Assessment of SCWO

In general, the operating conditions of the SCWO process are high temperature and high pressure, and it is necessary that an operator can carefully deal with any problem during the operation. The high temperature has the potential to cause burns from hot surfaces of the furnace. To minimise the risk of the hot furnace wall, thermal gloves were used to avoid burns and the door of the furnace was closed tightly and secured. To minimise the risk of overpressure, pressure must be continuously monitored during all experiments and a safety valve installed to the SCWO rig, which was set at 265 bar. Handling organic chemical compounds involves avoiding any direct contact between solution and skin, eyes or any part from the body of the operator because these organic compounds can have dangerous effects on health. Gloves, laboratory coat, safety glasses and a facemask were used to mitigate against contact with organic compounds and effluent of the reaction during the experiment. Each solution preparation was conducted in a fume cupboard to avoid inhalation of vapours. In addition, the remaining organic solutions after experimentation (reactant and effluent solutions) were collected in special bottles to be disposed of according to laboratory safety instructions. Lastly, all instruments depend on electric power to operate and they were all inspected regularly for electrical safety.

CHAPTER FOUR: SUPERCRITICAL WATER OXIDATION OF MONOETHANOLAMINE (MEA) IN THE ABSENCE AND PRESENCE OF ISOPROPYL ALCOHOL (IPA) AS CO-FUEL

4.1 Introduction

In order to employ the SCWO technology as a competitive treatment method and bring it to become a commercial scale, we must understand the destruction behaviour for nitrogen-containing wastewater of this technology and study their oxidant kinetics. Chapter four displays the results of MEA with and without IPA under various operating conditions and discusses the effects of selected operating conditions namely temperature, oxidant ratio, organic concentration and residence time, on the removal efficiency of MEA and by-products. It also investigates the effect of co-fuel addition, on destroying MEA and by-products distribution at selected operating conditions. Furthermore, it studies the SCWO kinetics for both cases to find the effect of IPA on the reaction parameters, which would contribute to increase the understanding of the role of co-fuel and feasibility of SCWO.

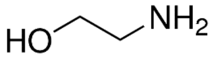
4.2 Selection of MEA

MEA was selected as a model chemical compound in this study. MEA contains amino function group and alcohol function group with a molecular formula of (C_2H_7NO). MEA is considered an important compound in various industries and would therefore be found in many process effluents such as manufacture detergent and textile materials, in effluent of thermal and nuclear power plants as it is employed as pH adjustment to reduce the corrosion in piping systems, in petrochemical industry and oil treatment. It is mainly used to remove CO_2 from natural gas, using in the cement industry to improve the strength and reduce the time of drying, production pharmaceuticals, using in printing inks to control pH, wood treating (Kim et al., 2010; Razali et al., 2010; Dow, 2019).

The physical properties of MEA (Sigma-Aldrich, UK, ≥ 99%) are shown in Table 4.1. It was colourless liquid during all runs, it was full miscible with water. The equation of the complete oxidation of MEA is:

$C_2H_7NO + 3.25O_2 \rightarrow 3.5H_2O + 2CO_2 + 0.5N_2$ ………………………………………… (4.1)

Table 4.1: Physical properties of MEA

CAS Number	*141-43-5*
Molar Mass (g/mol)	*61.08*
Density (g/ml)	*1.012*
Boiling point (°C)	*170*
Melting point (°C)	*10-11*
Water Solubility	*Miscible*
Colour	*Colourless*
Structure	

The main reasons for selecting MEA as a model of hazardous waste in this study is shown below:

1. MEA is widely used in various industries that are mentioned above, and this compound has an amino functional group (NH_2) and an alcohol functional group (OH).
2. It is found in real wastewater of various application such as thermal and nuclear plants (Kim et al., 2010) and petrochemical industry (Razali et al.,2010).
3. Limited studies on MEA were carried out under supercritical conditions; consequently, studying this compound will enrich the knowledge and provide novel kinetic data as well as it shows the behaviour of this compound at different conditions. In addition, the main by-product of this compound is ammonia (refractory compound), and it is significant to examine the effect of co-fuel on the ammonia reduction.
4. Most studies of MEA treatment did not have a complete removal efficiency, for example, MEA wastewater stream from petrochemical industry was treated by activated carbon, alum, zeolite and the COD removal efficiency results were 80%, 73% 64% respectively.

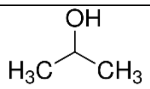
In a biological reactor, the removal efficiency of MEA was 92% after 10.5 days. Consequently, MEA would need to a long residence time for completing the destruction.

4.3 Selection of Isopropyl Alcohol (IPA)

IPA is a simple compound and monohydric alcohol. It was selected as co-fuel to compare its performance with propylene glycol (PG). IPA has physical properties that illustrate in Table 4.2. It was employed as a solvent in several applications such as a pharmaceutical industry and cleaning liquid. Several researches have referred to IPA as a significant co-fuel in SCWO (Yang et al., 2018; Bermejo et al., 2008; Al-Duri et al., 2016). Using co-fuel in SCWO may contribute to increase the rate of the reaction due to generation of extra free radicals and possible reduction in activation energy. Consequently, co-fuel would enhance the performance of SCWO. There are several reasons to select IPA as co-fuel.

1. Toxicity of IPA may be considered low compared with other organic solvents.
2. Numerous studies have referred to use IPA as co-fuel to improve the reduction of ammonia if compared with other co-fuels such as methanol and ethanol.

Table 4.2: Physical properties of IPA

CAS Number	*67-63-0*
Molecular formula	C_3H_8O
Molar Mass (g/mol)	*60.1*
Density (g/ml)	*0.786*
Boiling point (℃)	*82.6*
Melting point (℃)	*-89*
Water Solubility	*Miscible*
Colour	*Colourless*
Structure	

In summary, treatment MEA containing effluent by conventional methods is not a suitable solution due to its poor biodegradability (Kim et al., 2010) and MEA decomposes to produce ammonia that has influenced on the aquatic life.

4.4 Effect of System Operating Conditions

In this chapter, the SCWO process diagram and experimental procedures were previously illustrated in chapter three.

4.4.1 Experimental Work Plan

Table 4.3 gives a summary of operating conditions ranges. SCWO experiments were carried out at a range of temperatures, residence times, oxidant ratios, and MEA input concentrations. Furthermore, different ratios of IPA as co-fuel were investigated. Each parameter was individually investigated at 400 °C, 5 mM of MEA and SR of 1. The operating pressure was 250 bar during all experiments, and several studies have reported that increasing pressure did not influence the process efficiency (Cocero, 2001).

Table 4.3: Summary of the operating conditions used in SCWO of MEA experiments.

Variable	Range	Fixed conditions
Temperature (°C)	400 - 525	$[MEA]_o$ = 5 mM SR = 1SR
$[MEA]_o$ mM	2.5 - 10	Temp = 400 °C SR = 1SR
Oxygen Ratio	0.5 - 2 SR	Temp = 400 °C, $[MEA]_o$ = 5 mM
Temperature (°C)	400 - 525	$[MEA]_o$=$[IPA]_o$= 5 mM SR = 1SR
Oxygen Ratio	0.5 - 2 SR	Temp = 400 °C $[MEA]_o$=$[IPA]_o$= 5 mM
Ratio $[IPA]_o/[MEA]_o$	0.5 - 2	Temp = 400 °C, SR = 1SR
Residence time: 6-14 s for all experiments		

4.4.2 Effect of Residence Time

As shown in table 4.3 the residence times for MEA removal ranged from 6 to 14 s, based on keeping turbulent flow regime at all residence times. This was achieved by varying the feed flow rate, and the shortest and longest residence times were limited by the minimum and maximum delivery of the organics and oxidant HPLC pumps. During all runs, the time of stabilisation was 15 to 30 min in order to obtain accurate residence time as flow rates were fed. The effect of residence time on the COD removal % (without IPA) is displayed in Figure 4.1 at six different temperatures. Consistently with previous works in the field, longer residence times improved COD removal %.

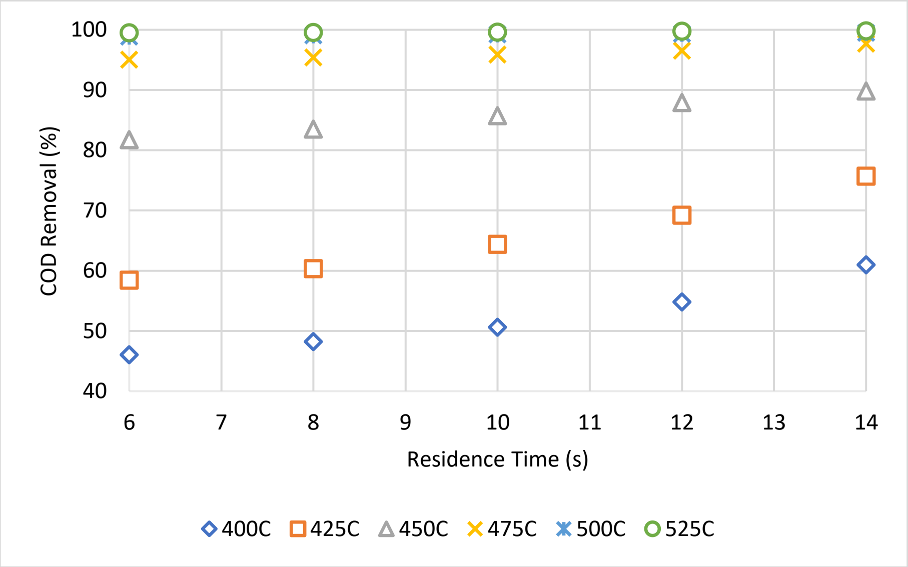


Figure 4.1: COD removal % against residence time at various operating temperatures, at 5 mM MEA, SR of 1

In general, at 400 °C the COD removal % increased with increasing the residence time from 46 % at 6 s to 61 % at 14 s (increased by 32.58%), while at higher temperatures the reaction rate and solubility are higher, and the influence of residence time is overtaken. For example, at 525 °C the COD removal % increased slightly from 99.5 % at 6 s to 99.8 % at 14 s. Figure 4.1 shows this effect clearly as the increase of the COD removal % from 400 to 525 °C decreased from 32.58 % to 0.3 % respectively. Several researchers have pointed out the positive effect of residence time on the enhancement of the organic conversion under supercritical water conditions (Savage et al., 2000; Qi et al., 2002; Ploeger et al., 2006).

Figure 4.2 displays the effect of residence time on the COD removal % at the same operating temperatures range in the presence of IPA, which expectedly showed the same trend. However, the IPA system clearly demonstrated enhanced COD removal %, but the residence time influence was overtaken by the IPA influence. For instance, at 400 °C, the COD removal % increased with increasing the residence time from 68.7 % at 6 s to 72 % at 14 s (increased by 4.8%) while the effect of the residence time on the COD removal % at 525 °C was from 98 % at 6 s to 99 % at 14 s (increased by 1%). Yang and his team pointed out methanol would be oxidised faster than IPA under supercritical water (Yang et al., 2018).

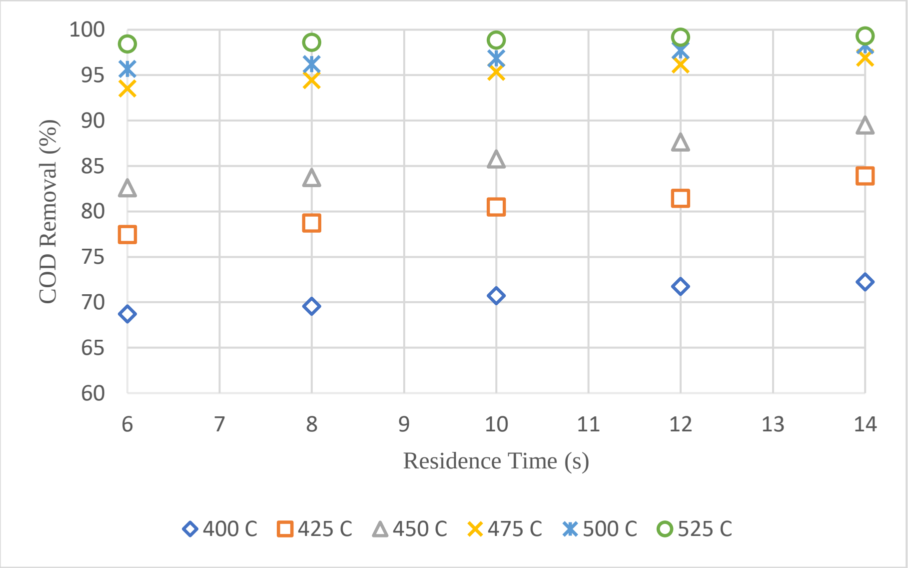


Figure 4.2: COD removal % against residence time at various temperatures at 5 mM MEA, 5 mM IPA, SR of 1

4.4.3 Effect of Operating Temperature

The range of operating supercritical temperatures of 400 to 525 °C was applied to study the effect of temperature on MEA oxidation using initial MEA concentration of 5 mM and 6 to 14 s residence time, at 1SR oxidant ratio. The selection of temperature range was based on the thermal ability of the furnace and keeping the turbulent flow regime at all conditions. In addition, an increment was 25 °C to study a reaction rate and in order to find parameters of the kinetic reaction.

At the range of residence time, Figure 4.3 display the effect of different temperatures on the COD conversion in the absence and presence of IPA respectively. The essential effect of temperature was observed on MEA oxidation. This role was illustrated in several works under supercritical water conditions. The operating temperature played a significant role in the enhancement of SCWO performance (Wang et al., 2011; Qi et al., 2002).

However, COD removal % of MEA increased from 46 % at 6 s and 400 ℃ to 99.5 % at the same residence time at 525 ℃, while at 14 s, the COD removal efficiency was enhanced from 60.99 % to 99.8 % due to increase the operating temperature from 400 to 525 ℃. This enhancement could be as a result to enhance the rate of reaction, and a high temperature contributes to generate free radicals at temperatures more than at 400 ℃. At higher temperatures, the reaction could consume a high percentage of oxygen that was provided to destroy the organic substance more than at low temperature (Al-Soqyani, 2017). The destruction of organic at high temperature may make SCWO an expensive technology to treat MEA. Thus, using co-fuel must be significant to destroy this compound at lower temperatures and residence times. IPA is one of the alcohols that used in the enhancement of the removal efficiency under supercritical conditions. Figure 4.1 displays the effect of various temperatures on the COD conversion.

Figure 4.3 displays the comparison between the effect of operating temperature on the enhancement of the COD removal % at 6, 10 and 14 s in the absence and the presence of IPA. The positive trend of temperature was consistent with the effect of temperature in several studies. Some researchers have pointed out the essential effect of increased temperature on the enhancement of the removal efficiency. In addition, the effect of temperature in the presence of co-fuel was significant due to the increase in the rate of reaction, increased the generation of free radical with increased temperature. Also, hydrogen peroxide and IPA may contribute to provide essential radicals such as $HO^\bullet$ and $HO_2^\bullet$. Then, various free radicals would attack MEA molecules and convert to water and wanted gases.

For example, The COD removal efficiency of MEA increased from 68.7 % at 6 s and 400 °C to 98 % at the same residence time and 525 °C (increased by 42.6 %). While at 14 s, the COD removal % was enhanced from 72 % to 99 % due to the increase in the operating temperature from 400 to 525 °C. This enhancement could be as a result to increase the rate of reaction, and a high temperature contributes to generate free radicals more than at 400 °C. Thus, these results have illustrated the significant effect of co-fuel on the COD conversion. The difference between the removal efficiency in the absence and presence of IPA at 400 °C was remarkable. For example, the increase in removal efficiency at 400 °C in the presence of IPA was 49 % at 6 s. Al-Duri et al. (2015) have demonstrated the positive effect of IPA on the TOC removal efficiency of DMF. However, the role of co-fuel could contribute to improve the performance of SCWO at low temperature. Consequently, the efficient of applied SCWO may improve if increasing the concentration of co-fuel or increasing the residence time.

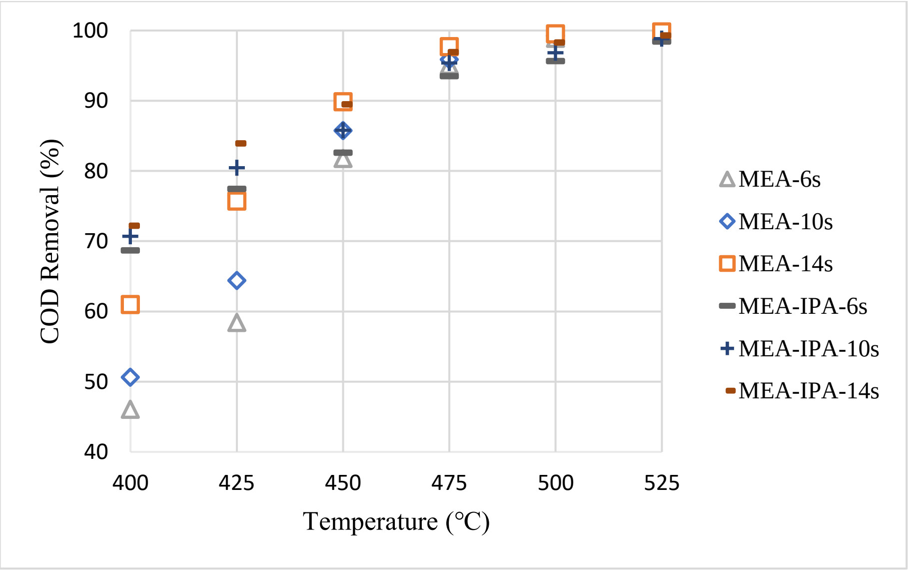


Figure 4.3: COD removal % against various temperatures at 5 mM MEA, 5 mM IPA, SR of 1 and 6, 10 and 14s

The destruction of MEA by SCWO led to produce intermediate compounds such as ammonium-nitrogen (NH_4-N) and nitrate (NO_3^-) and nitrite (NO_2^-). Figure 4.4 shows the effect of the different operating temperatures on the nitrogen species at 10 s and 5 mM MEA. NH_4-N was the main by-product of MEA oxidation under supercritical conditions (Yang et al., 2018). The results were illustrated the yield of NH_4-N increased with temperature while the NO_3^- and NO_2^- yields were still low because the conversion of MEA to NH_4-N was easy due to the structure of MEA contains an amino group (NH_2). The maximum NH_4-N yield increased to reach 29 % at 475 °C due to the increase the conversion of MEA with temperature, and the minimum NH_4-N yield was 13.5% at 400 °C due to lower the MEA conversion. At 525 °C, the yield of NH_4-N slightly decreased to reach 24.76 %. Several studies have pointed out the reduction of NH_4-N could occur at various conditions and converted mainly to N_2. Segond and his group have oxidised ammonia at 531 °C and 25 MPa, the reduction of ammonia was 17 %, at 30.6 s and the main product was N_2, and they referred to the complete destruction of ammonia was at 600 °C. (Segond et al., 2002).

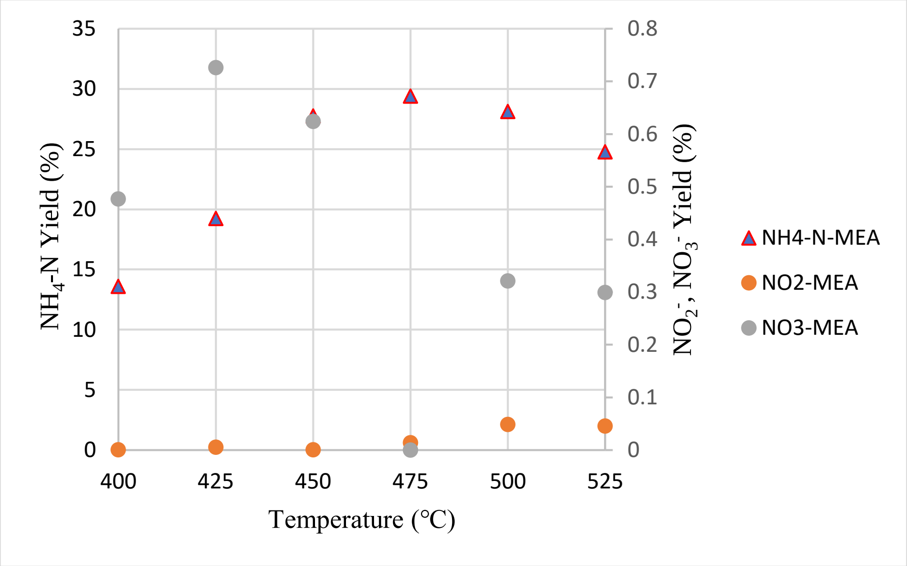


Figure 4.4: Nitrogen species yield as a function of temperature at 5 mM MEA, 10s and SR of 1.

Several researchers used co-fuels to destroy organic waste and by-products, and IPA would influence nitrogen species (Al-Duri et al., 2016). Figure 4.5 displays the effect of the different operating temperatures on the nitrogen species in the absence and presence of IPA at 10 s and 5 mM. In the IPA system, NH_4-N was the main by-product of MEA oxidation under supercritical conditions which was observed the yield of NH_4-N decreased with temperature. While the NO_3^- yield slightly occurred more than the yield of NO_3^- in the IPA-free system due to partial oxidation of NH_4-N to NO_3^-. The major product of oxidation ammonia was N_2, and the minor product was

NO_3^- (Segond et al., 2002). Consequently, the effect of IPA on the COD conversion contributed to increase the yield of NH_4-N at 400 °C and with increasing the temperature, the yield of NH_4-N decreased due to increase the generation of free radicals. For NO_2^- yield was still low in two systems. As a result, the maximum NH_4-N yield in the fuel-free system was 29 % at 475 °C, and the NH_4-N yield became 15.8 % in the presence of IPA. While at 525 °C, the effect of temperature and IPA occurred significantly to reduce the yield of NH_4-N from 24.76 % to 13.5 % in favour of gaseous N_2. This indicated that temperature would enhance the reduction of NH_4-N in presence of IPA.

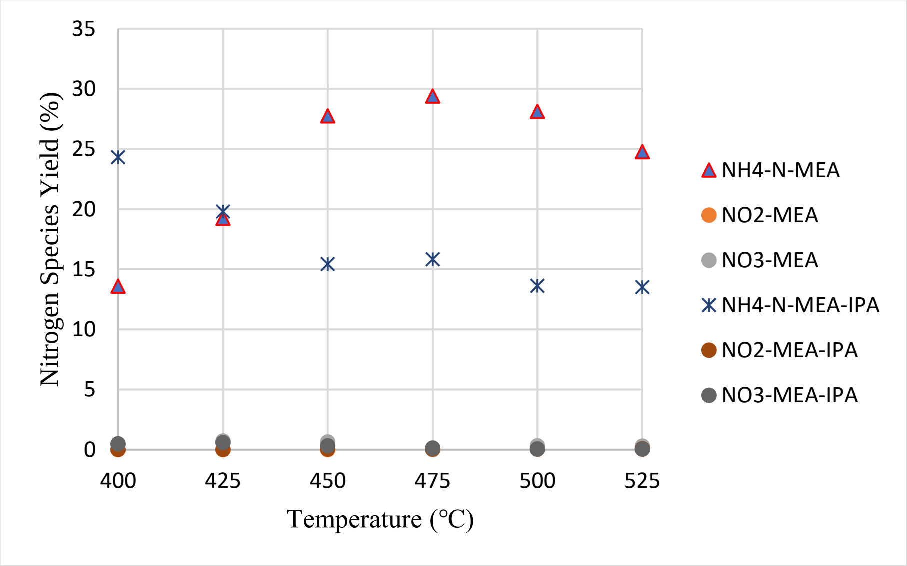


Figure 4.5: Nitrogen species yield as a function of various operating temperatures at 5 mM MEA, 5 mM IPA, SR of 1 and 10 s.

Figure 4.6 displays a comparison between the two systems. The nitrogen removal % in the presence of IPA improved with increasing the operating temperature, and IPA contributes to generate free radicals that have the power to attack and mineralise organic molecules to carbon dioxide, water and N_2. In addition, IPA has a high calorific value that contributes to the reduction of nitrogen (Yang et al., 2018). For example, the removal efficiency of nitrogen was enhanced from 61.6 % in the fuel-free system to 66 % in IPA system at 400 °C and 10 s while at 525 °C, it was enhanced from 75 % in the fuel-free system to 83 % due to increase the temperature. Also, at high temperature, the high percentage of required oxygen would consume. Thus, the co-fuel has a significant role to improve the COD and nitrogen removal efficiencies at SR of 1 and with increased the oxidant ratio, the results will enhance in next section.

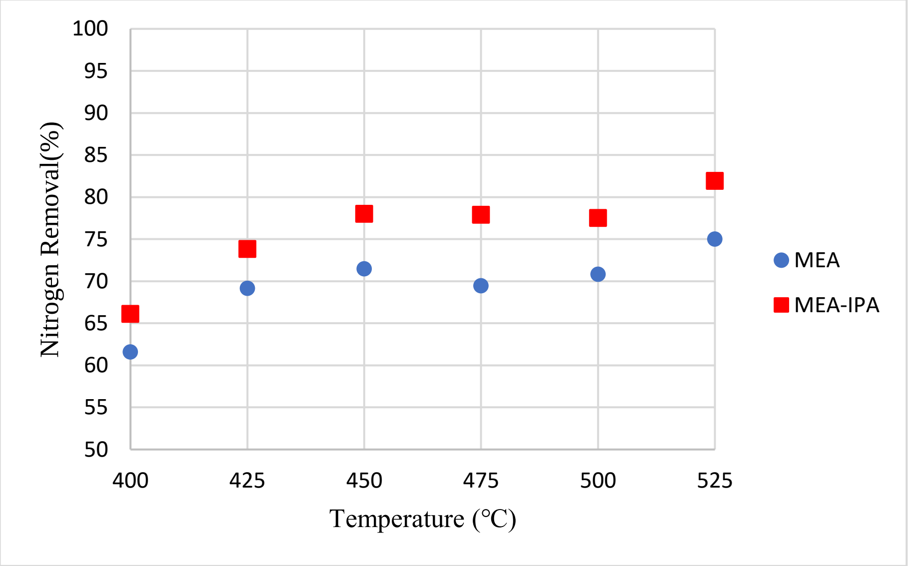


Figure 4.6: Nitrogen removal efficiency as a function of various operating temperatures at 5 mM MEA, 5 mM IPA, SR of 1 and 10 s.

4.4.4 Effect of Oxidant Ratio

The complete destruction equations for oxidation MEA and IPA systems are written below:

$C_2H_7NO + 3.25O_2 \rightarrow 2CO_2 + 3.5H_2O + 0.5N_2$ ………………………………………….... (4.1)

$C_3H_8O + 4.5O_2 \rightarrow 3CO_2 + 4H_2O$…………………………………….………………... (4.2)

The source of oxygen was hydrogen peroxide, and the equation of decomposition can be written:

$H_2O_2 \rightarrow H_2O+0.5O_2$ ………………………………………………………………… (4.3)

In this work, the effect of oxidant ratio was investigated on the COD removal efficiency and nitrogen species. The various amounts of oxygen were employed to oxidise MEA in the fuel-free and IPA systems under supercritical conditions to complete the destruction. The effect of oxidant ratio on the destruction of organic waste may be considered an essential factor. In the IPA system, the amount of oxygen represents enough oxygen for MEA and IPA under various supercritical conditions. The range of oxidant ratio was 0.5 to 2 SR. 0.5 SR represents the half amount of sufficient oxygen. 2 SR represents the double amount of sufficient oxygen. Also, the selected range of SR was based on the capacity of the HPLC pump. However, excessive oxidant ratios may contribute to increase the cost of oxidant and generate unfavoured products such as N_2O (Al-Duri et al., 2016)

COD removal efficiency was enhanced with increasing the oxidant ratio from 0.5 SR to 2 SR as shown in Figure 4.7. The oxidant would generate the free radicals required to perform oxidation. Free radical mechanism characterises the main pathways of supercritical water reactions (Pinto et al., 2006). Several studies have pointed out that the enhancement of the removal efficiency was to increase the oxidant ratio (DiNaro et al., 2000; Lee et al., 1990; Qi et al., 2002). For example, at 0.5 SR, the COD conversion improved from 34.8 % at 6 s with increasing the residence time to reach 51.7 % at 14 s. While at 2 SR the COD conversion enhanced from 75% at 6 s to 84 % at 14 s. However, the effect of oxidant ratio and the residence time contributed to the enhancement of the COD conversion.

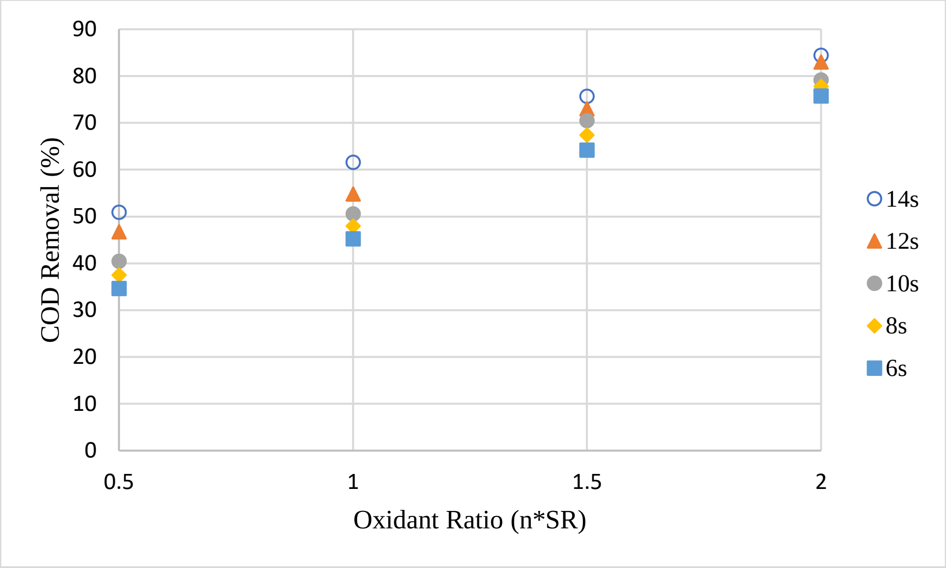


Figure 4.7: COD removal efficiency against various oxidant ratios at 400 °C, 5 mM MEA and various residence times.

Also, the effect of the oxidant ratio on nitrogen removal is as important as that on the COD conversion. In general, the results in Figure 4.8 show nitrogen species in liquid at 10 s and various oxidant ratios. The yield of NH_4-N decreased with increasing the oxidant ratio due to increased generation of free radicals, which further oxidised NH_4-N to gaseous nitrogen (N_2 and possibly N_2O). The nitrogen species trend illustrates the significant effect of increased amount of oxygen on the reduction of NH_4-N. For example, the yield of NH_4-N decreased from 19 % at 0.5 SR to 7.6 % (decreased by 60%) at 2 SR at 10 s and 400 °C. The main by-product of MEA conversion was NH_4-N because its structure contains the amino group (NH_2) (Yang et al., 2018) while the yields of NO_3^- and NO_2^- were still low. Increased the oxidant ratio of more than 2 SR and temperature may treat the by-product of MEA and improve the removal efficiency of organic substance.

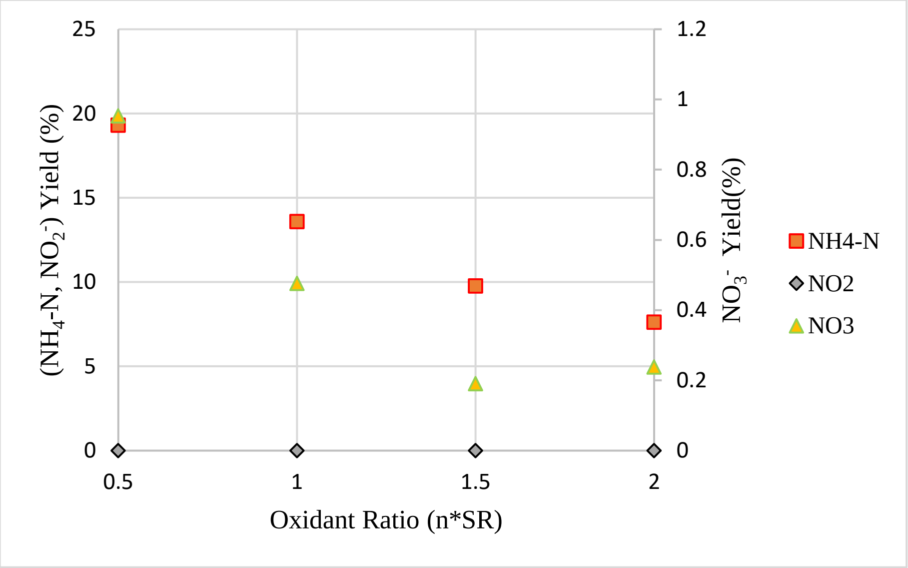


Figure 4.8: Nitrogen species yield as a function of the oxidant ratio at 5 mM MEA, 400 °C and 10 s.

In the IPA system, the effect of oxidant ratio on the COD conversion increased consistently with increased amount of oxygen from 0.5 SR to 2 SR. Figure 4.9 shows the enhancement the COD removal % as a result of oxygen increase in fuel-free and IPA systems. In addition to the free radicals generated by oxygen such as such as $HO^{\bullet}$ and $HO_2^{\bullet}$, IPA is a second source to generate free radicals such as $HO^{\bullet}$ and $HO_2^{\bullet}$ (Al-Duri et al., 2016) as well as $\bullet CH_3$, $\bullet HCO$ and $CH_3COO\bullet$. For example, at 0.5 SR the COD conversion was improved from 34.8 % at 6 s in the absence of IPA to 59 % in the presence of IPA (increased by 69.5 %), while the COD conversion was enhanced from 84 % (fuel-free system) to 87 % in the presence of IPA at 14 s and 2SR. In addition, the effect of oxidant ratio, IPA and the residence time contributed to the enhancement of the COD conversion.

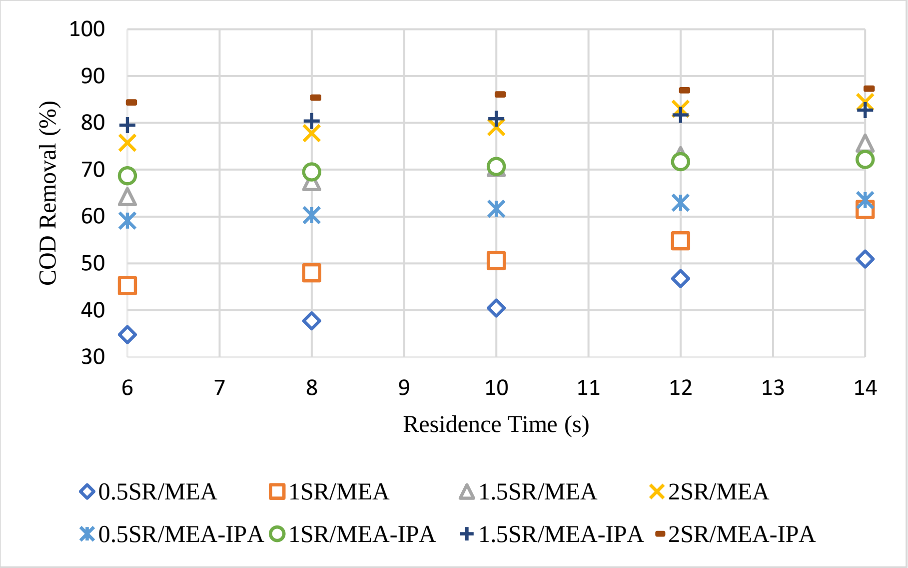


Figure 4.9: Effect of the oxidant ratio on COD removal % at various residence time and 400 °C, 5 mM MEA, 5 mM IPA.

In general, the result in Figure 4.10 shows nitrogen species in liquid at various oxidant ratios in the absence and presence of IPA. The results demonstrated the yield of NH_4-N significantly decreased with increasing the oxidant ratio. Nitrogen species trend illustrates the significant effect of increased the amount of oxygen in the reduction of NH_4-N in two systems. In IPA system, the yield of NH_4-N decreased from 30 % at 0.5 SR to 9 % at 2 SR at 10 s and 400 °C (decreased by 70 %). The NO_2^- yield was still low. Lowered yield of NH_4-N indicated to the essential role of oxidant in removing recalcitrant ammonia. In this work, the role of IPA was positive in the enhancement of COD removal efficiency but increased the COD conversion contributed to increase the yield of NH_4-N in IPA system if compared with the fuel-free system. For example, the yield of NH_4-N increased from 19 % at 0.5 SR (fuel-free system) to 30 % at 10 s, the same SR and 400 °C (increased by 57.89 %). The yield of NH_4-N increased from 7.6 % at 2 SR (system) to 9 % at 10 s, the same SR and 400 °C (increased by 18 %). Consequently, Increased the oxidant ratio more than 2 SR and increased IPA ratio would treat the by-products of MEA and improve the removal efficiency of organic substance at 400°C.

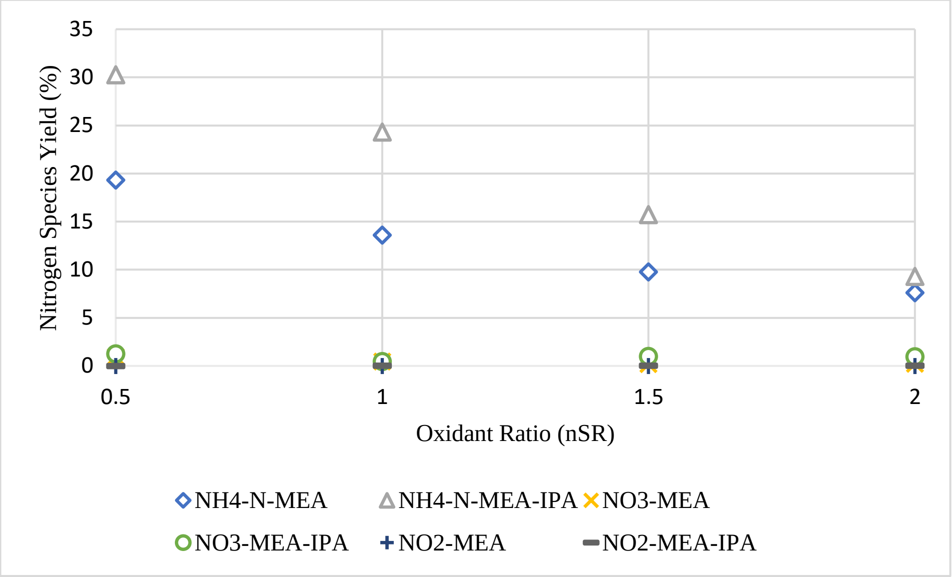


Figure 4.10: Effect of various oxidant ratios on nitrogen species at 10 s, 400 ℃, 5mM MEA and 5 mM IPA

Figure 4.11 displays the comparison between the effect oxidant ratio on the removal % of nitrogen in two systems. The nitrogen removal in the IPA system improved due to increase the oxidant ratio and IPA participated to generate free radicals that have powerful energizing to attack and mineralise organic molecules to carbon dioxide, water and N_2. Also, IPA has a high calorific value, then co-fuel would add heat to the reaction, and this heat would affect nitrogen removal (Yang et al., 2018; Al-Duri et al., 2016). For example, the removal efficiency of nitrogen was enhanced from 45.8 % in the fuel-free system to 54.9 % in IPA system at 400 ℃ and 0.5 SR, while at 2 SR it was enhanced from 71.6 % in the fuel-free system to 82.6 % in the presence of IPA (increased by 15 %) due to increase the oxidant ratio and the role of IPA. Thus, co-fuel has a significant role to improve the COD removal and nitrogen removal efficiencies.

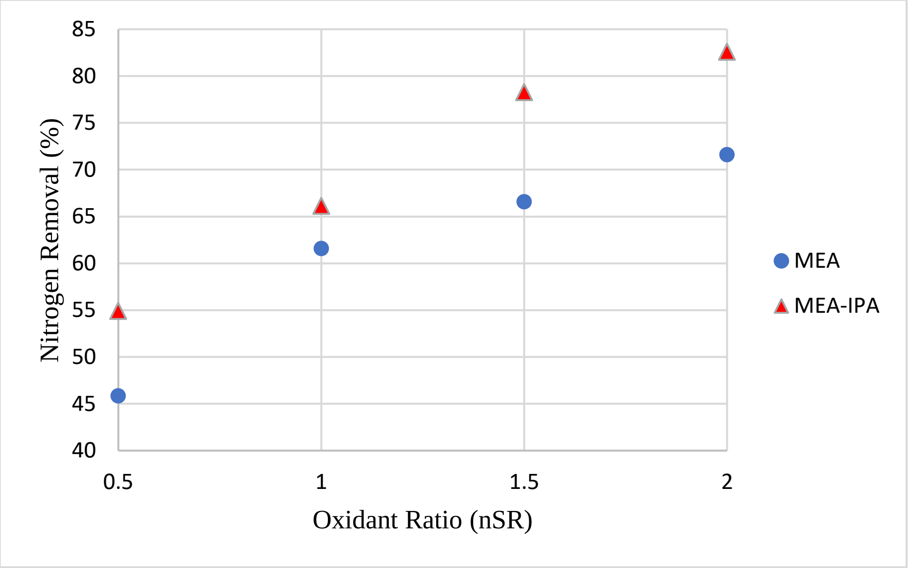


Figure 4.11: Nitrogen removal efficiency as a function of various oxidation ratio at 5 mM MEA, 5 mM IPA, and 10 s.

4.4.5 Effect of IPA_o/MEA_o Ratio

The primary purpose of this work is to evaluate the enhancement of the SCWO process performance using co-fuels. The effect of various concentrations of IPA on COD removal % and nitrogen species was investigated. Literature illustrated the significant role of IPA in enhancement the removal of nitrogen and improved the removal efficiency (Yang et al., 2018; Al-Duri et al., 2016). Several examples demonstrated the positive effect of methanol and ethanol on the performance of SCWO (Ploeger et al., 2006； Shimoda e al., 2016). The range of IPA/MEA was from 0.5 to 2 (i.e. 2.5-10 mM IPA) at 400 °C and 5 mM MEA. The selection of this range was based on the capacity of the HPLC pump, the concentration of organic (IPA+MEA) and operating temperature. In addition, the SCWO system was isothermal, and IPA would release high heat when using the high concentration. Consequently, various parameters contributed to choosing this range.

The effect of IPA ratio on the COD removal efficiency and by-products of MEA was investigated and the results are displayed in Figure 4.12. The effect of IPA ratio was observed to be positive on the COD removal efficiency, due to the increased powerful free radicals and increased the rate of reaction (Al-Duri et al., 2016; Bermejo et al., 2008). For example, at 10 s the COD removal efficiency was improved from 50.6 % (fuel-free system) to 62.6 % at 0.5 IPA ratio, to 79.9 % at 2 IPA ratio (increased by 58 %). The increment in the COD removal efficiency was as a result to increase the IPA concentration from zero to 10 mM. These results made IPA competent co-fuel to improve the removal efficiency at 400 °C. On the other hand, the effect of IPA ratio on COD % was observed as function of the residence time at various IPA ratios, which further clarifies the effect of IPA/MEA ratio.

Figure 4.13 displays the effect of IPA ratio on the nitrogen species. The NH_4-N yield increased to reach 24 % at 1 IPA ratio due to increased COD conversion, then decreased significantly to reach 15% at 2 IPA/MEA ratio. This indicates the positive role of IPA on the further conversion of NH_4-N to gaseous nitrogen (N_2) and is attributed to the affinity of IPA radicals for N-H bonds. The yield NO_3^- slightly increased with increasing IPA ratio. (Segond et al., 2002). The NO_2^- yield was still low.

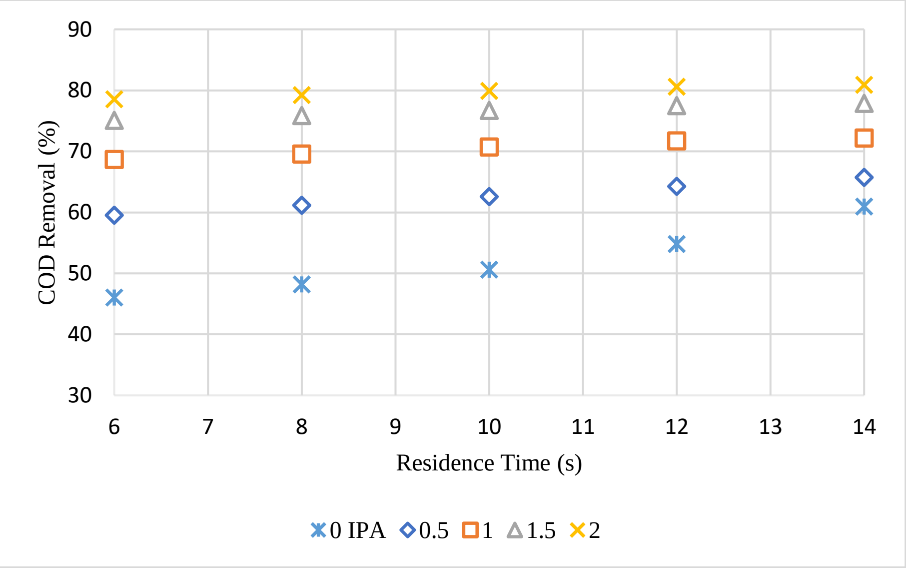


Figure 4.12: Effect of IPA ratio on COD removal efficiency at various residence times, 400°C, 5 mM MEA and SR of 1.

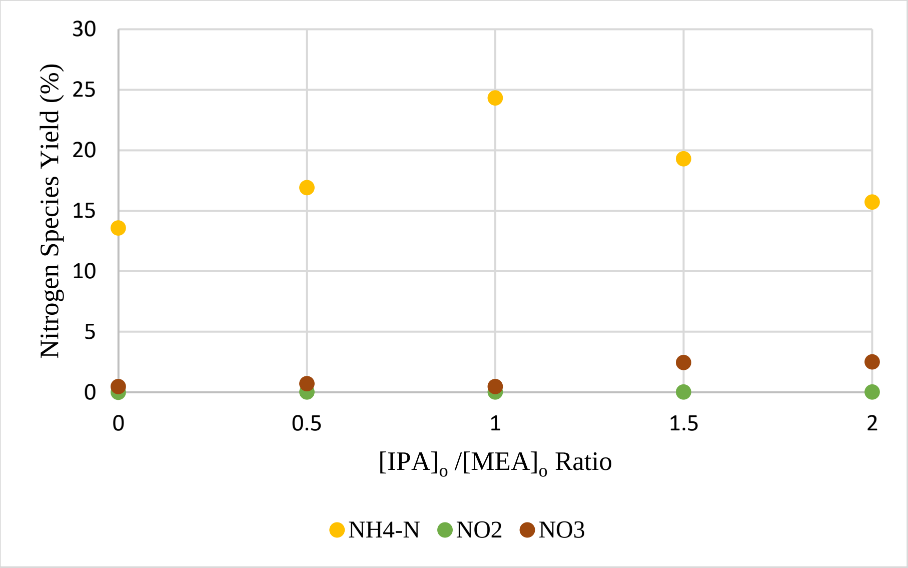


Figure 4.13: Effect of IPA ratio on nitrogen species at 400 °C, 5 mM MEA, SR of 1 and 10 s

The main goals of using co-fuel are increasing the removal efficiency and destroying by-products at a low temperature to reduce the cost of this technology. Thus, the destruction of nitrogen-containing compounds may be interested when the removal efficiency of nitrogen is high to avoid the disposal to the environment. The results of the effect of IPA ratio on nitrogen species are shown in Figure 4.13. Figure 4.14 displays the effect of IPA ratio on nitrogen removal %. The nitrogen removal efficiency enhanced with increased IPA ratio if compared with the result of the fuel-free system. For example, the removal efficiency increased slightly from 61 % (fuel-free system) to 62 % at 0.5 IPA ratio. At 2 IPA ratio, the enhancement of nitrogen removal % was essential with increasing the IPA ratio to reach 79.7 %. This enhancement in nitrogen removal efficiency would consider a significant indicator of the increased IPA concentration. Consequently, increased IPA ratio will contribute to destroy MEA and by-products.

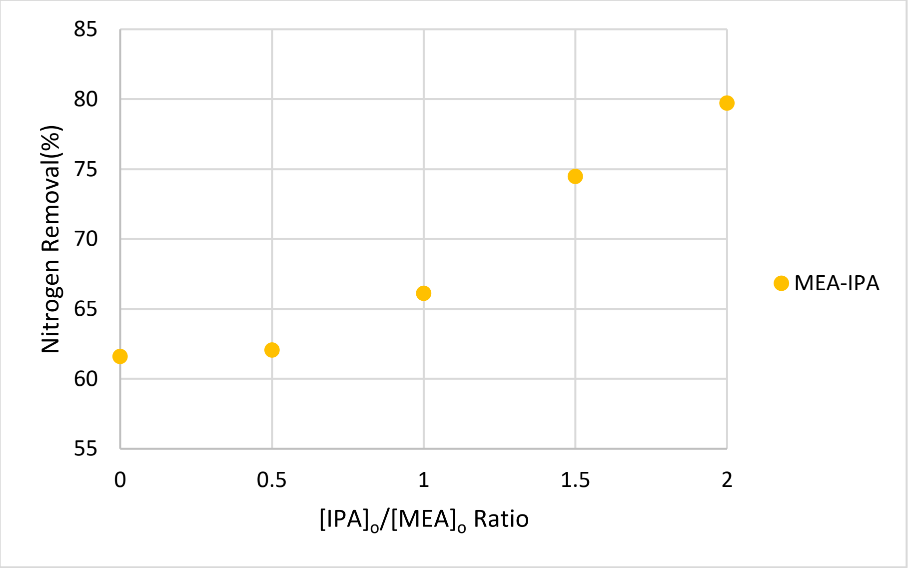


Figure 4.14: Effect IPA ratio on nitrogen removal % at 400 °C, 10s, SR of 1 and 5 mM MEA.

4.4.6 Effect of Initial Concentration of MEA

The effect of initial concentration was investigated at 400 °C, 1SR, and 6 to 14 s residence time range. The selection of the range of the initial concentration was controlled by the maximum flow rate of the HPLC pump for the organics and oxidant feed concentrations at the system temperature. In addition, the concentration of organic waste is less than 30 % organic content. (Fang and Xu, 2014) and this concentration would be a suitable concentration to be treated by SCWO.

Figure 4.15 displays the effect of initial concentration on COD removal %. The results illustrate the significant effect of the initial concentration on the COD conversion and nitrogen species. COD removal efficiency was enhanced from 40 % at 2.5 mM to 79 % at 10 mM and 10 s due to increase the initial concentration consequently increased the density of organic molecules and free radicals. Also, the effect of residence on the removal efficiency of COD was observed positive at various initial concentrations. Several studies pointed out the positive effect of increasing initial concentration; Pinto (2004) demonstrated the significant enhancement in TOC removal with increasing the concentration of quinoline, and Qi and his group demonstrated the positive effect of the initial concentration which they observed the removal efficiency of aniline improved with increasing the concentration. It is worth mentioning the removal efficiency of COD at 14 s, 400 °C, 10 mM and 1 SR was 83.6 % and increasing these parameters may contribute to enhance the COD removal efficiency. Also, the effect of the residence time was positive with increased the initial concentration. For example, COD removal % enhanced from 30 % at 6 and 2.5 mM to 50 % at 14 s. The enhancement of COD removal % with the residence time may consider essential thus, increased the residence time more than 14 s would improve the COD removal efficiency at 400 °C and 1 SR. Modified the operating conditions would improve the COD removal efficiency such as increased oxidant ratio and added co-fuel. The destruction of MEA at 400 °C would reduce the cost of energy.

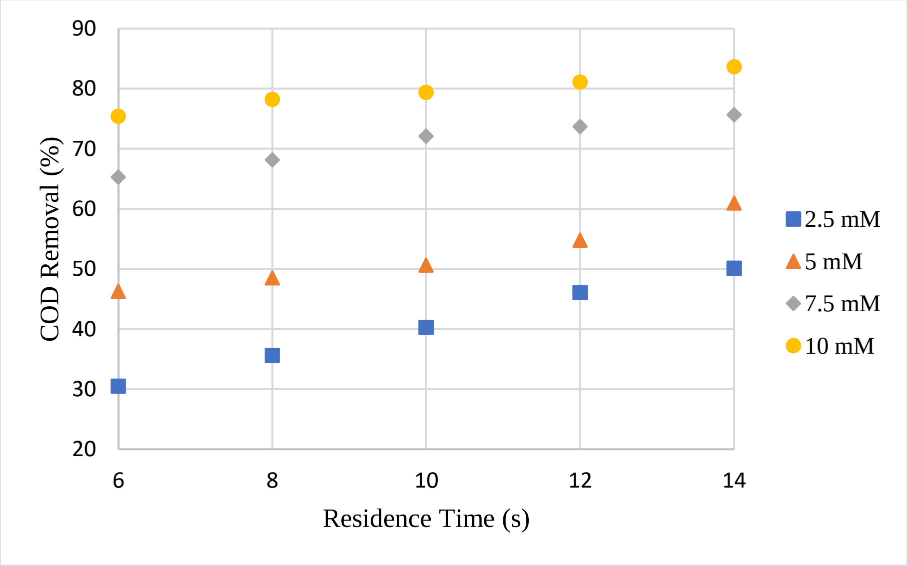


Figure 4.15: Effect of initial concentration of MEA on the COD removal efficiency at 400 °C, various residence times and SR of 1.

Figure 4.16 displays the effect of the initial concentration of MEA on nitrogen species in the liquid sample. The yield of NH_4-N was slightly enhanced with increasing the initial concentration, as it decreased from 20 % at 2.5 mM to 11 % at 10 mM, this reduction in the yield of NH_4-N was low when increasing the initial concentration from 5 mM to 10 mM. On the other hand, the other nitrogen species as NO_3^- and NO_2^- were low.

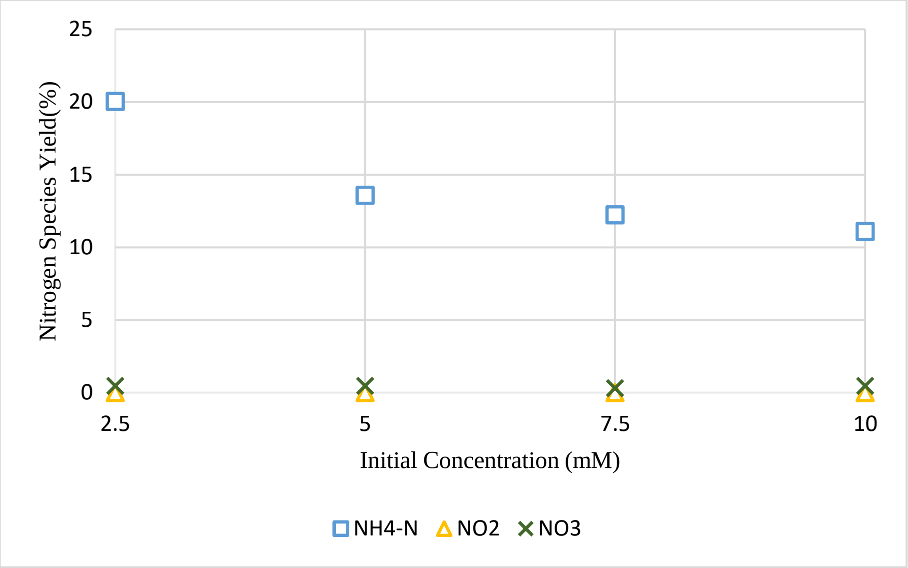


Figure 4.16: Effect of the concentration of MEA on nitrogen species at 400 °C, 10s and SR of 1.

As the main by-product of MEA was ammonia, the removal efficiency of nitrogen would be consistent with reducing the yield of NH_4-N. Figure 4.17 displays the effect of initial concentration on nitrogen removal %, which was enhanced with concentration. For example, the nitrogen removal efficiency increased from 41.7 % at 2.5 mM to 75 % at 10 mM due to increase the number of molecules then increase the rate of reaction, but the increase rate slowed down when the initial concentration increased from 7.5 mM to 10 mM. This may be attributed to the concentration of free radicals compared to N concentration. There are several examples demonstrated the increase of the initial concentration would not improve the removal efficiency and using the high concentration would generate some problems such as salt plugging.

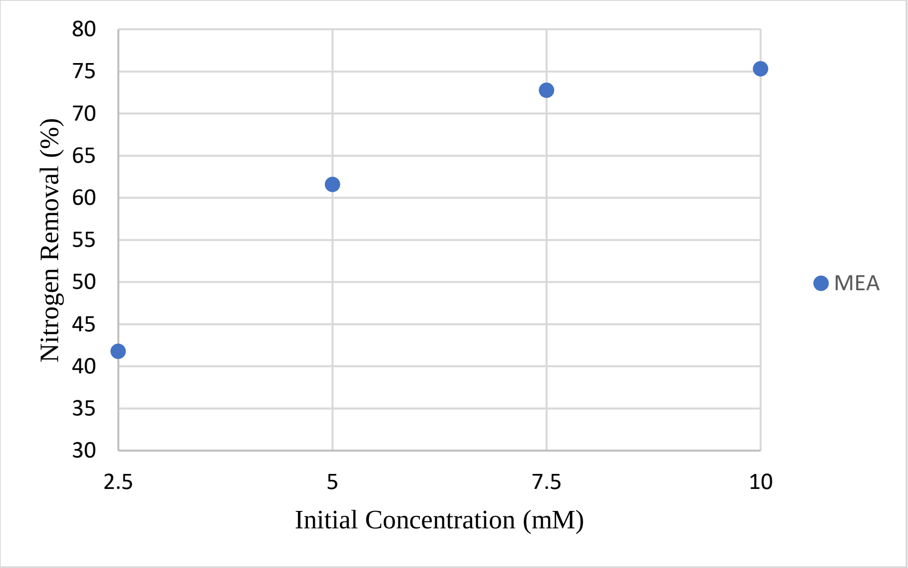


Figure 4.17: Effect of initial concentration of MEA on nitrogen removal efficiency at 400 °C, 10 s and SR of 1.

4.5 Global Kinetics of MEA Oxidation

It is necessary to study the global reaction rate and would supply valuable data for design purposes. The body of experimental data obtained regarding influences the various reaction parameters was employed to evaluate the reaction rates expressions namely the Arrhenius constants, rate constants and reactions orders were determined. The global rate law expression was employed to develop most SCWO kinetic models. Equation 4.4 illustrates the global rate law:

$$\frac{-d[Organic]}{dt} = k[Organic]^a[Oxidant]^b[Water]^c = Ae^{\frac{-Ea}{RT}}[Organic]^a[Oxidant]^b[Water]^c \ldots (4.4)$$

Where

k is the reaction rate constant in $M^{1-a-b-c}\,s^{-1}$.

A is the pre-exponential factor in $M^{1-a-b-c}\,s^{-1}$.

E_a is the activation energy in $J.mol^{-1}$.

R is the constant of universal gas (8.314 $J.mol^{-1}.K^{-1}$).

T is the reaction temperature in K.

[Organic] is the organics initial concentration in $mol.L^{-1}$.

[Oxidant]is the oxidant initial concentration in mol.L^{-1}.

a is the reaction order relating to an organic compound.

b is the reaction order relating to oxidant.

c is the reaction order relating to water.

Numerous SCWO kinetic studies have been accomplished for different wastes either a single model compound or a mixture of wastes under various temperature, residence times, oxidant ratios, concentrations of organic and using various reactor designs. In this study, two methods were applied to study kinetic of MEA:

1) Pseudo-first order approximation method
2) Integral method approximation

The medium of SCWO is water, and it formed more than 99 % of MEA SCWO; therefore, the water concentration considers constant. In other words, the reaction order with respect to water becomes zero.

4.5.1 Pseudo-First Order Approximation Method

Numerous researchers have studied the global kinetic for SCWO either single compound or mixture organics, and they have employed Pseudo first order to describe the global kinetic. The order of the reaction is one with respect to the organic compound ($a = 1$) and zero for oxygen ($b = 0$) (Pinto et al., 2006; Abelleira et al., 2013). This model might be a simple method to describe the global kinetic, but is a suitable starting point to evaluate the reaction rate constant k. The following equation represents the global power rate law for two systems:

$$rate = \frac{-d[MEA]}{dt} = k[MEA] \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots .. (4.5)$$

The experimental results of MEA oxidation are the COD values, and the equation (4.5) was modified to use the COD:

$$rate = \frac{-d[COD_{MEA}]}{dt} = k[COD_{MEA}] \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots . \ldots\ldots\ldots\ldots\ldots\ldots\ldots (4.6)$$

After integrating this equation (4.6), the new equation can be applied:

$$\ln\left(\frac{[COD]}{[COD_o]}\right) = -k.t \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (4.7)$$

Plotting Eq. (4.7) using experimental data at each temperature gives the rate constant *k* (s^{-1}) from the slope for each operating temperature as shown Figures 4.18 and 4.19 for the fuel-free and IPA systems, respectively.

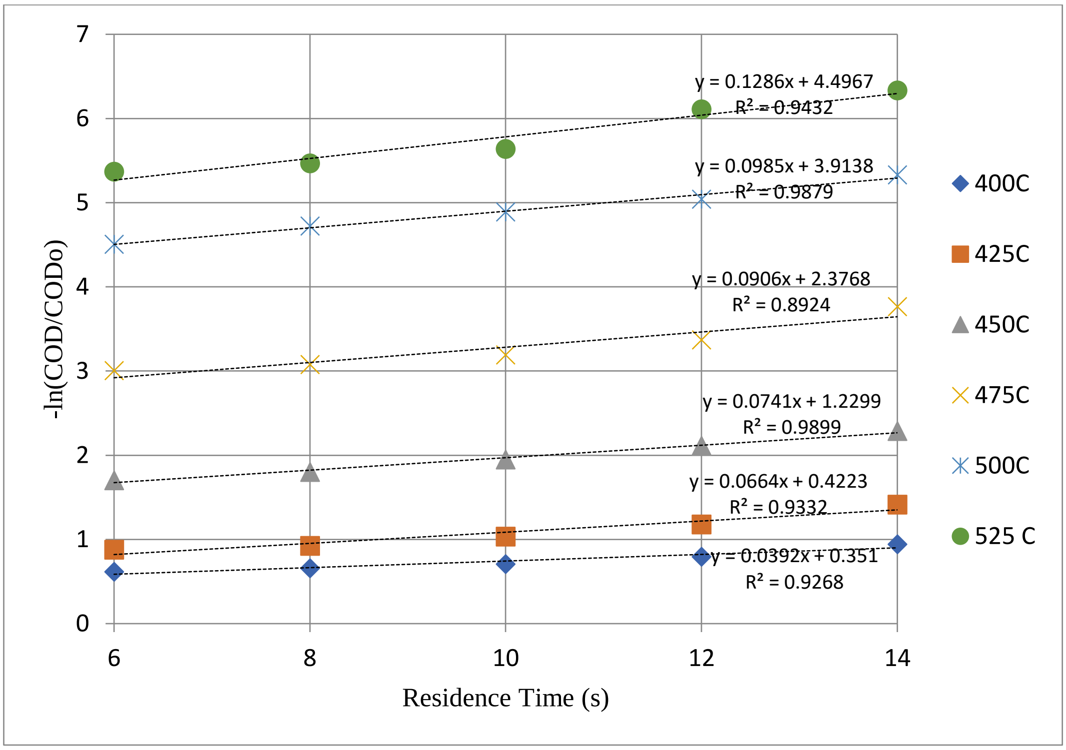


Figure 4.18: ln (COD/COD$_o$) against residence time for fuel-free system.

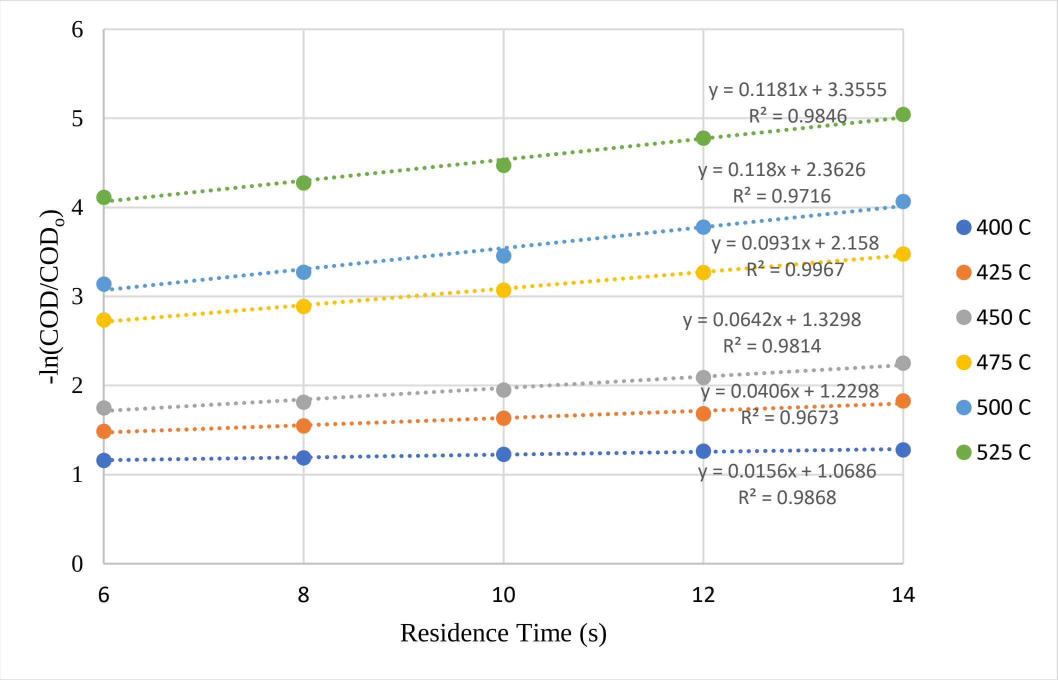


Figure 4.19: ln (COD/COD$_o$) against residence time for IPA system.

Then, where ln *k* is plotted against *1/T* as displayed in Figure 4.20. From this plot E_a and *A* were evaluated to be 37692 J.mol^{-1} and 37.7 s^{-1} respectively. The results are shown in Eq. 4.8. The same procedure was followed for the IPA system and the results are displayed in Figure 4.21 and Eq. 4.9.

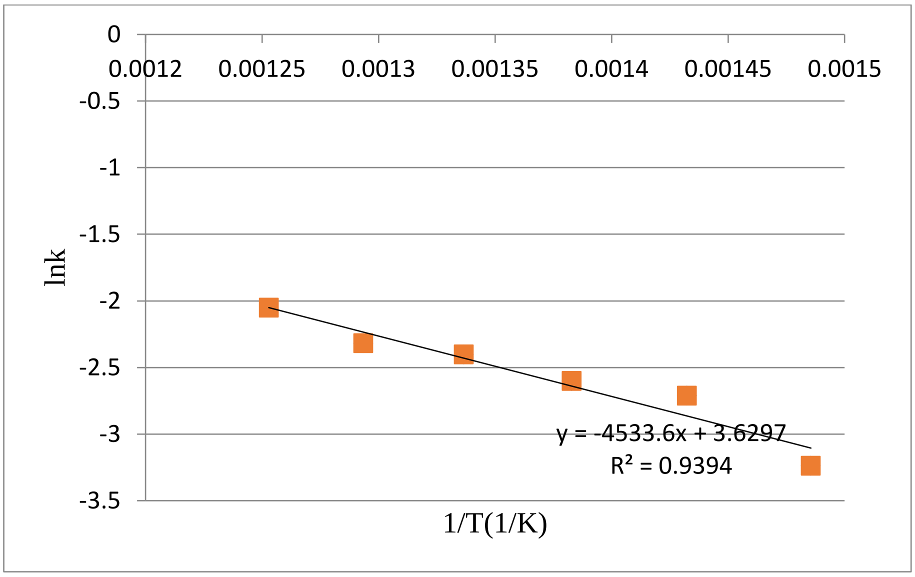


Figure 4.20: Arrhenius plot for the oxidation of MEA.

$$rate = \frac{-d[COD_{MEA}]}{dt} = 37.7 * (s^{-1}) \exp\left(-\frac{37692\,\frac{J}{mol}}{RT}\right)[COD_{MEA}] \ldots\ldots\ldots\ldots(4.8)$$

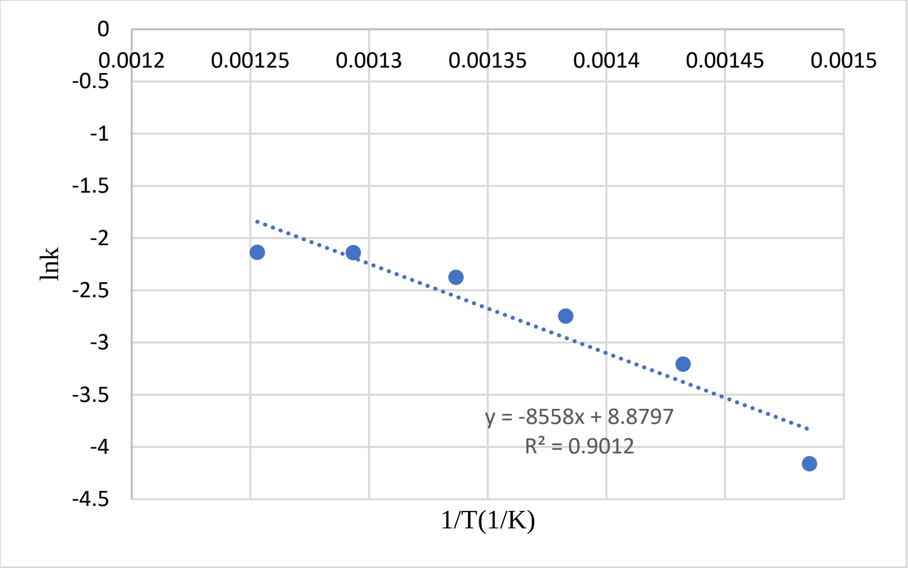


Figure 4.21: Arrhenius plot for the oxidation of MEA and IPA.

$$rate = \frac{-d[COD_{MEA+IPA}]}{dt} = 71.84 * 10^2\ (s^{-1})\ \exp\left(-\frac{71151\,\frac{J}{mol}}{RT}\right)[COD_{MEA+IPA}]. \quad (4.9)$$

4.5.1 Integral method approximation Method

Using an integral method was to understand the global rate expression of MEA oxidation, to express the kinetic data. The global kinetic parameters as activation energy and pre-exponential factor for MEA oxidation were calculated from applied a set of experiments to determine the rate of the reaction. The order of organic substance is one. Also, the operating temperature was considered as a function for the MEA destruction. Water formed more than 99 %, and the effect of oxygen concentration on the MEA oxidation may be minor, but it is essential to investigate the order of oxygen. Four experiments were performed to determine the order of oxidant at 400 °C, and the range of oxidant ratio was 0.5 to 2 SR (i.e. the oxygen concentration range in the absence of IPA was from 8.125 mM to 32.5 mM while the oxygen concentration range in the presence of IPA was from 19.375 mM to 77.5 mM. These experiments were present in section 4.4.4. The COD removal enhanced with increasing the oxidant ratio; thus, the effect must be investigated to determine the order of oxygen. While the previous model (Pseudo first order) the oxygen order assumed zero. The plug flow reactor design equation was used to calculate the order of oxygen, and equation 4.4 is rearranged by using the integral method with a = 1 and b > zero:

$$-rA = \frac{-d[MEA]}{dt} = k[MEA][O_2]^b = Aexp^{\left(-\frac{Ea}{RT}\right)}[MEA][O_2]^b \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots (4.10)$$

The assumption can consider the concentration of oxidant constant. The equation of plug flow reactor for the steady state was applied (Levenspiel, 1999) to be:

$$\frac{t}{[MEA]_o} = \int_0^x \frac{dx_{MEA}}{(-rA)} \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots (4.11)$$

t is residence time, $[MEA]_o$ is an initial concentration, (-rA) is a rate of reaction of MEA oxidation. The following equation is substituting (4.10) into the equation of the plug flow design reactor.

$$\ln\left(\frac{1}{(1 - X_{MEA})}\right) = k.t[O_2]_0^b \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots (4.12)$$

Then, in order to determine the value of b, it is necessary to find the slopes of fitted straight lines of MEA oxidation for four experiments at 400 °C, from plotted ln (1/1-X_{COD}) against the residence time (t). The results of two systems are shown in Figures 4.22 and 4.23. The slopes of lines represent $k[O_2]_0^b$. This term can be written after taking the natural logarithm to be:

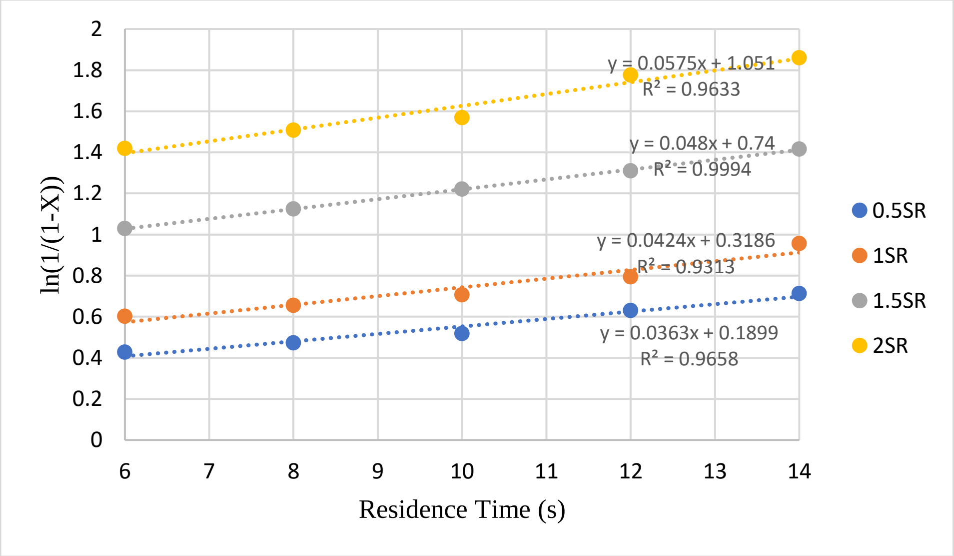


Figure 4.22: Natural logarithm of (1/(1-X)) versus residence time for MEA experiments with varying oxidant concentrations.

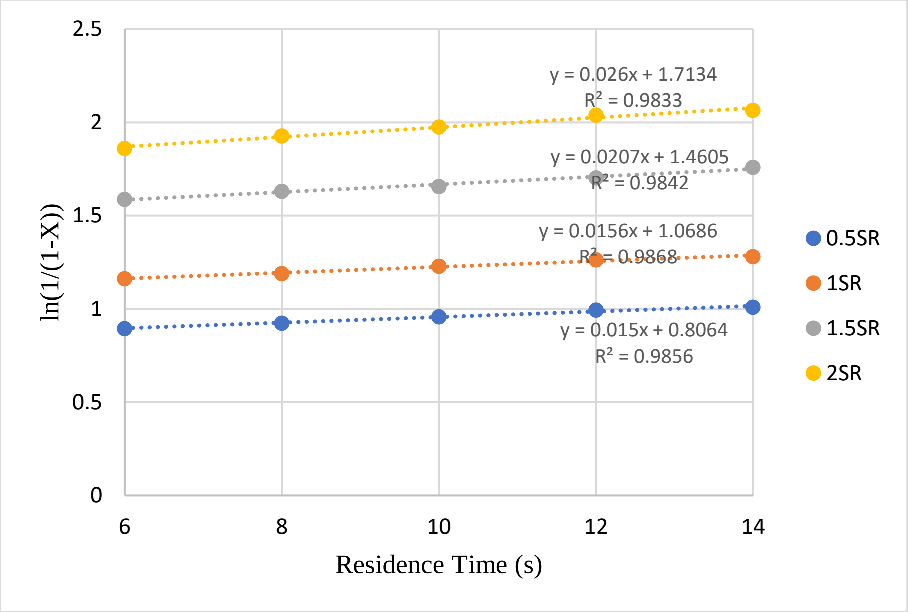


Figure 4.23: Natural logarithm of (1/(1-X)) versus residence time for MEA +IPA experiments with varying oxidant concentrations.

$$\ln(k[O_2]_o^b) = \ln(k) + b\ln([O_2]_o) \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots . (4.13)$$

The slopes from Figures 4.22 and 4.23 are plotted versus the concentration of oxygen to generate a straight line for the MEA system and the IPA system. The slopes of these lines represent the b value for each system. Figures 4.24 and 4.25 display the value of b.

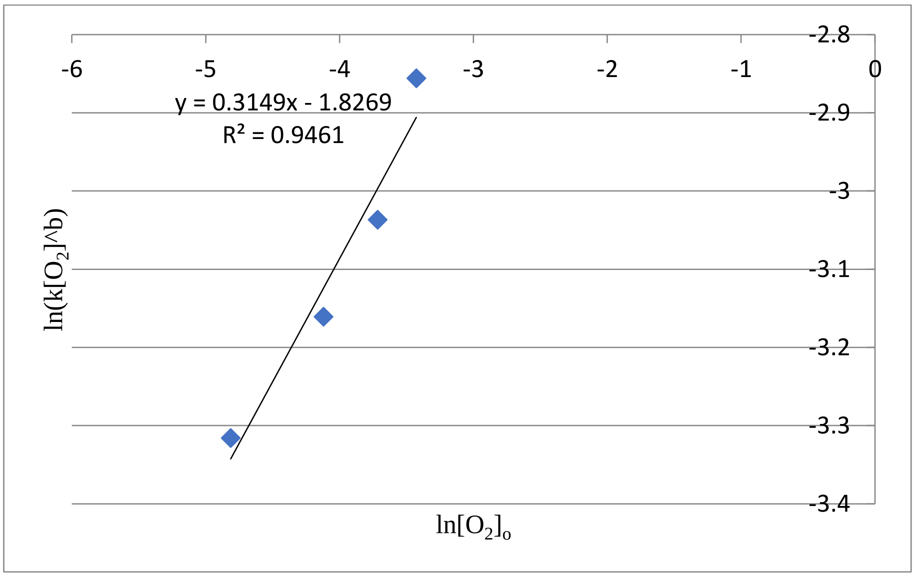


Figure 4.24: Oxygen reaction order.

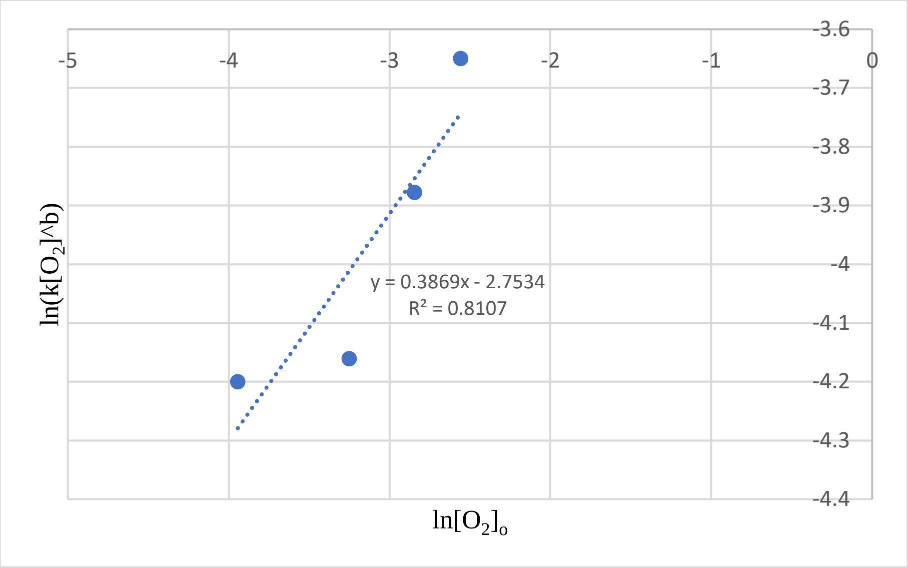


Figure 4.25: Oxygen reaction order (MEA and IPA).

The order of oxygen represents the slope of the straight line in Figure 4.24 and 4.25. The reaction orders are (a =1, b_{MEA}= 0.31, $b_{MEA+IPA}$= 0.38). It is necessary to determine the rate of the reaction by applying the equation (4.12) to be:

$$k = ln\frac{1}{(1-X_{MEA})} \times \frac{1}{t} \times \frac{1}{(O_2)^{0.31}} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (4.14)$$

$$k = ln\frac{1}{(1-X_{MEA+IPA})} \times \frac{1}{t} \times \frac{1}{(O_2)^{0.38}} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (4.15)$$

The new *k* values (two systems) are employed to determine the E_a and *A*, plotting the natural logarithm of the rate of reaction (*k*) versus inverse temperature (1/T) is shown in Figures 4.26 and 4.27. The E_a was calculated by multiplying the universal gas constant (8.314 $J.mol^{-1}.K^{-1}$) by the slope (i.e. 9591.8). *A* was calculated from ln *A*= intercept. Equations 4.16 and 4.17 illustrate the value of E_a and *A* in the generated global rate expression of MEA oxidation and MEA and IPA oxidation.

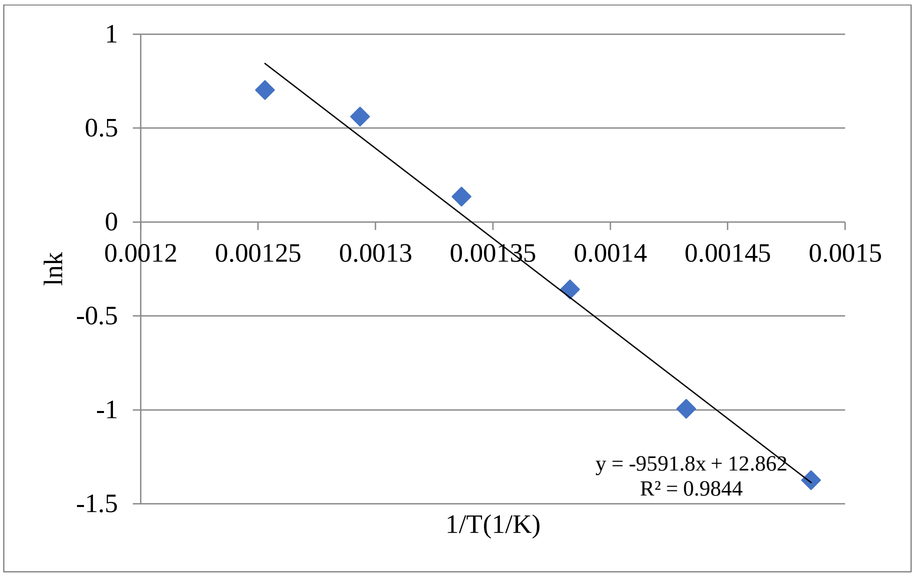


Figure 4.26: Arrhenius plot for MEA oxidation.

$$rate = -\frac{d[COD_{MEA}]}{dt} = 385.385 * 10^3(M^{-0.31}s^{-1})\exp\left(-\frac{79746\frac{J}{mol}}{RT}\right)[COD_{MEA}][O_2]^{0.31} \ldots (4.16)$$

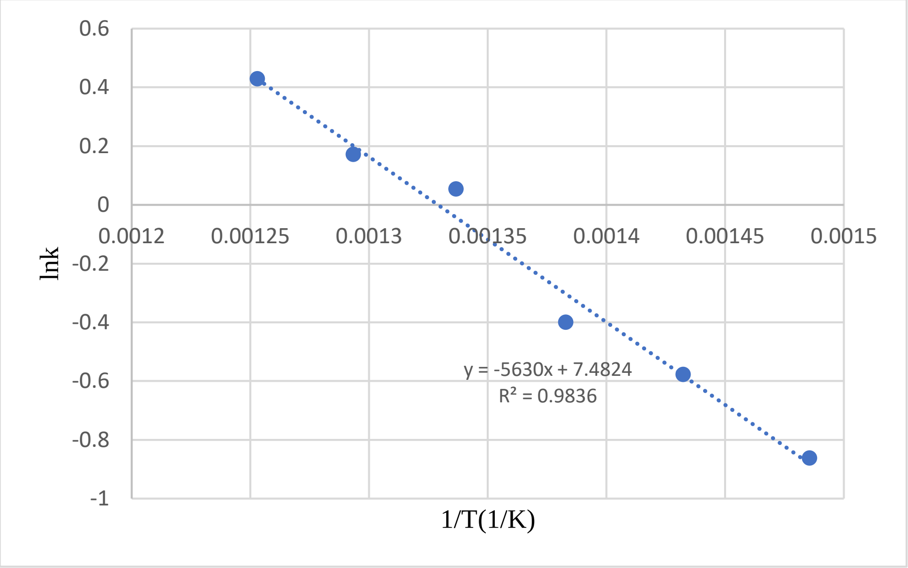


Figure 4.27: Arrhenius plot for MEA and IPA oxidation.

$$rate = -\frac{d[COD_{MEA+IPA}]}{dt} = 1.776 * 10^3(M^{-0.38}S^{-1})\exp\left(-\frac{46807\frac{J}{mol}}{RT}\right)[COD_{MEA+IPA}][O_2]^{0.38} \ldots (4.17)$$

The orders of oxygen were 0.31 and 0.38 for fuel-free and IPA systems respectively that indicated to the effect of oxidant on the MEA oxidation and MEA+IPA oxidation, consequently applying integral method could consider an appropriate way to understand the kinetic MEA and MEA+IPA. The literature of SCWO does not contain studies that show the kinetics of MEA to compare with these results.

4.6 Summary

- The operating temperature was the main parameter that significantly affected the efficiency of COD removal. The COD removal efficiency was greater than 99 % at 525 °C and 14s in the absence and presence of IPA. The effect of temperature and IPA on the nitrogen species could be positive. In the fuel-free system, the operating temperature contributed to an increase in COD conversion and an increase in the yield of NH_4-N. The effect of the residence time was positive at a low temperature and this effect decreased as the operating temperature increased. The effect of IPA was positive when the temperature increased. Increased the removal efficiency of nitrogen illustrated the role of IPA. The yields of NO_3^- and NO_2^- were low in the two systems.
- The effect of oxidant ratio on the COD removal was remarkable in the two systems, in the presence of IPA, the removal efficiency of COD enhanced with increased the oxidant ratio. The effect of the oxidant ratio on the nitrogen removal efficiency and NH_4-N was significant in two systems. The effect of the range of the residence time was also positive with different oxidant ratios.
- The IPA ratio had a positive effect on COD removal efficiency and nitrogen removal when the ratio increased to more than 1. This enhancement confirmed the significant role of IPA. Also, the effect of the residence time was positive with IPA ratio.
- The effect of the initial concentration was positive on the COD removal and nitrogen species. The effect of the residence time on the COD removal % was significant when increasing the initial concentration. Modifying the operating conditions, such as the oxidant ratio, or using co-fuel would contribute to improving the destruction of organic substances and by-products.

- Two methods were employed to study the kinetics analysis for the two systems. Applying the integral approximation method was essential to describing the kinetics analysis of the fuel-free system and the IPA system, where the order of oxygen has a value greater than zero (b_{MEA} = 0.31 and $b_{MEA+IPA}$= 0.38) and has influenced the destruction of MEA and MEA and IPA systems. Also, the results of this method illustrate the positive effect of IPA on the reduction E_a, which decreased from 79746 $J.mol^{-1}$ (fuel-free system) to 46807 $J.mol^{-1}$ (decreased by 41%).

CHAPTER FIVE: SUPERCRITICAL WATER OXIDATION OF MONOETHANOLAMINE (MEA) IN THE PRESENCE OF PROPYLENE GLYCOL (PG) AS CO-FUEL

5.1 Introduction

Chapter five investigates the addition of propylene glycol (PG) as co-fuel to the SCWO of MEA under a range of system condition namely temperatures, oxidant ratios, organics concentrations and residence times. Like Chapter 4, results are expressed in terms of COD removal %, nitrogen species yield and removal %. In addition, kinetic investigations were conducted, and reactions rate constants and rate expressions are presented.

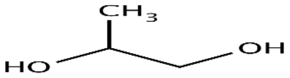
5.2 Selection of Propylene Glycol (PG)

PG is a simple compound and dihydric alcohol. It was selected as co-fuel to compare its result with fuel-free system results and isopropyl alcohol (IPA) results. Physical properties of PG are given in Table 5.1. To date, there are limited studies on PG as co-fuel in SCWO (Marrone et al., 2005), which would encourage research to provide novel knowledge on enhancement of SCWO performance. There are several reasons to select PG as co-fuel.

1. Toxicity of PG may be considered low if compared with other organic and it could be considered a good biodegradable substance.
2. Limited studies are available regarding the role of PG as co-fuel for to improve oxidation under supercritical conditions if compared with other co-fuels such as methanol, ethanol and IPA.
3. Propylene glycol contains two hydroxyl groups that contribute to generate free radicals and increases the pathways of reaction. According to Yang et al. one hydroxyl group has a high effectiveness in methanol, ethanol and IPA. Thus, two hydroxyl group may contribute to generate various pathways to produce different free radicals (Yang et al., 2018). Díaz et al. pointed out oxidation propylene glycol generated several pathways under temperature 400-500 K (Díaz et al., 2010). This mechanism contributed to generate high powerful radicals such as $HO^{\bullet}$ and $HO_2^{\bullet}$. Based on Gas chromatography–mass spectrometry analysis the oxidation mechanism of

propylene glycol is illustrated in Figure 5.1. Two proposed reaction pathways would be generated from the oxidation propylene glycol under supercritical conditions. Powerful radicals such as $HO^{\bullet}$ and $HO_2^{\bullet}$ are produced that contribute with radicals from hydrogen peroxide to attack molecules of MEA and increase the COD conversion.

Table 5.1: Physical properties of PG

CAS Number	*57-55-6*
Molecular formula	$C_3H_8O_2$
Molar Mass (g/mol)	*76.1*
Density (g/ml)	*1.036*
Boiling point (℃)	*187.4*
Melting point (℃)	*-59*
Water Solubility	*Miscible*
Colour	*Colourless*
Structure	

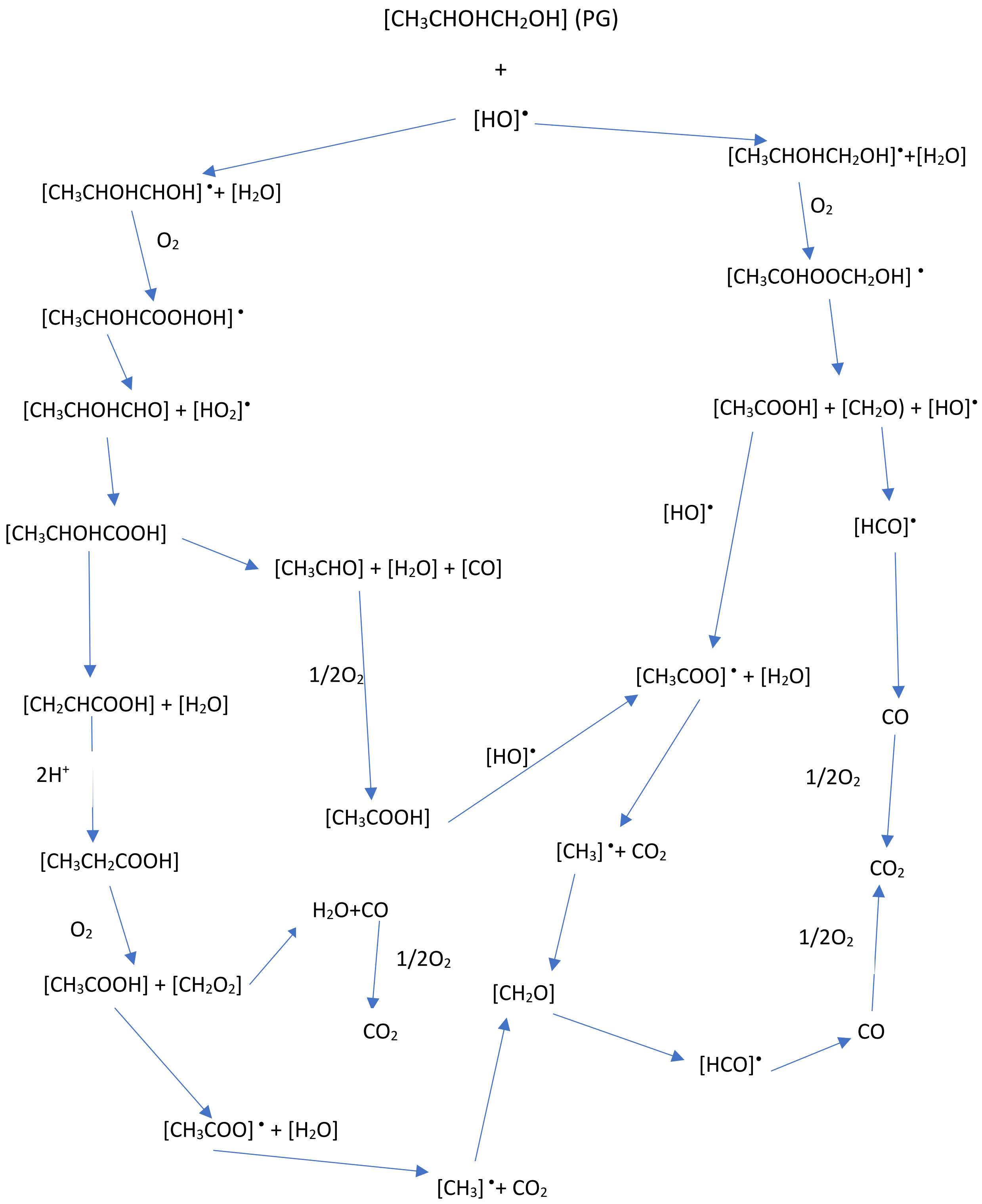


Figure 5.1: Proposed Mechanism of SCWO of PG

5.3 Effect of System Operating Conditions

In this chapter, the SCWO process diagram and experimental procedures were previously illustrated in chapter three.

5.3.1 Experimental Work Plan

In this section, the solution of MEA, PG and water was employed to carry out SCWO experiments at different temperatures, residence times, oxidant stoichiometric ratios, feed concentrations. Each parameter was individually examined at 400 ℃, 5 mM of MEA and SR of 1. The operating pressure was applied 250 bar during all experiments to obtain on supercritical phase and several studies have reported the increasing pressure has not influenced the efficiency of process under supercritical conditions (Cocero, 2001). Table 5.2 explains the summary of operating conditions ranges.

Table 5.2: Summary of the operating conditions of MEA and PG experiments.

Variable	Range	Fixed conditions
Temperature (^oC)	400 - 525	$[MEA]_o$ =$[PG]_o$= 5 mM SR = 1SR
$[MEA]_o$=$[PG]_o$ mM	2.5 - 10	Temp = 400 ℃ SR = 1SR
Oxygen Ratio	0.5 - 2 SR	$[MEA]_o$=$[PG]_o$= 5 mM Temp = 400 ℃
Ratio $[PG]_o$/$[MEA]_o$	0.5 – 2.5	Temp = 400 ℃ SR = 1SR $[MEA]_o$=5 mM
Residence time: 6-14 s for all experiments		

5.3.2 Effect of Residence Time

The range of residence time was selected to assess the removal efficiency of MEA from 6 to 14 s with keeping the turbulent flow regime at different residence times. In other words, the flow rate in the reactor was a turbulent flow at a high residence time and different temperatures, the short residence time was 6 s, as a result to the maximum flow rate could be delivered 20 ml.min^{-1} by the HPLC pump. Also, the oxidant ratio and organic concentration were taken an account to set up the range of residence times. The effect of residence time on the COD conversion of MEA in the absence and presence of co-fuel is displayed in Figure 5.2. The COD removal efficiency enhanced at long residence time. The increase of the reaction time for the reactants would improve the COD conversion. As expected, these results were consistent with more work in this field and increasing the residence time has positively influenced the destruction of organic substance (Savage et al., 2000; Qi et al., 2002; Ploeger et al., 2006).

In general, the effect of the residence time would be significant at different temperature. At 400 ℃, the COD conversion increased with increasing the residence time from 72.58 % at 6 s to 80 % at 14 s (increased by 10 %) due to provide the time to react between organic and oxidant molecules. While the effect of residence time on the COD removal efficiency at 525 ℃ was low because the rate of reaction and the solubility of organic material improved with temperature at different residence times. Also, increased operating temperature contributed to increase the oxygen consumption. For example, at 525 ℃ the COD conversion was enhanced from 99.58 % at 6 s to 99.9 % at 14 s (increased by 0.3 %). The effect of the residence time on the COD removal efficiency occurred at 400 and 425 ℃, then this effect decreased with increased the reaction temperature. As a result, the destruction of MEA would enhance with increase the residence time at low temperature, the trend of removal efficiency at 400 ℃ and 425 ℃ indicated to increase the residence time will contribute to improve the COD conversion. Figure 5.2 shows the effect of different residence time on the COD removal efficiency in the PG free system and the PG system.

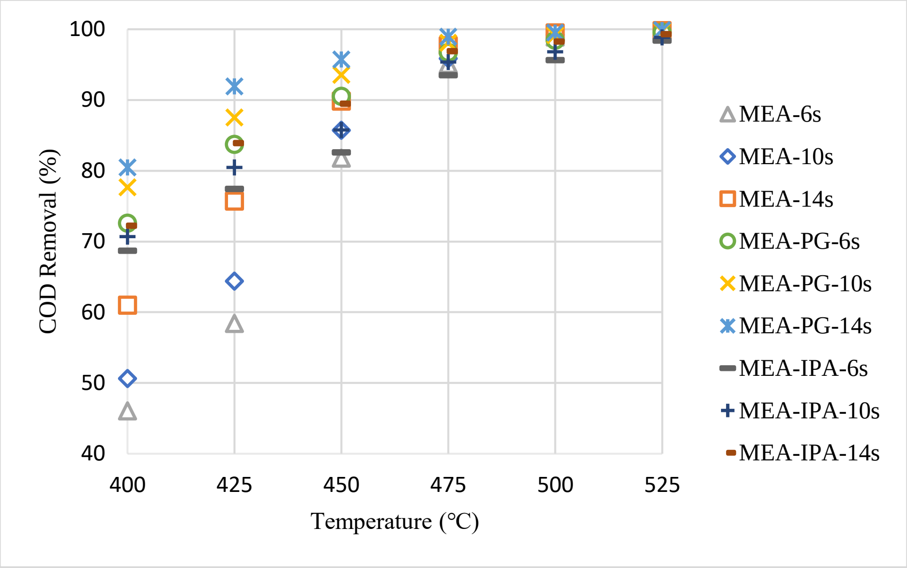


Figure 5.2: COD removal efficiency against various operating temperatures, 5 mM MEA, 5 mM PG, 5mM IPA, SR of 1 and at 6, 10, 14s.

Therefore, the comparison between the results of three systems (fuel-free system, PG system and IPA system) demonstrated the positive effect of the residence time on the COD conversion, but the effect of residence time at 400 °C and 425 °C occurred more than high temperature due to enhance the removal efficiency of organic compounds with increased operating temperature at various residences times. Despite the residence time having a positive trend, the effect of residence time on the destruction of organic waste in numerous studies would not be remarkable if compared with other operating conditions.

5.3.3 Effect of Operating Temperature

The range of operating supercritical temperatures was applied to study the effect of temperature on the MEA and PG oxidation from 400 to 525 °C, and the initial MEA concentration was 5 mM. The residence time ranged from 6 to 14 s at 1SR. The selection of the temperature range was based on the thermal ability of the furnace and keeping the turbulent flow regime at various temperatures and residence times.

Figure 5.3 displays the effect of the different temperatures on the COD conversion at the range of residence times in the absence and presence of PG. It was observed the essential role of temperature to improve MEA oxidation. This role was consistent with several researches under supercritical water conditions. The operating temperature played a significant role in the enhancement of the SCWO performance (Wang et al., 2011; Qi et al., 2002; Yu et al., 2015).

However, the COD removal efficiency of MEA in the presence of PG enhanced from 72.6 % at 6 s and 400 °C to 99.5 % (increased by 37%) at the same residence time and 525 °C. While at the long residence time 14 s, the COD removal was enhanced from 80 % at 400°C to 99.9 % (increased by 24.8 %) at 525 °C due to increase the operating temperature from 400 to 525 °C. This enhancement may be as a result to enhance the rate of reaction, and the high temperature would contribute to generate free radicals more than 400 °C, PG would consider a further source of powerful radicals such as $HO^•$ and $HO_2^•$. Consequently, the reaction rate would enhance from 400 to 525 °C. It is worth mentioning the destruction of MEA at low temperature would make SCWO as a competitive technology with various technologies to treat wastes.

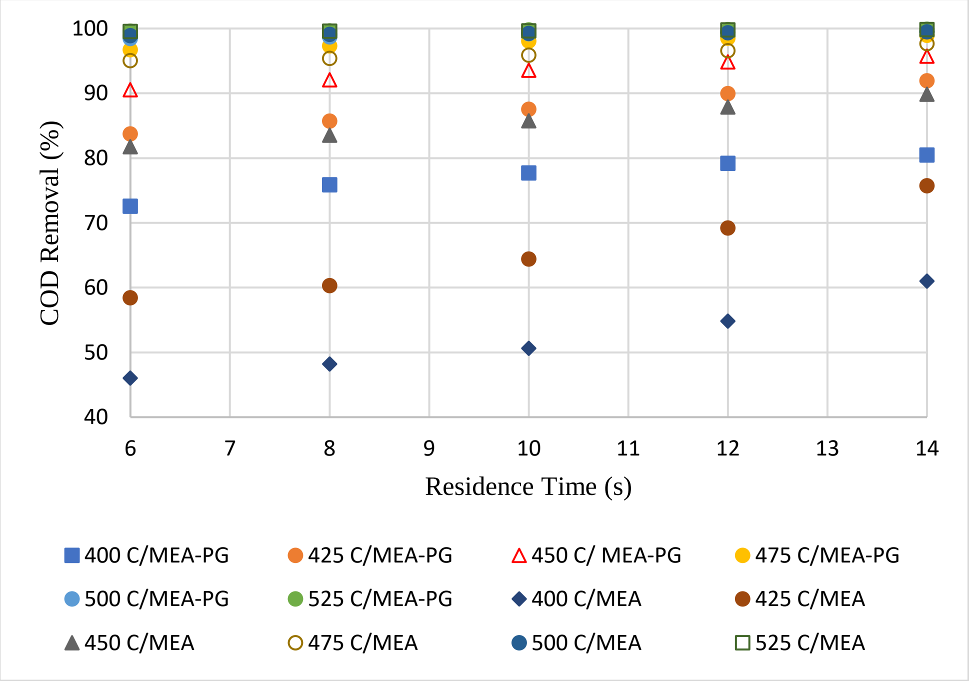


Figure 5.3: Effect of different temperatures on COD removal % at various residence time, at 5 mM MEA, 5 mM PG and SR of 1.

The comparison between the COD conversions in fuel-free system, PG system and IPA system at different operating temperatures is shown in Figure 5.2. In general, the effect of operating temperature on the COD removal efficiency was important and this role occurred significantly at 400 °C in the presence of co-fuels. Also, the increase of temperature contributes to increase the rate of the reaction. This enhancement of the COD conversion significantly occurred in the presence of PG more than IPA. The findings would promote three essential points including the number of the hydroxyl group in PG has a positive effect, increase the rate of reaction due to feed co-fuel, generation free radicals that have ability to attack organic molecules and mineralise to water, carbon dioxide and N_2 (Yang et al., 2018; Bermejo et al., 2008). In other words, PG played the significant role and it became a second source for free radicals. The results of IPA system at 400 °C confirmed one hydroxyl group would be less effective than two hydroxyl groups. For example, the COD conversion increased from 50.6 % (fuel-free system) to 70.7 % (IPA system) (increased by 39.7%) to reach 77.7 % at 400 °C (PG system) (increased by 53.5%). Thus, improving the operating conditions such as increasing oxidant ratio and ratio of PG would enhance the removal efficiency to avoid using high temperature as 525 °C. Consequently, the destruction of MEA at 400 °C, 10 s, 1 PG ratio and 1SR would be important to study this co-fuel and enhance the SCWO performance at low temperature.

Figure 5.4 displays the effect of the operating temperatures on nitrogen species in three systems at 10 s using no alcohol, 1 IPA/MEA and 1 PG/MEA respectively. In the PG system, NH_4-N was the main by-product of MEA oxidation under supercritical conditions which was observed the yield of NH_4-N decreased with temperature. While the NO_3^- yield occurred more than the yield of NO_3^- in fuel-free system due further oxidation of NH_4-N to NO_3^-, to reach 3.4 % at 450 °C. According to Segond et al. (2002) the major product of oxidation ammonia was N_2 and the minor product was NO_3^-. Consequently, the effect of PG on the COD conversion contributed to increase the yield of NH_4-N at 400 °C and the increase the yield of NO_3^- was as result to effect of PG on NH_4-N and with increasing the temperature, the yield of NH_4-N decreased due to increase the generation of free radicals with temperature and to provide another source for radicals (PG). The oxidation NH_4-N in the presence of PG at low temperature would consider an essential step to benefit from increased the co-fuel ratio to destroy ammonia at temperature less than 525 ℃. Two advantages would provide in using PG as co-fuel including the enhancement of COD removal % and the oxidation of the resistant by-product (ammonia). The results of co-fuel system illustrated the positive effect of PG than IPA at 400 ℃ and this effect on the destruction of NH_4-N occurred significant with increasing temperature. For example, the yield of NH_4-N decreased from 17 % at 400 ℃ to 12.9% at 525 ℃ (decreased by 24 %). However, increased temperature and the oxidant ratio would contribute to enhance the reduction of NH_4-N in the presence of PG. While the NO_2^- yield was still low in the PG system.

For the comparison among nitrogen species in three systems, the yield of NH_4-N generally decreased with temperature in co-fuel systems. This is meaning a positive effect of temperature and co-fuels on nitrogen species, but at 400 ℃, the yield of NH_4-N increased in the presence of co-fuels due to increase the conversion of MEA, and NH_4-N was a main by-product of MEA. Increased operating temperature contributed to reduce the yield of NH_4-N and oxidise to N_2 due to promote the generation radicals at high temperature. PG and IPA oxidised NH_4-N with increasing temperature but the effect PG on the NH_4-N at 400 ℃ was significant than IPA and with increasing temperature. For example, the yield of NH_4-N decreased from 24 % in the IPA system to 17 % in the PG system at 400 ℃ (decreased by 29 %). This enhancement at 400 ℃ and 1SR would be more positive if the concentration of PG increased. The maximum reduction of NH_4-N at 475 ℃ was 49.68% in the presence of PG and 45.5% in the presence of IPA. The yield of NO_3^- in the PG system occurred more than NO_3^- yield in the IPA system due to oxidise part from NH_4-N to N_2 and NO_3^-. For the NO_2^- yields were still low in three systems. However, the reduction of nitrogen species yield would be achieved if the operating conditions are modified as increasing temperature, oxidant ratio and co-fuel ratio.

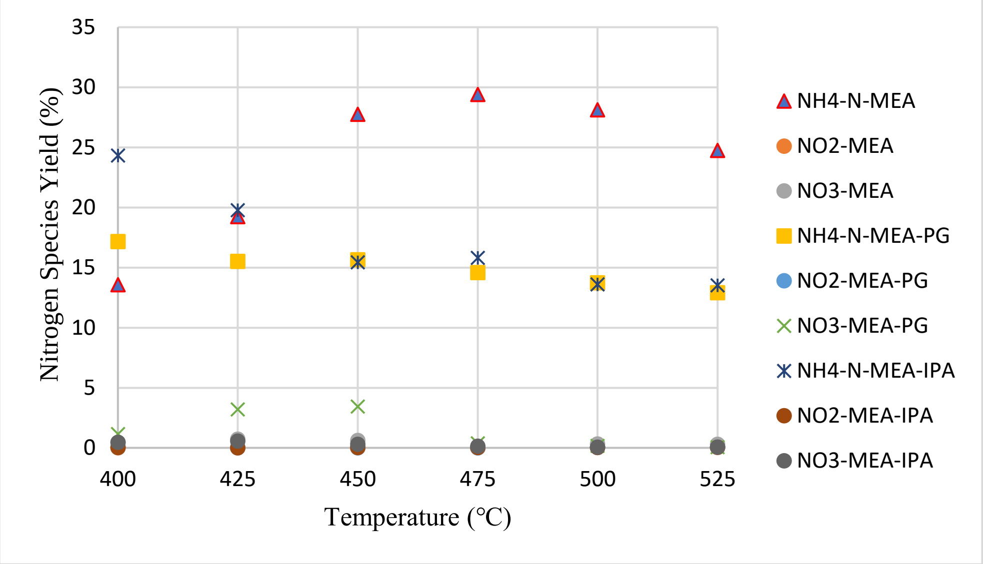


Figure 5.4: Nitrogen species yield as a function of various operating temperatures at 5 mM MEA, 5 mM PG, 5 mM IPA, SR of 1 and 10 s.

Figure 5.5 displays the nitrogen removal efficiency in the fuel-free system, PG system and IPA system. The nitrogen removal in the PG system was improved due to increase the operating temperature. Then, increased the rate of the reaction and abundant radicals with increasing temperature that have attacked and mineralised organic molecules to carbon dioxide, water and N_2. Also, the heat content of co-fuels may be added to the reaction. Yang et al. (2018) referred to the heat of the co-fuel was contributed to improve the nitrogen removal %. Al-Duri et al. (2016) have used IPA and they reported the heat content of co-fuel would contribute to enhance the removal % of nitrogen. In this work, the results illustrated the nitrogen removal % improved in the presence of co-fuels, and the effect of PG on the nitrogen removal % would be significant if compared with the effect of IPA. For example, the removal efficiency of nitrogen was enhanced from 74 % at 400 °C to 83.8 % at 525 °C in the PG system (increased by 13 %) because of temperature and PG, consuming a high percentage of oxygen at high temperature. The nitrogen removal % increased from 61.6 % in no co-fuel system to 74 % in PG system at 400 °C (increased by 20 %). The increment in the removal nitrogen % increased from 66 % IPA system to 74 % PG system (increased by 12 %) at 400 °C. This enhancement in removal of nitrogen would be important at 400 °C with modified operating conditions. Thus, the co-fuel has a significant role to improve the COD and nitrogen removal efficiencies. The results of PG system confirmed the positive role of PG in the enhancement of nitrogen removal.

In summary, the PG and IPA have improved the COD removal efficiency and reduced NH_4-N as well as improved the nitrogen removal%. Consequently, the effect of temperature and PG was significant to enhance the SCWO performance more than IPA, and the role of two hydroxyl groups was significant. According to several works in literature, the results of the effect temperature on the COD removal efficiency in three systems was consistent with the effect of the temperature on DMF, DBU and aniline (Al-Duri et al.,2015, 2016; Qi et al., 2002). In addition, if compared the results of SCWO with various treatment methods, SCWO would be a competitive method to destroy MEA in the short residence time with high removal efficiency.

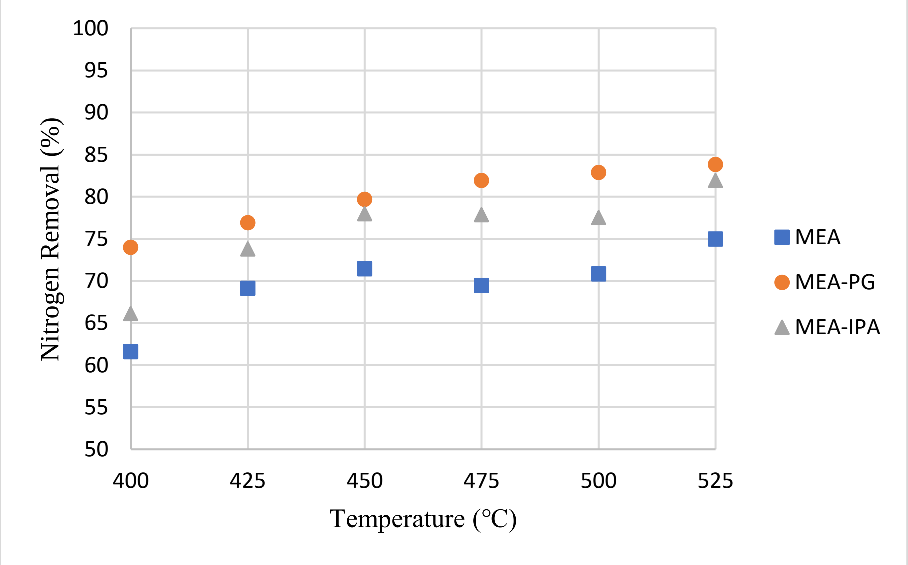


Figure 5.5: Effect of various operating temperatures on the nitrogen removal efficiency in three systems at 5 mM MEA, 5 mM PG, 5 mM IPA, SR of 1 and 10 s.

5.3.4 Effect of Oxidant Ratio

The complete destruction equations for oxidation MEA and IPA systems are written in chapter four (4.1 & 4.2), and the complete destruction equation for oxidation PG is written below:

$C_3H_8O_2 + 4O_2 \rightarrow 3CO_2 + 4H_2O$…………………………………………….………………….. (5.1)

In this work, the effect of oxidant ratio on the COD removal efficiency and nitrogen species was investigated. The various amounts of oxygen were employed to oxidise MEA and PG to complete the destruction at 400 °C, 5 mM MEA and 5 mM PG. The effect of the oxidant ratio may be considered an essential factor according to the literature. In the PG system, the amount of oxygen represents enough oxygen for oxidising MEA and PG which was based on the concentration of MEA and PG under supercritical conditions to determine the amount of oxygen. The range of oxidant ratio was 0.5 to 2 SR. Also, the selected range of SR based on the capacity of the HPLC pump. However, the increased oxidant ratio may increase the cost of oxidant and generate unfavoured products such as N_2O (Al-Duri et al., 2016).

In the PG system, the effect of oxidant ratio on the COD conversion occurred consistent with increased the amount of oxygen. The COD removal efficiency enhanced with increasing the oxidant ratio from 0.5 SR to 2 SR. Also, the effect of the oxidant ratio on nitrogen removal% was positive. Figure 5.6 shows the enhancement of the COD conversion due to increasing the amount of oxygen in the presence of PG. The amount of oxidant would contribute to generate free radicals that play an essential role to increase the rate of oxidation, and PG would consider a second source to generate powerful radicals such as $HO^{\bullet}$ and $HO_2^{\bullet}$. The free radical mechanism was a common reaction under supercritical conditions (Pinto et al., 2006). The results illustrated the positive effect of the residence time with various the oxidant ratios. For example, COD removal % was enhanced from 60.7 % at 6s to 70.5 % at 14s 0.5SR. Also, the oxidant ratio positively influenced on COD removal % for example, at 10 s and 0.5 SR, the removal efficiency improved from 66.7 % to 87 % at 2 SR (increased 30.4 %). This enhancement confirmed the role of the oxidant ratio and increased the amount of oxidant would generate radicals at 2SR more than 0.5 SR. Besides, PG has a significant effect on the COD removal % with different the oxidant ratio. For example, at 0.5 SR the COD conversion was improved from 40 % at 10 s in the fuel-free system to 66.7 % in the

PG system (increased by 66.75%). The maximum COD removal % was 91.6 % at 2SR and 14s in the presence of PG, the destruction of this compound at these conditions would be interest at 400 ℃ to avoid increase the operating temperature. This increase would confirm the positive effect of PG, and two hydroxyl groups played an important role. Finally, the effect of the oxidant ratio, PG and the residence time was contributed in the enhancement of the COD conversion. Figure 5.6 displays the comparison between the effect of oxidant ratio on the fuel-free system and the PG system.

The comparison between two co-fuels systems to assess the effect of the oxidant ratio on the COD removal efficiency would demonstrate the significant effect of PG on COD. This effect took a positive trend by increasing the amount of oxygen. The PG played an essential role to enhance the COD removal% more than IPA. For example, at 10 s, 0.5 SR, COD removal % enhanced from 61.6 % IPA system to 66.7 % PG system (increased by 8 %). However, PG influenced the COD removal more than IPA. The results illustrated the effect of two hydroxyl groups in PG on COD removal efficiency was more than one hydroxyl group in IPA. Consequently, the enhancement of the COD removal considers an important aim at 400 ℃ to reduce the cost of SCWO.

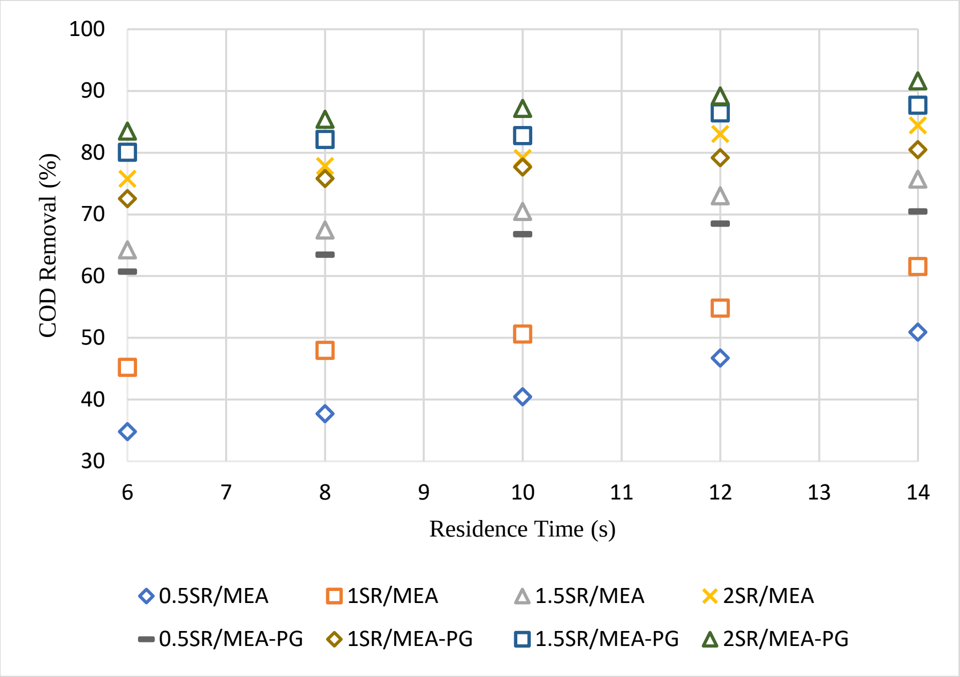


Figure 5.6: Effect of the oxidant ratio on the COD removal % at various residence time and 400 °C, 5 mM MEA, 5 mM PG.

In general, the results in Figure 5.7 show nitrogen species in a liquid sample at various oxidant ratios in three systems. The effect of the oxidant ratio on the nitrogen species in the presence of PG was investigated to determine the influence of co-fuel by-product of MEA as NH_4-N at different oxidant ratios and compare the results of PG system with results of IPA system and the fuel-free system. In this work, the role of PG was significant in the enhancement of the COD removal efficiency more than IPA but increased the COD conversion contributed to increase the yield of NH_4-N. The effect of oxidant ratio on the by-products was positive in the presence of PG. For example, the yield of NH_4-N decreased from 26.9 % at 0.5 SR to 8.9 % at 2 SR (decreased by 66.9%) due to increase the free radicals with increasing the oxidant ratio. The yield of NO_3^- illustrated there was a further oxidation of NH_4-N to gaseous nitrogen and NO_3^- in the presence of PG (Segond et al., 2002). This further oxidation would be considered an essential advantage in the PG system. In IPA system, the yield of NO_3^- was low. In other words, IPA would not have this advantage, and the yield of NH_4-N in IPA system was more than the yield of NH_4-N in PG system. For example, NH_4-N decreased from 30 % in the presence of IPA to 26.9 % in the presence PG at

0.5 SR. However, some authors have recommended in order to reduce nitrogenous products using 1 SR (Cocero et al., 2000). Another by-product was NO_2^- that was low in the fuel-free system, IPA system and PG system.

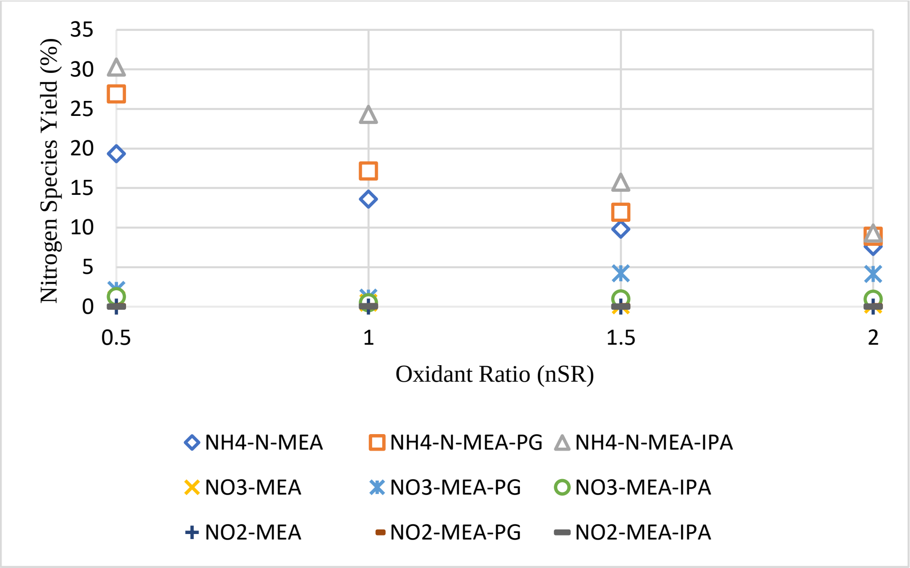


Figure 5.7: Effect of various oxidant ratios on nitrogen species in three systems at 10 s, 400 °C, 5 mM MEA, 5 mM PG and 5mM IPA.

Figure 5.8 displays the comparison between the effect of the oxidant ratio on the removal efficiency of nitrogen in fuel-free system and co-fuel systems. The nitrogen removal efficiency in the PG system was improved due to increase the oxidant ratio and the results illustrated the positive trend in the fuel-free system and the IPA system. PG participated to generate various free radicals such as $HO^\bullet$ and $HO_2^\bullet$ that have a powerful energising to attack and mineralise organic molecules to carbon dioxide, water and N_2 as well as PG would attack the by-product of MEA to oxidise ammonia and convert to N_2 and NO_3^-. According to Al-Duri et al. (2015) reported the free radicals were accelerated the rate of reaction. This enhancement in the removal nitrogen % in PG system would be as a result to add heat to the reaction. According to Yang and his group (2018) and Al-Duri et al. (2016) the heat reaction of IPA would enhance the removal efficiency of nitrogen. For example, the removal efficiency of nitrogen was enhanced from 45.8 % in the fuel-free system to 59 % in the PG system at 400 °C and 0.5 SR while at 2 SR, it was enhanced from 71.6 % to 84.0

% (increased by 17%). Consequently, two hydroxyl groups could contribute to improve the rate of the reaction (Yang et al., 2018). Thus, modified operating conditions and using co-fuel would enhance the COD removal and nitrogen removal efficiencies at 400 °C and different PG ratios.

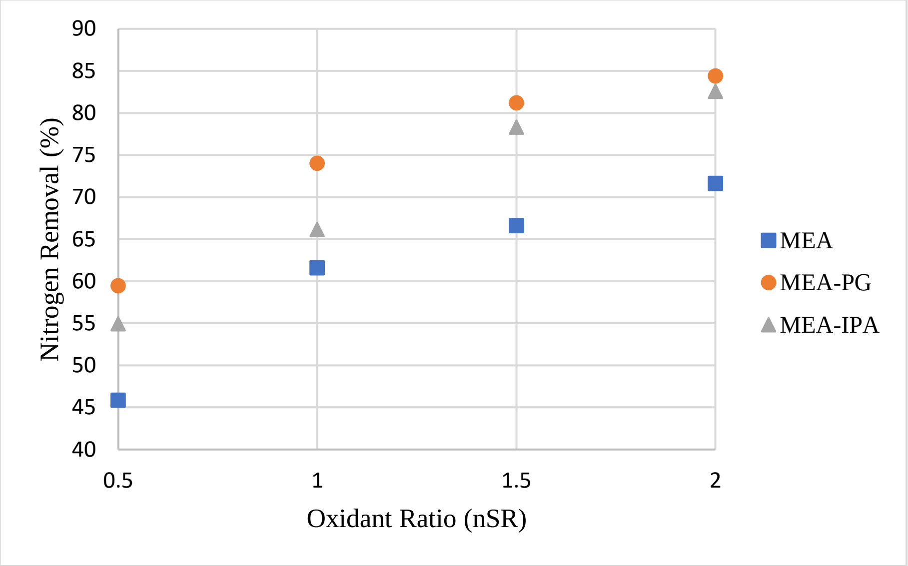


Figure 5.8: Nitrogen removal efficiency as a function of various oxidation ratio at 5 mM MEA, 5 mM PG, 5 mM IPA, 400 °C and 10 s.

5.3.5 Effect of PG_o/MEA_o Ratio

The main purpose of this work was how can improve the SCWO performance using co-fuel and what was the effect of PG on the conversion of organic substance and by-products. The effect of various concentrations of PG was investigated. Literature refers to use PG in rare works if compared with other co-fuels as IPA, ethanol and methanol (Yang et al., 2018; Al-Duri et al., 2016). Several examples were illustrated the positive effect of co-fuel on the SCWO performance (Ploeger et al., 2006； Shimoda e al., 2016). The range of PG_o/MEA_o was from 0.5 to 2.5 (i.e 2.5-12.5 mM PG) at 400 °C and 5 mM MEA. The selection this range was based on the capacity of the HPLC pump, the concentration of organic (PG+MEA) and operating temperature.

Figure 5.9 displays the results of the effect of the PG ratio on the COD conversion. The effect of PG ratio was significantly observed which the COD removal efficiency enhanced with increasing the PG ratio at 400℃. There are several reasons to enhance the removal efficiency of MEA including generation powerful free radicals and acceleration the rate of reaction (Al-Duri et al., 2016; Bermejo et al., 2008). For example, the COD removal efficiency was improved at 0.5 PG ratio from 71.7 % to 87.5 % (increased by 22%) at 2.5 PG ratio and 10 s. This enhancement could be positive if compared with the results at the same conditions in the IPA system. The removal efficiency was improved from 50.6 % in the fuel-free system at 10 s to 87.5 % in the PG system at 2.5 PG ratio and same conditions. Approximately 72.9 % was the increase in the COD removal % after increasing the concentration of PG from zero to 12.5 mM. This was remarkable enhancement in COD removal % at 400 ℃ and 1 SR. Thus, increased PG concentration more than 2.5 ratio would improve COD removal efficiency and this advantage will play significant role to improve the SCWO performance and to reduce the cost of energy. The destruction of MEA at low temperature was a major aim in this study. In addition, the effect of PG ratio on the COD % was improved with the range of the residence time at various PG ratios. For example, the COD % improved from 67 % at 6 s to 75.5 % at 14 s and 0.5 PG ratio while at 2.5 PG ratio, the COD removal efficiency improved from 83.7 % at 6 s to 93 % at 14 s. The linear enhancement of the removal efficiency at various PG ratios would indicate to increase the removal efficiency at 400 ℃ with increasing PG ratio.

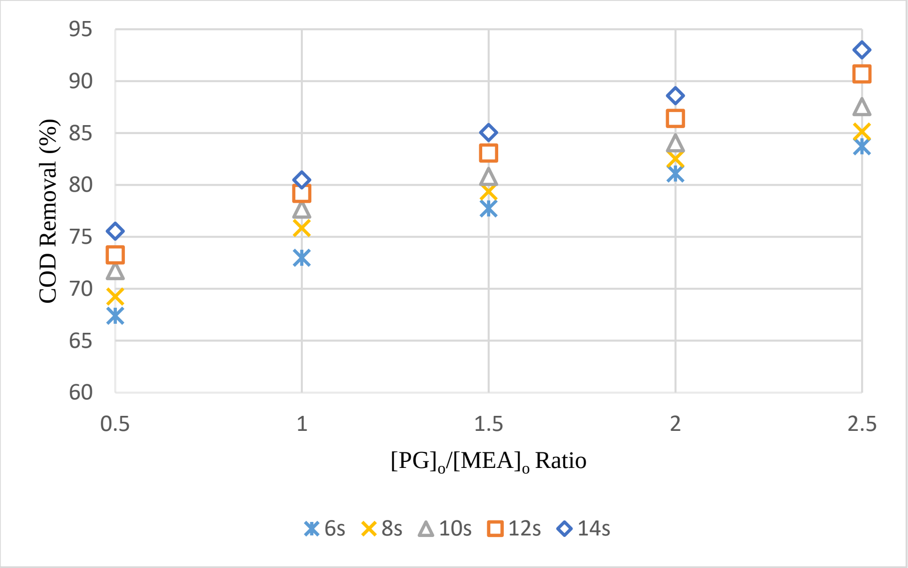


Figure 5.9: PG ratio against COD removal efficiency at various residence times, 400℃, 5 mM MEA and SR of 1.

Figure 5.10 shows the effects of PG/MEA and IPA/MEA ratios on nitrogen species. The NH_4-N yield increased to reach 17 % at 1 PG ratio due to increased COD conversion but further increase of PG ratio indicated further removal of NH_4-N by oxidation to gaseous N, therefore NH_4-N in liquid plummeted down to 9 % at 2.5 PG ratio. This indicates to the positive role of PG ratio on the COD removal efficiency and NH_4-N yield. The yield NO_3^- slightly increased with increasing PG ratio as a result to convert NH_4-N to N_2 and NO_3^- (Segond et al., 2002). NO_2^- yield remained low.

Comparison between the effects of PG and IPA on nitrogen species in Figure 5.10 demonstrates the higher influence of PG compared with IPA. For example, the yield of NH_4-N was reduced from 24 % in IPA system to 17 % in PG system (decreased by 29 %) at 1 the co-fuel ratio. Two hydroxyl groups in PG could illustrate this effect on NH_4-N and increased the yield of NO_3^- would consider another indicator that explains the reduction of NH_4-N and converts to N_2 as a major product and NO_3^- a minor product. While the effect IPA on NH_4-N was less than the effect PG. For the NO_2^- yield in co-fuel systems was low.

Figure 5.11 shows the effect of varying co-fuel ratio on the nitrogen removal %. For the current systems PG demonstrated more influence in improving N removal % than IPA, which is attributed to the added OH• and HO_2• radicals. For example, the removal efficiency increased slightly from 79.7 % (in IPA system) to 83 % (in PG system) at 2 co-fuel ratio while the removal efficiency of nitrogen increased with increasing the PG ratio from 61.6 % in the fuel-free system to 85 % at 2.5 PG ratio (increased by 37.98 %). This enhancement in nitrogen removal efficiency may consider a significant indicator about the role of PG ratio. Although, there is a competition between PG and IPA to improve nitrogen removal efficiency, PG has advantage on MEA and by-products removal, over IPA. Thus, increased PG ratio will contribute to destroy MEA and by-products at 400 °C. The destruction MEA and by-products at 400 °C would consider an essential step in the enhancement of the SCWO performance by using co-fuel and the PG system results at 10 s and 2.5 co-fuel ratio would be remarkable to avoid using a high temperature then reducing the cost of power. Also, two hydroxyl groups in PG could work an essential role more than one hydroxyl group in IPA.

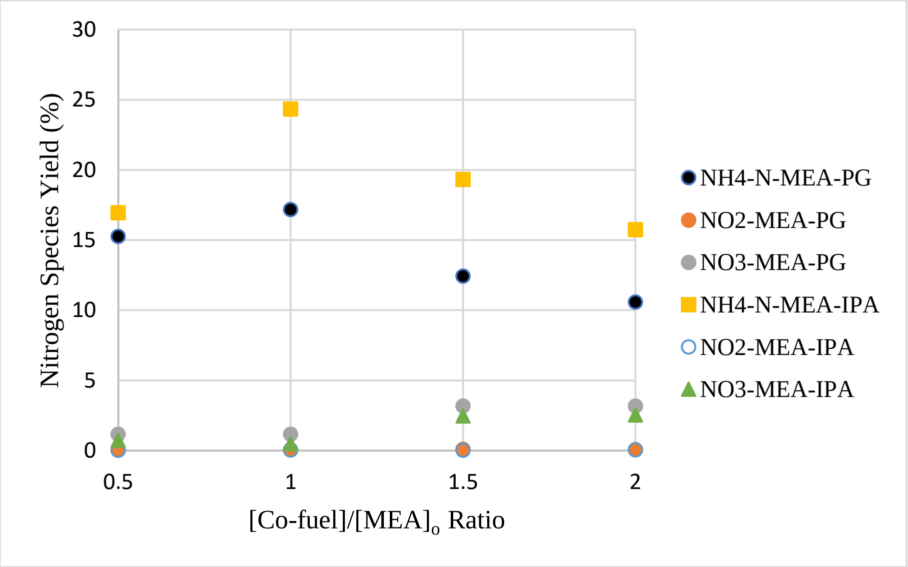


Figure 5.10: Effect of co-fuel ratio on nitrogen species at 400 °C, 5 mM MEA, SR of 1 and 10 s.

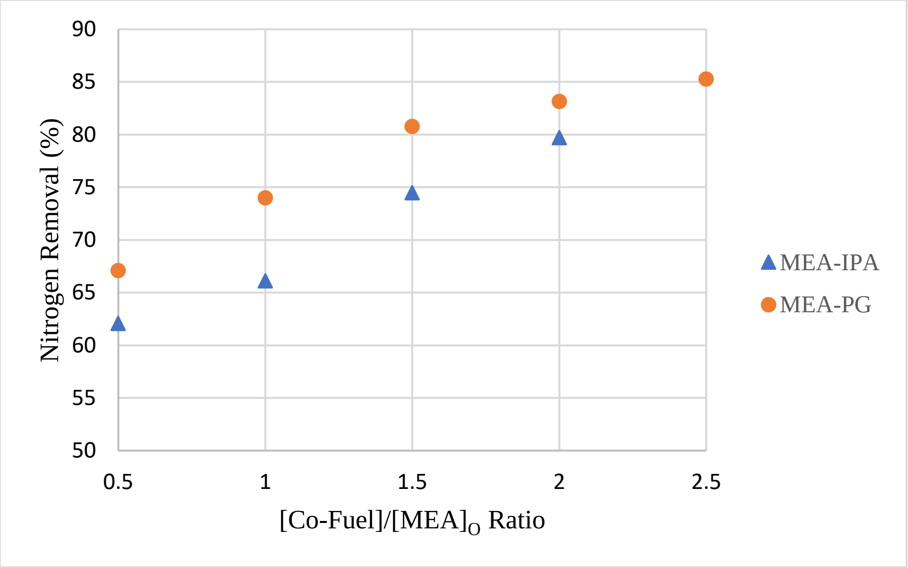


Figure 5.11: Effect of co-fuel ratio on the nitrogen removal efficiency at 5 mM, 400 °C, 10 s and SR of 1.

5.3.6 Effect of Initial Concentration of MEA

The effect of the initial concentration on the COD conversion was investigated under supercritical conditions to study the performance of SCWO when increasing the MEA concentration in the presence of PG. The selection of this initial concentration range was controlled by the maximum flow rate of the HPLC pump, the feeding concentration, the amount of oxygen and the temperature.

Similar to the MEA system, the effect of the initial MEA concentration on the COD removal efficiency was investigated for the MEA-PG system, and results are shown in Figure 5.12 over a range of residence times. The results illustrated the positive influence of the initial concentration on the COD and nitrogen removal efficiencies in the presence of PG. For example, COD removal efficiency increased from 63% at 2.5 mM to 86.9% (increased by 37.9%) at 10 mM and 10 s due to the increase in the initial concentration of MEA consequently increasing the rate of the reaction. PG played an essential role in enhancing the COD removal efficiency. According to Al-Duri et al. (2015), the reaction between alcohol and the oxidant contributed to generating free radicals. Free radicals are active intermediates that attack alcohol molecules and accelerate the reaction. For example, at 2.5 mM COD removal percentage was enhanced from 40% in the fuel-free system to 63% at 10 s while at 10 mM the removal efficiency was enhanced from 79% in the fuel-free system to 86.9% at 10 s. The results also illustrated the enhancement of the removal efficiency in the presence of PG and within the range of the various residence times. For example, COD percentage reached 91% in the presence of PG at 14 s and 10 mM. Several studies pointed out the positive effect of increasing the initial concentration, such as Pinto (2004), who demonstrated the significant enhancement in TOC removal when increasing the concentration of DMF. Qi et al. (2002) have demonstrated the positive effect of the initial concentration, which they observed when the removal efficiency of aniline improved with an increase in the concentration. The results can also improve with increasing the temperature, oxidant ratio or both.

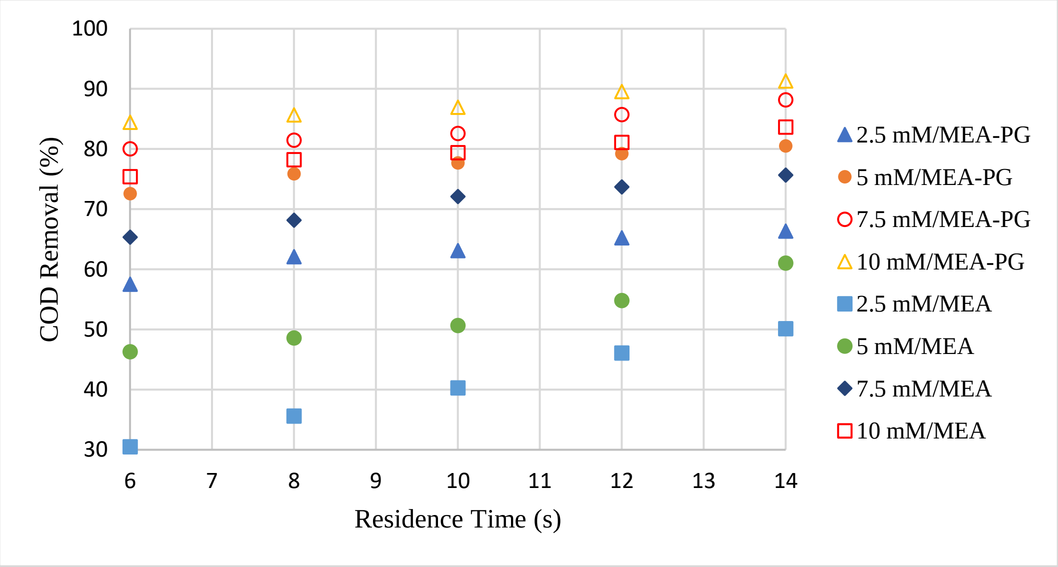


Figure 5.12: Effect of various residence times on COD removal efficiency at 400 °C at various initial concentrations of MEA (PG system) and SR of 1.

Figure 5.13 displays the effect of the initial concentration of MEA in the presence of PG on the nitrogen species. The results showed the positive effect of PG on NH_4-N. NH_4-N was converted into N_2 and NO_3^- due to PG provided a further oxidation. Thus, the yield of NH_4-N plummeted when the initial concentration of PG increased. For example, it decreased from 20.5 %

at 2.5 mM to 10.5 % at 10 mM because the density of organic and oxidant molecules accelerated the reaction. Also, increasing the concentration of PG would provide a second source for free radicals. This reduction in the yield of NH_4-N was remarkable when increasing the initial concentration from 2.5 mM to 7.5 mM. Then the reduction in the yield of NH_4-N slightly decreased. Consequently, increasing the concentration to more than 10 mM would not give remarkable results. However, the trend of COD percentage was consistent with the trend of the NH_4-N yield at various concentrations. Increasing the reduction of the yield of NH_4-N could be improved with changes to the conditions of the experiment, such as the oxidant ratio, using a high co-fuel ratio and temperature. In comparison, it was observed that the NO_3^- yield occurred in the presence of PG at 7.5 and 10 mM, but it was still low, and the NO_2^- yield was low in the presence of PG.

The yield of NH_4-N in both systems was low, and the effect of the initial concentration of MEA on nitrogen species was consistent, but at 5 mM in the presence of PG, the NH_4-N yield was slightly increased. Then, the yield of NH_4-N decreased at 7.5 to 10 mM to become approximately the same NH_4-N yield as in the PG free system. This indicates the influence of PG on the NH_4-N and increases the NO_3^- yield as a result of the ammonia oxidising to N_2 and NO_3^-. Increasing the PG concentration contributed to increasing the yield of NO_3^- between 7.5 to 10 mM while the NO_2^- yield remained low in fuel-free and PG systems.

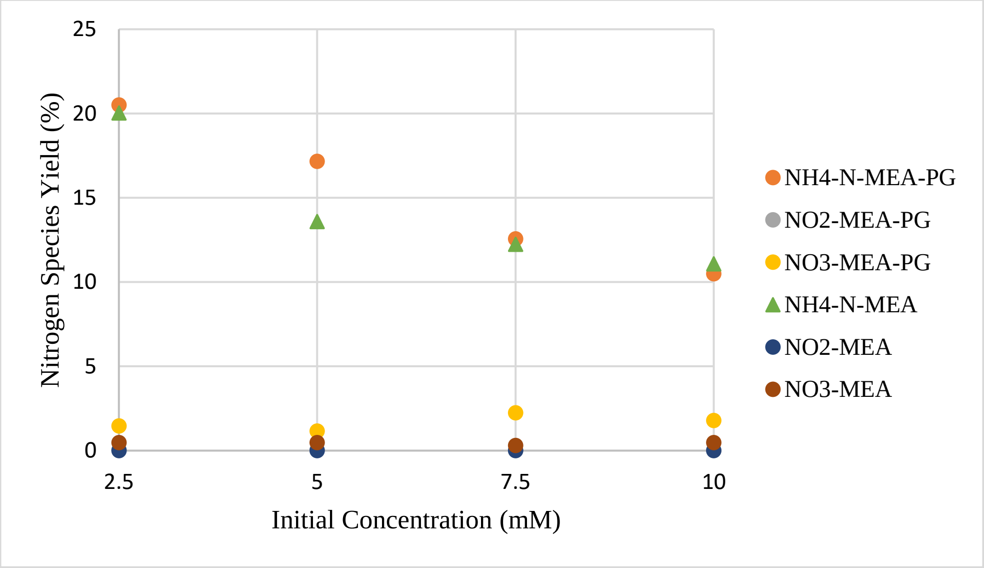


Figure 5.13: Effect of initial concentration of MEA and PG on nitrogen species at 400 °C, 10s and SR of 1.

The removal efficiency of nitrogen was significantly enhanced with increased the initial concentration of MEA in the presence of PG from 2.5 to 7.5 mM while at 10 mM the enhancement of the removal of nitrogen was slightly increased. For example, the nitrogen removal efficiency increased from 57 % at 2.5 mM to 81.6 % at 7.5 mM due to increase the rate of the reaction. Also, according to Yang et al. (2018) and Al-Duri et al. (2016), co-fuel would add heat to the reaction that improved the removal efficiency of nitrogen (the heat reaction of PG -1822 kJ.mol^{-1}: NIST). This enhancement in the removal % confirmed a positive effect of PG on nitrogen removal %. Figure 5.14 shows the linear improvement with increasing initial concentration from 2.5 to 7.5 mM. The comparison between the fuel-free system and the PG system was remarkable. For example, at 2.5 mM nitrogen removal % was improved from 41.7% (fuel-free system) to 57 % (PG system) (increased by 36.69%) and at 10 mM it enhanced from 75 % (fuel-free system) to 84.7 % (PG system) (increased by 12.9%). However, changing the operating conditions would contribute to improve the reduction of the nitrogen such as temperature and the oxidant ratio. Figure 5.14 displays the effect of initial concentration on the nitrogen removal efficiency for both systems.

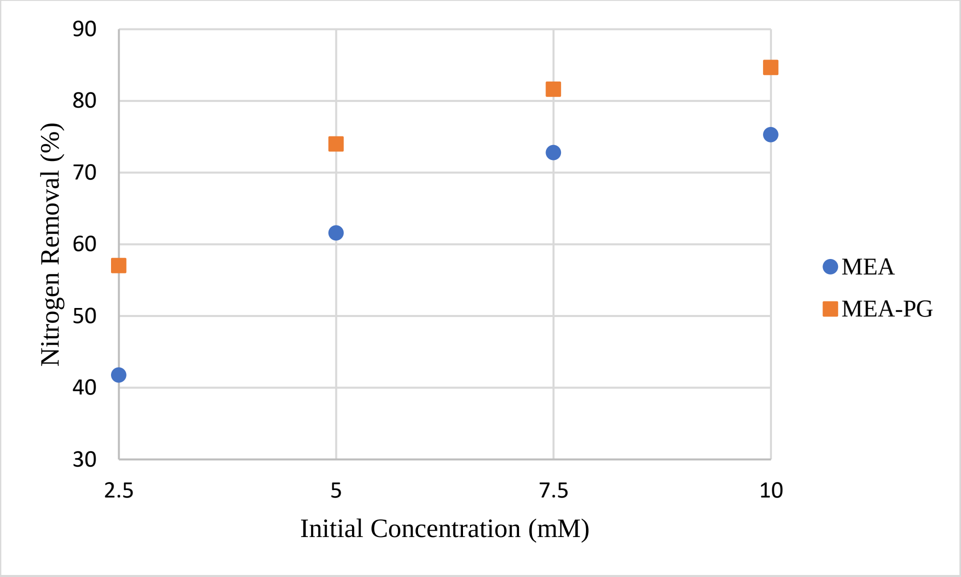


Figure 5.14: Effect of the initial concentration of MEA + PG on the nitrogen removal efficiency at 400 °C, 10 s and SR of 1.

5.4 Global Kinetics of MEA Oxidation

It is necessary to study the global reaction rate and would supply valuable data for design purposes. The body of experimental data obtained regarding influences the various reaction parameters was employed to evaluate the reaction rates expressions namely the Arrhenius constants, rate constants and reactions orders were determined. The global rate law expression was employed to develop most SCWO kinetic models. Equation 5.2 illustrates the global rate law:

$$\frac{-d[Organic]}{dt} = k[Organic]^a[Oxidant]^b[Water]^c = Ae^{\frac{-Ea}{RT}}[Organic]^a[Oxidant]^b[Water]^c \ldots (5.2)$$

k is the reaction rate constant in $M^{1-a-b-c}\,s^{-1}$.

A is the pre-exponential factor in $M^{1-a-b-c}\,s^{-1}$.

E_a is the activation energy in $J.mol^{-1}$.

R is the constant of universal gas ($8.314\ J.mol^{-1}.K^{-1}$).

T is the reaction temperature in K.

[Organic] is the organics initial concentration in $mol.L^{-1}$.

[Oxidant]is the oxidant initial concentration in $mol.L^{-1}$.

a is the reaction order relating to an organic compound.

b is the reaction order relating to oxidant.

c is the reaction order relating to water.

Numerous SCWO kinetic studies have been accomplished for different wastes either a single model compound or a mixture of wastes under various temperature, residence times, oxidant ratios, concentrations of organic and using various reactor designs. In this study, two methods were applied to study kinetic of MEA:

1) Pseudo-first order approximation method
2) Integral method approximation

The medium of SCWO is water, and it formed more than 99 % of MEA SCWO; therefore, the water concentration considers constant. In other words, the reaction order with respect to water becomes zero.

5.4.1 Pseudo-First Order Approximation Method

Numerous researchers have studied the global kinetic for SCWO either single compound or mixture organics, and they have employed Pseudo first order to describe the global kinetic. The order of the reaction is one with respect to the organic compound ($a = 1$) and zero for oxygen ($b = 0$) (Pinto et al., 2006; Abelleira et al., 2013). This model might be a simple method to describe global kinetics, but is a suitable starting point to evaluate the reaction rate constant *k*. The following equation represents the global power rate law system:

$$rate = \frac{-d[MEA_{PG}]}{dt} = k[MEA_{PG}] \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots .. (5.3)$$

The experimental results are the COD values from MEA oxidation in the presence of PG, and equation 5.3 was modified to use the COD:

$$rate = \frac{-d[COD_{MEA+PG}]}{dt} = k[COD_{MEA+PG}] \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots . \dots\dots\dots\dots\dots\dots (5.4)$$

After integrating this equation (5.4), the new equation can be applied:

$$\ln\left(\frac{[COD]}{[COD_o]}\right) = -k.t \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (5.5)$$

Plotting equation 5.5 using experimental data at each temperature gives the rate constant *k* (s^{-1}) from the slope for each operating temperature as shown in Figure 5.15 PG system.

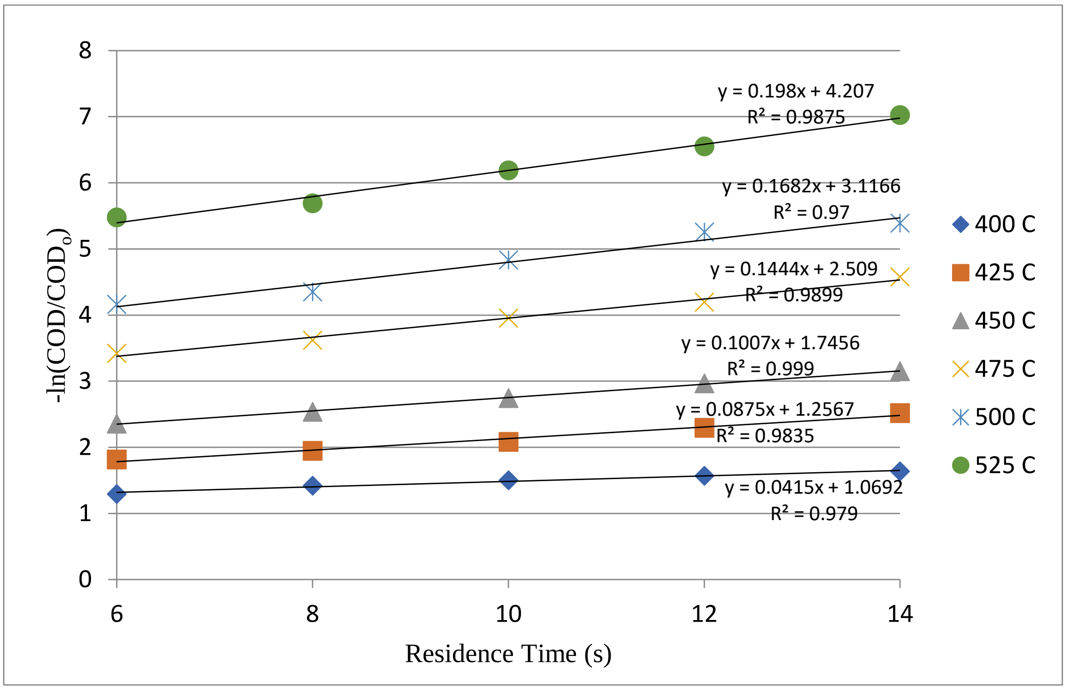


Figure 5.15: Natural logarithm of (COD/COD$_o$) against residence time for MEA and PG experiments at operating temperatures.

Then, where lnk is plotted against *1/T* as displayed in Figure 5.16. From this plot E_a and *A* were evaluated to be 52332 J.mol^{-1} and 589 s^{-1} respectively. The results are shown in equation 5.6.

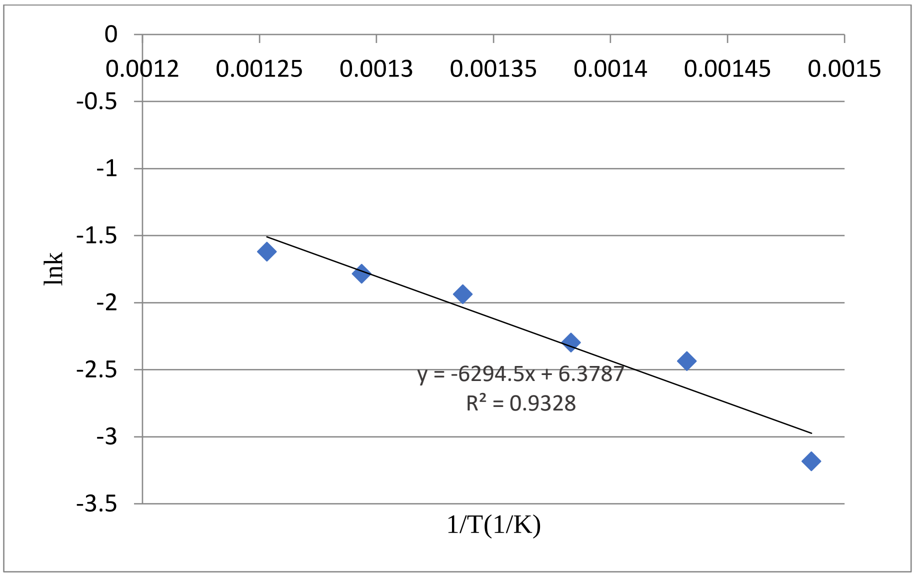


Figure 5.16: Arrhenius plot for the oxidation of MEA and PG.

$$rate = \frac{-d[COD_{MEA+PG}]}{dt} = 589 * (s^{-1}) \exp\left(-\frac{52332 \frac{J}{mol}}{RT}\right)[COD_{MEA+PG}] \ldots\ldots\ldots\ldots .(5.6)$$

5.4.2 Integral Approximation Method

Using the integral method was to understand the global rate expression of MEA oxidation in the presence of PG and to express the kinetic data. The global kinetic parameters as activation energy and pre-exponential factor for MEA oxidation were calculated from applied a set of experiments to determine the rate of the reaction, and the order of organic was considered one as well as the operating temperature considered as a function for the destruction of MEA and PG. Also, water formed more than 99 %. The effect of oxygen concentration on the MEA oxidation may be minor, but it is essential to investigate the order of oxygen. To determine the order of oxidant, four experiments were performed at 400 °C, and the range of oxidant ratio was 0.5 to 2 SR (i.e. the oxygen concentration range was from 18.125 mM to 72.5 mM). These experiments were present in section 5.3.4. The COD removal enhanced with increasing the oxidant ratio thus, the effect must be investigated to determine the order of oxygen. While in previous model (Pseudo first order) the oxygen order assumed zero, but the oxidant experiments have illustrated the effect of oxygen. The design equation of plug flow reactor was based to calculate the order of oxygen and equation 5.2 is rearranged by using the integral method with a = 1 and b > zero:

$$-rA = \frac{-d[MEA]}{dt} = k[MEA][O_2]^b = Aexp^{\left(-\frac{Ea}{RT}\right)}[MEA][O_2]^b \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots.\ldots\ldots\ldots\ldots\ldots\ldots (5.7)$$

The assumption can consider the concentration of oxidant constant. The plug flow reactor equation for the steady state was applied (Levenspiel, 1999) to be:

$$\frac{t}{[MEA]_o} = \int_0^x \frac{dx_{MEA}}{(-rA)} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (5.8)$$

t is a residence time, [MEA]$_o$ is an initial concentration, (-rA) is a rate of reaction of MEA oxidation.

The following equation is substituting integral method equation (5.7) in the performance equation of the plug flow reactor.

$$\ln\left(\frac{1}{(1 - X_{MEA+PG})}\right) = k.t[O_2]_0^b \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots.\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots. (5.9)$$

Then, in order to determine the value of b, it is necessary to find the slopes of fitted straight lines of MEA oxidation for four experiments at 400 °C from plotted ln (1/1-X$_{COD}$) against the residence time (t). The results of the PG system are shown in Figure 5.17. The slopes of lines represent $k[O_2]_0^b$. This term can be written after taking the natural logarithm to be:

$$\ln(k[O_2]_o^b) = \ln(k) + bln([O_2]_o) \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots. (5.10)$$

From Figure 5.17, these slops are plotted versus the concentration of oxygen to generate a straight line for the MEA and PG. The slope of this line represents the b value for PG system. Figure 5.18 displays the value of b.

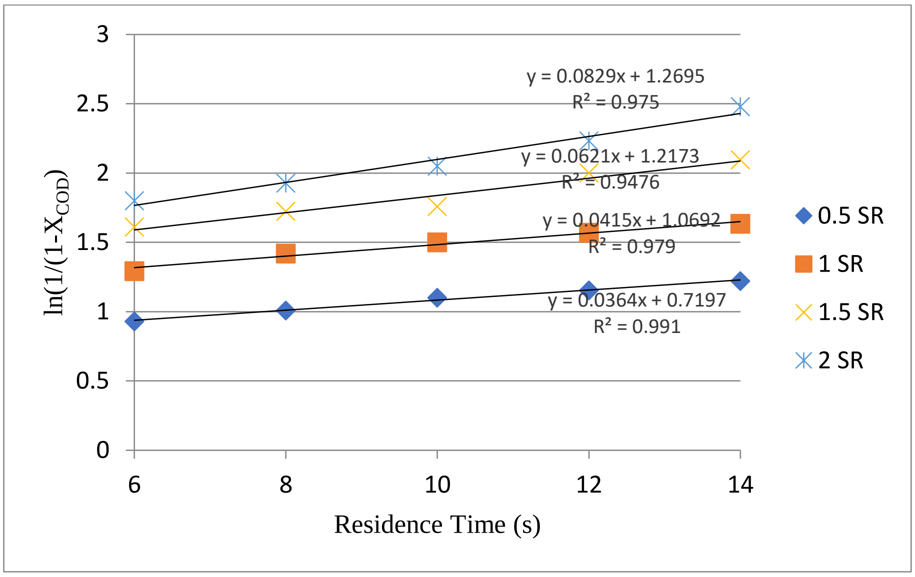


Figure 5.17: Natural logarithm of (1/(1-X)) versus residence time for MEA and PG experiments with varying oxidant concentrations.

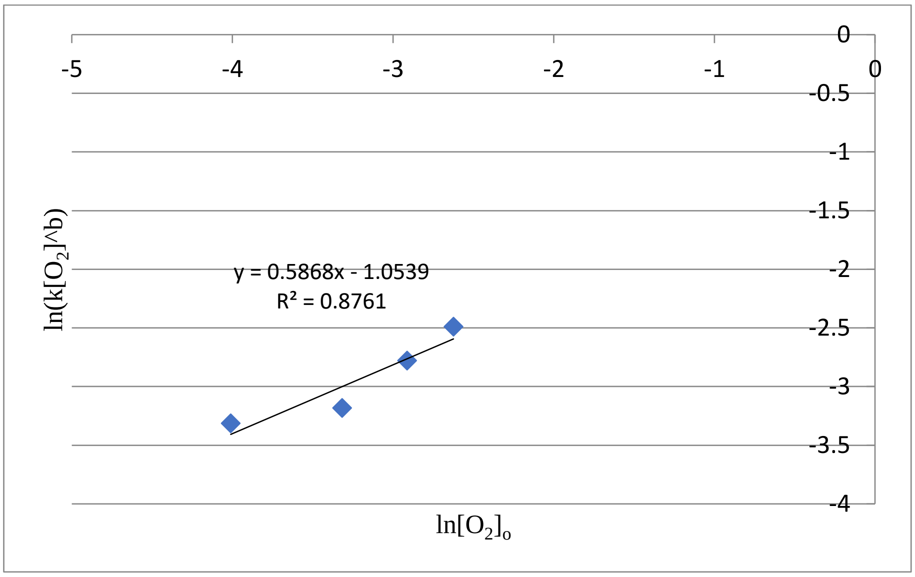


Figure 5.18: Oxygen reaction order

The order of oxygen represents the slope of straight line in Figure 5.19. The determination of reaction orders is (a =1, b_{MEA+PG}= 0.58). It is easy to determine the rate of the reaction by applying the equation (5.11) to be:

$$k = ln\frac{1}{(1-X_{MEA+PG})} \times \frac{1}{t} \times \frac{1}{(O_2)^{0.58}} \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots \quad (5.11)$$

The new *k* value is employed to determine the E_a and *A*, plotting the natural logarithm of the rate of reaction (*k*) versus inverse temperature (1/T) is shown in Figure 5.19. The E_a was calculated by multiplying the universal gas constant (8.314 $J.mol^{-1}.K^{-1}$) by multiplying the slope. *A* was calculated from ln *A*= intercept. Equation 5.12 illustrates the value of E_a and *A* in the generated global rate expression of MEA and PG oxidation.

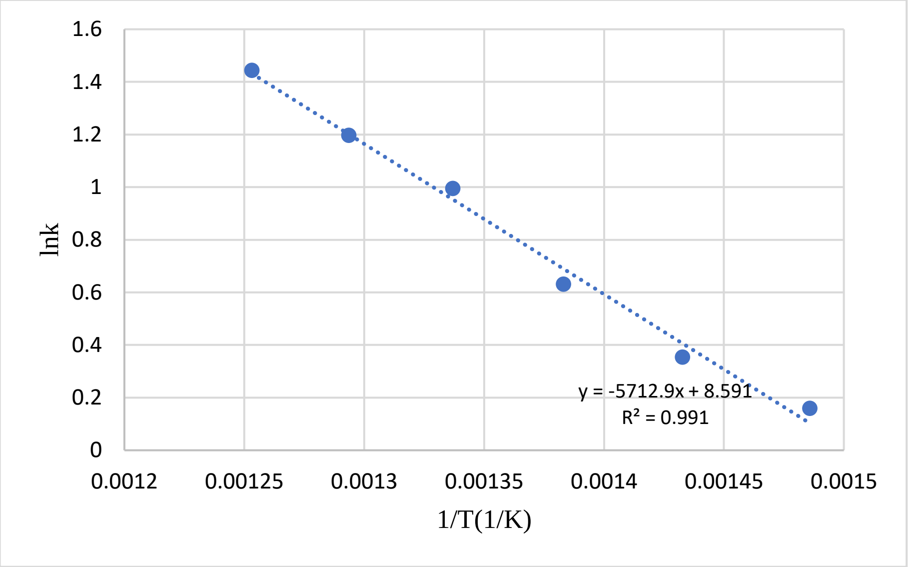


Figure 5.19: Arrhenius plot for MEA and PG oxidation.

$$rate = -\frac{d[COD_{MEA+PG}]}{dt} = 5.382 * 10^3 (M^{-0.58} s^{-1}) \exp\left(-\frac{47497 \frac{J}{mol}}{RT}\right) [COD_{MEA+PG}][O_2]^{0.58} \ldots (5.12)$$

The order of oxygen was 0.58 (PG system) that indicated to the effect of oxidant on the MEA+PG oxidation was clear, consequently applying integral method could consider a suitable way to understand the kinetic MEA+ PG. The literature of SCWO does not contain a reference that illustrates the kinetic of MEA + PG to compare with these results.

5.5 Summary

The operating conditions had different influences on the oxidation of MEA in the presence of PG. The following points summarise Chapter five:

- The effect of operating temperature on the COD removal efficiency was significant in the presence of PG. The maximum removal efficiency was 99.9 % at 525 °C. Also, the effect of PG was remarkable at 400 °C and it positively influenced the nitrogen species with increasing temperature. Comparison between the fuel-free system, IPA system and PG system was significant. The effect of PG was remarkable on the COD removal efficiency and by-products more than IPA. Moreover, a further oxidation for NH_4-N in the PG system was clear and increased the yield of NO_3^- confirmed a positive role of PG. Consequently, the enhancement in the removal efficiency of nitrogen illustrated the essential effect of PG.
- The effect of oxidant ratio on the COD removal efficiency was remarkable in the presence of PG, the effect of the oxidant ratio and PG on the by-product was positive when the oxidant ratio was increased to more than 1 SR. Furthermore, the removal efficiency of nitrogen was enhanced in the presence of PG and when increasing the oxidant ratio. The effect of PG on the COD removal efficiency and the removal efficiency of nitrogen was positive more than IPA.
- The PG ratio enhanced the COD removal and nitrogen removal efficiencies at 400 °C. The maximum removal of COD and nitrogen at the PG ratio of 2.5 was 93 % at 14 s and 85 % at 10 respectively. Also, the effect of PG on the reduction of NH4-N increased with the concentration of PG more than 1. The influence of PG on by-products of MEA was positive when compared with the influence of IPA.
- The effect of initial concentration in the presence of PG significantly influenced COD removal and nitrogen efficiencies. This effect was positive on nitrogen species when increased the initial concentration from 2.5 to 7.5 mM. The results of PG system were considered significant if compared with the results of the fuel-free system.

- The enhancement of COD removal and nitrogen removal in the presence of PG at different operating conditions was remarkable due to the activity of two hydroxyls groups. These results confirmed the role of two hydroxyl groups was better than a single hydroxyl group.
- The kinetic analysis showed a positive effect of co-fuel on $E_{a,}$, which decreased from 79746 J.mol^{-1} (fuel-free system) to 46807 J.mol^{-1} (IPA system). E_a decreased to reach 47497 J.mol^{-1} in the presence of PG. The order of oxygen confirmed the effect of the oxidant on the destruction of MEA in the fuel-free system, IPA system and PG system.

CHAPTER SIX: SUPERCRITICAL WATER OXIDATION OF 3-METHYLPYRDINE (3MP) IN THE ABSENCE AND PRESENCE OF ISOPROPYL ALCOHOL (IPA) AS CO-FUEL

6.1 Introduction

MEA was selected as a model compound to be treated by SCWO because it was found in the environment as a real waste. The main by-product of MEA is ammonia due to containing an amino group. PG was employed as a co-fuel in this work to investigate the effect of two hydroxyl groups on the removal of MEA. Also, comparison between the effect of PG and IPA on MEA and ammonia was to assess the role of PG. The results were remarkable in the presence of PG. The influence of two hydroxyl groups on the COD removal%, nitrogen removal % and nitrogen species was positive more than the one hydroxyl group. On the other hand, the results of the destruction of MEA (fuel-free system) was significant, and the MEA could be destroyed without co-fuel. Thus, 3MP was selected as a resistant model compound to assess the feasibility of PG. 3MP is a derivative of pyridine that would be a challenge to be destroyed under supercritical conditions.

This chapter will deal with 3MP at various operating conditions. 3MP is a nitrogen-containing hydrocarbon (heterocyclic). It was selected to test the capability of co-fuel to aid TOC removal and the destruction of intermediates compounds. This chapter displays the investigated results of 3MP with and without IPA under various operating conditions. Discussion the effect of selected operating conditions as temperature, oxidant ratio, organic concentration and residence time are on the removal efficiency of 3MP and by products. In addition, study the kinetics of two cases and the effect of IPA on Arrhenius parameters would illustrate the feasibility of IPA.

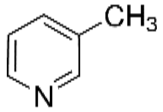
6.2 Selection of 3MP

3MP was selected as model of a heterocyclic, aromatic N-containing hazardous hydrocarbon. It contains a methyl function group with a molecular formula of (C_6H_7N). 3MP considers a necessary compound in several industries. Thus, it was found in the effluent of different applications such as dyes, pharmaceutical and pesticides (Carini et al., 2001; Mohan et al., 2005).

The physical properties of 3MP (Sigma-Aldrich, UK, 99 %) are shown in Table 6.1. The equation of the complete oxidation of 3MP is:

$$C_6H_7N+ 7.75O_2 \rightarrow 3.5H_2O+6CO_2+0.5N_2 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (6.1)$$

Table 6.1: Physical properties of 3MP

CAS Number	*108-99-6*
Molar Mass (g/mol)	*93.129*
Density (g/ml)	*0.956*
Boiling point (℃)	*144*
Melting point (℃)	*-18*
Water Solubility	*Miscible*
Colour	*Colourless*
Structure	

3MP was investigated in this work, for the following reasons:

1. It is widely used as a raw material and solvent in various industries such as pharmaceutical and agricultural, dyes, niacin, textile, polymer and fuels.
2. It is found in real wastewater effluent of various application (Carini et al., 2001; Mohan et al., 2005).
3. Limited studies are on the treatment of 3MP. Consequently, treatment of this compound by SCWO will enrich the knowledge and provide the novel kinetics data as well as it shows the behaviour of this compound at different conditions.

Most studies for treatment 3MP did not achieve a complete removal. For example, 3MP wastewater stream was destroyed by Ozonation and biological treatment and the removal efficiency was 75% at 80 min. Also, 3MP was treated by activated carbon. The removal efficiency of 3MP increased with increasing pH of a solution and the temperature that has influenced on the removal efficiency when increased the temperature from 10 to 40 °C. The maximum removal efficiency was less than 80 %. Consequently, two units of treatment must be used to destroy 3MP.

In summary, treatment of 3MP containing effluent by biological methods or another technology would not be a suitable solution due to its poor biodegradability (Stern et al., 1997). Also, it decomposes to produce nitrogen species as ammonia, nitrate and nitrite that have influenced on the aquatic life. For these reasons, effects of 3MP on the environment must be avoided. Thus, study this case would improve the SCWO performance and provide the further knowledge about this compound as well as the role of co-fuel. Furthermore, 3MP is a derivative of pyridine that has a high resistant to supercritical conditions. This study will provide a further source about the kinetics of 3MP.

6.3 Effect of Operating Conditions

In this chapter, SCWO process diagram and experimental procedures were previously illustrated in chapter three.

6.3.1 Experimental Work Plan

In this section, solution of 3MP and water was employed to carry out SCWO experiments and solution of 3MP, IPA and water was employed to carry out SCWO experiments at different temperatures, residence times, oxidant stoichiometric ratios, 3MP feed concentrations. Each parameter was individually examined at 4 mM of 3MP and SR of 1. The operating pressure was applied 250 bar during all experiments to obtain on supercritical phase and several studies have reported the increasing pressure has not influenced on the efficiency of process under supercritical conditions (Cocero, 2001). Table 6.2 explains the summary of operating condition ranges.

Table 6.2 summarises the range of operating conditions.

Variable	Range	Fixed conditions
Temperature (ºC)	425 - 525	$[3MP]_o$ = 4 mM SR = 1SR
$[3MP]_o$ mM	2 - 8	Temp = 450 ℃ SR = 1SR
Oxygen Ratio	0.75 - 2 SR	Temp = 425 ℃, $[3MP]_o$ = 4 mM
Temperature (ºC)	425 - 525	$[3MP]_o$=$[IPA]_o$= 4 mM SR = 1SR
Oxygen Ratio	0.75 - 2 SR	Temp = 425 ℃ $[MEA]_o$=$[IPA]_o$= 4 mM
Ratio $[IPA]_o/[3MP]_o$	0.5 – 2.5	Temp = 425 ℃, SR = 1SR $[3MP]_o$ = 4 mM
Residence time: 6-14 s for all experiments		

6.3.2 Effect of Residence Time

The range of residence time was selected to investigate the removal efficiency of 3MP from 6 to 14 s with keeping the turbulent flow regime at different residence times. The effect of residence time on the TOC conversion of 3MP oxidation (fuel-free system) displays in figure 6.1. It was observed the removal efficiency at high residence time 14 s was better than the removal efficiency at a short residence time because the time of reaction between the reactants (organic molecular and oxidant molecular) will improve the TOC conversion.

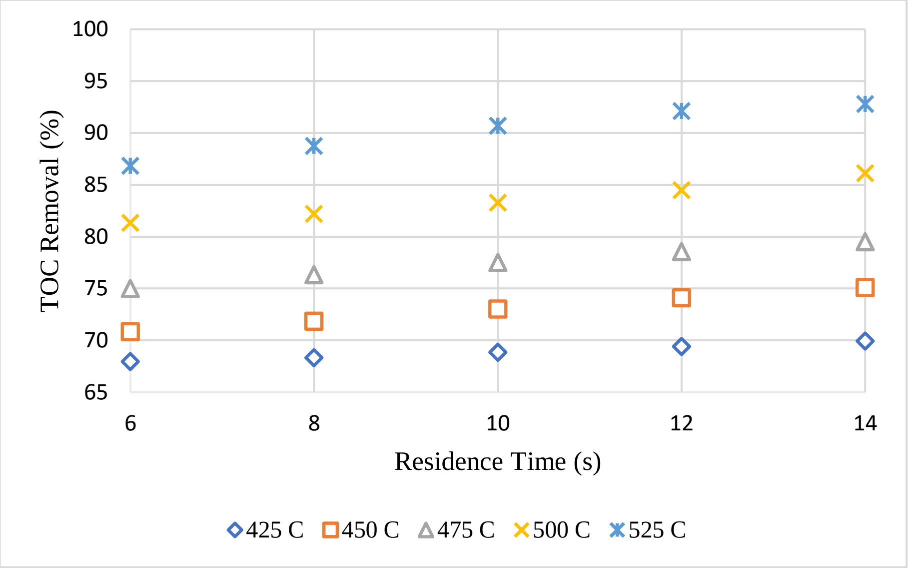


Figure 6.1: TOC removal % against residence time at various operating temperatures, at 4 mM 3MP, SR of 1

The TOC conversion increased with increasing residence time at different operating temperatures. For example, the removal efficiency was enhanced from 67.9 % at 6 s to 69.9 % at 14 s (increased by 2.9 %) due to provide sufficient time to react between organic and oxidant molecules, but this enhancement was low. While the effect of residence time on the TOC removal efficiency at 525 °C was significant because the rate of reaction and the solubility of organic material improved with temperature. For example, at 525 °C the TOC conversion was enhanced from 86.8 % at 6 s to 92.8 % at 14 s (increased by 7%). Figure 6.1 shows the effect of residence time on the TOC removal efficiency. As a result, the destruction of 3MP would enhance with the residence time at high temperature. In addition, several researchers have pointed out the positive effect of residence time on the enhancement the organic removal under supercritical conditions (Savage et al., 2000; Qi et al., 2002; Ploeger et al., 2006). Consequently, these results are consistent with other work in this field.

Figure 6.2 displays the effect of residence time on the TOC removal % with various operating temperature in the presence of IPA. The results were illustrated the TOC removal efficiency enhanced with increasing the residence time. Although the system was contained IPA as co-fuel to enhance the removal efficiency, but IPA slightly improved the TOC conversion with the residence time. Yang and his team pointed out methanol would be oxidised faster more than IPA under supercritical conditions (Yang et al., 2018). The positive effect of the residence time on the removal efficiency could be illustrated for example, at 425 °C the TOC conversion increased with increasing the residence time from 71 % at 6 s to 73.7 % at 14 s (increased by 3.8%). The effect of the residence time on the TOC removal efficiency at 525 °C was improved from 89.8 % to 93 % (increased by 3.5 %). This enhancement in TOC % was observed with various temperature. In summary, the effect of the residence time in the IPA free system and the IPA system would be positive. The role of IPA was significant with residence time while the effect of the residence time on TOC% was significant at high temperature in the absence of IPA due to co-fuel improved the TOC removal % at different residence times.

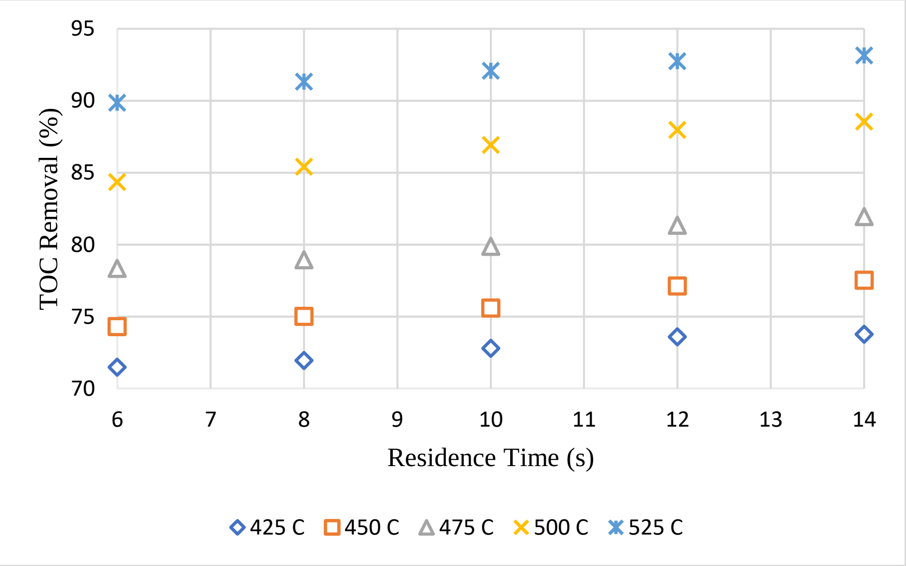


Figure 6.2: TOC removal efficiency against the residence time at various temperatures at 4 mM 3MP, 4 mM IPA, SR of 1

6.3.3 Effect of Operating Temperature

A range of operating temperatures, from 425 to 525°C, was applied to study their effect on 3MP oxidation; the initial 3MP concentration was 4 mM. The residence time ranged from 6 to 14 s at 1 SR. The range of temperatures selected was based on the thermal ability of the furnace, while keeping the turbulent flow regime at various temperatures and residence times.

The influence of temperature on the destruction of 3MP was remarkable in the fuel-free system and the IPA system. Figure 6.3 displays the effect of a range of various temperatures on the efficiency of the TOC removal at 10 s in the absence and the presence of IPA.

In the fuel-free system, the TOC removal % of 3MP increased from 67.9% at 6 s and 425°C to 86.8% (it increased by 27.8%) at the same residence time with a temperature of 525°C. With a long residence time of 14 s, the efficiency of the TOC removal was enhanced from 69.9% to 92.8% (it increased by 32.76%). The increase in the operating temperature from 425 to 525°C promoted the destruction of 3MP. As expected, this enhancement could be a result of an increase in the reaction rate. The high temperature could accelerate the generation of free radicals and increase the solubility of the organic substance, and the reaction at 525°C could consume a high percentage of the oxygen provided to destroy an organic substance. The removal efficiency of 3MP at 525°C indicated that it would not be easy to destroy this substance at 525°C. Changing in operating conditions or using a co-fuel to improve the removal efficiency could be a suitable solution. The destruction of the organic substance at a high temperature would make SCWO an expensive technology for treating 3MP. On other hand, several studies (for instance, Carini et al., 2001; Mohan et al., 2005) have referred to the fact that removing this compound using a biological treatment was expensive because 3MP has poor biodegradability. Thus, it could be destroyed at a low temperature using a co-fuel under supercritical conditions. IPA is one of the alcohols used in enhancing the removal efficiency under supercritical conditions and the results for the efficiency of the COD removal for the MEA and IPA system illustrated the positive effect of IPA in terms of increasing the COD removal.

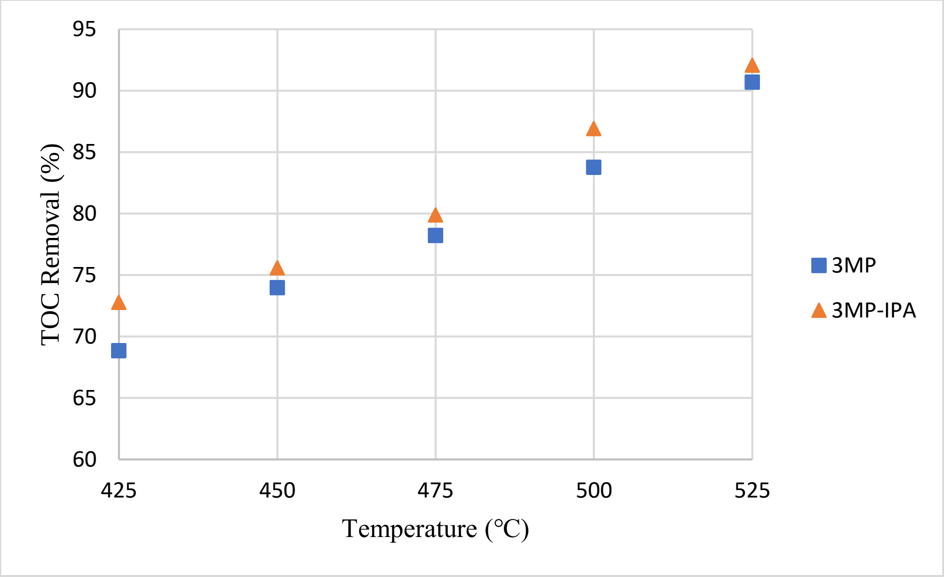


Figure 6.3: TOC removal efficiency against various temperatures at 10 s, 4 mM 3MP, 4 mM IPA, SR of 1

In the presence of IPA, the rate of the TOC removal was enhanced with the temperature increased at different residence times. In addition, the effect of the co-fuel is significant because the co-fuel accelerates the reaction rate and increases the generation of free radicals as the temperature increases. IPA provides various powerful radicals, such as $HO^{\bullet}$ and $HO_2^{\bullet}$, that could attack 3MP molecules and convert 3MP to water and gases. Some researchers have demonstrated the positive effect of increasing the temperature in terms of enhancing the removal efficiency (Ma and Zou, 2015; Al-Duri et al., 2016).

For example, the TOC removal of 3MP increased from 71% at 6 s and a temperature of 425°C to 89.8% at the same residence time and a temperature of 525°C (it increased by 26.47%). With a long residence time of 14 s, the rate of TOC removal was enhanced from 73.7% to 93% (26 %). The role of IPA was positive in terms of increasing the destruction of 3MP. These results illustrate the significant effect of IPA on the rate of TOC removal. Although IPA has a positive influence on the removal of 3MP, the removal efficiency in the presence of IPA at 425°C was slight if compared with the rate of TOC removal in the absence of IPA under the same operating conditions. Modifying the operating conditions could enhance the conversion of 3MP in the presence of IPA. For example, the efficiency of the TOC removal at 425°C increased from 68.8% at 10 s (the fuel-free system) to 72.7% (the IPA system) (it increased by 5.6%).

It is necessary to enhance the removal efficiency of wastewater at a low temperature to avoid high costs for power. The role of IPA does not seem remarkable when compared with the results of the MEA and IPA system at 400°C. There may be two reasons for these results. MEA is not a resistant compound when compared with 3MP, and a high temperature and long residence time would be needed for IPA when compared with methanol and ethanol (Yang et al., 2018).

The oxidation of 3MP under supercritical conditions would produce ammonium-nitrogen (NH_4-N), nitrate (NO_3^-) and nitrite (NO_2^-). Figure 6.4 shows the effect of the operating temperatures on the nitrogen species at 10 s. NH_4-N was the main by-product of 3MP oxidation at a high temperature. The yield of NH_4-N was low when compared with the yield of NH_4-N generated through MEA oxidation. The structure of MEA shows it contains an amino group whereas 3MP contains nitrogen and, according to Yang et al. (2018), the by-products of pyridine are N_2 and NH_4-N and so the yield of NH_4-N was low in the effluent of 3MP. The results demonstrated the yield of NH_4-N increased as the temperature increased. The NO_3^- and NO_2^- yields remained low. The maximum NH_4-N yield increased to 9.7% at 525 °C due to an increase in the conversion of 3MP as the operating temperature increased, and the minimum NH_4-N yield was 0.38% at 425°C. Applying a high temperature and increasing the oxidant ratio accelerate the reduction in NH_4-N and improves the efficiency of the TOC removal. In addition, several studies (Segond et al., 2002; Oe et al., 2007; Cocero et al., 2000) demonstrated a reduction in NH_4-N occurred under high supercritical conditions, and the main by-products of the oxidation of ammonia were N_2 as well as the NO_3^- and N_2O that were generated if the oxidant ratio was increased by more than 1 SR. Segond and his colleagues (2002) oxidised ammonia at 531°C and 25 MPa; ammonia was removed by 17% at 30.6s, and they referred to how the ammonia was completely destroyed at 600°C. Killilea et al. (1992) suggested a high temperature of 600°C would be needed to convert ammonia to N_2.

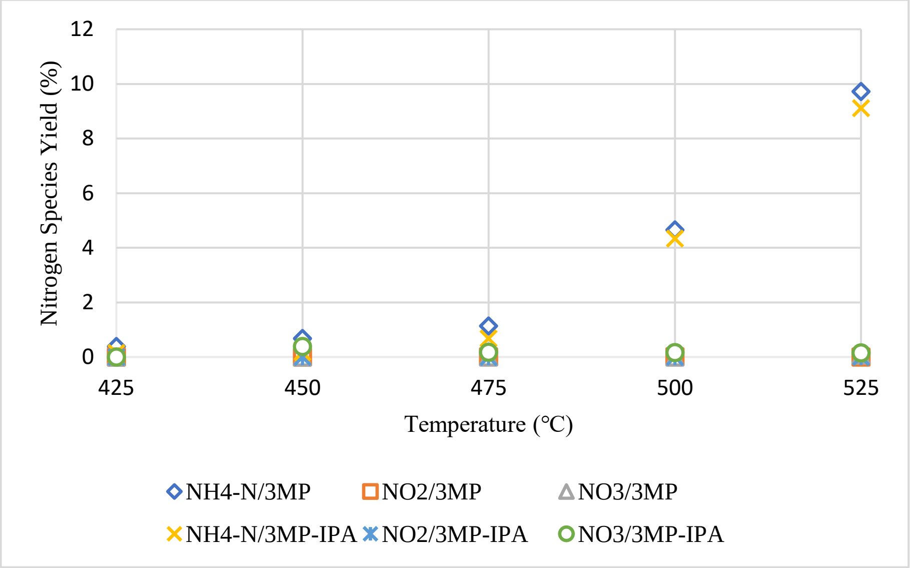


Figure 6.4: Nitrogen species yield as a function of temperature at 4 mM 3MP, 4 mM IPA, SR of 1 and 10 s.

Ammonia generation as a by-product during the treatment of nitrogen-containing compounds would be a main problem due to the fact a high temperature is needed to remove ammonia from wastewater. Several researchers (Al-Duri et al. 2016; Bermejo et al. 2008) have reported using co-fuels to destroy organic waste and by-products. IPA is used to destroy nitrogen species. Bermejo et al. (2008) investigated ammonia and IPA as a co-fuel and they demonstrated how the removal efficiency of ammonia increased as the temperature increased above 710 °C. Figure 6.4 displays the effect of the operating temperatures on the nitrogen species in the presence of IPA and without IPA at 10 s and 4 mM 3MP. In the IPA system, NH_4-N was the main by-product of 3MP oxidation under supercritical conditions. The yield of NH_4-N slightly decreased as the temperature increased whereas the NO_3^- yield was slightly higher than the yield of NO_3^- in the fuel-free system due to the partial oxidisation of NH_4-N to NO_3^- (Segond et al., 2002). The NO_2^- yield was still low in the two systems. As a result, the maximum NH_4-N yield in the fuel-free system was 9.7% at 525°C and the NH_4-N yield became 9.1% in the presence of IPA. The effect of temperature and IPA was clearly seen with respect to the removal efficiency of nitrogen.

Figure 6.5 displays the removal free efficiency of nitrogen in the fuel and the IPA systems. The increase in the rate of nitrogen removal was significant with the increased temperature in the two systems. The rate of nitrogen removal in the presence of IPA improved with the increased operating temperature. IPA reacts rapidly with the oxidant to produce free radicals, which are considered to be unstable intermediates. Then, intermediates react with organic molecules, which are converted to carbon dioxide, water and N_2 (Al-Duri et al., 2015). In addition, IPA has a high calorific value, which contributed to the reduction in nitrogen (Yang et al., 2018). In the fuel-free system, nitrogen in 3MP at 475°C was partially converted to NH_4-N while, in the IPA system, the enhancement was linear in relation to the temperature. For example, the removal efficiency of nitrogen increased from 74% in the fuel-free system to 81% in the IPA system at 425°C and 10 s while, at 525°C, it increased from 82.0 % in the fuel-free system to 85.7 % due to an increase in the temperature. The results of the nitrogen removal demonstrated a significant point: nitrogen in 3MP was mainly converted to N_2 and NH_4-N. Finally, the operating temperature influenced the conversion of 3MP while the co-fuel had a positive effect on the efficiency of the nitrogen removal.

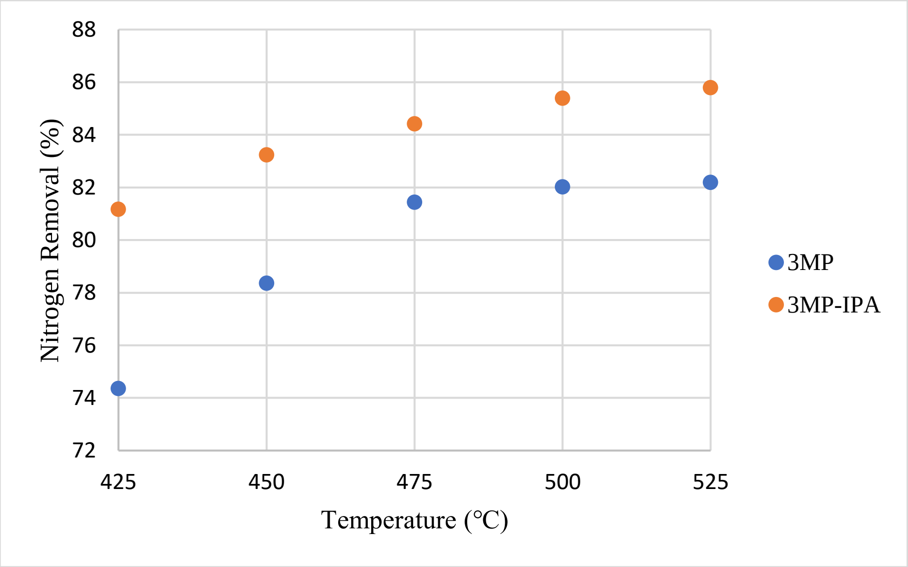


Figure 6.5: Nitrogen removal efficiency as a function of various operating temperatures at 4 mM 3MP, 4 mM IPA, SR of 1 and 10 s.

6.3.4 Effect of Oxidant Ratio

The complete destruction equations for oxidation 3MP and IPA systems are written below:

$C_6H_7N + 7.75O_2 \rightarrow 6CO_2 + 3.5H_2O + 0.5N_2$ ……………………………………..……... (6.1)

$C_3H_8O + 4.5O_2 \rightarrow 3CO_2 + 4H_2O$………………………………………….…………..……... (6.2)

The source of oxygen was hydrogen peroxide, and the equation of decomposition can be written:

$H_2O_2 \rightarrow H_2O+0.5O_2$ …………………………………………………………………… (6.3)

The use of various oxidant ratios is an essential condition for determining the enhancement in the rate of TOC removal and nitrogen removal. In this section, the effect of the oxidant ratio on the destruction of 3MP and by-products was investigated. Different amounts of oxygen were employed to oxidise 3MP in the absence and presence of IPA under supercritical conditions to complete the destruction. In the IPA system, the amount of oxygen represents enough oxygen for 3MP and IPA, and this was depended on the concentration of 3MP and IPA under various supercritical conditions. The range in the oxidant ratio was 0.75 to 2 SR. Furthermore, the selected range of SR was based on the capacity of the HPLC pump. However, an increased oxidant ratio increases the cost of the oxidant and generates unwanted by-products, like N_2O.

The influence of the oxidant ratio on the TOC conversion was consistent with an increase in the amount of oxygen. The efficiency in terms of the TOC removal and nitrogen removal was enhanced when the oxidant ratio was increased from 0.75 SR to 2 SR. Figure 6.6 shows the increase in the rate of TOC removal in both systems at 425°C. According to Pinto et al. (2006), the free radical mechanism characterises the primary pathways of supercritical water reactions. Thus, the amount of oxidant significantly influenced the rate of TOC removal. For example, at 10 s the rate of TOC removal increased from 63.8% to 86.5% (it increased by 35.5%) at 0.75 SR and 2 SR, respectively. The increase of the TOC removal at 425 °C was significant in terms of avoiding the use of a high temperature. The effect of the oxidant ratio on the nitrogen species and rate of nitrogen removal was also positive. Several studies (for instance, DiNaro et al., 2000; Lee et al., 1990; Qi et al., 2002) have pointed out the removal efficiency increased as a result of an increase in the oxidant ratio.

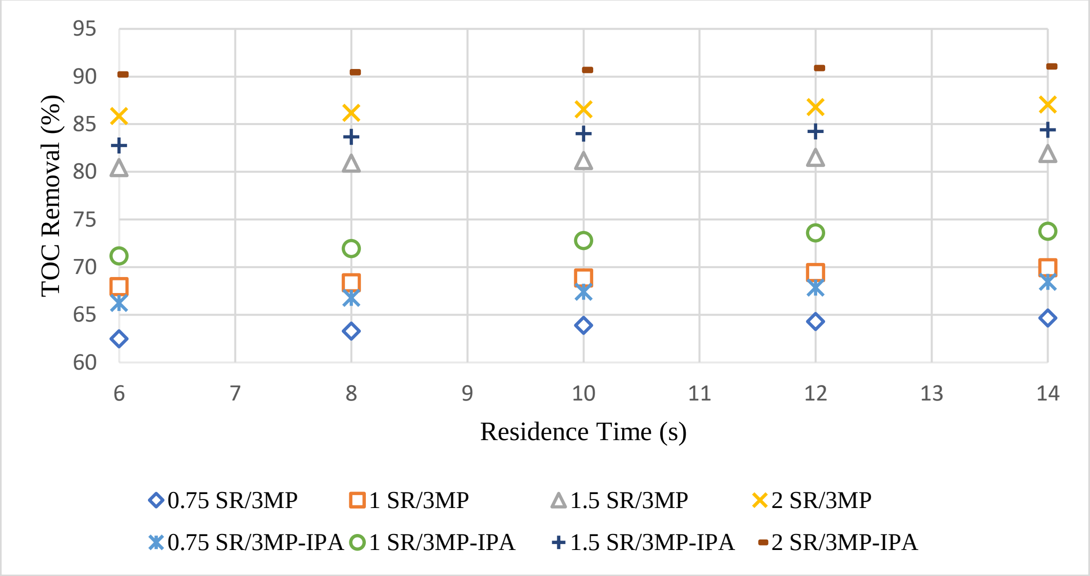


Figure 6.6: Effect of the various oxidant ratios on TOC removal efficiency at 425 °C, 4 mM 3MP, 4 mM IPA and various residence times.

The destruction of 3MP also improved as the residence time increased. For example, at 0.75 SR the TOC removal improved from 62% at 6 s to 64.6% at 14 s (it increased by 4% as the residence time increased. At 2 SR, the TOC removal efficiency increased from 85.8% at 6 s to 87% at 14 s (it increased by 1.39%). The effect of the residence time on the TOC removal efficiency was positive with different oxidant ratios.

According to Al-Duri et al. (2016), IPA helps to generate free radicals, such as $HO^{\bullet}$ and $HO_2^{\bullet}$, that could play an essential role in increasing the rate of oxidation and hydrogen peroxide as an oxidant also has a role. Thus, the effect of the oxidant ratio on the rate of TOC removal was consistent with an increase in the amount of oxygen, as it was observed that the efficiency of the TOC removal increased as the oxidant ratio increased from 0.75 SR to 2 SR. Figure 6.6 shows the increase in TOC conversion due to the increase in the amount of oxygen and addition of IPA. The trend for TOC removal in the absence and presence of IPA was significant. The free radical mechanism was a common reaction under supercritical conditions (Pinto et al., 2006). For example, at 0.75 SR the rate of TOC removal increased from 62% at 6 s in the fuel-free system to 66% in the IPA system while the rate of TOC removal increased from 87% in the fuel-free system to 91% in the IPA system at 14 s and 2 SR.

The results in Figure 6.7 show the results for nitrogen species in a liquid sample with various oxidant ratios and 10 s. It was observed that the yield of NH_4-N decreased as the oxidant ratio increased. The trend for the nitrogen species would illustrate the significant effect an increase in the amount of oxygen can have on a reduction in NH_4-N. The main reason for improving the removal of NH_4-N is that it could generate powerful radicals that have a predominant mechanism under supercritical conditions. These radicals, as $HO^•$ and $HO_2^•$, could attack organic molecules and convert them to water and gases. The results for the nitrogen species were low, and these results confirmed that the nitrogen in 3MP was mainly converted to N_2 rather than other liquid nitrogen species. For example, the yield of NH_4-N decreased from 0.6% at 0.75 SR to 0.1% at 2 SR at 10 s at a temperature of 425℃. The main by-product of the 3MP conversion was N_2 and, according to Yang et al. (2018), the main by-product of heterocyclic was N_2. The yields of NO_3^- and NO_2^- were still low. Despite the fact the yield of NH_4-N was low, the amount of oxygen influenced the yield of NH_4-N. An increase in the amount of oxygen helped to increase the conversion of TOC and oxidise ammonia to N_2 and N_2O. However, the removal of nitrogen as a gas may be regarded as a suitable way to avoid elevating the temperature to over 600℃ and destroying NH_4-N.

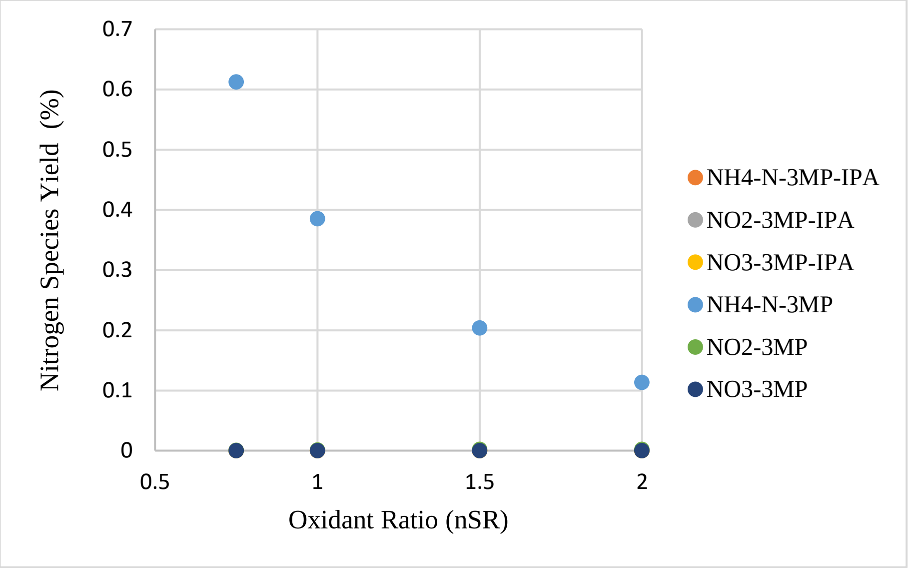


Figure 6.7: Nitrogen species yield as a function of the oxidant ratio at 4 mM 3MP, 4 mM IPA 425 °C and 10 s.

The results in Figure 6.7 show nitrogen species in a liquid sample at various oxidant ratios in the presence of IPA. As expected, the yields of NH_4-N, NO_2^- and NO_3^- were low and these findings confirmed the role of IPA, and nitrogen in 3MP was converted to N_2. The yield of NH_4-N decreased as the oxidant ratio increased. Although the yield of NH_4-N was low in the fuel-free system, IPA contributed to the reduction in NH_4-N due to an increase in the generation of free radicals. Various free radicals play an essential role in improving the destruction of 3MP and by-products. Thus, an investigation of the removal efficiency of nitrogen in a liquid sample demonstrated this point.

Figure 6.8 displays the effect of the oxidant ratio on the removal efficiency of nitrogen in the two systems. The increase in the removal of nitrogen was consistent with the different oxidant ratios, and the increase in the rate of nitrogen removal was linear with respect to the amount of oxygen. The role of IPA was significant. The nitrogen removal in the IPA system improved as the oxidant ratio increased and heat was added through IPA oxidation, IPA has a high calorific value (ΔH_r) (-1908 kJ.mol^{-1}). The reaction heat for IPA helps to enhance the rate of nitrogen. IPA generates radicals that have a powerful energising effect in terms of attacking and mineralising organic molecules into carbon dioxide, water and N_2 (Al-Duri et al., 2015). For example, at 425℃ the efficiency of the nitrogen removal increased from 68.9% in the fuel-free system to 76% (it increased by 10%) in the IPA system and 0.75 SR while, at 2 SR, it increased from 85% in the free system to 88% (it increased by 3.5%). The increase in the rate of the removal of nitrogen at 0.75 SR was remarkable due to the addition of IPA.

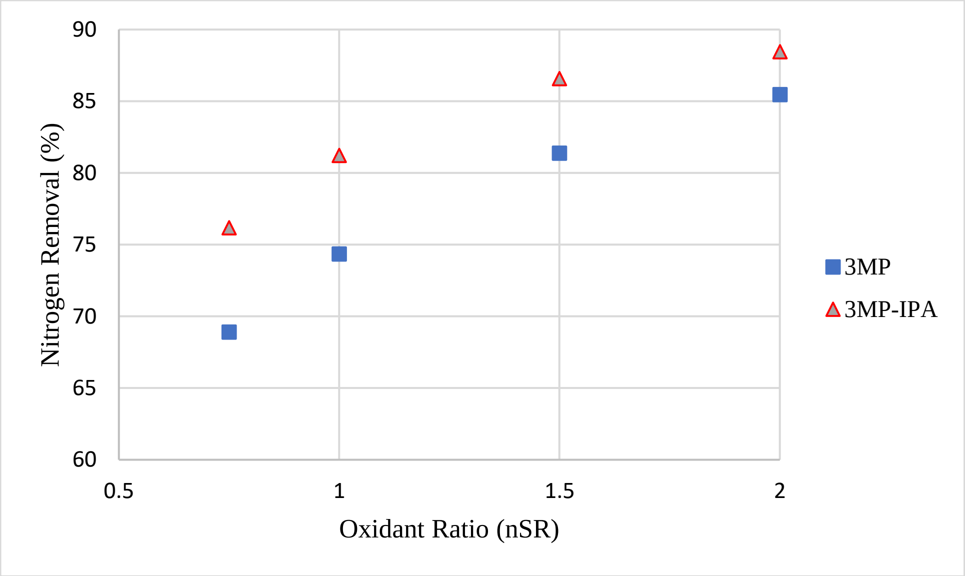


Figure 6.8: Nitrogen removal efficiency as a function of various oxidation ratio at 4 mM 3MP, 4 mM IPA, 425 °C and 10 s.

6.3.5 Effect $IPA_o/3MP_o$ Ratio

The literature illustrated the significant role of IPA in enhancing the destruction of nitrogen and improving removal efficiency (Yang et al., 2018; Al-Duri et al., 2016). Several examples demonstrated the positive effect of methanol and ethanol on SCWO performance (Ploeger et al., 2006； Shimoda e al., 2016). The range of IPA/3MP ratio was 0.5 to 2.5 (i.e. 2 - 10 mM IPA) at 425 °C and 4 mM 3MP.

The effect of the IPA ratio on the TOC removal efficiency and on the by-products of 3MP was investigated. Figure 6.9 displays the results of the IPA ratio. The effect of the IPA ratio was observed to be significant. TOC removal efficiency was enhanced with increasing the IPA concentration. This was attributed to the generation of extra powerful free radicals such as HO•, HO_2• and increased rate of reaction. IPA oxidation would add further heat to the reaction (Al-Duri et al., 2016; Bermejo et al., 2008). The effect of the IPA ratio at 2mM (IPA) was not positive and the enhancement was clear with increasing the IPA ratio. For example, at 425 °C the TOC removal efficiency improved from 68% at 0.5 IPA ratio, to 78% at 2.5 IPA ratio and 10s (increased by 14.7%). This enhancement could be positive if compared with the removal efficiency in the absence of IPA. There was approximately a 13% increment in the TOC removal efficiency after increasing the IPA concentration from zero to 10 mM. These results made IPA a competitive co-fuel to improve the removal efficiency at a short residence time and low temperature. In addition, the effect of residence time on the efficiency of TOC removal was positive at various IPA ratios. The influence of the IPA ratio on the destruction of 3MP was positive, but it was not remarkable if compared with the results of IPA and MEA systems.

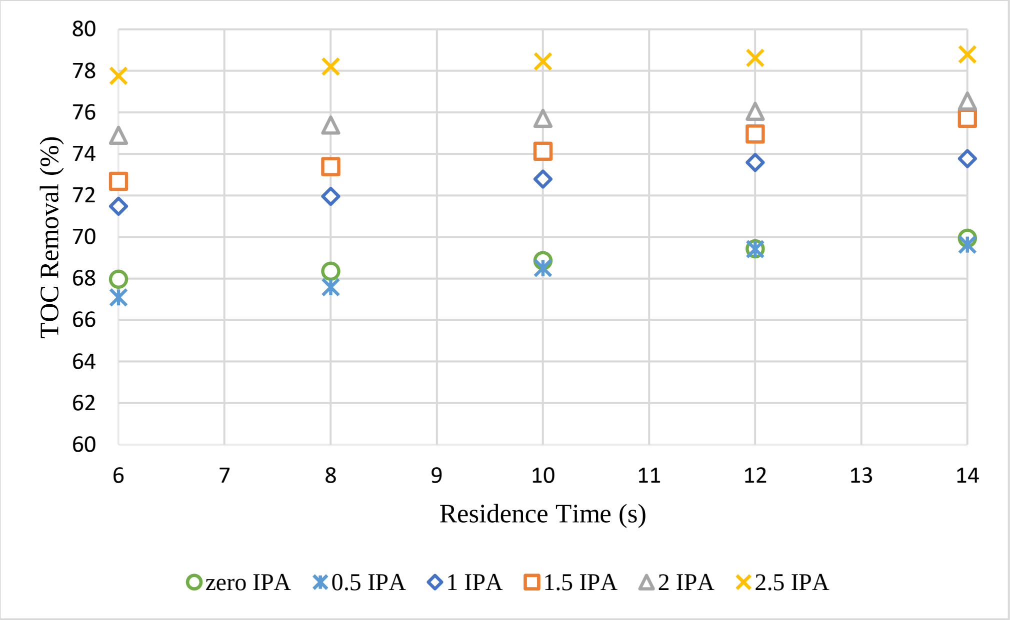


Figure 6.9: Effect of IPA ratio on the TOC removal efficiency at various residence times, 425 °C, 4 mM 3MP and SR of 1.

Results of the effect of the IPA ratio on nitrogen species are illustrated in figure 6.10, as well as the effect of IPA ratio on the nitrogen removal %. The nitrogen removal efficiency was enhanced with increasing the IPA ratio if compared with the result of the fuel-free system. The enhancement was linear with increasing IPA concentration. The influence of a 0.5 IPA ratio on nitrogen removal % was low. For example, the removal efficiency increased slightly from 74% (fuel-free system) to 77.5% at 0.5 IPA ratio, while the nitrogen removal efficiency increased to reach 87 % with increasing the IPA ratio to 2.5. This enhancement in nitrogen removal efficiency is considered a significant indicator of IPA concentration. Consequently, an increased IPA ratio would contribute to destroying 3MP and by-products. The effect of IPA on the nitrogen removal was clear, and Yang et al. (2018) have confirmed this role. The influence of IPA on nitrogen speciation was positive too. Although the NH_4-N yield was low (fuel-free system) as well as the yield of NO_2^- and NO_3^-, the reduction of NH_4-N was positive in the IPA system and improved nitrogen removal % confirmed this point. Lowered nitrogen species and total nitrogen in an aqueous solution were due to the IPA activity and it would add further heat to the reaction. In addition, 3MP is a derivative of Pyridine, therefore the main by-product was nitrogen.

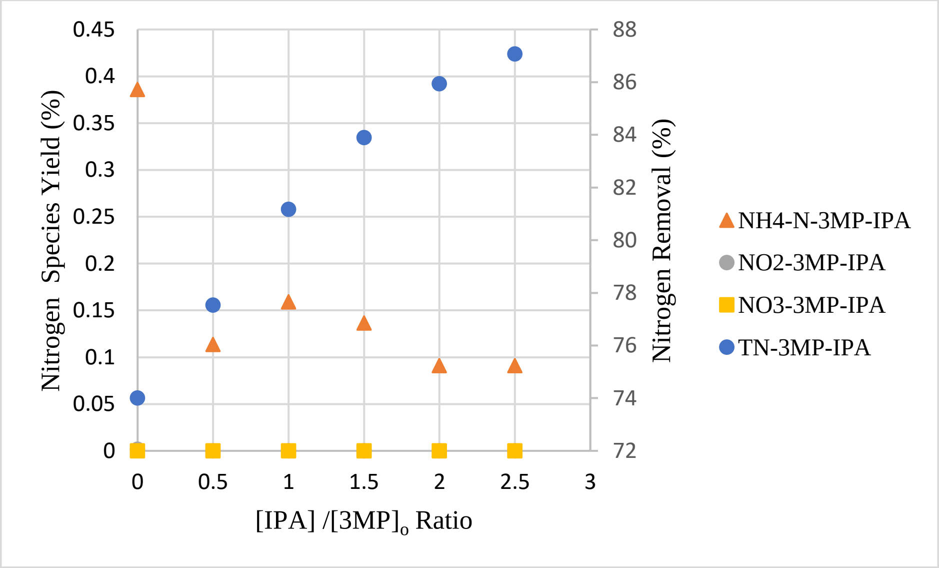


Figure 6.10: Effect of IPA ratio on the nitrogen removal efficiency and nitrogen species yield at 4 mM 3MP, 425 °C, 10 s and SR of 1.

6.3.6 Effect of Initial Concentration of 3MP

The effect of initial concentration was investigated under supercritical conditions to study the performance of SCWO when increasing the concentration of 3MP, and without using co-fuel and at 450 °C. The range of the initial concentration was 2-8 mM. Selecting this range for the initial concentration was based on the maximum flow rate of the HPLC pump, the feeding concentration, temperature and the amount of oxygen. In addition, this concentration is less than 30% wt. and would be a suitable concentration to be treated by SCWO (Fang and Xu, 2014).

Figure 6.11 shows the effect of initial concentration on the TOC removal efficiency. The enhancement of the TOC removal % was linear. TOC removal efficiency was enhanced from 64.8 % at 2 mM to 89 % at 8 mM (increased by 37 %) and 10 s because increased initial concentration accelerated the rate of the reaction at 450°C. Residence time has a slight influence on the removal efficiency. For example, TOC removal % improved from 63.5% at 6 s to 65.9% at 14 s and 2 mM. Several studies pointed out the positive effect of increasing initial concentration, such as Pinto (2004) who demonstrated the significant enhancement in TOC removal efficiency with increasing the concentration of DMF, and Qi et al. (2002) demonstrated the positive effect of the initial concentration of aniline with increasing the initial concentration. It is worth mentioning that the removal efficiency of 3MP at 14 s, 450 °C, 8 mM and 1 SR was 89.8 % and that with changing operating conditions the TOC removal efficiency would be enhanced.

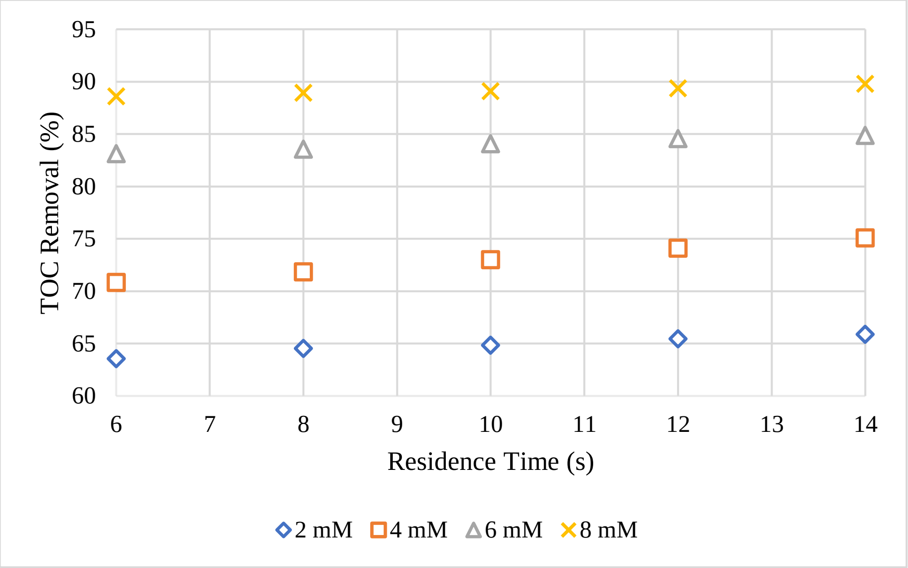


Figure 6.11: Effect of initial concentration of 3MP on the TOC removal efficiency at 450 °C, various residence times and SR of 1.

Figure 6.12 displays the effect of the initial concentration of 3MP on the nitrogen species yield and the nitrogen removal efficiency in the liquid sample. The results showed the main product was N_2. According to Yang et al. (2018), N_2 and ammonia are the main by-products of the oxidation pyridine. Thus, the results of removal efficiency of nitrogen illustrated this point and the main product of 3MP oxidation is N_2. For example, the nitrogen removal efficiency increased from 64.8 % at 2 mM to 87 % (increased by 34%) at 8 mM due to an increase in the rate of the reaction with the initial concentration. This enhancement would indicate an increase in the maximum initial concentration of more than 8 mM at 450 °C. Modifying the operating conditions would improve nitrogen removal %. The yield of NO_3^- and NO_2^- remained low. The initial concentration positively influenced the yield of NH_4-N and this yield decreased from 1.17% to 0.06%. The reduction of NH_4-N confirmed the enhancement of removal efficiency. In addition, the trend of TOC removal % was consistent with the removal efficiency of nitrogen at various concentrations.

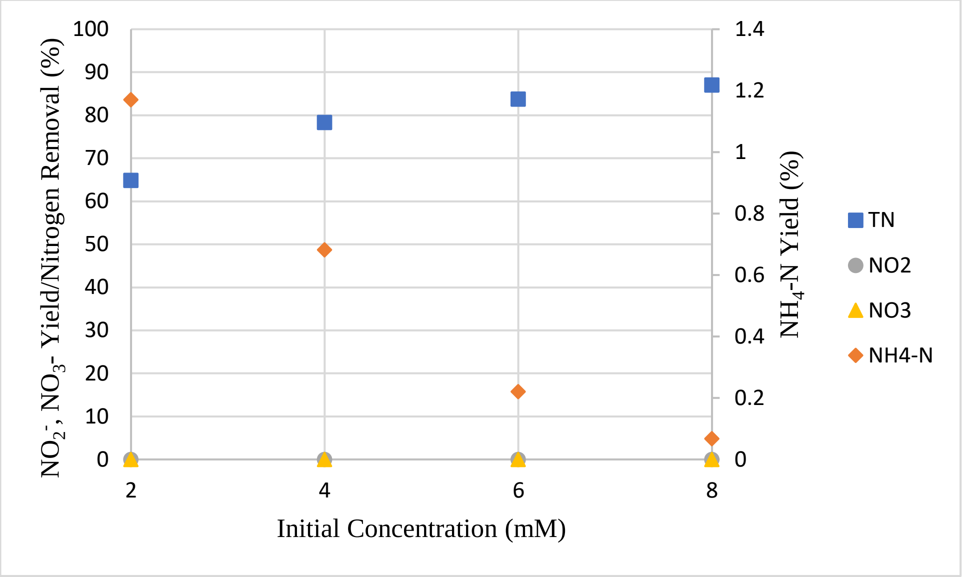


Figure 6.12: Effect of initial concentration of 3MP on nitrogen species and removal efficiency of nitrogen at 450 °C, 10 s and SR of 1.

6.4 Global Kinetics of 3MP Oxidation

It is necessary to study the global reaction rate and would supply valuable data for design purposes. The body of experimental data obtained regarding influences the various reaction parameters was employed to evaluate the reaction rates expressions namely the Arrhenius constants, rate constants and reactions orders were determined. The global rate law expression was employed to develop most SCWO kinetic models. Equation 6.4 illustrates the global rate law:

$$\frac{-d[Organic]}{dt} = k[Organic]^a[Oxidant]^b[Water]^c = Ae^{\frac{-Ea}{RT}}[Organic]^a[Oxidant]^b[Water]^c \ldots (6.4)$$

Where

k is the reaction rate constant in $M^{1\text{-}a\text{-}b\text{-}c}$ s^{-1}.

A is the pre-exponential factor in $M^{1\text{-}a\text{-}b\text{-}c}$ s^{-1}.

E_a is the activation energy in $J.mol^{-1}$.

R is the constant of universal gas (8.314 $J.mol^{-1}.K^{-1}$).

T is the reaction temperature in K.

[Organic] is the organics initial concentration in mol.L^{-1}.

[Oxidant]is the oxidant initial concentration in mol.L^{-1}.

a is the reaction order relating to an organic compound.

b is the reaction order relating to oxidant.

c is the reaction order relating to water.

Numerous SCWO kinetic studies have been accomplished for different wastes either a single model compound or a mixture of wastes under various temperatures, residence times, oxidant ratios, concentrations of organic and using various reactor designs. In this study, two methods were applied to study kinetic of 3MP:

1) Pseudo-first order approximation method
2) Integral approximation method

The medium of SCWO is water, and it formed more than 99 % of 3MP SCWO; therefore, the water concentration considers constant. In other words, the reaction order with respect to water becomes zero.

6.4.1 Pseudo-First Order Approximation Method

Numerous researchers have studied the global kinetic for SCWO either single compound or mixture organics, and they have employed Pseudo first order to describe the global kinetic. The order of the reaction is one with respect to the organic compound ($a = 1$) and zero for oxygen ($b = 0$) (Pinto et al., 2006; Abelleira et al., 2013). This model might be a simple method to describe the global kinetic, but is a suitable starting point to evaluate the reaction rate constant k. The following equation represents the global power rate law for two systems:

$$rate = \frac{-d[3MP]}{dt} = k[3MP] \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots.. (6.5)$$

The experimental results are the TOC values from 3MP oxidation, and the equation (6.5) was modified to use the TOC:

$$rate = \frac{-d[TOC_{3MP}]}{dt} = \ k[TOC_{3MP}] \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots. \dots\dots\dots\dots\dots\dots\dots (6.6)$$

After integrating this equation (6.6), the new equation can be applied:

$$\ln\left(\frac{[TOC]}{[TOC_o]}\right) = \ -k.t \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots (6.7)$$

Plotting equation (6.7) using experimental data at each temperature gives the rate constant *k* (s^{-1}) from the slope for each operating temperature as shown figures 6.13 and 6.14 for the IPA-free and IPA systems, respectively.

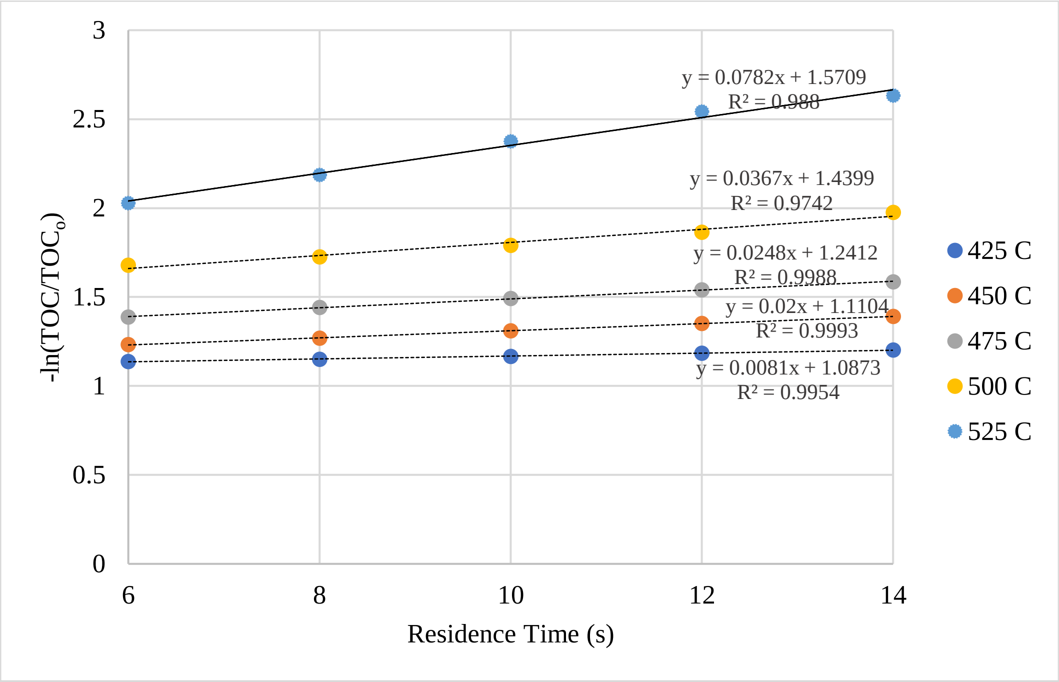


Figure 6.13: Natural logarithm of (TOC/TOC$_o$) against residence time for 3MP experiments at various operating temperatures.

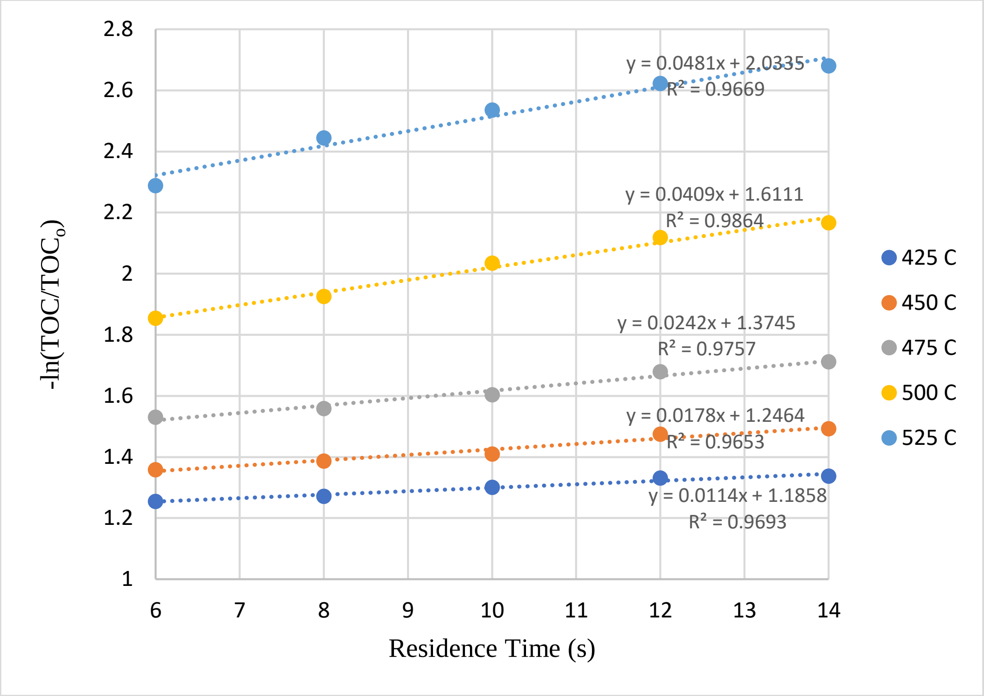


Figure 6.14: Natural logarithm of (TOC/TOC$_o$) against residence time for 3MP and IPA experiments at operating temperatures.

Then, where ln k is plotted against *1/T* as displayed in figure 6.15. From this plot E_a and *A* were evaluated to be 95295 J.mol^{-1} and 120*10^3 s^{-1} respectively. The results are shown in equation 6.8. The same procedure was followed for the IPA system and the results are displayed in figure 6.16 and equation. 6.9.

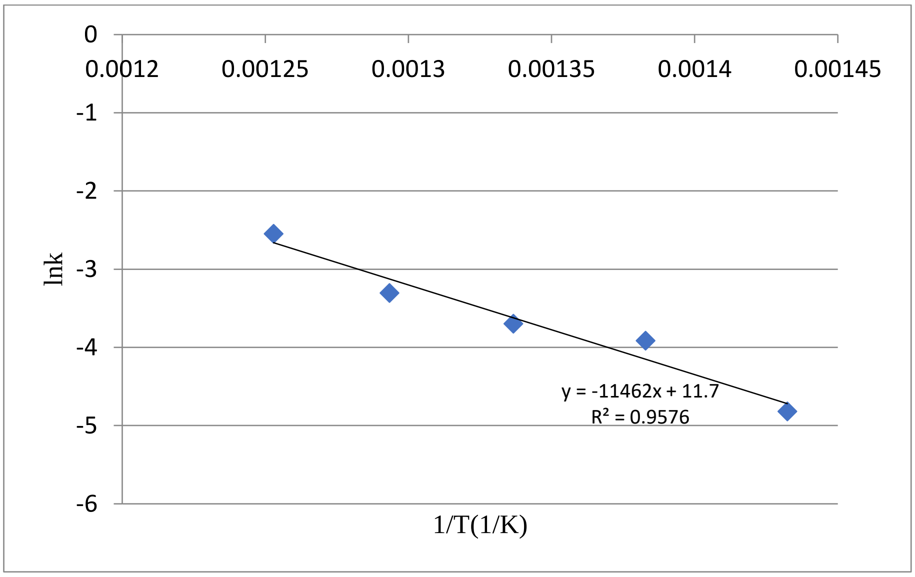


Figure 6.15: Arrhenius plot for the oxidation of 3MP.

$$rate = \frac{-d[TOC_{3MP}]}{dt} = 120.571 * 10^3 * (s^{-1}) \exp\left(-\frac{95295\frac{J}{mol}}{RT}\right)[TOC_{3MP}] \ldots\ldots\ldots\ldots(6.8)$$

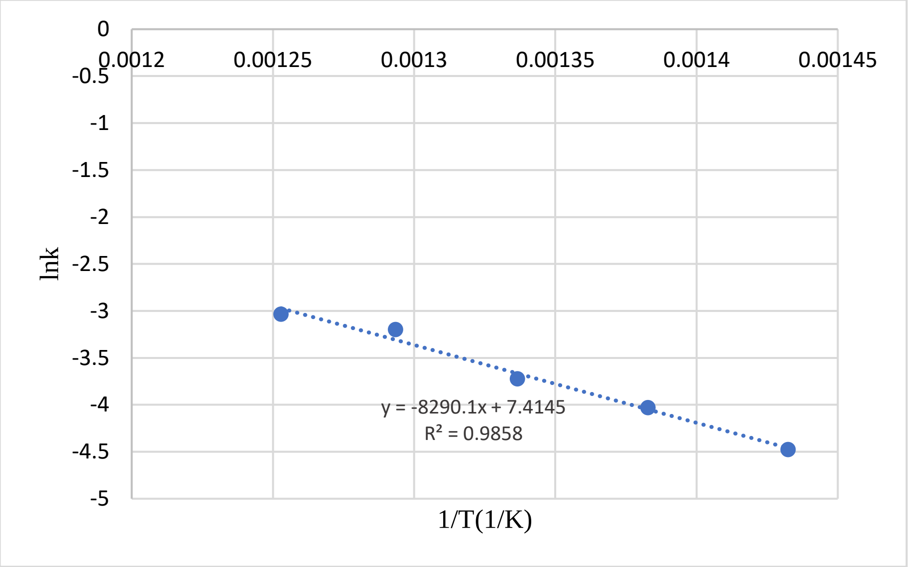


Figure 6.16: Arrhenius plot for the oxidation of 3MP and IPA.

$$rate = \frac{-d[TOC_{3MP+IPA}]}{dt} = 1659\ (s^{-1}) \exp\left(-\frac{68923\frac{J}{mol}}{RT}\right)[TOC_{3MP+IPA}] \ldots\ldots\ldots\ldots(6.9)$$

6.4.2 Integral Approximation Method

Using an integral method was to understand the global rate expression of 3MP oxidation, to express the kinetic data and to calculate the global kinetic parameters as activation energy and pre-exponential factor. These parameters for 3MP oxidation were calculated from applied a set of experiments to determine the rate of the reaction, and the order of organic was applied one. Also, the operating temperature was considered as a function for the 3MP destruction. Water formed more than 99 %, and the effect of oxygen concentration on the 3MP oxidation may be minor, but it is essential to investigate the order of oxygen. To determine the order of oxidant, four experiments were applied at 425 °C, 250 bar, and the oxidant ratio ranged from 0.75 to 2 SR (i.e the oxygen concentration range was from 23.25 mM to 62 mM while the oxygen concentration range in the presence of IPA was from 36.75 mM to 98 mM). These experiments were present in section 6.3.4. The TOC removal was enhanced with increasing the oxidant ratio thus, the effect must be investigated to determine the order of oxygen. The previous model (Pseudo first order) assumed the oxygen order zero while the oxidant experiments were illustrated the effect of oxygen. The plug flow reactor design equation was based to calculate the order of oxygen and equation 6.4 is rearranged by using integral method with a = 1 and b > zero:

$$-rA = \frac{-d[3MP]}{dt} = k[3MP][O_2]^b = Aexp^{\left(-\frac{Ea}{RT}\right)}[3MP][O_2]^b \ldots\ldots\ldots\ldots\ldots\ldots\ldots.\ldots\ldots\ldots\ldots\ldots\ldots (6.10)$$

The assumption can consider the concentration of oxidant constant. The plug flow reactor equation for steady state was applied (Levenspiel, 1999) to be:

$$\frac{t}{[3MP]_o} = \int_0^x \frac{dx_{3MP}}{(-rA)} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (6.11)$$

t is a residence time, [3MP]₀ is an initial concentration, (-rA) is a rate of reaction of 3MP oxidation. The following equation is substituting integral method equation (6.10) in the plug flow reactor performance equation.

$$\ln\left(\frac{1}{(1-X_{TOC})}\right) = k.t[O_2]_0^b \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots.\ldots\ldots\ldots\ldots\ldots\ldots. (6.12)$$

Then, in order to determine the value of b, it is necessary to find the slopes of fitted straight lines of 3MP oxidation for four experiments at 425 °C, from plotted ln (1/1-X_{TOC}) against the residence time (t). The results of two systems are shown in figures 6.17 and 6.18. The slopes of lines represent $k[O_2]_0^b$. This term can be written after taking the natural logarithm to be:

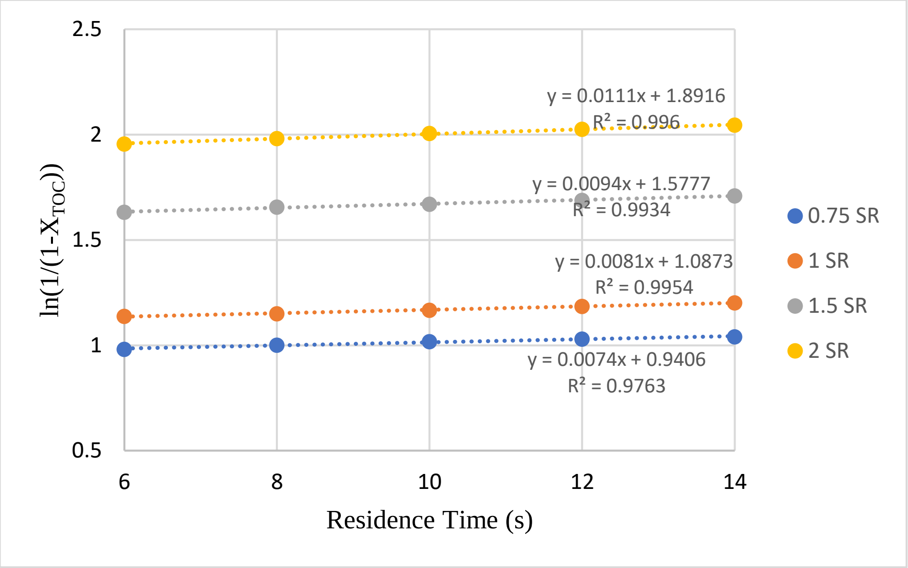


Figure 6.17: Natural logarithm of $(1/(1-X_{TOC}))$ versus residence time for 3MP experiments with varying oxidant concentrations.

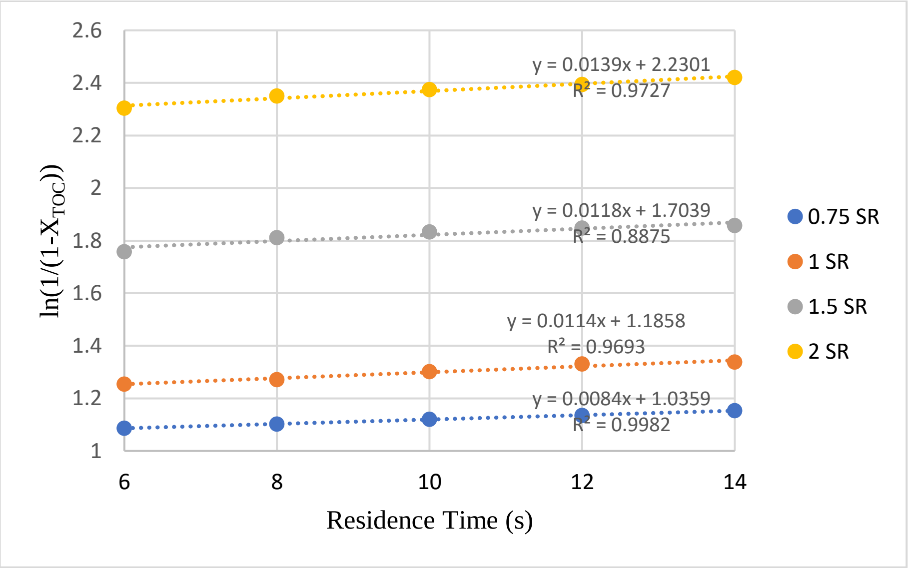


Figure 6.18: Natural logarithm of $(1/(1-X_{TOC}))$ versus residence time for 3MP +IPA experiments with varying oxidant concentrations.

$$\ln(k[O_2]_o^b) = \ln(k) + b\ln([O_2]_o) \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots . (6.13)$$

From figure 6.17 and 6.18, these slopes are plotted versus the concentration of oxygen to generate a straight line for the 3MP system and the 3MP and IPA system. The slope of each line represents b value for each system.

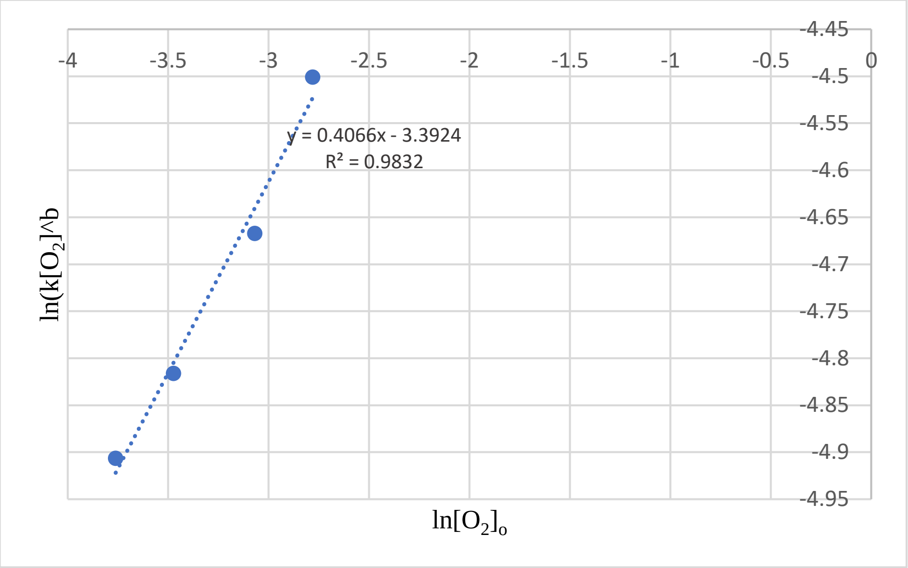


Figure 6.19: Determination of oxygen reaction order (3MP system).

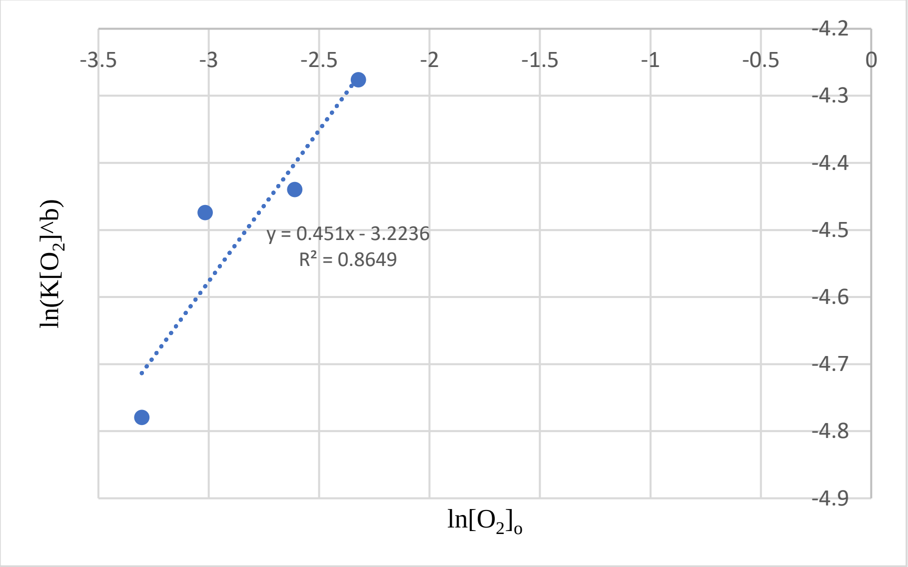


Figure 6.20: Determination of oxygen reaction order (3MP+IPA system).

The order of oxygen represents the slope of straight line in Figures 6.19 and 6.20. The determination of reaction orders was (a =1, b_{3MP}= 0.40, $b_{3MP+IPA}$= 0.45). It is easy to determine the rate of the reaction by applying the equation (6.12) to be:

$$k = ln\frac{1}{(1-X_{3MP})} \times \frac{1}{t} \times \frac{1}{(O_2)^{0.4}} \quad \ldots \ldots \ldots (6.14)$$

$$k = ln\frac{1}{(1-X_{3MP+IPA})} \times \frac{1}{t} \times \frac{1}{(O_2)^{0.45}} \quad \ldots \ldots \ldots (6.15)$$

The new *k* values (for two systems) are employed to determine the E_a and *A*, plotting the natural logarithm of the rate of reaction (*k*) versus inverse temperature (1/T) is shown in figures 6.21 and 6.22. The E_a was calculated by multiplying the universal gas constant (8.314 $J.mol^{-1}.K^{-1}$) by multiplying the slope. *A* was calculated from ln *A*= intercept. Equations 6.16 and 6.17 illustrate the value of E_a and *A* in the generated global rate expression of 3MP oxidation and 3MP and IPA oxidation.

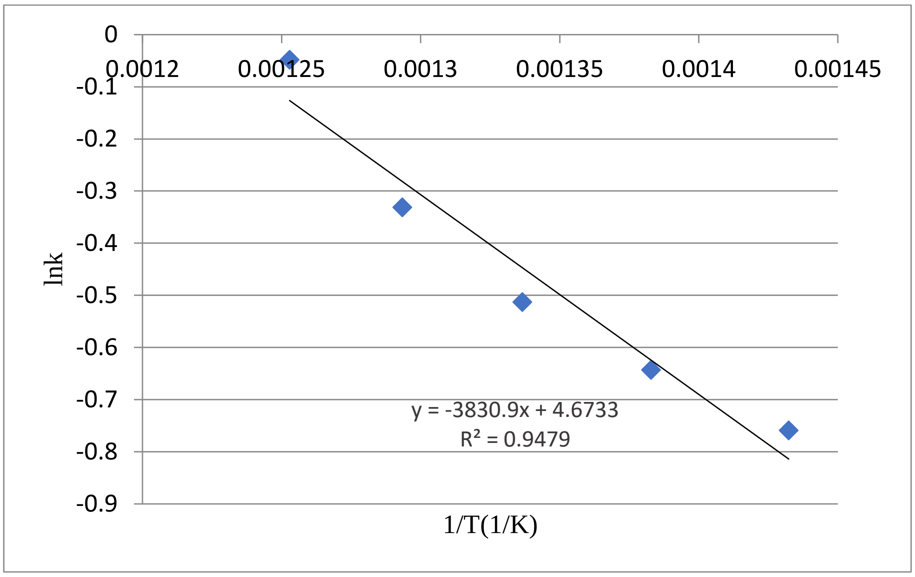


Figure 6.21: Arrhenius plot for 3MP oxidation

$$rate = -\frac{d[TOC_{3MP}]}{dt} = 107\ (M^{-0.4}s^{-1})\exp\left(-\frac{31850\frac{J}{mol}}{RT}\right)[TOC_{3MP}][O_2]^{0.4} \ldots (6.16)$$

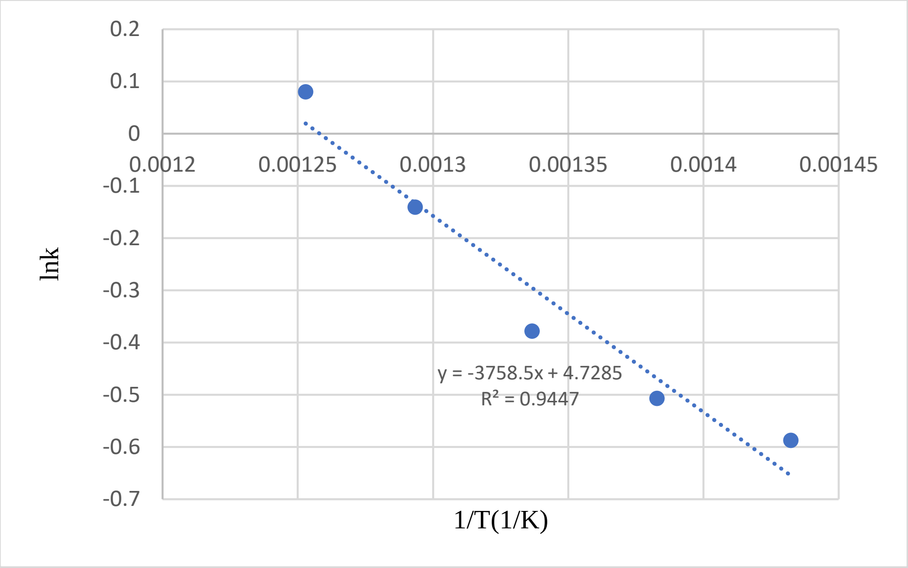


Figure 6.22: Arrhenius plot for 3MP and IPA oxidation.

$$rate = -\frac{d[TOC_{3MP+IPA}]}{dt} = 113\ (M^{-0.45}s^{-1})\ \exp\left(-\frac{31248\,\frac{J}{mol}}{RT}\right)[TOC_{3MP}][O_2]^{0.45} \ldots (6.17)$$

The order of oxygen was 0.4 and 0.45 for IPA free and IPA systems respectively that indicated to the effect of oxidant on the 3MP oxidation and 3MP+IPA oxidation, consequently applying integral method could consider an appropriate way to understand the kinetics of 3MP and 3MP+IPA.

6.5 Summary

- 3MP is a derivative of pyridine that is considered a compound that is resistant to supercritical water conditions. The effect of operating temperature on the TOC removal efficiency was positive in the fuel-free system and IPA system. The high removal efficiency of TOC was 93% at 525 °C in the presence of IPA. Nitrogen species were low at 425 °C and NH_4-N increased with increasing temperature in the fuel-free system. The removal efficiency of nitrogen in the liquid sample was enhanced with increasing temperature due to the nitrogen in 3MP converted to N_2. The maximum removal efficiency of nitrogen at 525°C reached 82% (fuel-free system) and 85.7% (IPA system).

- The effect of oxidant ratio on the conversion of TOC was significant in the two systems. In the presence of IPA, the removal efficiency of TOC was enhanced with increasing the oxidant ratio, but the effect of IPA was not essential, due to resistant compound of 3MP and it needs to increase the concentration of IPA. The effect of the oxidant ratio on nitrogen removal efficiency was significant in the presence of IPA.
- The effect of the residence time was of interest at various temperatures, oxidant ratios, IPA ratios and initial concentrations.
- The ratio of IPA has a positive effect on TOC removal efficiency the nitrogen removal efficiencies when increased this ratio to more than 1. The maximum efficiency of TOC removal was 78% at a 2.5 IPA ratio. The influence of IPA was slightly significant on TOC removal at 425 °C.
- The effect of initial concentration on the TOC removal and nitrogen removal efficiencies was significant at 450°C. The maximum TOC removal efficiency was 89 % at 8 mM and 10s. The initial concentration positively influenced the reduction of the NH_4-N yield. Also, the removal efficiency of nitrogen significantly improved with increasing the concentration of 3MP.
- Two methods were employed to study the kinetics analysis for the two systems. The integral approximation method is essential to describing the kinetics analysis of the IPA free system and IPA system, where the order of oxygen has a value greater than 0 (b_{MEA} = 0.40 and $b_{MEA+IPA}$= 0.45) and the oxidant influenced the destruction of 3MP and 3MP in the presence of IPA. Moreover, the results of this method illustrated a slight effect of IPA on the reduction of $E_{a,}$ which reduced from 31850 $J.mol^{-1}$ (fuel-free system) to 31248 $J.mol^{-1}$.

CHAPTER SEVEN: SUPERCRITICAL WATER OXIDATION OF 3METHYLPYRIDINE (3MP) IN THE PRESENCE OF PROPYLENE GLYCOL (PG) AS CO-FUEL

7.1 Introduction

This chapter displays the effect of PG on SCWO of 3MP under various operating conditions and discusses the effect of selected operating conditions as temperature, oxidant ratio, organic concentration and residence time on the removal efficiency of 3MP and by products. In addition, study the kinetic of this case and find the effect PG on Arrhenius parameters would contribute to increase the understanding the behaviour of co-fuel and feasibility of SCWO. It also shows a comparison between the effects of IPA and PG on 3MP under different operating temperatures, oxidant ratios and co-fuel/3MP ratios.

7.2 Effect of System Operating Conditions

In this chapter, the SCWO process diagram and experimental procedures were previously illustrated in chapter three.

7.2.1 Experimental Work Plan

In this section, the solution of 3MP, PG and water was employed to carry out SCWO experiments at different temperatures, residence times, oxidant stoichiometric ratios, feed concentrations. Each parameter was individually examined at 4 mM of 3MP and SR of 1. The operating pressure was applied 250 bar during all experiments to obtain on supercritical phase. Table 7.1 explains the summary of operating condition ranges.

Table 7.1: Summary of the operating conditions used in SCWO of 3MP and PG experiments.

Variable	Range	Fixed conditions
Temperature (°C)	425 - 525	$[3MP]_o = [PG]_o$= 4 mM SR = 1SR
$[3MP]_o=[PG]_o$ mM	2 - 8	Temp = 450 ℃ SR = 1SR
Oxygen Ratio	0.75 - 2 SR	$[3MP]_o=[PG]_o$= 4 mM Temp = 425 ℃
Ratio $[PG]_o/[3MP]_o$	0.5 – 3	Temp = 425 ℃ SR = 1SR $[3MP]_o$=4 mM
Residence time: 6-14 s for all experiments		

7.2.2 Effect of Residence Time

The range of the residence time was selected to assess the removal efficiency of 3MP from 6 s to 14 s, keeping the turbulent flow regime at different residence times. In other words, the flow rate in the reactor was a turbulent flow at a high residence time and different temperatures; the short residence time was 6 s because the maximum flow rate could be delivered at 20 ml.min^{-1} by an HPLC pump. Also, the oxidant ratio and organic concentration were considered to set up the range of residence times. During all runs, the stabilisation time was set at 15 to 30 min to obtain accurate residence times as flow rates were fed. The effect of residence time on the TOC removal of 3MP oxidation (PG system) displays in Figure 7.1. It was observed that the TOC removal efficiency during the long residence time of 14s was better than the removal efficiency during the short residence time of 6s because the increase in the reaction time for the reactants (organic molecular and oxidant molecular) will improve the TOC conversion. However, the effect of the residence time on the removal efficiency has been demonstrated in several studies in this field (Savage et al., 2000; Qi et al., 2002; Ploeger et al., 2006).

The effect of the residence time was significant at different operating temperatures. At 425 ℃, the TOC conversion increased with the increase in the residence time from 81.9 % at 6 s to 84.9 % at 14 s (increased by 3.6 %) to provide enough time for the reaction between organic and oxidant molecules. At 525 °C, the TOC removal efficiency increased from 94.9 % at 6 s to 97.5 % at 14 s (increased by 2.7 %). The enhancement of the TOC removal efficiency was positive with the residence time, and the temperature of 525 °C at different residence times would reduce this effect. Also, at 525 °C, the rate of reaction and solubility of organic material improved at various residence times. However, the main advantage in SCWO is the destruction of an organic substance in the short residence time compared with biological treatment methods that need a long residence time and do not have complete removal efficiency. 3MP was treated by ozonation and biological treatment methods and the maximum degradation of initial concentration was 75% at 80 min (in the ozone unit).

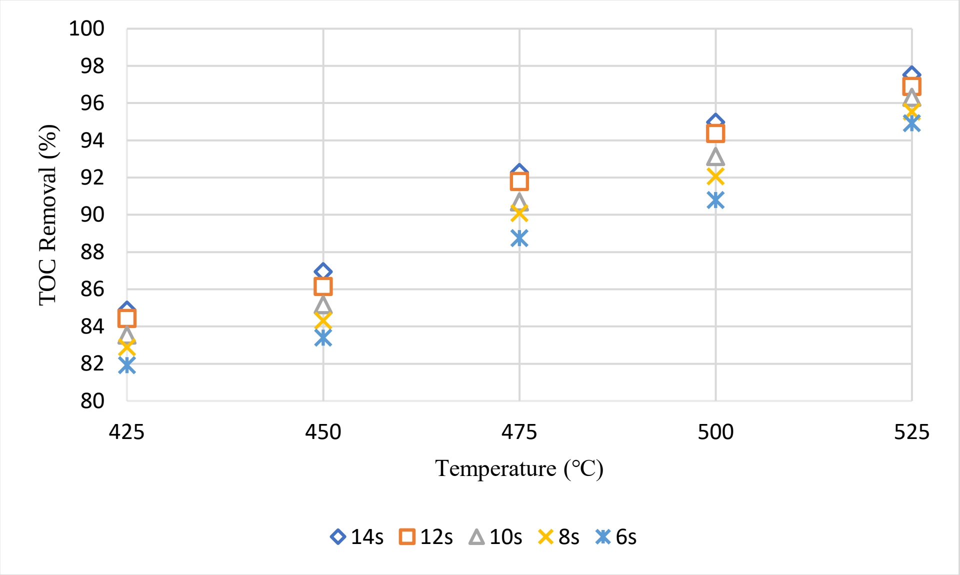


Figure 7.1: Effect of residence time on the TOC removal efficiency at various temperatures, 4 mM 3MP, 4 mM PG, SR of 1.

The increased operating temperatures at various residence times enhanced the removal efficiency of organic compounds in three systems. Also, the influence of PG and IPA on the TOC removal efficiency was consistent at 425 °C and 525 °C. The improvement of the TOC removal efficiency in a fuel-free system at 525 °C confirmed the residence time would improve the TOC removal efficiency at a high temperature.

7.2.3 Effect of Operating Temperature

A range of operating supercritical temperatures was applied to study the effect of temperature on the 3MP and PG oxidation from 425 °C to 525 °C, and the initial concentration of 3MP was 4 mM. The residence time ranged from 6 s to 14 s, and the oxidant ratio was 1SR. The selection of the range of operating temperatures was based on the thermal ability of the furnace and keeping the turbulent flow regime at various temperatures and residence times.

Figure 7.2 displays the effect of the range of different temperatures on the TOC conversion at the range of residence times in the presence of PG. As expected, it was observed that the essential role of temperature was to improve 3MP oxidation. The enhancement of the destruction of 3MP was consistent with the role of the operating temperature in numerous studies under supercritical water conditions (Wang et al., 2011; Qi et al., 2002; Yu et al., 2015). The effect of PG was remarkable with the range of temperatures.

For example, the TOC removal efficiency in the presence of PG was enhanced from 81.9 % at 6 s and 425 ℃ to 94.9 % at the same residence time and 525 ℃. With the long residence time of 14s, the TOC removal efficiency was enhanced from 84.9 % at 425℃ to 97.5 % at 525 ℃. The high operating temperature improved the destruction of 3MP. The solubility of organics increased with temperature and the generation of free radicals also increased with temperature. Besides the operating temperature, PG was a remarkable source to feed the reaction with powerful free radicals. These radicals attack the organic molecules and accelerate the destruction of organic substances. Consequently, the rate of reaction is enhanced due to the increase in free radicals and the increases the operating temperature. The destruction of 3MP at a low temperature would make SCWO a competitive technology with which to treat 3MP.

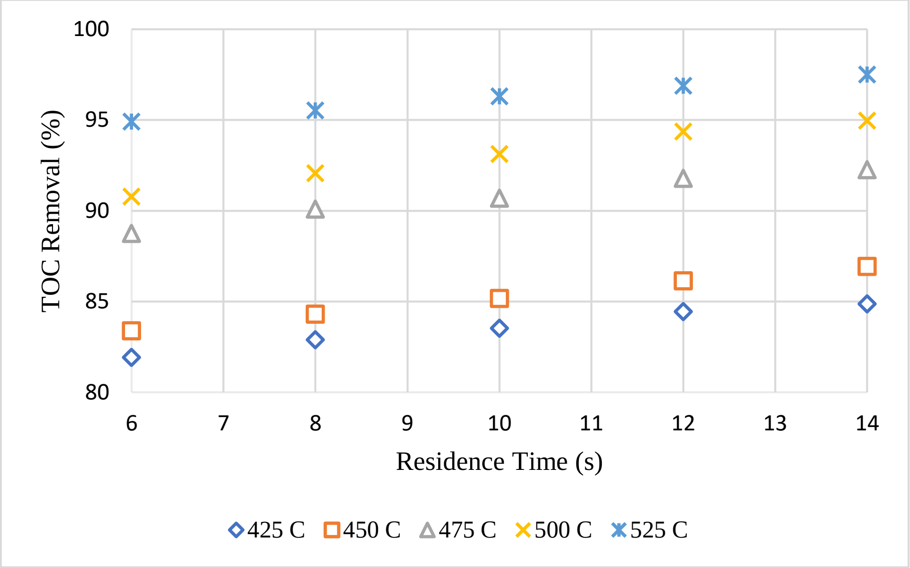


Figure 7.2: Effect of various operating temperatures on TOC removal % at various residence time, at 4 mM 3MP, 4 mM PG SR of 1.

The results of the fuel-free system, IPA system, and PG system demonstrated that the influence of two hydroxyl groups in PG on the TOC removal percentage was remarkable. The effect of IPA in this work was slightly significant, and the enhancement of the COD removal percentage (IPA +MEA system) was due to MEA being a simple aliphatic and non-resistant compound. The comparison between the TOC removal efficiencies in three systems at 10 s is shown in Figure 7.3. The effect of the operating temperature on the removal efficiency was positive. The increase in temperature contributed to enhancing the removal efficiency in three systems. The findings of the efficiency of TOC removal show that the essential point, including the number of hydroxyl groups in PG, can generate several reaction pathways (Yang et al., 2018). The rate of reaction would increase due to the addition of the co-fuel (Bermejo et al., 2008). For example, the TOC removal efficiency at 425 °C increased from 68.8 % (fuel-free system) to 72.7 % (IPA system) (increased by 5.6 %) to reach 83.5 % (PG system) (increased by 21%). In other words, the increase in the removal efficiency in the presence of PG was four times that for IPA. This enhancement in the removal efficiency confirmed the positive effect of PG. Also, 3MP is a highly resistant compound. Thus, the destruction of 3MP would be considered a challenge for testing the feasibility of PG. Finally, modifying the operating conditions, such as the increase in temperature, oxidant ratio, and PG concentration, would enhance the removal efficiency at 425 °C. The removal of 3MP at a low temperature is a significant goal.

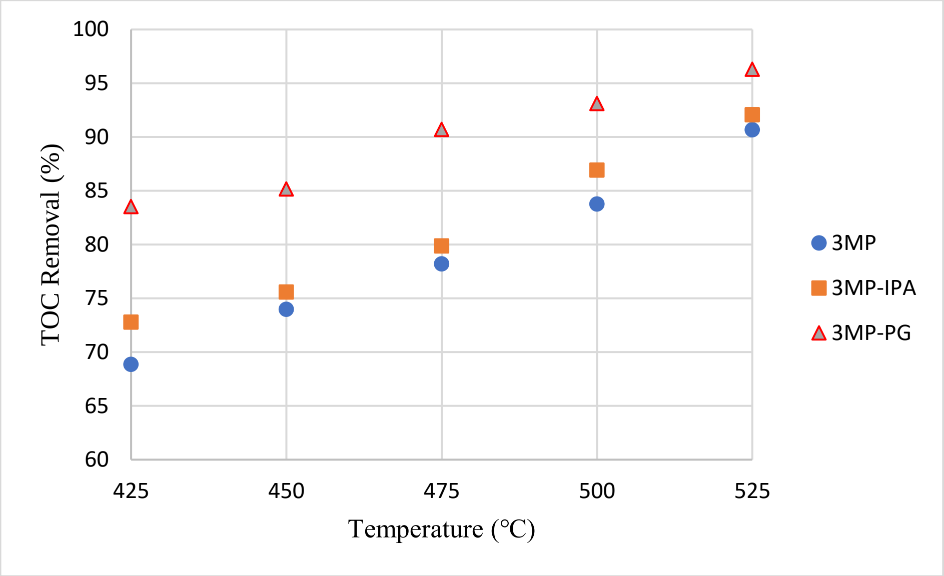


Figure 7.3: Effect of the operating temperature on the TOC removal efficiency at 10 s, 4 mM 3MP, 4 mM IPA, 4 mM PG, and SR of 1.

Figure 7.4 shows the effects of the operating temperatures on nitrogen species in three systems at 10 s. In the PG system, NH_4-N and NO_3^- were the main by-products of 3MP oxidation in the liquid sample; it was also observed that the yield of NH_4-N increased with the temperature, but it was less than the yield of NH_4-N in the fuel-free system. While the NO_3^- yield occurred more than the yield of NO_3^- in the fuel-free system and the IPA system at 425 °C. Then, the yield of NO_3^- decreased with the increasing temperature. There are two reasons for the increase in the yield of NO_3^- at 425 °C: the increased conversion of 3MP led to an increase in the yield of NH_4-N and, according to Segond et al. (2002), ammonia is oxidised to NO_3^- (minority) and N_2 (majority). The second reason and according to Cocero et al. (2000), NO_3^-, NO_2^-, and N_2O occurred with the increase in the oxidant ratio. In other words, the oxidation of PG was a remarkable source of free radicals. The enhancement in the efficiency of TOC removal in the presence of PG illustrated the advantage of PG. The NH_4-N yield decreased with the increasing temperature in the presence of PG due to the influence PG on by-products of 3MP at high temperatures and consuming a high percentage of oxygen. Although the reduction in NH_4-N was only slight in the presence of PG due to the TOC removal efficiency of 96 % at 10 s and 525 °C, the destruction of 3MP requires high temperatures or an increase in the oxidant ratio to provide enough oxygen to destroy 3MP and their by-products. The comparison between the yield of NH_4-N from MEA and 3MP led to the yield of ammonia from 3MP oxidation being less than the yield of ammonia from MEA because the MEA structure contains an amino group. Consequently, the yield of ammonia from 3MP would be considered low, and the nitrogen in 3MP was converted to N_2. For example, the yield of NH_4-N increased from 0.1 % at 425 °C to 8 % at 525 °C. The yield of NO_3^- decreased from 9 % at 425 to 0.9 % at 500 °C while the yield of NO_2^- remained low.

The comparison of three systems illustrated that the yield of NH_4-N slightly decreased at a high temperature in the PG system. This is a positive effect of PG on nitrogen speciation with the increase in the operating temperature, but this enhancement in the reduction of ammonia in the presence of PG was more than IPA at 525 °C; the NO_2^- yield was still low in the three systems. The NO_3^- yield increased in the presence of PG if compared with the findings of the fuel-free system and the IPA system.

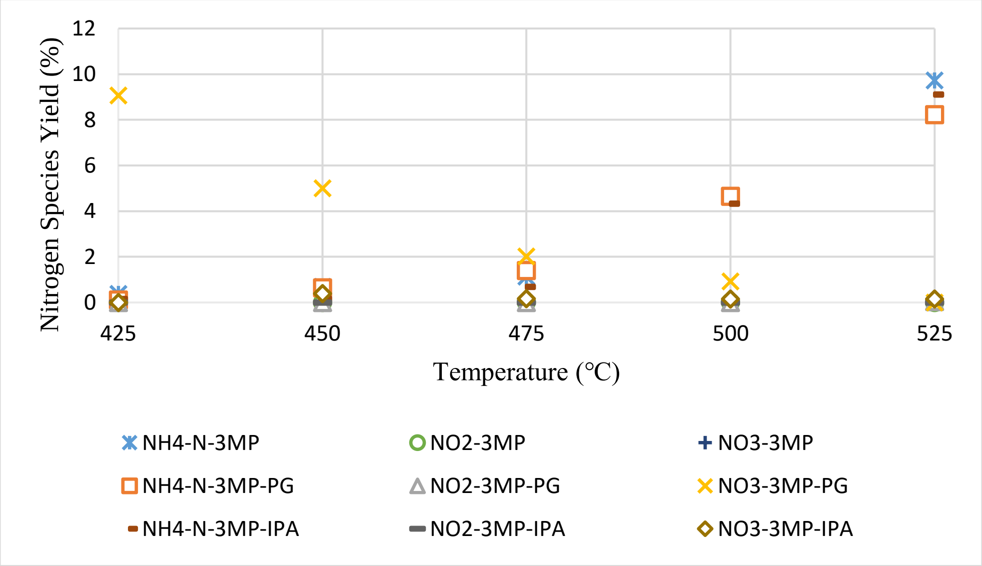


Figure 7.4: Nitrogen species yield as a function of various operating temperatures at 4 mM 3MP, 4 mM PG, 4 mM IPA, SR of 1 and 10 s.

Figure 7.5 displays the nitrogen removal efficiency in the three systems. The nitrogen removal in the presence of PG was improved with the increase in the operating temperature due to the increase in the rate of the reaction, and abundant of powerful radicals that attack and mineralise organic molecules to carbon dioxide, water, and N_2. According to Yang et al. (2018) and Al-Duri et al. (2016), co-fuel would add further heat to the reaction to improve the removal of nitrogen. For example, the removal efficiency of nitrogen was enhanced from 82 % at 425 ℃ to 89 % at 525 ℃ in the PG system and at 10 s (it increased by 8.5 %). The high temperature and PG contributed to the increase of the nitrogen removal efficiency. The increment of nitrogen removal in the presence of PG was 10.8 % while in the presence of IPA, it was 9.4 % at 425 ℃ and 10 s. Consequently, PG has a significant role in improving nitrogen removal efficiency more than IPA.

In summary, the PG has improved the TOC removal efficiency and slightly reduced NH_4-N as well as significantly improved the nitrogen removal in comparison with the role of IPA. Consequently, the effect of temperature and PG significantly enhanced SCWO performance. According to several studies, the results of the effect temperature on the TOC removal efficiency in the three systems was consistent with the effect of the temperature on DMF, DBU, and aniline (Al-Duri et al., 2015; 2016; Qi et al., 2002). The structure of 3MP contributes to the production of N_2 as the main gaseous product. Finally, if the results of SCWO are compared with various treatment methods, SCWO would be a competitive method for the destruction of 3MP in a short residence time with high removal efficiency. Also, the feasibility of using PG as the co-fuel is important as it improves the TOC removal efficiency and nitrogen removal efficiency more than IPA.

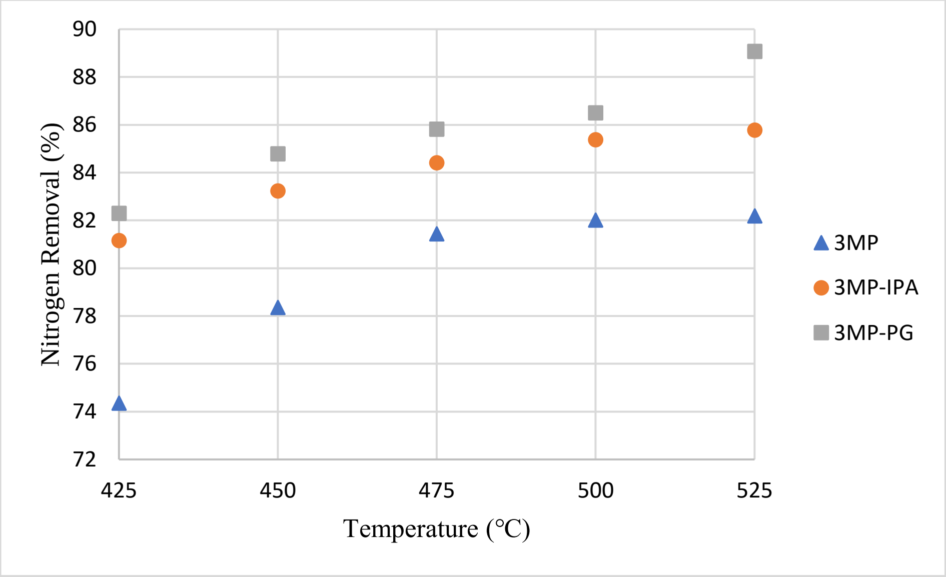


Figure 7.5: Effect of various operating temperatures on the nitrogen removal efficiency in three systems at 4 mM 3MP, 4 mM PG, 4 mM IPA, SR of 1 and 10 s.

7.2.4 Effect of Oxidant Ratio

The oxidation equations for the oxidation of 3MP and IPA systems are in chapter six (equations 6.1 and 6.2), and the oxidation equation for oxidation PG is:

$C_3H_8O_2 + 4O_2 \rightarrow 3CO_2 + 4H_2O$……………………………………….………………... (7.1)

In this work, the effect of the oxidant ratio on the TOC removal efficiency and nitrogen species was investigated. Various amounts of oxygen were employed to oxidise 3MP and PG to complete the destruction at 425 °C. The effect of the oxidant ratio is an essential factor, according to the literature. In the PG system, the amount of oxygen represents sufficient oxygen for oxidising 3MP and PG, which is based on the concentration of 3MP and PG under various supercritical conditions to determine the amount of oxygen. The range of the oxidant ratio was from 0.75 to 2 SR. However, the increased oxidant ratio increases the cost of the oxidant and generates unwanted products like N_2O (Al-Duri et al., 2016). Also, the selected range of oxidant ratio was based on the capacity of the HPLC pump.

The effect of the oxidant ratio on the TOC removal efficiency was consistent with the increase in oxygen in the presence of PG. The TOC removal efficiency was enhanced by increasing the oxidant ratio from 0.75 SR to 2 SR. Also, the effect of the oxidant ratio on nitrogen removal was significant. Figure 7.6 shows the enhancement of the TOC removal. The enhancement of the efficiency of TOC removal due to the abundance of radicals that play an essential role in increasing the rate of oxidation as well as PG is considered a remarkable source for generating free radicals such as $HO^{\bullet}$ and $HO_2^{\bullet}$. Two hydroxyl groups are active and generate several reaction pathways (Yang et al., 2018). The free radical mechanism is a predominant reaction under supercritical conditions (Pinto et al., 2006). For example, at 0.75 SR, the efficiency of the TOC removal increased from 75 % at 6 s to 89.8 % (it increased by 19.7%) in the PG system and 2 SR, and the efficiency of the TOC removal increased from 78 % at 14 s and 0.75 SR to 91.9 % (it increased by 17.8%) in the presence of PG and 2 SR. Also, the effect of residence time on the TOC removal was positive. Consequently, the effect of the oxidant ratio, PG, and residence time remarkably improved the TOC removal efficiency at 425 °C and 2 SR and will avoid the use of high temperatures.

The comparison between the results of the three systems to assess the effect of the oxidant ratio on the TOC removal efficiency demonstrated the significant effect of PG on the TOC removal. This effect has a positive trend with the increase in oxygen, and PG played an essential role in enhancing the TOC removal at 0.75 to 2 SR. For example, at 0.75 SR and 10 s, the TOC removal was enhanced from 63.8 % (fuel-free system) to 67 % (IPA system) (it increased by 5 %), while in the presence of PG, the removal efficiency increased to 77 % (it increased by 20.6 %). The increase in the efficiency of TOC removal in the presence of the PG system was four times more than that in the presence of IPA. In other words, the oxidant ratio and PG have a positive effect on the TOC removal efficiency at 0.75 SR. However, two hydroxyl groups in PG influenced the TOC removal more than IPA. Consequently, the enhancement of TOC removal in the presence of PG is considered an essential goal at 425 °C to reduce the input power.

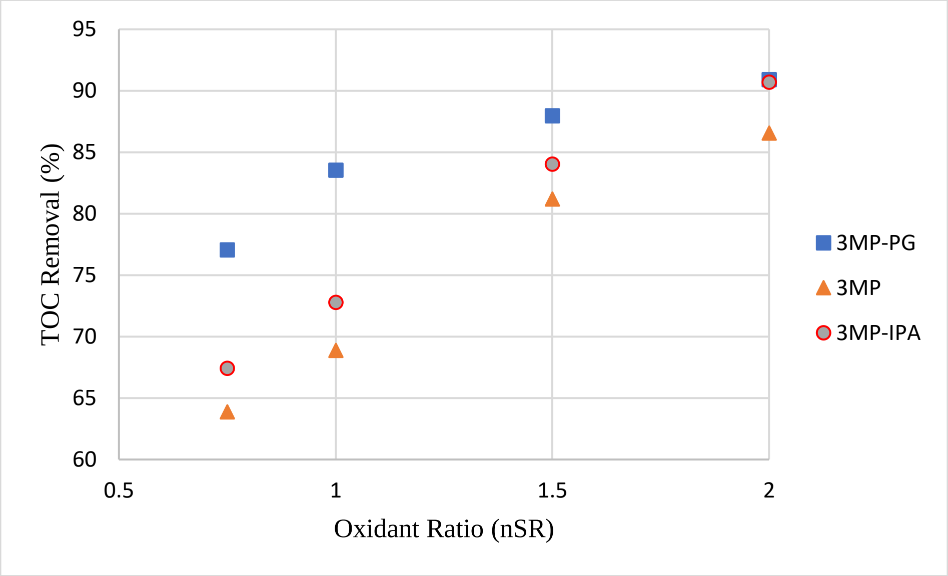


Figure 7.6: Effect of the oxidant ratio on TOC removal % at 10s, at 425 °C, 4 mM 3MP, 4 mM PG and 4 mM IPA.

The results in Figure 7.7 show nitrogen species in a liquid sample at various oxidant ratios in the presence of PG and these results are compared with the results of the IPA free system and the IPA system. The results demonstrated the yield of NH_4-N decreased with the increase in the oxidant ratio due to the increase in generating free radicals. Also, PG contributed to the generation of free radicals such as $HO^{\bullet}$ and $HO_2^{\bullet}$. Despite the yield of NH_4-N decreasing with the increase in the oxidant ratio, it was still low because the main product of the oxidation of pyridine was N_2 and ammonia (Yang et al., 2018). In other words, the increased yield of NO_3^- in the presence of PG was because the ammonia was oxidised to N_2 and NO_3^-. Increased NO_3^- in the presence of PG would be considered a significant advantage and positive indicator of the further oxidation of ammonia at 425 °C. For example, the yield of NO_3^- decreased with increase in the oxidant ratio from 14 % to 4.7 %. The NO_2^- yield was low in two systems. However, increasing the oxidant ratio to more than 2 SR would treat the by-product of 3MP and improve the organic substance removal efficiency.

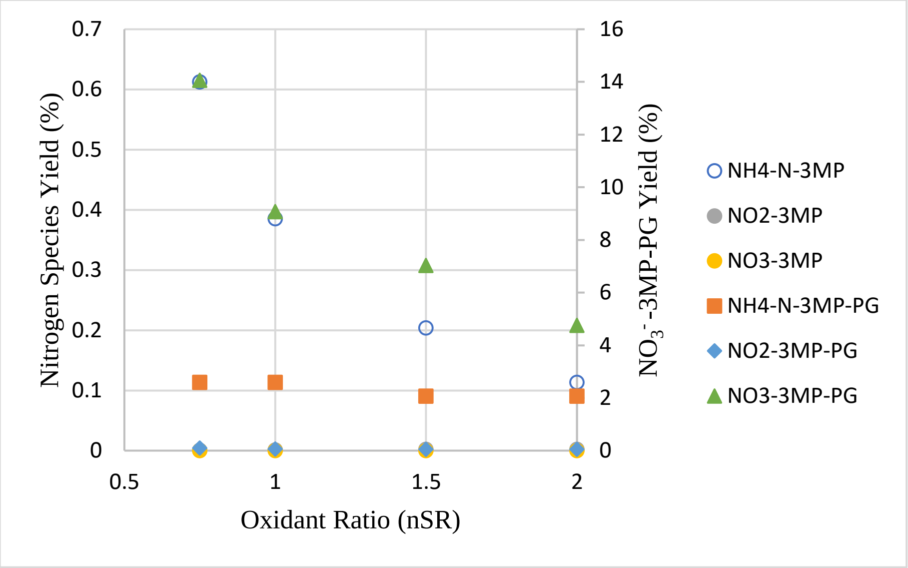


Figure 7.7: Effect of various oxidant ratios on nitrogen species in two systems at 10 s, 425 °C, 4 mM 3MP and 4 mM PG.

The effect of the oxidant ratio on nitrogen species has been investigated in three systems. The role of PG was significant in the enhancement of the TOC removal efficiency at low 0.75 SR. The effect of PG on NH_4-N was positive despite the low yield of NH_4-N in the absence of co-fuel, but the reduction in the yield of NH_4-N in the presence co-fuel was observed. The NO_3^- yield occurred in the PG system. The efficiency of the nitrogen removal illustrated the effect of the oxidant ratio and PG and IPA on nitrogen.

Figure 7.8 shows the effect of the oxidant ratio on the removal efficiency of nitrogen in the three systems. The nitrogen removal efficiency in the PG system was improved due to the increase in the oxidant ratio. The results show that the role of PG is positive compared with IPA. According to Yang et al. (2018), the heat reaction of IPA would enhance the removal efficiency of nitrogen more than ethanol and methanol. The heat of the reaction for PG and IPA are -1822 kJ.mol^{-1} and -1908 kJ.mol^{-1} respectively.

The trend of the nitrogen removal efficiency in Figure 7.8 is linear, and this trend promotes the advantage of the increased oxidant ratio. For example, the removal efficiency of nitrogen was enhanced from 68.9 % in the fuel-free system to 76.8 % (it increased by 11.4%) in the presence of PG at 425 °C, 10 s, and 0.75 SR, while in the presence of IPA, the nitrogen removal efficiency was 76 % (it increased by 10 %). At 2 SR, the removal efficiency increased from 85 % in the fuel-free system to 90 % in the presence of PG, while in the presence of IPA, the removal efficiency of nitrogen reached 88 %. The results show the effect of PG was more significant than those for IPA.

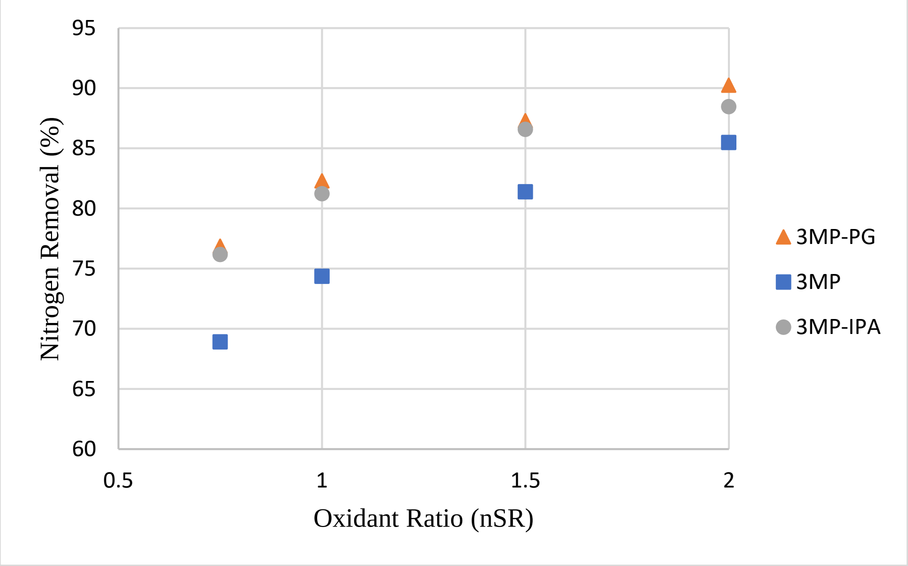


Figure 7.8: Nitrogen removal efficiency as a function of various oxidation ratio at 4 mM 3MP, 4 mM PG, 4 mM IPA, and 10 s.

7.2.5 Effect of $PG_o/3MP_o$ Ratio

The destruction of 3MP at 425 °C is considered a challenge due to this organic compound's derivation from pyridine. Different operating conditions have been applied to destroy 3MP such as a high temperature of 525°C, increasing the oxidant ratio, as well as the addition of co-fuel. In this study, the use of various concentrations of PG to investigate the influence of co-fuel on the removal of TOC and of nitrogen is considered a significant approach to destroying 3MP at 425°C. Some studies highlight the positive effect of the concentration of co-fuel (Oe et al., 2007; Al-Duri et al., 2016). The range of $PG_o/3MP_o$ extended from 0.5 to 3 (i.e. 2–12 mM PG) at 425 °C and 4 mM 3MP. The factors forming the basis for selecting this range were mentioned in Chapter Six.

Figure 7.9 displays the results of the effect of the PG and IPA ratios on TOC removal efficiency. The effect of the PG ratio was remarkable. TOC removal efficiency was improved by the increase in concentration of PG. These results confirmed the activity of the PG ratio compared with the results of the IPA ratio. There are several reasons to explain the improvement in TOC removal efficiency, including an abundance of powerful free radicals generated by PG, increasing the rate of reaction (Al-Duri et al., 2016; Bermejo et al., 2008). Nevertheless, the IPA ratio results were slightly positive due to IPA containing one hydroxyl group, and according to Yang et al. (2018), the order of activity for the hydroxyl group was methanol > ethanol > IPA. For example, TOC removal efficiency was improved from 81% at 0.5 PG ratio to 92% at 3 PG ratio and 10 s (increasing by 13.58%). This enhancement was positive compared with the results of TOC removal efficiency in the absence of PG under the same conditions. Removal efficiency was enhanced from 68.8% in the fuel-free system at 10 s to 92% under the same conditions and with the PG ratio of 3. The increment in TOC removal efficiency was approximately 33.7% when increasing the PG concentration from 0 to 12 mM. In addition, the effect of PG ratio on the percentage of TOC was slightly improved with the range of residence time at various PG ratios. For example, the TOC percentage improved from 80% at 6 s to 84% at 14 s and 0.5 PG ratio, while at the PG ratio of 3, TOC removal efficiency improved from 90% at 6 s to 93% at 14 s. The linear enhancement of the removal efficiency at various PG ratios would indicate increasing removal efficiency at 425 °C when increasing the PG ratio. Consequently, the PG ratio played an essential role in improving SCWO performance at 425 °C. The comparison between the PG ratio and the IPA ratio is clear in Figure 7.9. The effect of PG ratio on TOC removal efficiency demonstrated the influence of two hydroxyl groups on the destruction of 3MP, compared with one hydroxyl group. For example, at 10 s and 0.5 co-fuel ratio, TOC removal was enhanced from 68% in the presence of IPA to 81% in the presence of PG (an increase of 19%), while under the same conditions the effect of IPA on removal efficiency was not significant. The low ratio of PG (2 mM) improved removal efficiency as much as 19%. This increment would become significant when increasing the concentration of PG from 2 mM to 12 mM to destroy 3MP at 425 °C. Finally, the destruction of 3MP at 425 °C is considered a positive indicator of the role of PG and of the effect of the two hydroxyl groups.

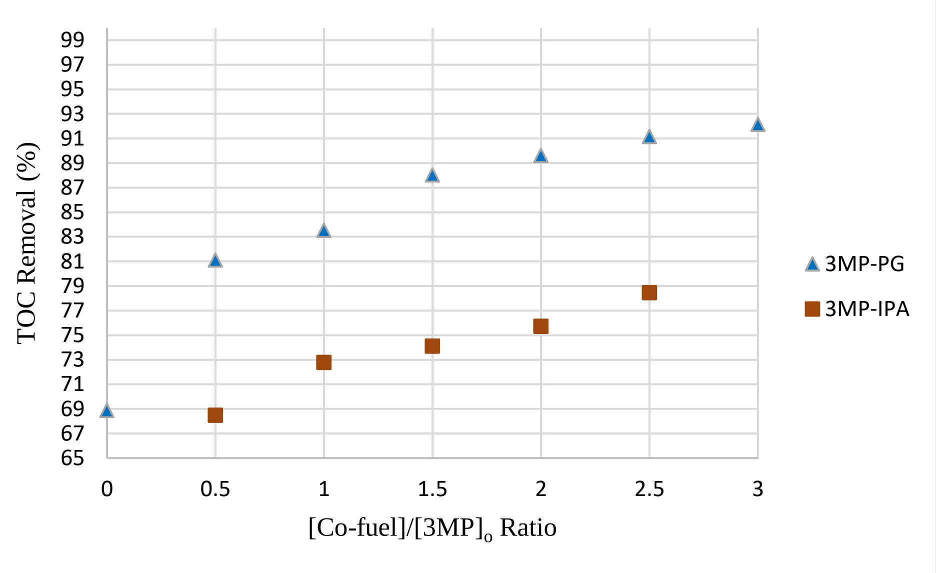


Figure 7.9: Effect of co-fuel ratio on the TOC removal efficiency at 10s, 425°C and SR of 1.

The effect of PG and IPA ratios on NH_4-N was consistent, despite the low yield of NH_4-N in the fuel-free system due to nitrogen's release as a gas, and because 3MP is a derivative of pyridine. According to Yang et al. (2018), N_2 and ammonia are the main products of pyridine oxidation. In the case of monoethanolamine (MEA), the main by-product is ammonia, due to MEA contains an amino group. The NO_2^- yield was a trace concentration in the IPA and PG systems. In the presence of PG, a yield of NO_3^- occurred in the liquid sample. The occurrence of NO_3^- in PG systems (i.e. PG + MEA and PG + 3MP) illustrates the advantage of PG, because NO_3^- is a by-product of the oxidation of ammonia. The results of nitrogen species confirmed this fact, while NO_3^- yield occurred low in the presence of IPA. Consequently, PG had a positive influence on ammonia and converted ammonia to NO_3^- at 425 °C. The effect of two hydroxyl groups in co-fuel on ammonia was positive, and several reaction pathways generated as a result of the activity of two hydroxyl groups. Figure 7.10 shows the effect of the co-fuel ratio on nitrogen species. The efficiency of nitrogen removal illustrates the effect of PG and IPA on 3MP.

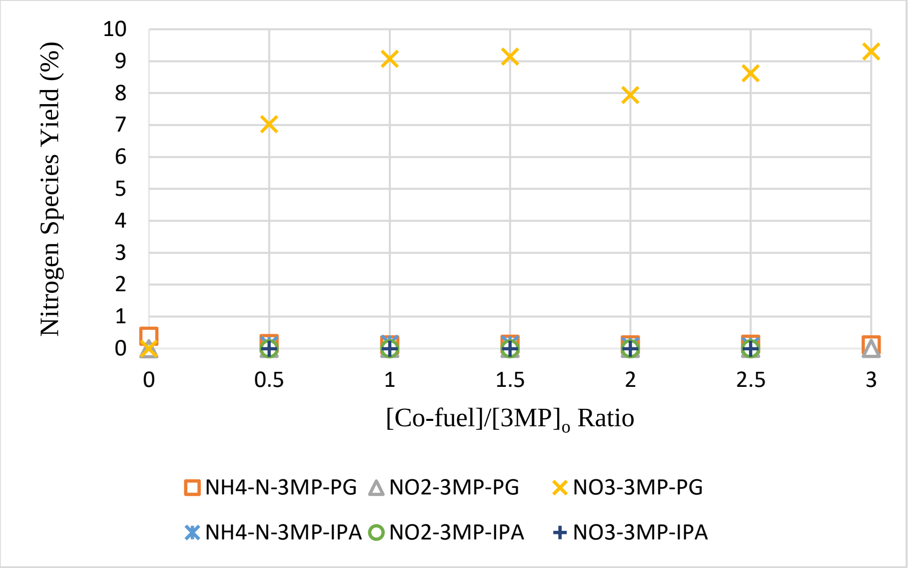


Figure 7.10: Effect of co-fuel ratio on nitrogen species at 425 °C, 4 mM 3MP, SR of 1 and 10 s.

The main goals with using co-fuel are increasing removal efficiency and destroying by-products at low temperatures to reduce the costs of using this technology. Thus, destruction of nitrogen-containing compounds would be essential when nitrogen removal efficiency is high, in order to protect the environment. Figure 7.11 shows the effect of the co-fuel ratio on the efficiency of nitrogen removal. Nitrogen removal efficiency was improved with the increase in the PG ratio, compared with the result of the IPA system at different PG ratios. The improvement in the efficiency of nitrogen removal was linear with increasing the concentration of co-fuel. For example, the removal efficiency increased from 80% to 88%, at 0.5 ratio and 3 ratio respectively, in the presence of PG. Also, the removal efficiency of nitrogen was increased from 77.5% in the presence of IPA to 80% in the presence of PG at 0.5 co-fuel ratio (an increase of 3%). The removal of nitrogen was improved on the increase of PG and IPA. The increased concentration of PG from 0 to 12 mM was positive and improved removal of nitrogen from 74% to 88% at a PG ratio of 3 (increasing by 18.9%). This enhancement in nitrogen removal efficiency is considered a significant indicator regarding the role of the PG ratio. PG would have a more positive effect on TOC removal and by-products than IPA. Thus, increased PG ratio would contribute to destroying 3MP and its by-products at 425 °C. The destruction of 3MP and by-products at 425 °C is considered an essential step in the improvement of SCWO performance when using PG. In addition, the two hydroxyl groups in PG have a more essential role than that of a single hydroxyl group in IPA.

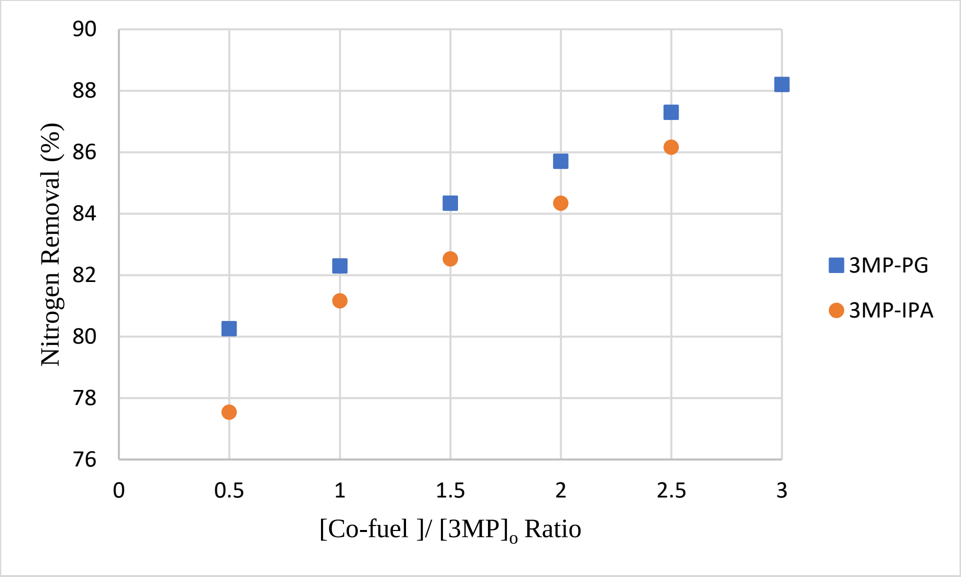


Figure 7.11: Effect of co-fuel ratio on the nitrogen removal efficiency at 4 mM 3MP, 425 °C, 10 s and SR of 1.

7.2.6 Effect of Initial Concentration of 3MP

The effect of an initial concentration on TOC removal efficiency and nitrogen species was investigated under supercritical conditions, in order to study the performance of SCWO in increasing 3MP concentration when using PG. The range of residence time was 6 to 14 s, 450 °C and 1 SR. The selection factors for the range of concentration was mentioned in Chapter Six.

An investigation was conducted into the effect of initial concentration on TOC removal efficiency. The results illustrated the significant effect of initial concentration on TOC conversion and nitrogen species. In Figure 7.12, the improvement in the efficiency of TOC removal is linear and the effect of PG is positive.

For example, TOC removal efficiency was enhanced from 81% at 2 mM to 93% at 8 mM and 10 s, because PG played an essential role in enhancing TOC removal efficiency compared with the results of the fuel-free system. Free radicals generated from PG has a significant influence on improvement in TOC removal efficiency, and the role of PG became clear with temperature, oxidant ratio and ratio of co-fuel. For example, at 2 mM TOC removal efficiency was enhanced from 64.8% in the absence of PG to 81% (it increased by 25%) at 10 s, while at 8 mM TOC removal efficiency was increased from 89% in the fuel-free system to 93% (it increased by 4.49%) in the presence of PG. This improvement could further the role of PG; in its absence, increased initial concentration positively influenced TOC removal efficiency. Also, reaction time could have a significant role in enhancing TOC removal efficiency. For example, the maximum TOC efficiency reached 93.8% in the presence of PG at 14 s and 8 mM. It could improve with changing operating conditions such as oxidant ratio or co-fuel ratio to improve removal efficiency at 450 °C. Figure 7.12 displays the effect of the initial concentration of 3MP on TOC removal efficiency using the PG system. Several studies highlight the positive effect of increasing the initial concentration.

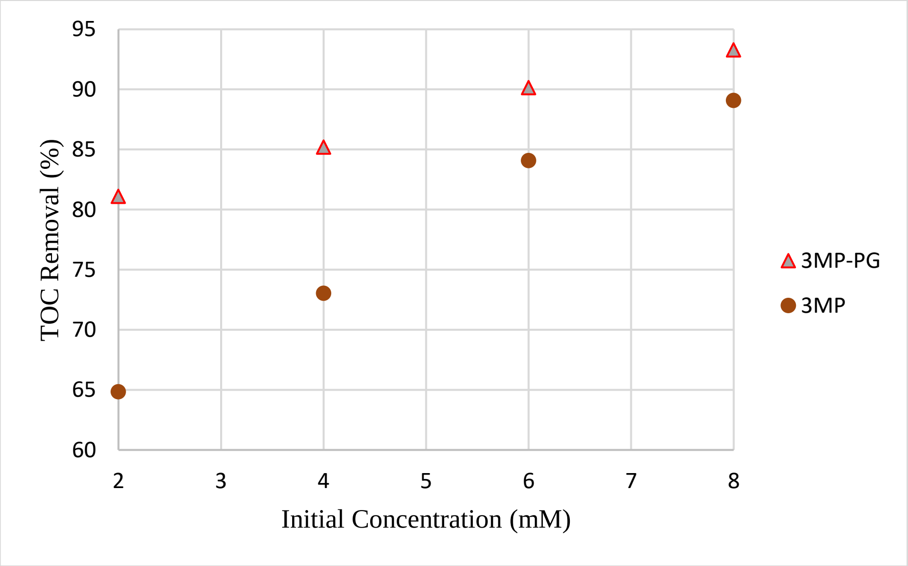


Figure 7.12: Effect of the initial concentration of 3MP (PG free system & PG system) on the TOC removal efficiency at 450 °C, at 10s and SR of 1.

Figure 7.13 displays the effect of the initial concentration of 3MP in the presence of PG on the nitrogen species in the liquid sample. The results show that the main by-products in the presence of PG were mainly NO_3^- and, less so, NH_4-N, the occurrence of NO_3^- confirming the oxidation of ammonia. In other words, PG generates radicals, increasing the conversion of 3MP and producing ammonia, which is converted to N_2 and NO_3^-. The NO_3^- yield decreased as the initial concentration increased. For example, the NO_3^- yield decreased from 7.8% at 2 mM to 2.0% at 10 s and 8 mM, because the high density of molecules of organic and oxidant would accelerate the reaction, whereas the NH_4-N yield was low for both systems. Also, NO_2^- yield remained low. The comparison between the two systems would become clear on investigation of the removal efficiency of nitrogen in the liquid sample, because the nitrogen species yield seemed low and nitrogen in 3MP would be released as N_2.

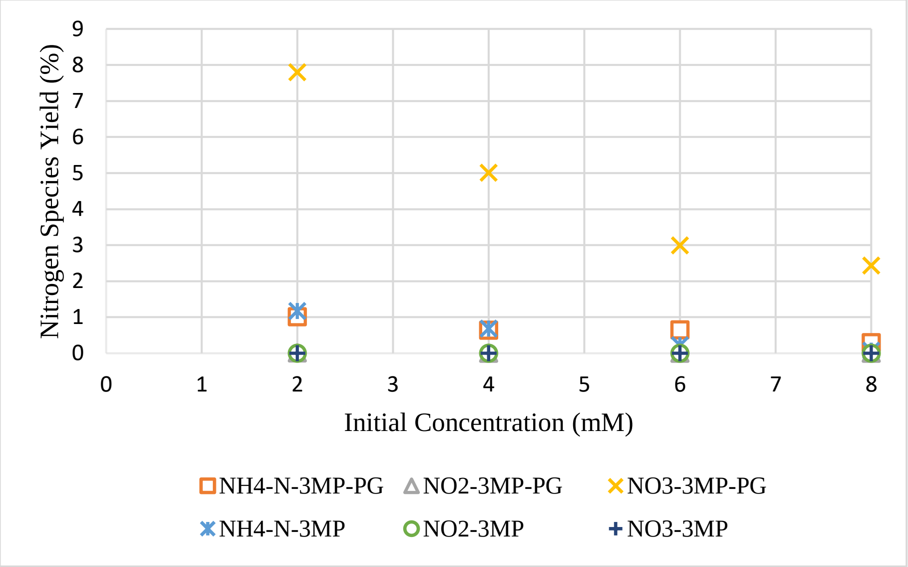


Figure 7.13: Effect of initial concentration of 3MP and PG on nitrogen species at 450 °C, 10 s and SR of 1.

The destruction of nitrogen-containing compounds is important to avoid the decomposition of these compounds and their conversion to unwanted by-products such as ammonia, nitrate and nitrite. These by-products pose dangers to aquatic life and human health. The presence of PG and increased initial concentration contributed to improving nitrogen removal efficiency. Figure 7.14 displays the enhancement in efficiency of nitrogen removal and illustrates the positive effect of PG. There are some reasons that may explain the improvement in removal efficiency, including increasing the initial concentration of 3MP and PG, thus increasing the rate of the reaction and increasing the generation of free radicals. 3MP is a derivative of pyridine and, in accordance with the literature, nitrogen in pyridine was converted to mainly N_2 and a small amount of ammonia, and co-fuel would add further heat to the reaction. The removal efficiency of nitrogen was significantly enhanced by increasing the initial concentration in the presence of PG from 2 to 8 mM. For example, nitrogen removal efficiency increased from 74% at 2 mM to 91% at 8 mM (it increased by 22.9%). This improvement in nitrogen removal using the PG system is considered remarkable at 450 °C and 8 mM.

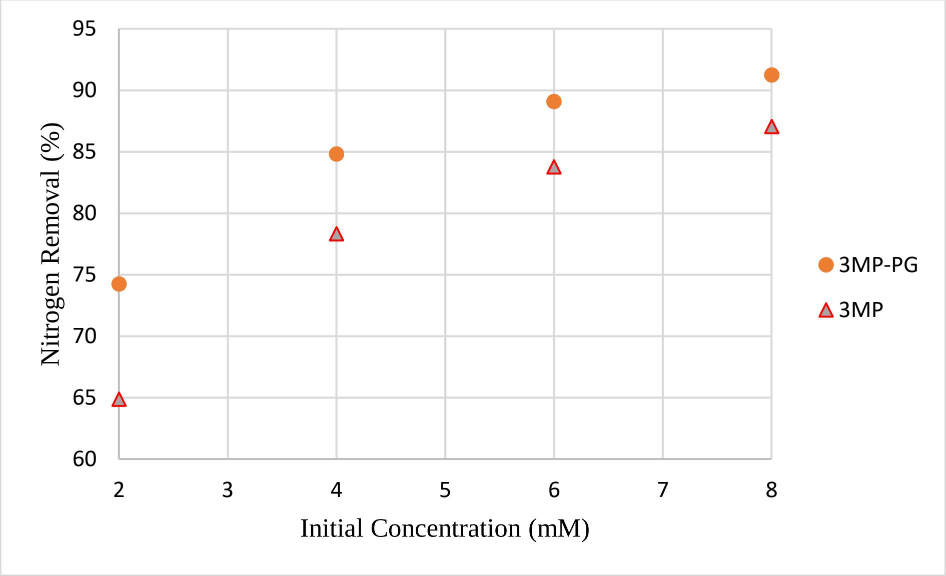


Figure 7.14: Effect of the initial concentration of 3MP and PG on the nitrogen removal efficiency at 450 °C, 10 s and SR of 1.

The improvement in nitrogen removal efficiency between 6 and 8 mM could be low for the two systems; consequently 8 mM may be considered the maximum concentration and increasing the initial concentration more than this value may slightly improve the removal of nitrogen. Comparison of the PG free and PG systems shows the positive influence of PG. For example, nitrogen removal was improved from 64.8% (fuel-free system) to 74% (PG system) at 10 s and 2 mM. This increment was approximately 14%, while at 8 mM the increment in the nitrogen removal was approximately 4.59%. The effect of PG on nitrogen removal efficiency was significant at various initial concentrations. According to Yang et al. (2018), IPA has a more positive effect on nitrogen removal than ethanol and methanol, due to the possibility of IPA adding further heat to the reaction compared with ethanol and methanol. PG would have the same advantage and its heat of reaction is high (-1822 kJ.mol^{-1}). At the temperature of 450 °C, modification of operating conditions is essential to improve the characteristics of the effluent.

7.3 Global Kinetics of 3MP Oxidation

It is necessary to study the global reaction rate and would supply valuable data for design purposes. The body of experimental data obtained regarding influences the various reaction parameters was employed to evaluate the reaction rates expressions namely the Arrhenius constants, rate constants and reactions orders were determined. The global rate law expression was employed to develop most SCWO kinetic models. Equation 7.2 illustrates the global rate law:

$$\frac{-d[Organic]}{dt} = k[Organic]^a[Oxidant]^b[Water]^c = Ae^{\frac{-Ea}{RT}}[Organic]^a[Oxidant]^b[Water]^c \ldots (7.2)$$

k is the reaction rate constant in M$^{1-a-b-c}$ s^{-1}.

A is the pre-exponential factor in M$^{1-a-b-c}$ s^{-1}.

E_a is the activation energy in J.mol^{-1}.

R is the constant of universal gas (8.314 J.mol^{-1}.K^{-1}).

T is the reaction temperature in K.

[Organic] is the organics initial concentration in mol.L^{-1}.

[Oxidant]is the oxidant initial concentration in mol.L^{-1}.

a is the reaction order relating to an organic compound.

b is the reaction order relating to oxidant.

c is the reaction order relating to water.

Numerous SCWO kinetic studies have been accomplished for different wastes either a single model compound or a mixture of wastes under various temperature, residence times, oxidant ratios, concentrations of organic and using various reactor designs. In this study, two methods were applied to study kinetic of 3MP:

1) Pseudo-first order approximation method
2) Integral method approximation

The medium of SCWO is water, and it formed more than 99 % of 3MP SCWO; therefore, the water concentration considers constant. In other words, the reaction order with respect to water becomes zero.

7.3.1 Pseudo-First Order Approximation Method

Numerous researchers have studied the global kinetic for SCWO either single compound or mixture organics, and they have employed Pseudo first order to describe the global kinetic. The order of the reaction is one with respect to the organic compound ($a = 1$) and zero for oxygen ($b = 0$) (Pinto et al., 2006; Abelleira et al., 2013). This model might be a simple method to describe the global kinetic, but is a suitable starting point to evaluate the reaction rate constant *k*. The following equation represents the global power rate law for this system:

$$rate = \frac{-d[3MP_{PG}]}{dt} = k[3MP_{PG}] \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots.. (7.3)$$

The experimental results are the TOC values from 3MP oxidation in the presence of PG, and the equation (7.3) was modified to use the TOC:

$$rate = \frac{-d[TOC_{3MP+PG}]}{dt} = k[TOC_{3MP+PG}] \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots.\ldots\ldots\ldots\ldots\ldots\ldots\ldots (7.4)$$

After integrating this equation (7.3), the new equation can be applied:

$$\ln\left(\frac{[TOC]}{[TOC_o]}\right) = -k.t \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots.\ldots (7.5)$$

Plotting equation (7.5) using experimental data at each temperature gives the rate constant *k* (s^{-1}) from the slope for each operating temperature as shown in Figure 7.15 in the PG system.

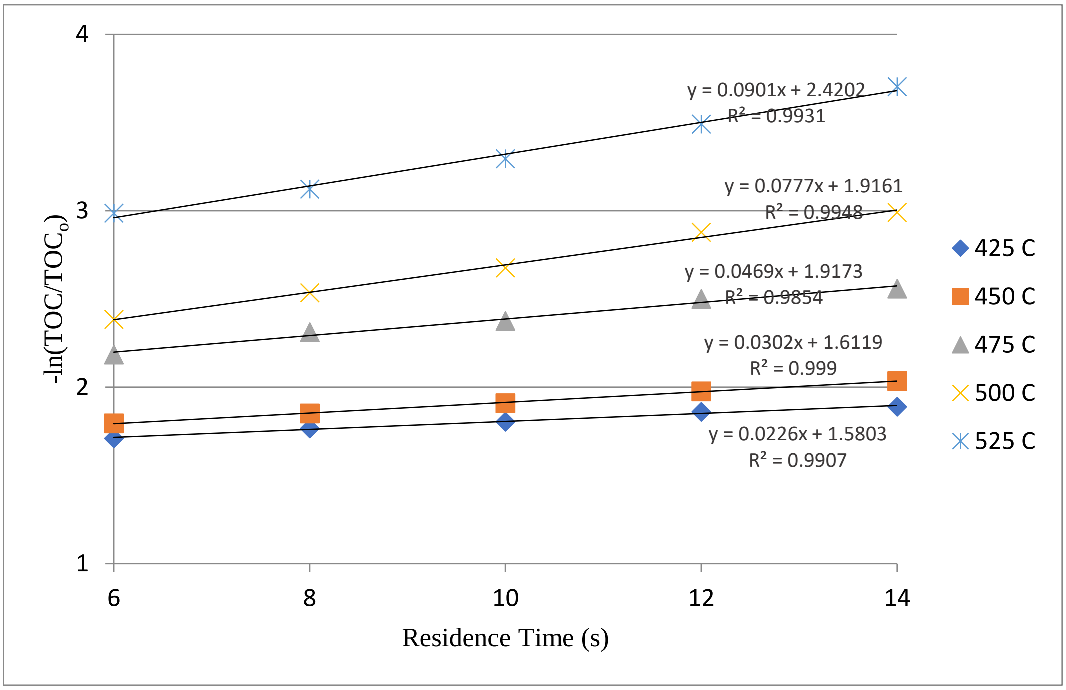


Figure 7.15: Natural logarithm of (TOC/TOC$_o$) against residence time for 3MP and PG experiments at various operating temperatures.

Then, where Ln k is plotted against $1/T$ as displayed in Figure 7.16. From this plot E_a and A were evaluated to be 68802 J.mol^{-1} and $3*10^3$ s^{-1} respectively. The results are shown in equation 7.6.

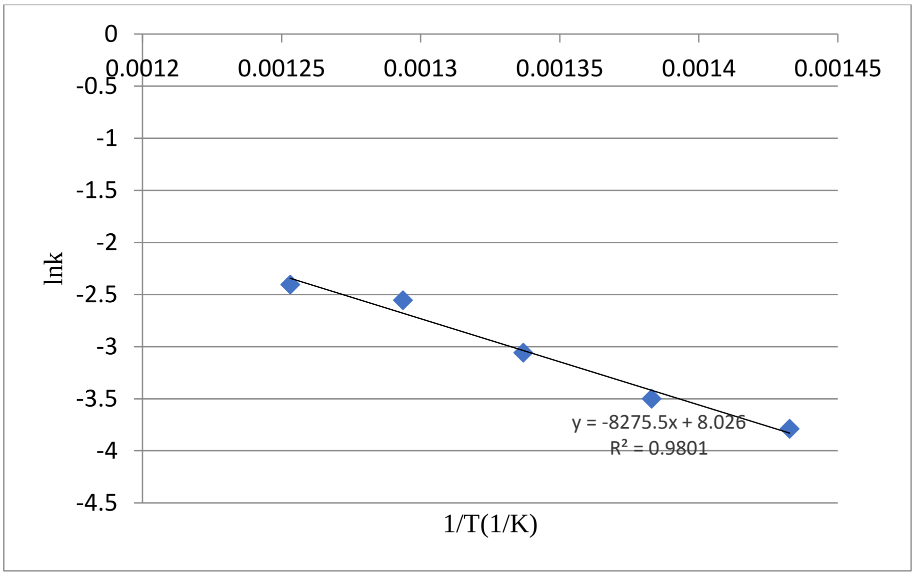


Figure 7.16: Arrhenius plot for the oxidation of 3MP and PG.

$$rate = \frac{-d[TOC_{3MP+PG}]}{dt} = 3 * 10^3 (s^{-1}) \exp\left(-\frac{68802 \frac{J}{mol}}{RT}\right) [TOC_{3MP+PG}] \ldots\ldots\ldots\ldots.(7.6)$$

7.3.2 Integral Approximation Method

Using integral method was to understand the global rate expression of 3MP oxidation and to express the kinetic data. The global kinetic parameters as activation energy and pre-exponential factor for 3MP oxidation were calculated from applying a set of experiments to determine the rate of the reaction, and the order of organic was applied one. The operating temperature was considered as a function for the destruction of 3MP. Water formed more than 99 %. The effect of oxygen concentration on the 3MP oxidation may be minor, but it is essential to investigate the order of oxygen. To determine the order of oxidant, four experiments were applied at 425 °C, 250 bar and the range of oxidant ratio was 0.75 to 2 SR (i.e the oxygen concentration range was from 35.25 mM to 94 mM). These experiments were present in the section 7.2.4. The TOC removal efficiency was enhanced with increasing the oxidant ratio thus the effect must be investigated to determine the order of oxygen. While in previous model (Pseudo first order) the oxygen order assumed zero. The design equation of plug flow reactor was based to calculate the order of oxygen and equation 7.2 is rearranged by using integral method with a = 1 and b > zero:

$$-rA = \frac{-d[3MP]}{dt} = k[\mathrm{3MP}][O_2]^b = Aexp^{\left(-\frac{Ea}{RT}\right)}[\mathrm{3MP}][O_2]^b \ldots\ldots\ldots\ldots\ldots\ldots\ldots.\ldots\ldots\ldots\ldots\ldots\ldots (7.7)$$

The assumption can consider the concentration of oxidant constant. The plug flow reactor equation for steady state was applied (Levenspiel, 1999) to be:

$$\frac{t}{[\mathrm{3MP}]_o} = \int_0^x \frac{dx_{\mathrm{3MP}}}{(-rA)} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (7.8)$$

t is a residence time, $[\mathrm{3MP}]_o$ is an initial concentration, (-rA) is a rate of reaction of 3MP oxidation. The following equation is substituting integral method equation (7.7) in the plug flow reactor performance equation.

$$\ln\left(\frac{1}{(1-X_{\mathrm{TOC}})}\right) = k.t[O_2]_0^b \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots . (7.9)$$

Then, in order to determine the value of b, it is necessary to find the slopes of fitted straight lines of 3MP oxidation for four experiments at 425 °C from plotted ln (1/1-X$_{\mathrm{TOC}}$) against residence time (t). The results of PG system are shown in Figure 7.17. The slopes of lines represent $k[O_2]_0^b$. This term can be written after taking the natural logarithm to be:

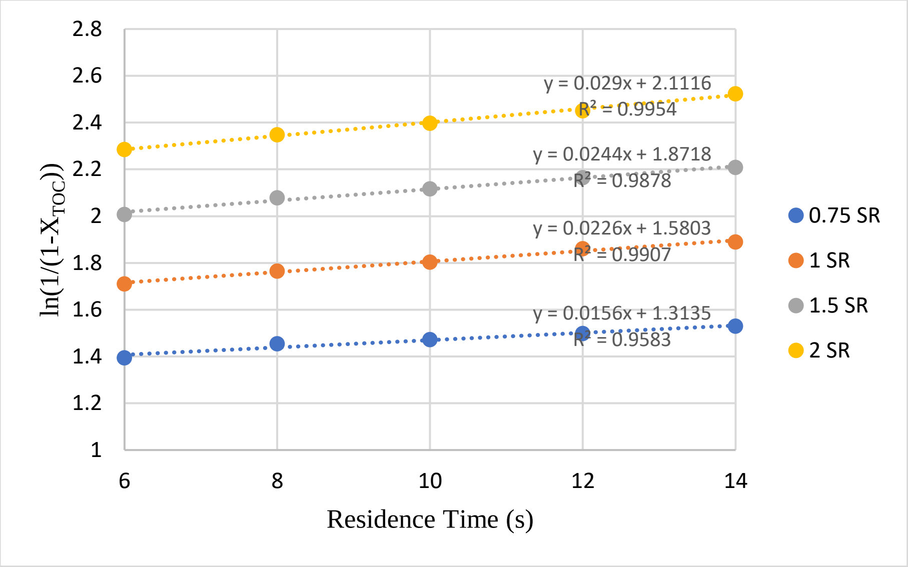


Figure 7.17: Natural logarithm of (1/(1-X$_{\mathrm{TOC}}$)) versus residence time for 3MP +PG experiments with varying oxidant concentrations.

$$\ln(k[O_2]_o^b) = \ln(k) + b\ln([O_2]_o) \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots . (7.10)$$

From Figure 7.17, these slopes are plotted versus the concentration of oxygen to generate a straight line for the 3MP and PG system. The slope of this line represents the b value for PG system.

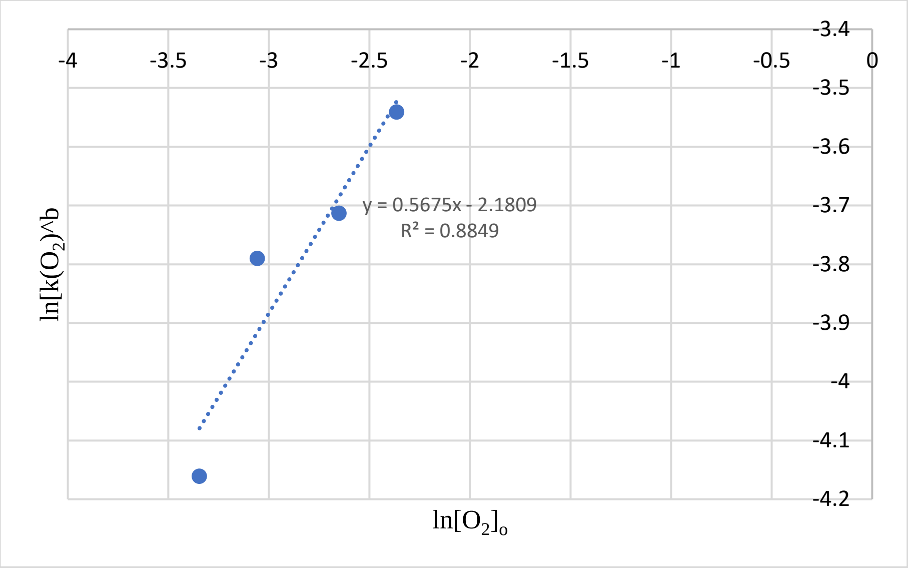


Figure 7.18: Determination of oxygen reaction order.

The order of oxygen represents the slope of straight line in Figure 7.18. The determination of reaction orders is (a =1, b_{3MP+PG}= 0.56). It is easy to determine the rate of the reaction by applying the equation (7.11) to be:

$$k = ln\frac{1}{(1-X_{3\mathrm{MP}+PG})} \times \frac{1}{t} \times \frac{1}{(O_2)^{0.56}} \dots\dots\dots\dots\dots.\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots (7.11)$$

The new *k* values are employed to determine the E_a and *A*, plotting the natural logarithm of the rate of reaction (*k*) versus inverse temperature (1/T) is shown in Figure 7.19. The E_a was calculated by multiplying the universal gas constant (8.314 $J.mol^{-1}.K^{-1}$) by multiplying the slope. *A* was calculated from ln *A*= intercept. Equation 7.12 illustrates the value of E_a and *A* in the generated global rate expression of 3MP and PG oxidation.

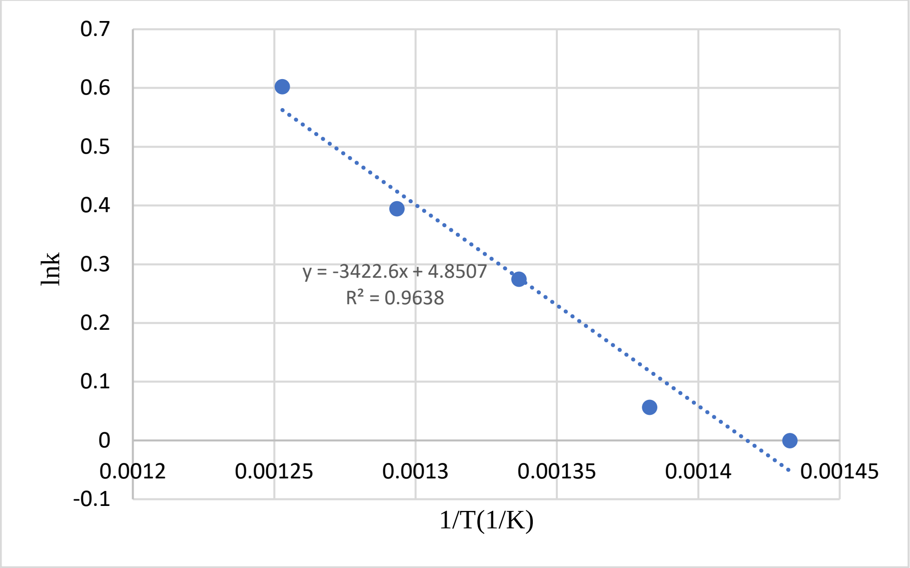


Figure 7.19: Arrhenius plot for 3MP+PG oxidation.

$$rate = -\frac{d[TOC_{3MP+PG}]}{dt} = 127\ (M^{-0.56}s^{-1})\ \exp\left(-\frac{28455\frac{J}{mol}}{RT}\right)[TOC_{3MP+PG}][O_2]^{0.56} \ldots (7.12)$$

The order of oxygen was 0.56 in the PG system that indicated to the effect of oxidant on the 3MP+PG oxidation, consequently applying integral method could consider an appropriate way to understand the kinetics of 3MP+ PG oxidation.

7.4 Summary

- The operating temperature was the main parameter that positively influenced TOC removal efficiency. The high removal efficiency was 97.5 % at 525 °C in the 3MP and PG system. The TOC results could be considered significant when compared with the results of the fuel-free system and IPA system. Two hydroxyl groups have played an essential role in producing free radicals and improving the efficiency of TOC removal. This system confirmed the effect of IPA was slightly positive. PG influenced the removal efficiency of nitrogen and this influence was positive in the MEA and PG system because PG contributed to oxidise ammonia and converted to N_2 and NO_3^-. The maximum removal efficiency of nitrogen at a high temperature was 89%. For nitrogen species, the effect was positive with increasing temperatures.

- The effect of the oxidant ratio on TOC removal efficiency was positive in the presence of PG. The oxidant and PG would play an essential role in providing different powerful radicals such as HO• and HO_2•. These radicals would attack organic molecules and enhance the destruction of 3MP. The removal of nitrogen was improved by increasing the oxidant ratio in the presence of PG. The results of the PG system were significant when compared with the results of the fuel-free system. The high removal efficiency of nitrogen and TOC at 2SR and 10 s were 90% and 90.9%, respectively.
- The enhancement of efficiency of TOC removal by increasing the ratio of PG confirmed the significant effect of PG, and two hydroxyl groups in PG would positively influence the destruction of 3MP more than single hydroxyl group in IPA at 425°C. The maximum TOC removal efficiency was 93% at 14 s and 425°C. Therefore, using a high ratio of PG may lead to essential results. This advantage of two hydroxyl groups must be studied to improve the performance of SCWO. Nitrogen removal efficiency increased with increasing PG ratio more than IPA, reaching 88% at 3 PG ratio. PG affected the nitrogen species more than IPA.
- The initial concentration would have a significant effect on TOC removal efficiency in the PG system. The efficiency of nitrogen removal positively increased when increased the initial concentration from 2-6 mM, and PG had a positive influence on nitrogen removal efficiency.
- Increased the yield of NO_3^- in the presence of PG indicated to a further oxidation of ammonia. In the IPA system, the yield of NO_3^- was low. The oxidation of ammonia at temperatures lower than 525 °C would be important goal.
- The kinetic analysis (integral method) showed a slight effect of IPA on E_a, which decreased from 31850 $J.mol^{-1}$ (fuel-free system) to 31248 $J.mol^{-1}$, while in the presence

of PG, E_a reduced to reach 28455 $J.mol^{-1}$. The role of PG seems to be more significant than that of IPA. The order of oxygen was not zero and this illustrated the effect of oxygen on the destruction of 3MP.

CHAPTER EIGHT: CONCLUSIONS AND RECOMMENDATIONS

8.1 Introduction

This work has covered the general aim of increasing the understanding of hydrothermal reactions and investigating the SCWO performance of treating diluted nitrogen-containing model compounds at various operating conditions in both the presence and the absence of a co-fuel. These compounds were MEA and 3MP found in effluents of various industries. IPA and PG were used to investigate the effect of monohydric alcohol and dihydric alcohol on the removal efficiency of organic compounds and their by-products. For these reasons, SCWO technology was chosen to collect experimental data which was then used to describe the global kinetic reaction rate for both compounds.

8.1.1 MEA

MEA was oxidised under various supercritical conditions in the presence and absence of co-fuel. All experiments were carried out in a tubular reactor and a laboratory scale. The effect of temperature, oxidant ratio, co-fuel ratio and initial concentration on the removal efficiency and nitrogen species was investigated. The results illustrated temperature was essential. For example, the COD removal efficiency was more than 99% at 10 s and 525 ℃ in the absence of co-fuel. The effect of co-fuel on the percentage of COD was remarkable at 400 ℃. The results confirmed that the effect of PG on the COD percentage was more significant than IPA. PG would be a second source for free radicals that influenced the destruction of MEA at 400℃. For example, the COD removal efficiency was enhanced at 10 s from 50.6% to 70.7% in the presence of IPA (with an increase of 39.7%) and reached to 77.6% in the presence of PG (showing an increase of 53%). The oxidant ratio and the initial concentration had a positive effect on the COD conversion. The amount of oxygen significantly improved the efficiency of COD removal in the MEA, PG and IPA systems. The co-fuel ratio has an essential effect at a minimum temperature of 400 ℃ on the efficiency of COD removal. From the results, PG was proved to be more effective than IPA. In general, PG plays an important role to improve the COD removal efficiency than IPA at different conditions. Two hydroxyl groups in PG have a positive influence the enhancement of SCWO performance rather than the single hydroxyl group in IPA. The results of COD removal and TOC removal in this work confirmed the advantage of two hydroxyl groups.

The effect of different conditions in the absence and presence of co-fuel on by-products of MEA was investigated. The primary by-product of MEA is NH_4-N in an aqueous sample. In the absence of co-fuel, the yield of NH_4-N increased when the operating temperature was increased from 400 to 525 °C and 1SR, and the maximum yield of NH_4-N at 475°C was 29 %. The effect of the PG was positive with increasing operating temperature. In the presence of PG or IPA, the yield of NH_4-N increased at 400 °C, but this increase in the IPA system was more than the PG system due to PG instigating more oxidation than IPA. The occurrence of NO_3^- in the PG system confirmed this advantage and NH_4-N was converted to N_2. The effect of PG on the yield of ammonia was more significant than IPA. In the fuel-free system, NH_4-N required a high temperature to be treated or using of another unit to reduce the yield of ammonia. For example, using a biological reactor would contribute to destroying the remained ammonia in effluent of the SCWO reactor.

The amount of oxygen in the three systems had a positive effect on NH_4-N. The yield of NH_4-N decreased when the oxidant ratio was increased in the absence and presence of co-fuel. In the presence of PG, the yield of NH_4-N decreased when the oxidant ratio was increased, and the yield of nitrate ion slightly increased. The co-fuel ratio also improved the reduction of NH_4-N, and PG had a more positive influence than IPA. The initial concentration influenced the main by-product. The oxidation of NH_4-N in the PG system occurred under different conditions.

The enhancement of the efficiency of nitrogen removal by SCWO is considered an essential goal. The various supercritical conditions were investigated to determine which had a positive effect on the removal efficiency of nitrogen. In the MEA system, the removal of nitrogen improved with temperature, oxidant ratio and concentration. In the presence of a co-fuel, the improvement was significant when compared with the results of the fuel-free system. IPA and PG would contribute to enhance the removal efficiency of nitrogen. The influence of PG on the removal efficiency would be more positive than IPA.

A kinetic analysis was achieved using the Pseudo first order and integral approximation methods. The results illustrated the difference in the kinetic parameters. The kinetic analysis demonstrated the positive effect of co-fuel on the E_a when using the integral approximation method. E_a decreased from 79746 J.mol^{-1} to 46807 J.mol^{-1} due to the addition of IPA, while PG reduced E_a to 47497 J.mol^{-1}. The integral approximation method described the global rate reaction for the three systems and illustrated the effect of the amount of oxygen on the results. The orders of the oxidants used for each system were 0.31 in the fuel-free system, 0.38 in the IPA system and 0.58 in the PG system. Unfortunately, there is not enough data to compare the results of this research and other literature.

8.1.2 3MP

3MP is a heterocyclic compound that would be considered as a resistant compound to SCWO. 3MP was investigated under various supercritical conditions in the 3MP system, IPA system and PG system, and a laboratory scale was used to carry out all experiments. The effect of temperature, oxidant ratio, co-fuel ratio and concentration were all investigated. The results illustrated that in the presence of PG, the temperature had a significant impact. The TOC removal efficiency was enhanced to reach 97.5% at 14 s and 525 °C in the presence of PG, while the effect of temperature in the absence of co-fuel at 525 °C was 92.8%. The effect of PG on the efficiency of TOC was remarkable and was more than IPA at different operating temperatures. For example, the TOC removal efficiency increased at 10 s and 425 °C from 68.8% to 72.7% in the presence of IPA (showing an increase of 5.6%) and reached to 83.5% in the presence of PG (showing an increase of 21%). Furthermore, the effect of the oxidant ratio and the initial concentration on the TOC conversion was positive. The amount of oxygen significantly improved the radical generation in the absence and presence of co-fuel. PG enhanced the TOC efficiency more than IPA.

3MP is a challenge as this compound is destroyed under SCWO due to its need for high temperatures and using PG would be a suitable alternative. The co-fuel ratio has a remarkable effect at the minimum temperature of 425 ℃ on TOC removal. The results demonstrate the PG ratio influenced the efficiency of TOC removal more than the IPA ratio. For example, the efficiency of TOC removal increased from 78% in the IPA system and 91% PG system (showing an increase of 16% at a 2.5 co-fuel ratio). Therefore, PG could play a more significant role than IPA to improve the TOC removal efficiency at different conditions. The high activity of PG is able to enhance the removal efficiency as it contains two hydroxyl groups.

The effect of different conditions in the absence and presence of co-fuel on by-products of 3MP was investigated. The primary by-products were NH_4-N and NO_3^-: their yields were low. In the absence of co-fuel, the yield of NH_4-N increased by increasing operating temperature from 425 to 525 ℃ and 1SR. The effect of the co-fuel on nitrogen species was significant. In the presence of co-fuel, the yield of NH_4-N decreased with increasing temperature. In the PG system, the nitrate ion increased if compared with the other two systems. Although the yield of NH_4-N was low, the oxidant ratio positively influenced the nitrogen species. Also, the initial concentration contributed to reduce the yield of NH_4-N. The use of co-fuel had a clear effect on total nitrogen in the aqueous sample.

Primary products of pyridine oxidation were N_2 and NH_4-N. Thus, the efficiency of 3MP nitrogen removal was significant. The various supercritical conditions of the three systems have a positive effect on the removal efficiency of nitrogen. In the fuel-free system, the removal of nitrogen increased with temperature, oxidant ratio and initial concentration which was significantly improved by the presence of co-fuel. IPA or PG would contribute to add heat to the reaction and enhance the removal efficiency of nitrogen. The effect of PG was remarkably more efficient on the removal of nitrogen than IPA.

A kinetic analysis was carried out by using Pseudo first order and integral approximation. The results have illustrated the difference in the kinetic parameters. The kinetic analysis demonstrated a positive effect of co-fuel on the E_a when using an integral approximation method. E_a decreased from 31850 J.mol^{-1} (fuel-free system) to 31248 J.mol^{-1} in the presence of IPA while the contribution of PG reduced E_a to 28455 J.mol^{-1}. The effect of PG on E_a was clear. The integral approximation method described the global reaction rate for all three systems and illustrated the effect the amount of oxygen has on the results. The orders of the oxidants for the fuel-free system, IPA system and PG system were 0.4, 0.45 and 0.56 respectively.

Briefly, SCWO is high effective in destroying two nitrogen-containing compounds. The results of PG demonstrated the effect of two hydroxyl groups on the efficiency of COD and TOC is more significant than IPA. Thus, PG will be added to promote the SCWO performance. Also, the results of the removal of nitrogen in the presence of PG have confirmed the significant effect of two hydroxyl groups rather than one hydroxyl group.

8.2 Recommendations

From the observations of this study, the author suggests the following recommendations to support further research.

Using PG as a co-fuel would considerably enhance SCWO performance. Despite the results of the PG system were of significant interest. It is important to oxidise PG with various compounds such as mixture compounds or real waste to test the feasibility of PG and investigate the technical challenges. The use of a multi-injection reactor could be important to study the effect of PG on the removal efficiency of nitrogen species. Increasing the PG ratio under various operating conditions is important to destroy MEA and 3MP and their by-products at minimum temperature.

The treatment of the two nitrogen-containing compounds in this work would generate a low quantity of inorganic salts. In other words, salt precipitation did not occur in this study. Consequently, this research can be applied in the future to treat these compounds without concern of salt production on a large scale if a stream of real waste contains a low concentration of salts and the main organic substance in stream is MEA or 3MP.

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