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EVALUATION OF OZONE FOR THE REMOVAL OF PHENOLIC COMPOUNDS IN WASTEWATER FROM THE MERISOL PLANT (SASOLBURG)

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(0110094T)

A research report submitted to the Faculty of Science, University of the Witwatersrand, Johannesburg, in partial fulfilment of the requirements for the degree of Master of Science.

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University of Witwatersrand, Johannesburg, 2008

DECLARATION

I declare that this research report is my own, unaided work. It is being submitted for the Degree of Masters of Science in the University of Witwatersrand, Johannesburg. It has not been submitted before for any degree or examination in any other University.

(Signature of the candidate)

-------**22**------Day of----**May**------**2008**

ABSTRACT

Ozone was evaluated for the removal of phenolic compounds in wastewater from the Merisol Plant. Oxidation was conducted under both acidic (pH = 4.70) and basic (pH = 10.45) conditions. Phenol and acetic acid (as well as traces of formic, butyric and propionic acids) were identified as major components in the Merisol effluent. The results from the study have indicated that the phenol concentrations in the Merisol effluent were reduced from an average of 355 mg/L to below detectable levels within 60 min of oxidation period under both acidic and basic conditions. Furthermore, the effluent COD concentration was reduced from approximately 1200 mg/L to: 678 mg/L at 40 ppm O_3; 590 mg/L at 80 ppm O_3; and to 579 mg/L at 120 ppm O_3 under acidic conditions. Under basic conditions, the effluent COD concentration was reduced to: 656 mg/L at 40 ppm O_3; 510 mg/L at 80 ppm O_3; and 397 mg/L at 120 ppm. These results were well below the required 1000 mg/L COD specification level. Moreover, the results also indicated that oxidation of the Merisol effluent sample under basic conditions yielded better results when compared to oxidation under the normal pH of the effluent (acidic).The degradation products of phenol ozone oxidation were identified as formic, butyric and propionic acids. These acids occurred in various proportions during the oxidation and were also removed during the process.

In conclusion, ozone oxidation technology has proven to capably treat the Merisol effluent to the required specifications. This technology may be applied to increase the degree of compliance of the Merisol Plant and that of Sasol One with regard to the Department of Water Affairs and Forestry (DWAF) phenol specification under the discharge water licence conditions.

In loving memory of my late grandmother
Mamaetso Getsho Maggie Mooketsi

Ke tshwene makopo gake naiwe ke naiwa mmeleng, setlogolo sa batshweneng!!

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LIST OF ABBREVIATIONS

ATAR	**African Tar Acids Refiners**
COD	**Chemical Oxygen Demand**
CTL	**Coal to Liquids**
DAD	**Diode Array Detector**
DWAF	**Department of Water Affairs and Forestry**
EPA	**Environmental Protection Agency**
FID	**Flame Ionization Detector**
GAC	**Granular Activated Carbon**
GC-MS	**Gas Chromatograph Mass Spectrometry**
GTL	**Gas to Liquids**
HPLC	**High Performance Liquid Chromatography**
LOD	**Limit of Detection**
LOQ	**Limit of Quantitation**
OCN	**Ortho-cresol Novolen**
RSD	**Relative Standard Deviation**
TNPE	**Tar Napthalene Phenolic Extraction**
UV	**Ultra Violet**

CHAPTER ONE

1. INTRODUCTION

Sasol is a South African based company which produces petrochemicals from coal and natural gas. Sasol has been using the Lurgi coal-gasification process for over half of a century in a process widely known as coal-to-liquids (CTL). During the coal gasification process, steam, oxygen and coal are fed into a gasifier to produce synthesis gas (mixture of CO_2 and H_2) which is used as a feed to the Fischer-Tropsch reactor for producing various petrochemical products. However, during the gasification process large amounts of heavily contaminated wastewater is produced. Contaminants in this wastewater may include the following: phenols, ammonia, organic acids, sulphides, carbon dioxide, etc. Some research work has shown that phenol and ammonia concentrations in this wastewater can be over 4000 mg/L and 3000 mg/L, respectively (Gai *et al,* 2007). Furthermore, the chemical oxygen demand (COD) concentration for this wastewater is about 20 000 mg/L.

Because of the presence of valuable chemicals in this water such as phenolics and ammonia this wastewater is treated in various processes to recover most of the chemicals and to make it more amendable for treatment in a biological process where after it is finally discharged into the environment. It is known that in China wastewater from the coal gasification process has for a long time caused serious environmental problems (Gai *et al,* 2007). However, recently there has been great emphasis on cleaner production in the CTL business since coal has become more attractive as a source of energy owing to high and volatile oil prices as well as political instability and tension in the Middle-East. Gai *et al* (2007) stated that there are two common problems encountered during the treatment processes of the wastewater in the CTL business with reference to China. Firstly, they point out that there is poor removal of phenols and secondly poor removal of sour gases (e.g.CO_2 and H_2S) from the wastewater (Gai *et al,* 2007).

Of particular relevance and significance to this research work is the phenolics in this wastewater from the coal-gasification process. Sasol Secunda has been supplying partially processed gas water to the Merisol Plant in Sasolburg for further processing and beneficiation since the conversion of Sasol One site from coal to natural gas feed stock.

1.1 Origin of the Phenolic Effluent from the Merisol Plant

The Merisol Plant is located within the Sasol One site in Sasolburg and is a global player in the manufacturing of various phenolic products such as phenol, o/m/p-cresols, xylenols and C_3-C_4 alkyl phenols. Since the decommissioning of the Gasification Plant with the conversion of Sasol One to natural gas feed stock, the Merisol Plant has been receiving partially processed gas water from the Sasol Secunda Plant via rail transport. This gas water is treated in several processes to remove various valuable chemicals (tar acids) in various plants (i.e. TNPE, OCN, and ATAR). During these various processes and chemical work-up, effluent containing 3 - 5% phenolics is produced within the works. This phenol rich effluent, referred as to as the C-stream, is stored into three effluent tanks with a capacity of 5000 m^3 each.

This effluent is normally pre-treated to remove suspended solids and oils before recovery of phenolics via solvent extraction using butyl acetate as a solvent. Diisopropyl ether (DIPE) and methyl isobutyl ketone (MIBK) can also used as solvents for phenol extraction though it is not employed at Sasol (Gai *et al*, 2007). The phenolics in the organic phase are further recovered from the solvent via a scrubbing column and the aqueous phase from the extractors is routed to the packed column to remove any remaining butyl acetate via steam injection. The waste from the packed column is then discharged via the Chemical Sewer for treatment at the Bioworks. However, due to process instabilities and variations in the feed, the quality of this effluent or wastewater is such that it contains significant amounts of phenolics (mainly phenol) and some amounts of acetic acid resulting from the decomposition of butyl acetate. As a result this effluent has

chemical oxygen demand (COD) ranging between 500 and 4000 mg/L and this is mostly due to the unrecovered phenol content. The pH values encountered in this effluent can vary from 4.5 to 9.6. Currently, this effluent is discharged from the Merisol Plant at approximately 21 m^3/h to the Sasol One Bioworks via the Chemical sewer system. This effluent is routinely tested for the COD concentration before any discharge is permitted. The discharge is permitted only if the COD concentration is < 1000 mg/L.

1.2 Effluent Treatment at the Sasol One Bioworks

At the Bioworks effluent (Chemical Sewer, Industrial Sewer and Domestic Sewer) from various plants are combined and treated to produce effluent of acceptable quality by using biofilters or trickling filters as shown in Figure 1.

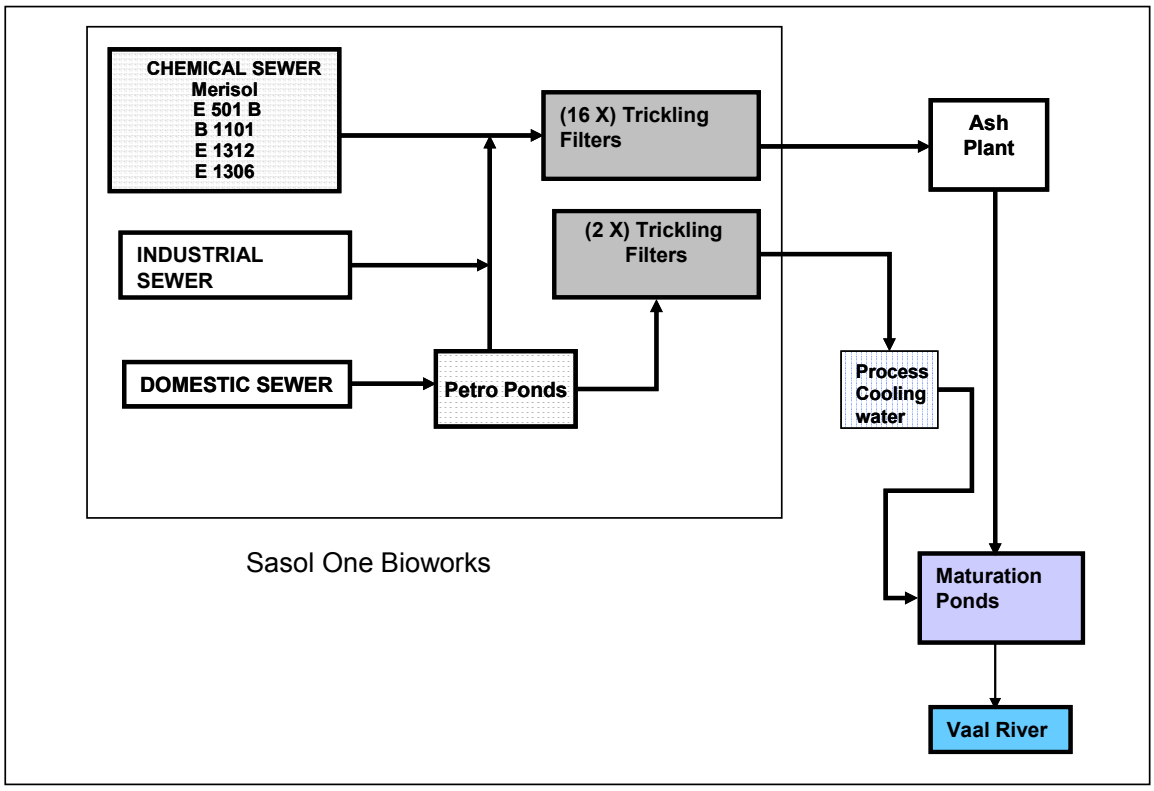


Figure 1: Simplified process flow diagram of the Sasol One effluent system

The Sasol One Bioworks use biofilters as a main treatment process for the purification of effluent emanating from the Sasol One Plants. The biofilters are

packed-bed biological reactors used for wastewater treatment. They are either packed with rocks or plastic media where biofilm grows. The biofilm grows on the packing material (rock or plastic) and the organisms are fed with substrate in the wastewater as the water trickles through the media. The Sasol One Bioworks has 18 trickling filters packed with rock media and were commissioned fifty years ago. The treated effluent is used for both ash transportation and as cooling water make-up as shown in Figure 1. This effluent is later discharged into the Vaal River via a series of maturation dams.

1.3 Impact of the Merisol Effluent on the Sasol One Bioworks

Current indications are that the Sasol One Bioworks Plant is quickly running out of capacity (both hydraulic and organic load) to treat any additional effluent. This is as a direct result of several expansion projects that were realised in the past years as well as the collapse of four other trickling filter units within recent years, obviously due to aging of the infrastructure. Due to the status quo at the Sasol One Bioworks Plant, plans to upgrade the plant have been a priority and are underway. However, the upgrading process may require a lot of initial capital investment as well as time for construction. Because of this situation, the Infrachem Water and Waste Management have recently become more stringent to the plants within the Sasol One site with regard to the quality and quantity of the effluent that is discharged to the Bioworks.

Currently there are contracts drawn up between the Business Units (plants) and the Infrachem Water and Waste Management which stipulates the quantity and quality of effluent a certain plant can discharge to the Bioworks and any violations may lead to serious fines. Thus there has been a significant drive or push from the Infrachem Water and Waste Management site to address the capacity problem by forcing plants to improve on the quality of their effluent. Many plants on the Sasol One site including the Merisol Plant are currently evaluating various ways of improving the quality of their effluent before discharging to the Bioworks. The effluent quality from the Merisol Plant could

directly impact the performance of the Sasol One Bioworks and thus poor effluent quality would be generated and this will subsequently impact the quality of the Sasol One final effluent in terms of phenol and COD. According to the license conditions between Sasol One and the Department of Water Affairs and Forestry (DWAF), the maximum phenol and COD concentrations in the effluent discharged should not exceed 1.0 mg/L and 80 mg/L, respectively.

Currently, the Merisol Plant is investigating several options including, but not limited, to the following: process modification to increase the recovery of the phenolics, Fenton's oxidation, membrane filtration, activated carbon, peroxide oxidation and advanced oxidation processes using ozone and UV, hydrogen peroxide or the combinations thereof. The Environmental Science and Technology (EST) Group at Sasol Technology R&D were tasked to investigate some of these processes for the treatment of the Merisol's effluent. Currently the plan is to investigate the advanced oxidation processes where ozone alone and the combination with hydrogen peroxide will be used. Extensive research work on the treatment of wastewater containing phenolic compounds using various processes is available in the literature. However, in most cases certain pre-treatment steps may be required due to the variations in the chemical composition of the wastewater and therefore the applicability of these processes has to be performed empirically before piloting and implementing on a full-scale. Possible implementation of the ozone treatment system may be realised at the Merisol Plant should positive results be obtained. This would serve as a good example for many business units within Sasol towards striving for greener production and sustainable business practices.

1.4 RESEARCH OBJECTIVES

1.4.1 General Objectives

This study was aimed at evaluating ozone oxidation for the removal of phenolics (phenol) in the wastewater from the Merisol Plant.

1.4.2 Specific Objectives

- To quantify the amount of phenols removed during the ozonation process.
- To determine the COD removal efficiency of the ozonation process.
- To reduce the phenolics to < 50 mg/L and COD to < 1000 mg/L in the effluent during the ozonation process.
- To determine the efficiency of the low pH and high pH ozonation treatment processes.
- To quantify and qualify the oxidation products (organic acids) during oxidation treatment.

1.5. JUSTIFICATION OF THE RESEARCH PROJECT

The Merisol Plant has for a number of times not shown consistent compliance with the quality of the effluent discharged to the Sasol One Bioworks. The internal effluent discharge standard for the Merisol Plant is a maximum of 1000 mg/L COD. However, the effluent has COD concentration significantly in excess of 1000 mg/L recommended for discharge by the Infrachem Water and Waste Management and this is directly related to the presence of phenolic compounds in this effluent. This matter is of significant concern to the Infrachem Water and Waste Management because of a number of possible implications:

1) The Sasol One internal COD discharge standard for the Merisol Plant is exceeded significantly and as a result there is poor compliance by the business unit. During these situations the plant has to divert the off-specification effluent into holding tanks, and when the storage capacity

has been exceeded this sometimes results in unnecessary production down times.

2) The Sasol One Bioworks is facing serous capacity problems because of high organic (COD) and hydraulic loads from various plants within the site. The design capacity of the Sasol One Bioworks is 29 T/d COD, and the current load is between 26 – 27 T/d COD. This significantly exceed the recommended operation safety margin of 20 %. For this reason, there is very strict quality control and monitoring by the Water and Waste Management on all effluents entering the Bioworks at the Sasol One site.

3) High phenol content in the wastewater could result in Sasol One exceeding the Department of Water Affairs and Forestry (DWAF) phenol specification of 1 mg/L. This has huge implications on the licence to operate.

4) Phenol is a toxic and hazardous substance and can result in the deterioration and ultimately death of a biological system even at low concentrations (Hill and Robinson, 1975; Li and Humphrey, 1989). Therefore, there is an inherent risk of a total loss of the biosystem (trickling filters) at Sasol One Bioworks. The catastrophic effect on the trickling filters at the Sasol One Bioworks due to possible phenol shock load would result in production loss for Sasol.

CHAPTER TWO

2. LITERATURE REVIEW

2.1 Brief Review on Treatment Processes for Phenolic Wastewaters

Phenolic substances are usually present in large amounts in many industrial wastewaters such as petrochemical, steel mill, coking plants, coal-gas processes, synthetic resins and pharmaceuticals (Mukherejee *et al*, 2007). Phenols in aquatic systems are toxic to both fish and human beings. Most of these substances are harmful and highly toxic due to their stability in aqueous media (Beltran-Heredia *et al,* 2001*)*. Because of this and of their refractory character they have been included in the US Environmental Protection Agency (EPA) list of priority pollutants and also in the European Union (EU) Directive (80/778/EC), (Llompart, *et al*, 2002). Phenols just like most organic compounds find their way in to the environment via discharge from industrial effluents. According to Mukherejee *et al* (2007), typical phenol concentration in the effluent from a crude refinery is around 125 mg/L. Furthermore, the highest concentration of phenolics in wastewater is generated from the coke processing facilities with typical concentrations usually in excess of 1000 mg/L (Mukherejee *et al*, 2007).

The Environmental Protection Agency (EPA) has set a limit for phenol concentration in wastewaters to 0.1 mg/L because of possible contamination of drinking water sources by industrial activities. The EU Directive (80/778/EC) states a maximum concentration of 0.5 μg/L for total phenol in drinking water (Llompart, *et al*, 2002). The World Health Organisation (WHO) has a limit of 0.1 μg/L phenols in drinking /potable water (Mukherejee *et al*, 2007).

In the light of the above, there has been a continued research interest to study different approaches for the removal of phenols in wastewaters. The deciding factor for the appropriate technology is mostly based on efficiency as well as the economics.

Below are some of the examples of various processes that have been researched extensively for their effective reduction/removal of phenols in water and wastewaters: oxidation via ozone, chlorine and its derivatives, hydrogen peroxide Fenton oxidation, UV radiation, and removal by activated carbon, membrane processes, and more recently advanced oxidation processes (AOPs). AOPs involve the generation of hydroxyl radicals for oxidizing and destroying of organic contaminants. The hydroxyl radicals are very reactive and unselective and should be produced in sufficient quantities during AOPs. According to some researchers there has been a major shift from conventional treatment processes such as carbon adsorption, chlorine oxidation, stripping and biotreatment towards AOPs (Kusic *et al*, 2006). Some of the reasons for this move away from conventional treatment processes include the following: slow kinetics, transfer of pollutant from one media to the other resulting in secondary waste, selectivity and production of carcinogenic halogenated hydrocarbons (Kusic *et al*, 2006).

Oxidation of phenols using ozone has been a preferred way because ozone treatment does not result in potentially toxic by-products compared to other oxidants such as chlorine. Furthermore, by-products from the ozonation process are mainly readily biodegradable (e.g. oxalic acid, formic acid and acetic acid), (Beltran-Heredia *et al,* 2001; EPA Guidance Manual, 1999).

2.2 Ozone Chemistry in Water and Wastewater Treatment

Ozone is a powerful oxidizing agent (E° = 2.07 V) and its use in water and wastewater treatment is well known (Kusic *et al*, 2006; Munter, 2001; Oh *et al*, 2007; and Benitez, 1996). Table 1 shows the relative oxidation power of some oxidizing species.

Table 1: Relative oxidation power of some oxidizing species (Munter, 2001)

Oxidizing species	Relative oxidation Power(V)
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

Ozone is mainly used for the decolourisation, degradation of organics, disinfection, oxidation, and for elimination of taste and odours. Ozonation of organics in water is a fast process (e.g. colour removal) but complete mineralization to CO_2 and H_2O is a very slow process.

Mechanism of ozone reaction in aqueous solution

The reaction of ozone with organic compounds occurs via two different mechanisms, direct and indirect. The direct mechanism involves an electrophilic addition and cyclo-adition (Yiacoumi and Vithayaveroj, 2001).

The electrophilic addition takes place in unsaturated organic molecules with high electron density sites such as the following chromophores: C=C (e.g. phenol), C=N and N=N (Yiacoumi and Vithayaveroj, 2001; Zhou and Smith; and Magara *et al,* 1995). This reaction occurs under acidic to neutral conditions.

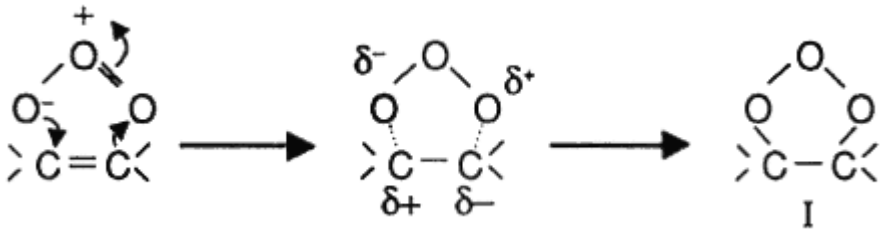


Figure 2: Direct oxidation of an alkene by ozone

Figure 2 illustrates a 1-3 dipolar cyclo addition reaction of ozone with an alkene resulting in the formation of a compound called ozonide. Under acidic conditions, this ozonide can disintegrate into an aldehyde, a ketone or a zwitter ion (Lenntech, 2007).

Ozone is also known to rapidly react directly with simple oxidizable ions such as S^{2-} resulting in the formation of SO_3^{2-} and SO_4^{2-} anions (Gogate and Pandit, 2004).

The indirect mechanism involves the reaction via free hydroxyl radicals which are produced during the decomposition of ozone. This mechanism occurs under alkaline conditions (pH > 8.5) where ozone decays into hydroxyl radicals via various chain radicals. These radicals can attack and oxidize organic molecules (Yiacoumi and Vithayaveroj, 2001; and Munter, 2001). The decomposition rate of ozone increases with increase in pH. The half life of ozone at pH 10 is approximately less than one minute (Munter, 2001).

The chemistry of ozone in pure water is rather complex and various aqueous reactions have been proposed as represented by equations 1 to 7 (Yiacoumi and

Vithayaveroj, 2001). The following reactions describe various reactions that occur when ozone is dissolved in water:

$O_3 + OH^- \rightarrow O_2^{\bullet -} + HO_2^{\bullet}$……..……..(1)

$HO_2^{\bullet} \rightarrow O_2^{\bullet -} + H^+$ (pKa = 4.8).....(2)

$O_2^{\bullet -} + O_3 \rightarrow O_2 + O_3^{\bullet -}$……..…..……..……..…...(3)

$HO_3^{\bullet} \rightarrow O_2 + OH^{\bullet}$……...……...…(4)

$HO_2^{\bullet} \leftrightarrow H^+ + O_2^{\bullet -}$…….... (5)

$O_3^{\bullet -} + H^+ \rightarrow HO_3^{\bullet}$ (pH ≈ 8).…….….(6)

$O_3 + OH^{\bullet} \rightarrow HO_2 + O_2$……..……(7)

Equation 1 describes a reaction of the hydroxide ion with ozone, which initiates a series of chain reactions. The formation of hydroxyl radicals in equation 4 via secondary decomposition of ozone is thought to be a rapid process (Gogate and Pandit, 2004). The hydroxyl radical is an important oxidant because of its high oxidation power. Its formation is also favoured at relatively high pH levels. Unlike ozone, the hydroxyl radical is indiscriminative in attack and oxidizes organic matter eventually to CO_2 and H_2O. This is the main reason ozonation is mostly conducted under alkaline conditions.

An appropriate pathway must exist before ozone can react with pollutants or substrates. Some researchers believe that kinetic factors most often dictate ozone-induced oxidation processes even though the thermodynamics may be favourable (Gogate and Pandit, 2004). This is an important factor because it has direct implications on the engineering and design aspect of a particular treatment system.

The oxidation of aqueous phenol by ozone has been studied extensively (Wu *et al*, 2000) and there have been suggestions that one of the oxidation pathway is via indirect radical mechanism whereas the other thoughts are that phenol degradation by ozone occurs via direct mechanisms (Wu *et al*, 2000). However, the work performed by Wu *et al* (2000) totally eliminated the indirect mechanism of phenol

reaction with ozone by conducting experiments under (pH>12) conditions favouring radical formation (Wu *et al*, 2000). In order to prove this, strong radical scavengers such as t-butanol and sodium carbonate were added which proved not to interfere with phenol removal. It was also noted that the rate constant of phenol oxidation decreased logarithmically with increasing initial phenol concentration. The reaction rate constant (k) of phenol oxidation by ozone under ambient conditions is in the order of 10^3 to10^4 M^{-1}•s^{-}1 and that of the hydroxyl radical is in the order of 10^9 to10^{11} M^{-1}•s^{-}1 (Munter, 2001).

The advantages and disadvantages of using ozone for water and wastewater treatment are many and are very specific to a particular application. For an example, in drinking water disinfection, the disadvantage will be the fact that ozone does not provide for a residual to guard against the recurrence of micro-organisms. On the other hand the advantage is that ozone does not result in the formation of chlorinated organic compounds which are suspected carcinogens. However, listed below are the main advantages and disadvantages of using ozone for various applications.

2.2.1 Main advantages of ozone

- Environmentally friendly
- Increases oxygen levels in wastewater
- Increases the biodegradability of wastewaters
- No chlorination by-products

2.2.2 Main disadvantages of ozone

- Ozone is sparingly soluble in water therefore it leads to poor mass-transfer from gas phase to liquid phase
- High cost of generation
- Very short half-life
- Formation of free radicals

2.2.3 Important parameters during ozonation process

Based on an exhaustive literature analysis performed by Gogate and Pandit (2004), the following are the most important operating parameters for the ozonation process for maximum degradation of pollutants in an energy efficient way.

- System pH: as mentioned earlier, at higher pH values ozone tends to form radicals which attack pollutants in an indiscriminate manner. Of importance is that if the operating pH of the system is above the pK value of the pollutant (i.e. pollutant not in molecular form), not much enhancement in the degradation rate will be achieved.

- Partial pressure of ozone: Although the high partial pressure leads to increased degradation, it is important to ensure that the ozone transfer into the solution is maximized or optimum.

- Contact time and interfacial area: The use of static mixers increases the maximum contact time and available interfacial area which leads to maximum ozone transfer into the solution.

- Radical scavengers: Depending on the mode of ozone radical scavengers (e.g. bicarbonate ions and humic substances) could drastically affect the efficiency of the process. These scavengers do not significantly affect the direct mechanisms. Thus it is important to consider the presence of these radicals when modelling the kinetics of degradation of a pollutant.

- Temperature: It is well known that the rate constant of reaction increases with increasing temperature, this will also be true for ozonation processes. However, temperatures also affect the dissolution of ozone in aqueous solution. Ozone is more soluble at low temperatures and less soluble at high temperatures.

- Catalysts: The presence of catalysts such as alumina and other metals can increase the efficiency of the ozonation process.

- Combination with other oxidation technologies: There are many examples where ozone oxidation is coupled with other technologies and the following are examples: ozone-ultrasound; ozone-UV; ozone-hydrogen peroxide, Ozone-GAC.

2.2.4 Mechanism for dissolving ozone in water

Ozone is sparingly soluble in water and for this reason several advances have been made in getting maximum ozone transfer from the gaseous phase into the liquid phase. At 20˚C, the solubility of 100% ozone is a mere 570 mg/L (EPA Guidance Manual, 1999). Ozone transfer into the liquid phase is usually a rate-limiting step during ozone water treatment processes (Zhou and Smith, 2002). Ozone transfer into the water phase is normally achieved via a contactor. Typical contactors used for ozone transfer are bubble diffuser, injectors and turbine/static mixers. Of interest to us is the bubble diffuser which was also employed during this study. Bubble diffusers contactors are the most commonly employed contactors found in many water treatment works in the United States as well as in the rest of the world (EPA Guidance Manual, 1999). They employ ceramic or stainless steel diffusers that are used to generate bubbles. They are constructed to achieve 85 – 90% ozone transfer efficiency with typical water depths ranging from 5.5 to 6.7 m (Zhou and Smith, 2002). There are several reasons as to why the bubble diffuser contactor is still used in most ozonation plants and below its advantages and disadvantages are summarised.

Advantages of the bubble diffuser contactor *(Zhou and Smith, 2002 and EPA Guidance Manual, 1999):*

- Demonstrated performance
- Effective ozone transfer (ca. 90%)
- Low hydraulic headloss
- Operational simplicity
- Less maintenance requirements

Disadvantages of the bubble diffuser contactor *(Zhou and Smith, 2002 and EPA Guidance Manual, 1999):*

- Deep contact basins (for effective mass transfer), this requires specialized construction which is normally costly
- Vertical channelling of bubbles (leads to loss of mass transfer)
- Potential clogging of pores (requires maintenance and attention)
- Maintenance of gaskets and piping

CHAPTER THREE

3. METHODOLOGY

3.1 Reagents/Chemicals

All chemicals used were of analytical grade (AR) or HPLC pure. The organic acids, formic (C_1), acetic (C_2), propionic (C_3), butyric (C_4) and pentanoic (C_5) were purchased from Sigma-Aldrich. Acetonitrile (Far UV) for HPLC and methanol (HPLC pure) were obtained from Acors Organics (New Jersey, USA). Phosphoric acid (85%) was obtained from Merck Chemicals. Dioxane (GC) was obtained from Sigma-Aldrich.

Water used for preparing standard and reference solutions was of ultra pure quality and was obtained from a Millipore Elix® 10 UV water purification system.

Ozone gas was obtained by passing pure oxygen gas via a laboratory ozone generator.

3.2. Preparation of Solutions and Reference Standards

3.2.1 Organic acids standards for HPLC analysis

A 100 mL standard stork solution containing individual standard organic acids, namely acetic (0.10 g ± 0.008 g), formic (0.10 g ± 0.008 g), propionic (0.10 g ± 0.008 g), butyric (0.10 g ± 0.008 g) and pentanoic acid (0.10 g ± 0.008 g) was prepared and the volumetric flask was diluted to the mark with acidified water (Solvent B at pH 2.7).

Solvent B was prepared by adding 20 mL of acetonitrile into a 2 L volumetric flask containing 1800 mL of Millipore water. The pH of this solution was acidified to pH 2.7 by using phosphoric acid.

A test sample containing formic acid (265 ppm), acetic acid (345 ppm), propionic (20 ppm), butyric (40 ppm) and pentanoic acid (20 ppm) was used to determine the intra assay precision of the HPLC method.

Three standards of organics acids (C_1 to C_5) solutions (50, 100, and 200 ppm) including a blank were prepared by diluting the parent stock solution and were injected in duplicates in order to determine the limit of detection (LOD) and LOQ limit of quantitation of the organic acids. The linearity was also computed using the prepared standard solutions

3.2.2 Sample preparation for HPLC analysis

A drop of phosphoric acid was added to the sample in the vial (2 mL) using a micro-syringe. Prepared samples were put on the instrument carousel ready for injection in the HPLC instrument.

3.2.3 Standard preparation for GC-MS analysis

A standard stork solution was prepared by mixing possible phenolics in the Merisol effluent into a 1000 mL volumetric flask. There following components were added to the flask (the balance was zeroed each time before addition of any component):

1. 5.00 g ± 0.10g aniline (Let weight be W_1)
2. 5.00 g ± 0.10 g 2,6-xylenol (Let weight be W_2)
3. 70.00 g ± 0.10 g o-cresol (Let weight be W_3)
4. 75.00 g ± 0.10 g phenol (Let weight be W_4)
5. 9.00 g ± 0.10 g o-ethyl phenol (Let weight be W_5)
6. 20.00 g ± 0.10 g 2,5-xylenol(Let weight be W_6)
7. 45.00 g ± 0.10 g 2,4-xylenol (Let weight be W_7)

8. 80.00 g ± 0.10 g p-cresol (Let weight be W_8)
9. 80.00 g ± 0.10 g m-cresol (Let weight be W_9)
10. 10.00 g ± 0.10 g 2,3-xylenol (Let weight be W_{10})
11. 5.00 g ± 0.10 g 3,4-xylenol (Let weight be W_{11})
12. 10.00 g ± 0.10 g p-ethyl (Let weight be W_{12})
13. 35.00 g ± 0.10 g 3,5-xylenol (Let weight be W_{13})
14. 17.00 g ± 0.10 g m-ethyl phenol (Let weight be W_{14})
15. 10.00 g ± 0.10 g naphthalene (Let weight be W_{15})

And let the total weight be $W_T = W_1 + W_2 + W_3 + W_4 + W_5 + W_6 + W_7 + W_8 + W_9 + W_{10} + W_{11} + W_{12} + W_{13} + W_{14} + W_{15}$.

Therefore the individual concentrations could be calculated by the following:

$$\%\text{Concentration} = \frac{W_X}{W_T} X100$$

Where W_x = individual weight of the compound added and W_T is the total weight of the sample in a 1000 ml flask. A 2 mL of the standard solution was used for analysis.

3.2.4 Sample preparation for GC-MS analysis

Approximately 1.02% of dioxane was added to the water samples (2 mL) as an internal standard for quantification purposes.

3.3 Equipment/Instrumentation

Ozone gas was generated by passing pure oxygen gas via Ozomatic LAB 802 ozone generator equipped with ozone analyser BMT 963 press instrument.

Analysis of the of C_1 to C_5 organic acids in the raw and treated sample was performed with the use of Agilent 1100 Series HPLC equipment equipped with Diode array (DAD) and multiple wavelength detectors Agilent 1100 Series. A

symmetry column – C18 (250 X 4.6mm X 5μm) and a personal computer equipped with Agilent Chemstation Software were used.

Analysis to determine of the presence of phenols in the sample was carried out with the use of Agilent Technologies 6890 N gas chromatography instrument linked to the mass spectra while the quantification was done using a FID detector. The GC instrument was equipped with column FFAP (50m X 0.20mm ID X 0.33μm) and accessory Agilent instrument. A personal computer equipped with Agilent Chemstation Software was used for data processing.

Analysis to determine COD concentration of the samples was carried out with the use of Nanocolor® 500D series photometer. The Nanocolor® COD 1500 and COD 15 000 kits were used for the determination of low and high COD concentration levels in the samples, respectively.

3.4 Sample Collection and Collection Method

Effluent sample was obtained from the Merisol Plant during the period 01 June 2007 to 22 June 2007 via grab sample procedure. Each time, an average of five litres of a sample was obtained on daily basis and was transferred into a 250 L drum to make a representative composite effluent sample.
This sample was collected over a period of three (3) weeks during stable operation of the plant and represented typical effluent from the Merisol Plant under normal operating conditions. Collected sample was stored in a refrigerated room (4˚C) during the entire sampling and experimental period. During the experiments a small portion of a sample was drawn from the 250 L container and any unused sample was discarded to avoid contamination of the original sample.

3.5 Ozone Oxidation Experiments

During the study, two sets of ozone oxidation experiments were conducted. The first study was conducted at the natural pH of the sample (4.70) and the second

study was conducted at pH 10.45. The sample pH was adjusted using a solution of NaOH.

Ozone oxidation experiments were conducted in a glass bubble-column reactor (2.5 L) equipped with a porous ceramic diffuser at the bottom. The ozone gas was produced by passing oxygen via the ozone generator. A gas mixture of ozone/oxygen was introduced at the bottom of the reactor through the sample. Any unreacted ozone from the reactor was trapped into the KI solutions (1 and 2) connected to the bubble column via a teflon connector (see Figure 3).

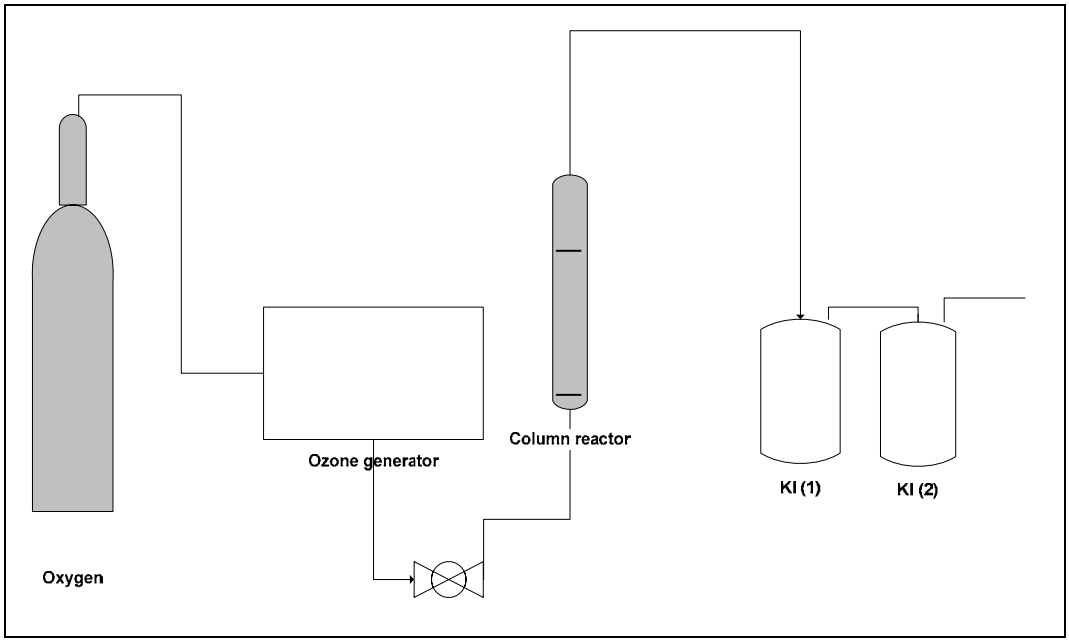


Figure 3: Experimental set-up for ozone oxidation studies

During the experiment, a 500 mL of a wastewater sample was introduced into the reactor and the ozone gas (20 L/h) was bubbled through the column. The concentration of ozone gas entering the reactor was controlled at 40, 80 and 120 ppm for a predetermined period of exposure. The exposure period was varied from 0 to 60 min for each ozone concentration setting at an interval of 10 min. A sample was obtained from the reactor after every 10 min by using a syringe. This

sample was analysed to determine the phenol, COD and organic acids concentrations.

This procedure was run in triplicates under all three ozone gas concentration settings (40, 80 and 120 ppm).Table 2 below summarizes the matrix used during the ozone oxidation experiments.

Table 2: Matrix for the ozone oxidation experiments

Time (minutes)	Ozone (ppm)	Runs
0	40	Triplicate
10	40	Triplicate
20	40	Triplicate
30	40	Triplicate
40	40	Triplicate
50	40	Triplicate
60	40	Triplicate
0	80	Triplicate
10	80	Triplicate
20	80	Triplicate
30	80	Triplicate
40	80	Triplicate
50	80	Triplicate
60	120	Triplicate
0	120	Triplicate
10	120	Triplicate
20	120	Triplicate
30	120	Triplicate
40	120	Triplicate
50	120	Triplicate
60	120	Triplicate

A total of 126 samples including the untreated samples at time zero were obtained and were sent for various analyses to be discussed in the next section.

3.6 Analysis of the Sample

The treated and untreated samples were subjected to various tests/analysis to determine the effect ozone oxidation on the organic contents of the sample. The following were conducted: COD, HPLC and, GC-MS analyses.

3.6.1 Chemical oxygen demand COD –Crude quantification of organics

The work conducted by Zhu *et al* (2004) on the oxidation of phenol using iron (III) catalyzed ozonation has recommended the use of chemical oxygen demand (COD) as an indication when determining the efficiency of phenol oxidation process than the use of phenol and its degradation products.

COD is defined as the amount of a specified oxidant that reacts with the sample under controlled conditions (APHA, 1995). The oxidant of choice is normally dichromate ($Cr_2O_7^{2-}$) ion because of its unique chemical characteristics. During these tests the dichromate ion is reduced into chromic (Cr^{3+}) ion (Standard Methods). The quantity of the oxidant consumed is expressed in terms of oxygen equivalence. COD is often used as a measure of pollutants in natural waters and wastewater. During these test both organic and inorganic carbon constituents of the sample are subject to oxidation, however, the organic fraction predominates (APHA, 1995). The COD method allows for oxidation of most organic compounds where 95 to 100% oxidation is possible (APHA, 1995). It is however known that some compounds such as pyridine and related compounds resist oxidation (APHA, 1995).

The COD method employed for analysing the samples during the study was method 5220 D of the (APHA, 1995). This is a closed reflux colorimetric method and was chosen to avoid volatilization of components in the sample and to cater for possibly high COD concentration. This method has coefficient of variation of ± 5%.

3.6.2 High performance liquid chromatography (HPLC) – Identification of organic acids

Many authors have indicated that ozonation of phenol leads to the formation of lower molecular weight acids such as propionic acid, oxalic acid and formic acids, etc (Zhu *et al*, 2004;. von Gunten, 2002 and Kasprzyk-Hordern *et al,* 2003).

In addition phenol degradation products such as maleic and fumaric acids are also known to occur under various oxidation conditions (Idris and Saed, 2002) A technique usually employed to identify these degradation products is high performance liquid chromatography and gas chromatography (Sano *et al,* 2007 and Zhu *et al,* 2004).

Liquid chromatography employs liquid as a mobile phase and the stationary phase used are mainly of the octadecylsilyl ("ODS") nature. The octyl phase is sometimes recommended. The mobile phase is either acetonitrile or methanol containing water (Faust, 1992).

Separation in a column is based upon the relative abilities of the stationary phase to interact with analytes. During injection of a sample in a column, molecular components of the sample can either be adsorbed on the stationary phase or remain in the mobile phase. Strongly adsorbed sample components spend more time in the stationary phase than weakly adsorbed components. Subsequently, the retention time is directly proportional to the amount of adsorption on the stationary phase (Braun, 1987).

High performance liquid chromatography has also been utilized for many years at Sasol to characterize many effluents such as the Fischer-Tropsch effluents (containing mainly volatile fatty acids). The HPLC instrument used during the study was equipped with diode array (DAD) ultra violet (UV) detector. Below are the analytical conditions used during the study:

Solvent A	: Acetonitrile 0 %
Solvent B	: Water (pH 2.6) 100%
Column	: Symmetry column-C18 (250mm X 4.6mm X 5µm)
Flow rate	: 1 ml/min
Oven temperature	: 40ºC
Injection volume	: 50µl
DAD wavelength	: 210nm

Analysis stop time : 20 min

Post run time :10 min

Pressure limits: : 0-200 bar

Table 3: Solvent gradient time

	Time (min)	% B
1	8.00	90.0
2	12.00	80.0
3	18.00	50.0
4	20.00	0.00
5	30.00	0.00

Retention times and UV spectra of detected peaks were compared with those of standard analytes stored in the spectrum library. In a case of good agreement between retention times (5% window) and spectra (match value above 950) the name of the identified compound was assigned to the peak and the concentration was calculated from the calibration table based on the peak area

3.6.3 Gas chromatography (GC) – Identification and quantification of phenolics

Gas chromatography technique use gas as a mobile phase with either solid (referred to as gas-liquid chromatography) or a non-volatile liquid (gas-liquid chromatography) as a stationary phase (Faust, 1992). For separation and/or identification, the analysed sample must either be of gaseous nature or should have appreciable vapour pressure at the temperature of the column (Faust, 1992).
GC-MS is a combination of gas chromatography and the mass spectra which enables quick identification of analytes. GC-MS is also employed in the environmental field for monitoring of pollutants (Slobodínk *et al*, 1997; Llompart *et al*, 2002). Phenol and its derivatives in the aquatic environment can also be monitored using GC. However, the resulting peaks are generally broad and result in rapid deterioration of the columns (Llompart *et al*, 2002).
The analytical conditions below were used during the study:

Instrument:	Agilent Technologies 6890N
Column	:(FFAP (50m × 0.20mmID × 0.33μm))
Insert	: LNR HP 4mmID, SGL Tap
Hamilton Syringe	: 10 µl
Maximum Column Temp	: 325 °C
Injector Temperature	: 260 °C
Detector Temperature	: 300 °C
Carrier Gas	: Hydrogen
Flow	: 1.3 ml/min
Average Velocity	: 40 cm/sec
Pressure	: 23.94 psi
Split ratio	: 150:1
Sample Volume	: 1.0 µl

Oven Temperature Profile

Initial Temperature	: 60 °C
Hold Time 1	: 5 min
Programme Rate 1	: 6 °C/min
Hold Temperature 1	: 240°C
Programme Rate 2	: 10°C/min

The phenolics in the samples were quantified via an internal standard calibration (dioxane) and Dietz response factors on a FFAP capillary column. The detection limit for the instrument was calibrated at 10 ppm.

CHAPTER FOUR

4. RESULTS AND DISCUSSION

In this section the results obtained during the ozone oxidation study performed on the Merisol effluent under acidic and basic conditions are discussed. The discussion focuses on the removal of phenol as well as the resulting degradation products. This study does not give an in-depth analysis on the kinetics and degradation attributes of the phenols but rather focuses on the observed trends.

4.1 Results on the COD analysis

Figure 4 shows the results obtained during the COD analysis of the treated and untreated water samples during ozone oxidation experiment. The results were obtained for the treated samples at 40, 80 and 120 ppm ozone concentrations under the natural pH of the sample (pH 4.7).

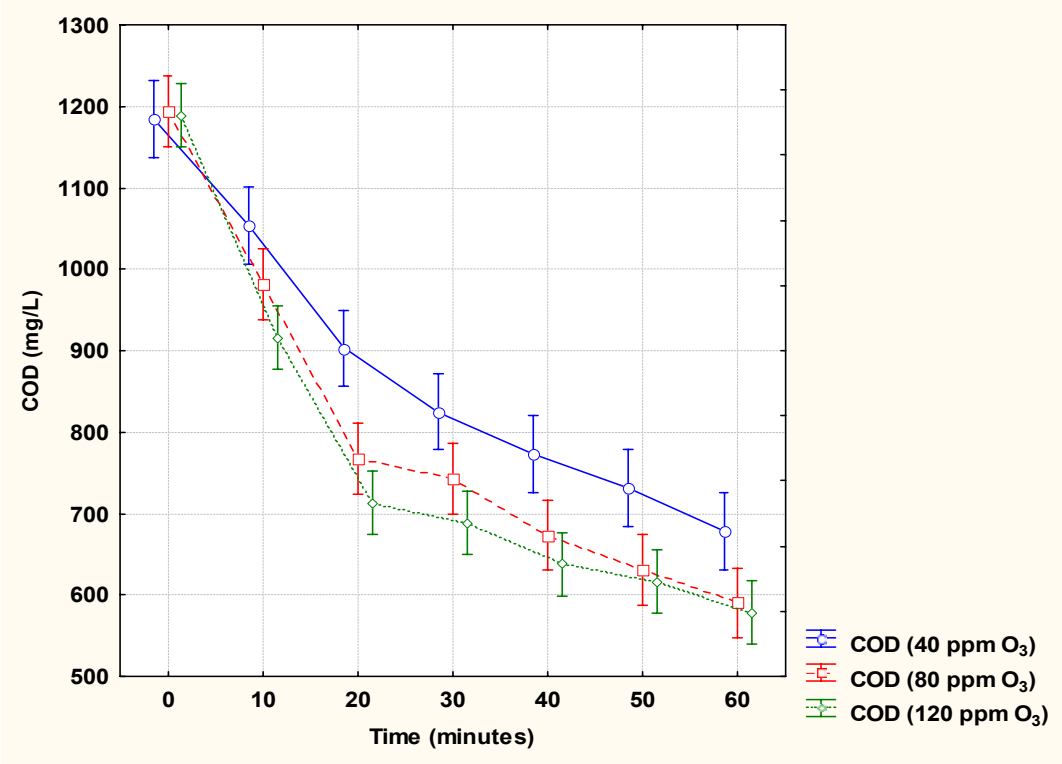


Figure 4: COD concentration of the sample vs. time during oxidation under 40, 80 and 120 **ppm** at pH 4.7 (acidic conditions)

The results in Fig. 4 indicate that the COD concentration of the effluent sample decreased with increasing oxidation time. This trend was observed for all three ozone concentrations understudy. In addition, the results show that the 80 and 120 ppm ozone treatments resulted in COD concentrations below 600 mg/L at 60 min oxidation time. This is equivalent to a COD decrease of approximately 60%.

Furthermore, the results also indicate that there were no significant differences between the 80 and 120 ppm ozone treatment of the samples as shown by overlapping bars (at 95% confidence level).

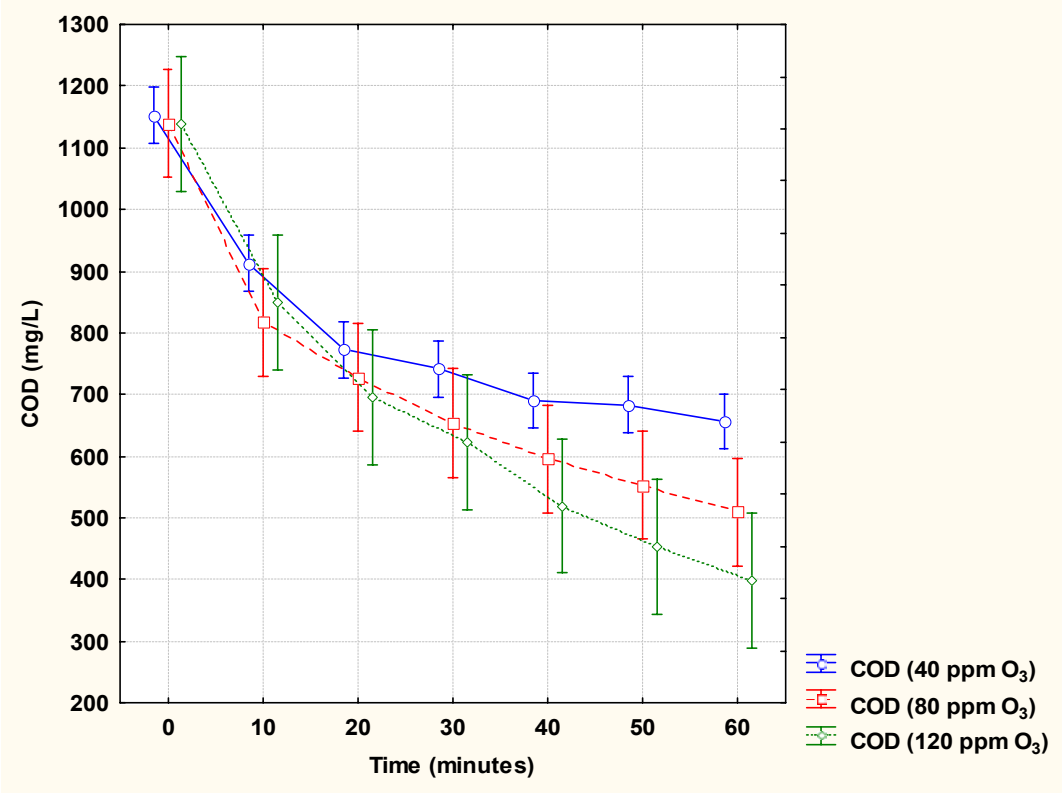


Figure 5: COD concentration of the sample vs. time during oxidation at 40, 80 and 120 **ppm** of ozone at pH 10.45 (basic conditions)

As seen in Fig. 4 previously, the results in Fig. 5 also show a decreasing COD concentration with increasing oxidation time for all three ozone concentrations understudy. Again, the 40 ppm ozone treatment resulted in the least COD

removal efficiency. In addition the Figure 5 shows that the graph for the 40 ppm ozone treatment was rather asymptotic when compared to the 80 and 120 ppm ozone concentrations. This is directly related to poor COD removal efficiency with increasing time.

However, these results indicate that the 120 ppm ozone treatment resulted in COD concentrations below 400 mg/L at 60 min. This was significantly lower when compared to the same treatment under acidic conditions. Although the average COD concentration values for the 120 ppm ozone treatment were generally lower (with the exception at 10 min) than the 80 ppm ozone, the results indicate that the differences were statistically not significant (overlapping error bars at 95% confidence level).

4.2 Identification of organic acids – HPLC analysis

Identification of the organic acids in the water samples was carried out by using the HPLC technique. This method also allowed for proper quantification and identification.

The results in Table 4 show the results obtained during intra assay determination of the HPLC instrument during sample analysis.

Table 4: Intra assay determination of the HPLC instrument

Acid *	Run1	Run2	Run3	Measured mean conc.	Prepared conc.	SD	% RSD
Formic	264	267	265	265.3	265.0	1.25	0.5
Acetic	346	345	347	346.0	345.0	0.82	0.2
Propionic	21	24	20	21.7	20.0	1.70	7.8
Butyric	39	41	43	41.0	40.0	1.63	4.0
Pentanoic	22	22	19	21.0	20.0	1.41	6.7

* All concentrations are in ppm

From the results in Table 4 it was evident that the method had good reproducibility. There was very low variation in the acid concentrations with

relatively low standard deviations except for propionic acid. The results indicate that the precision of the instrument was of acceptable standards with all %RSD values < 8 %. This allowed for good quantification and identification of the organic acids in the samples. Furthermore, the results indicated good accuracy when comparing the measured mean with the true mean of the prepared samples.

The following results were obtained during the determination of the LOD and LOQ during HPLC analysis.

Table 5: Results on LOD and LOQ determination

Acid	R^2	LOD (ppm)	LOQ (ppm)
Formic	0.9999	9	27
Acetic	0.9999	3	9
Propionic	0.9999	4	12
Butyric	0.9999	1	3
Pentanoic	0.9999	2	6

Figure 6 below shows a chromatograph of the acid standards obtained during the HPLC run. Visible in this figure are formic, acetic, propionic, butyric, and pentanoic acids all in concentration of approximately 100 ppm. They are shown in the order of increasing retention time.

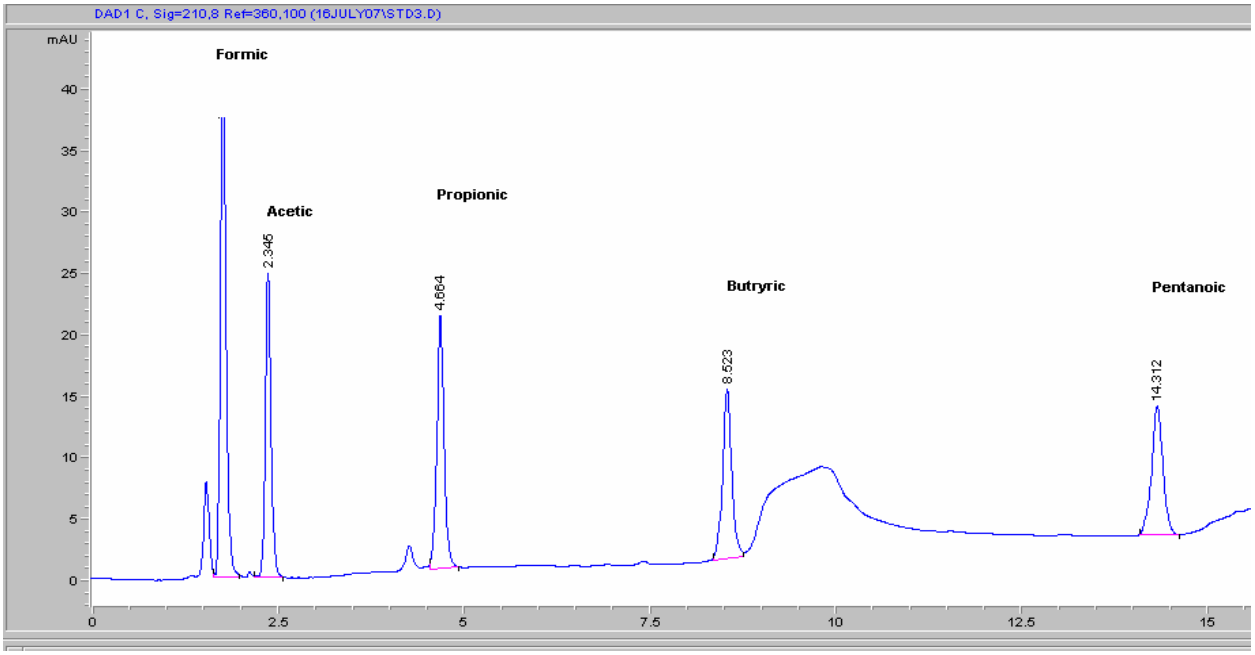


Figure 6: Chromatogram of the organic acid standard of approximately 100 ppm per acid mixture

Organic acids present in the water samples were identified by comparing their retention times with those of the known standards. Both the standards and the samples were analysed under the same operating conditions.

Identification of the unknown organic acids in the sample was carried out by superimposing the chromatographs of both the sample and the standard solution. Figure 7 shows an overlay of the organic acid standards (blue) with the sample (red) chromatographs. Note that all organic acids in the sample were identified with the exception of pentanoic acid.

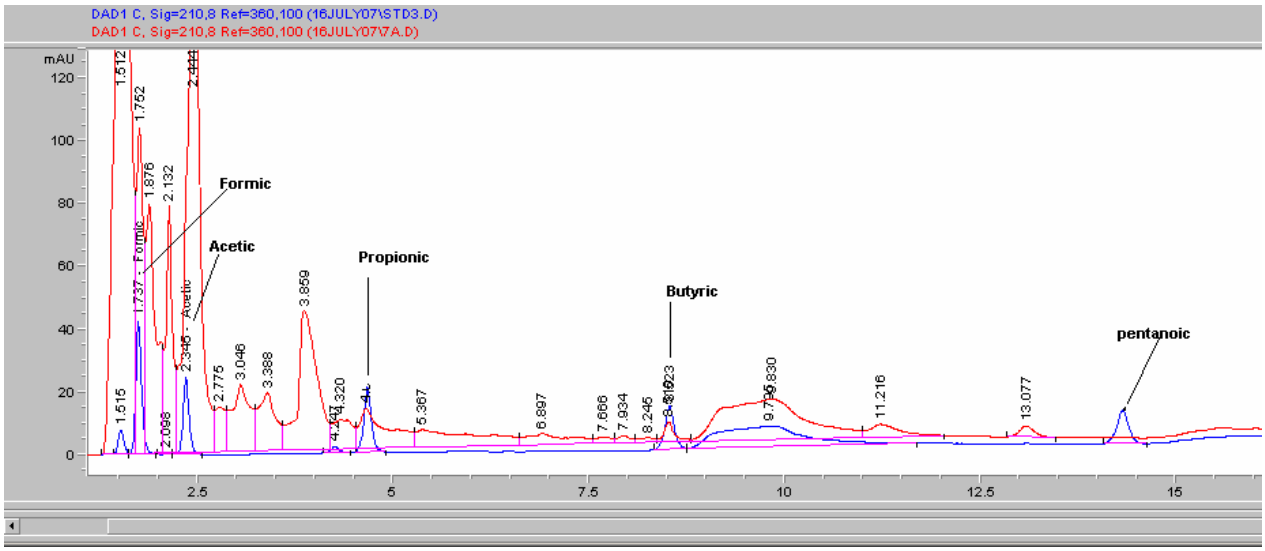


Figure 7: Overlay of the organic acid standards and the water sample chromatographs indicating identified organic acids in the sample

The results obtained when analysing the water samples during ozone oxidation experiments (under acidic and basic conditions) by HPLC are presented in Figures 8, 9 and 10 as well in Tables 6, 7 and 8. Because of the variability in the results from various runs the data was normalized by considering the concentration of the acid at time t (C) and dividing it with initial concentration (C_0).The ratio of C/C_0 allowed for a proper comparison of the trends observed during the oxidation of the water samples. Ratio values of $C/C_0 > 1$ would indicate that a particular acid was produced during oxidation whereas values of $C/C_0 < 1$ would mean that that there was a removal of the measured component in the water.

The results in Figure 8 show the trends that were observed when treating the Merisol effluent at 40 ppm ozone concentration under both acidic and basic conditions.

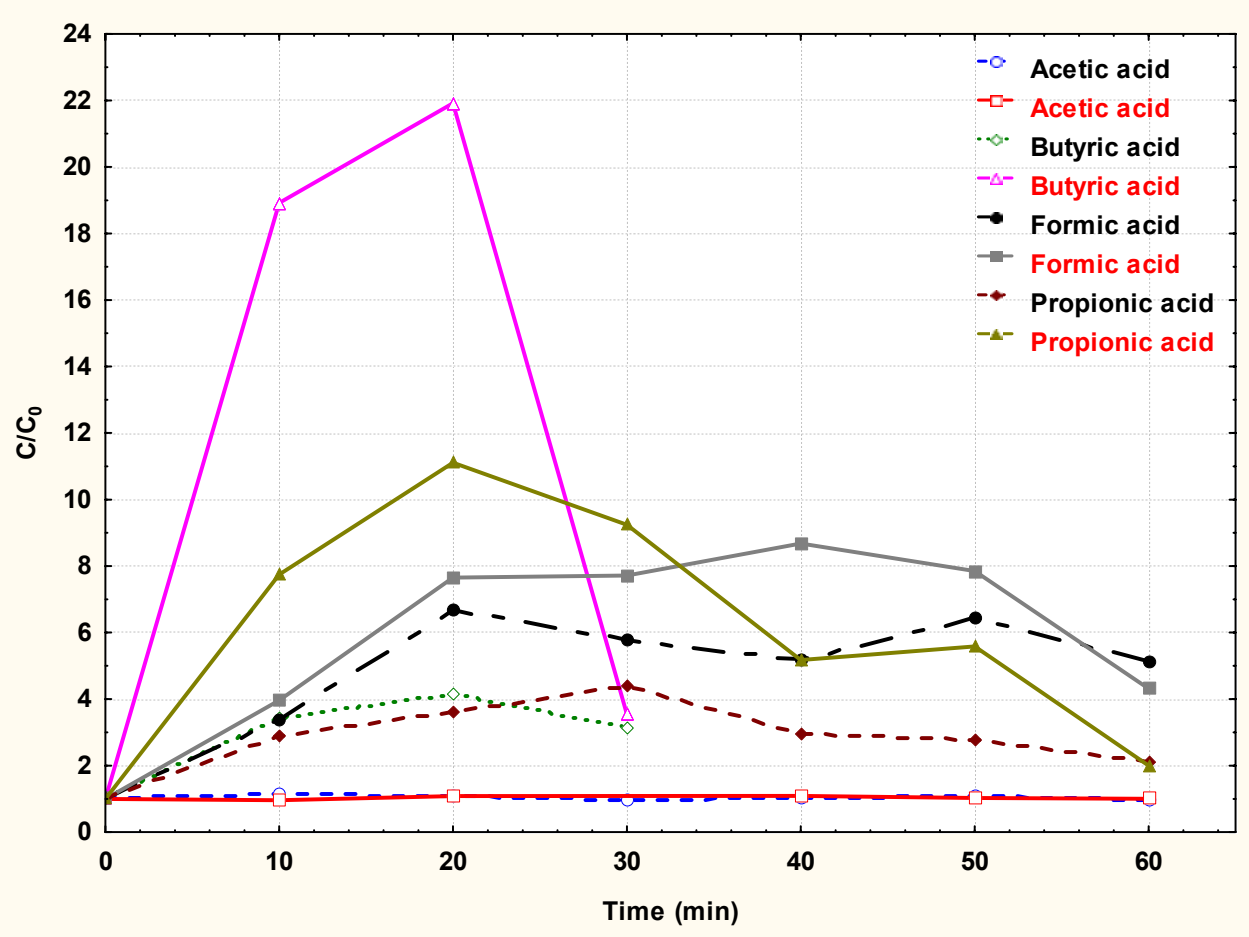


Figure 8: Normalized scatter plot of acid concentrations vs. time at 40 ppm ozone. Key: Red text = acidic conditions and black text = basic conditions

The results in Figure 8 and Table 6 indicate that there was a presence of acetic (299.3 ppm), butyric (16.0 ppm), formic (49.0 ppm) and propionic acids (10.5) in the untreated sample (i.e. at t = 0). Furthermore, the results indicate that acetic acid was in larger proportion when compared to the other acids. However, this observation was expected since the Merisol Plant utilises butyl acetate as a solvent for phenol extraction. Butyl acetate can be hydrolysed to butanol and acetic acid /acetate ion under acidic and basic conditions.

The results also indicate that the concentrations of all acids (with the exception of acetic) were noted to increase initially with increasing exposure time during oxidation. However, the concentration of butyric acid was noted to diminish beyond detectable levels after 30 min of oxidation under both acidic and basic conditions. Although the production of butyric acid was much more under acidic conditions, the degradation trends it followed were similar to the one observed under basic conditions.

The trends observed for formic and propionic acids were similar for both acidic and basic conditions. The trends for acetic acid were rather unique in a sense that its concentration remained almost unchanged throughout the entire oxidation period under both acid and basic condition.

Table 6: Average and %RSD results obtained at 40 ppm under both acidic and basic conditions

	Average concentrations (ppm) and % RSD values under acidic conditions						
Time (min)	**0**	**10**	**20**	**30**	**40**	**50**	**60**
Acetic	299.3(5.8)	288 (14.7)	325 (12.2)	N.D (N.A)	325.3 (22.5)	307.3 (2.1)	301 (2.6)
Butyric	16.0 (0.0)	302.7 (14.3)	350.7 (26.3)	56.7 (51.4)	N.D (N.A)	N.D (N.A)	N.D (N.A)
Formic	49.0 (8.7)	194 (33.6)	375 (9.6)	378 (9.6)	425.3 (21.2)	384.7 (21.6)	211.3 (16.5)
Propionic	12.5 (6.7)	81.3 (8.4)	116.7 (N.A)	97 (21.6)	54.3 (26.6)	58.7 (38.4)	21.0 (12.6)
	Average concentrations (ppm) and % RSD values under basic conditions						
Acetic	285.7(6.3)	319.3 (8.1)	303.3 (14.5)	268 (8.2)	286 (2.4)	305 (5.2)	272.3 (5.6)
Butyric	23.3(17.3)	80 (80.6)	97 (46.6)	72.5 32.2)	N.D (N.A)	N.D (N.A)	N.D (N.A)
Formic	21 (9.5)	71 (29.7)	140.3 (53.6)	121.3 (39.1)	109.3 (42.3)	135.7 (40.7)	107.3 (51.4)
Propionic	12 (27.3)	32 (40.9)	39.7 (24.2)	48.3 (9.8)	32.7 (51.3)	30.3 (39.3)	23 (85.6)

N.A = Not Available; N.D = Not Detected

The results in Figure 9 and Table 7 also indicate that there was a presence of organic acids with the exception of pentanoic acid in the untreated water sample. This observation was similar to the results discussed previously in Figure 8 and Table 6. The concentration of acetic acid was again observed to be in larger proportions when compared to the other acids. As previously observed in Figure

8, the results in Figure 9 and Table 7 indicate that the average concentration of acids were noted to increase initially with increasing exposure time during oxidation and this was followed by a decrease in the concentration. It is also important to note that the % RSD values obtained during the experiment were significantly > 15%. However, this observation was not surprising because the treated samples could still be unstable after exposure to ozone and also due to possible time delay in analysing the samples. Furthermore, it is important to note that the general trends obtained during the study were of more significance than the absolute values. In general the results also indicated that the concentration of organic acids was relatively higher under acidic conditions at any given point during oxidation.

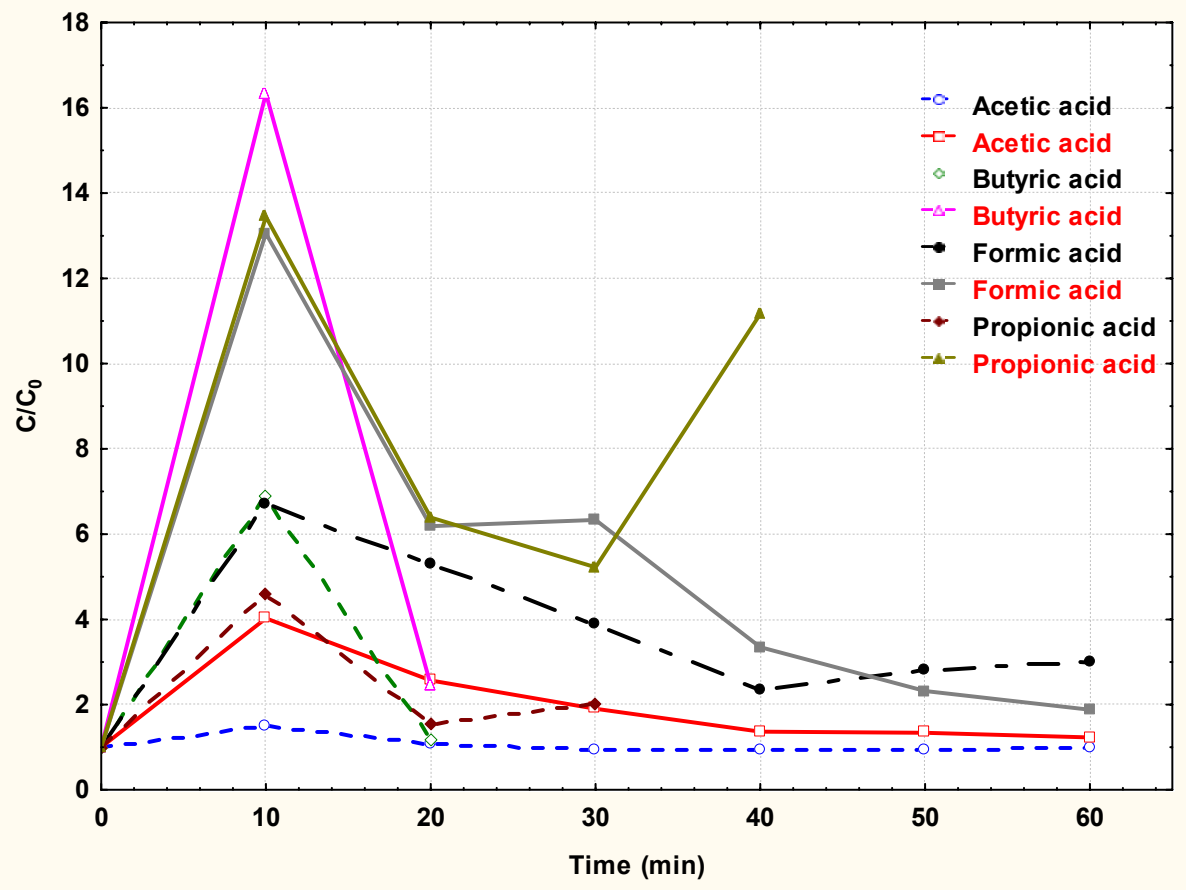


Figure 9: Normalized scatter plot of acid concentrations vs. time at 80 ppm ozone

In general the results also indicated that the concentration of organic acids was relatively higher under acidic conditions at any given point during oxidation.

The concentration of butyric acid was noted to diminish beyond detectable levels after 20 min of oxidation under both acidic and basic conditions. The diminishing of butyric acid concentrations were observed to be 10 min earlier when compared to the previous scenario at 40 ppm ozone. The concentrations of propionic acid were also noted to decrease beyond detectable levels at 30 min and 40 min oxidation periods under basic and acidic conditions, respectively.

The concentration of acetic acid was observed to remain mostly unchanged (with the exception at 10 min) under basic conditions. Under acidic conditions, a significant increase was noted during the first 10 min but later decreased significantly. Note that although no acetic acid was detected at 30 min under acidic oxidation conditions, it was later detected throughout the rest of the oxidation period. Although there were significant differences in the measured concentrations of acetic acid under acidic and basic conditions, the observed trends during oxidation experiments were rather similar.

Table 7: Average and %RSD results obtained at 80 ppm ozone under both acidic and basic conditions

Average concentrations (ppm) and % RSD values under acidic conditions							
Time (min)	**0**	**10**	**20**	**30**	**40**	**50**	**60**
Acetic	206.7(9.9)	832 (19.7)	530.3(43.2)	N.D (N.A)	282.3 10.9)	276.7(13.4)	254.0(3.6)
Butyric	13.0 (0.0)	212.3(27.7)	32.0 (N.A)	N.D (N.A)	N.D (N.A)	N.D (N.A)	N.D(N.A)
Formic	45.0 (40.4)	587.3(11.0)	278.3(60.7)	285 (31.3)	150.7(18.1)	104.3(29.5)	84.7(31.4)
Propionic	13.0 (16.7)	80.7 (31.9)	38.3 (34.0)	31.3(50.1)	67.0 (N.A)	N.D (N.A)	N.D(N.A)
Average concentrations (ppm) and % RSD values under basic conditions							
Acetic	244.3(45.7)	372 (7.7)	258.7(16.6)	230.7(8.7)	224.7 (5.0)	231(8.7)	243.3(N.A)
Butyric	23.0 (64.2)	158.3 (0.0)	27(N.A)	N.D (N.A)	N.D (N.A)	N.D (N.A)	N.D (N.A)
Formic	19.3 (43.5)	130 (24.3)	102.7(27.0)	75 (25.6)	45 (4.6)	54.3 (24.8)	57.7 (N.A)
Propionic	8.7 (66.3)	39.7 (18.9)	13.3 (28.3)	17.5(N.A)	N.D (N.A)	N.D (N.A)	N.D (N.A)

N.A = Not Available; N.D = Not Detected

Furthermore, the results in Figure 9 and Table 7 indicate that the concentrations of butyric acid and propionic acid decreased beyond detection levels under both acidic and basic oxidation conditions.
In addition the butyric acid concentrations were noted to decrease relatively faster than propionic acid concentrations under both oxidation conditions

The results obtained when treating the water sample at elevated ozone concentration (120 ppm) under both acidic and basic conditions are depicted in Figure 10 and tabulated in Table 8.

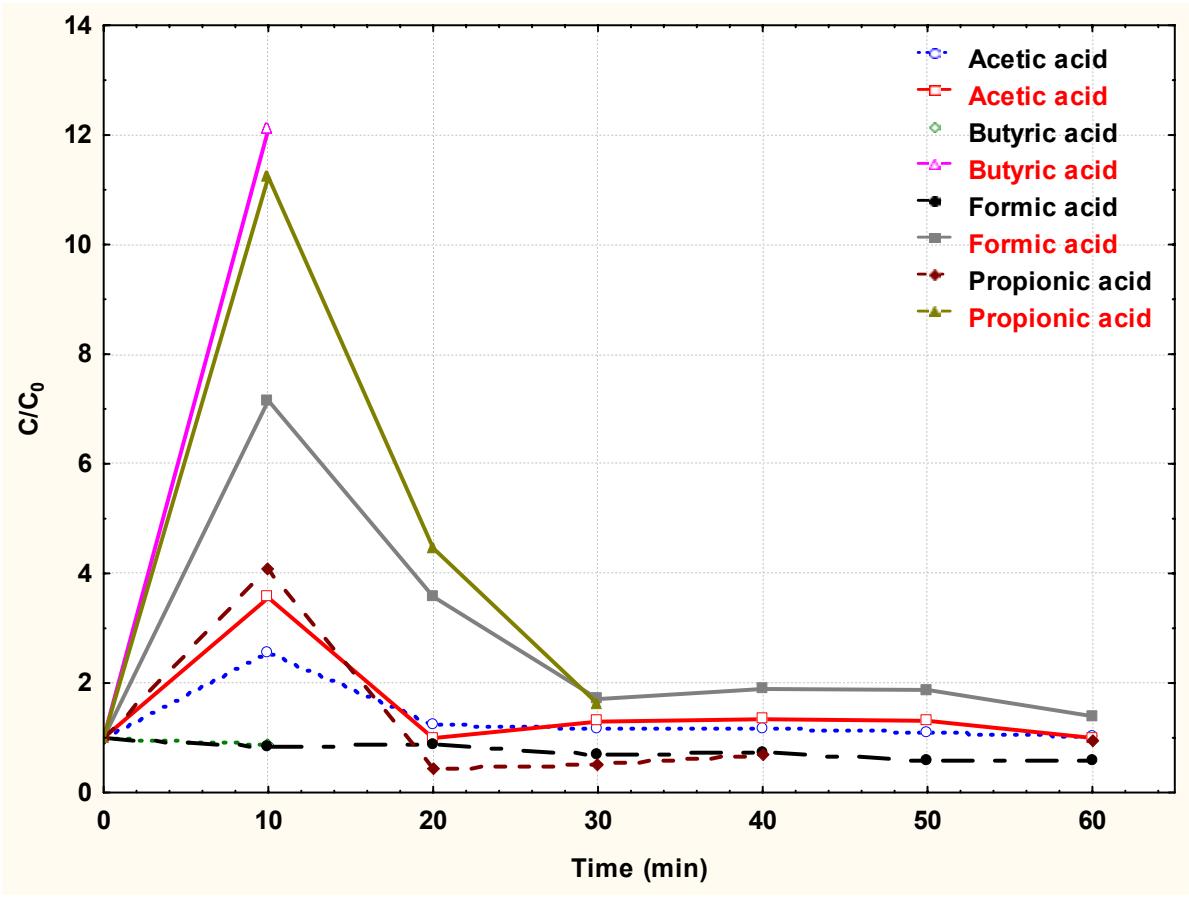


Figure 10: Normalized scatter plot of acid concentrations vs. time at 120 ppm ozone

The results obtained in Figure 10 and Table 8 indicates that a similar trend in the measured concentration of acids over time was observed at 120 ppm oxidation conditions. An initial increase in the acid concentrations followed by a decline and a rather steady concentration was noted as previously under 40 and 80 ppm

oxidation conditions. However, this observation was not true for butyric and formic acids under basic oxidation conditions which showed an initial decline.

The concentrations of butyric and propionic acids were noted to diminish with increased oxidation time under both acidic and basic conditions. This observation was similar to the previous scenario at 80 ppm ozone concentration.

Table 8: Average and %RSD results obtained at 120 ppm ozone under both acidic and basic conditions

Average concentrations (ppm) and % RSD values under acidic conditions							
Time (min)	**0**	**10**	**20**	**30**	**40**	**50**	**60**
Acetic	194.7 (30.0)	692 (N.A)	193.7 (N.A)	N.D (N.A)	261.0 (15.8)	255.3 (15.4)	194.0 (54.0)
Butyric	19(0.0)	230 (N.A)	N.D (N.A)	N.D (N.A)	N.D (N.A)	N.D (N.A)	N.D (N.A)
Formic	50.3 (6.1)	360 (11.4)	180 (34.2)	86 (50.4)	95.3 (39.0)	94.3 (44.9)	70.3 (57.5)
Propionic	15 (10.9)	73 (40.7)	29 (48.8)	12.5(47.1)	N.D (N.A)	N.D (N.A)	N.D (N.A)
	Average concentrations (ppm) and % RSD values under basic conditions						
Acetic	176.7 (N.A)	452 (5.0)	222.0 (N.A)	206.7	203.7 (11.2)	191.7 (6.4)	182.3 (N.A)
Butyric	31.7 (49.3)	27.7 N.A)	N.D (N.A)	N.D (N.A)	N.D (N.A)	N.D (N.A)	N.D (N.A)
Formic	54.3 (45.4)	45.7(24.3)	47.7 (41.2)	37.7(19.4)	38.7 (26.5)	32.0 (8.8)	32.0 (N.A)
Propionic	11.5 (N.A)	47.0 (N.A)	5.0 (16.7)	6.0 (N.A)	8.0 (N.A)	N.D (N.A)	11.0 (N.A)

NA = Not Available; N.D = Not Detected

In addition, the results in Table 8 indicate that in general the concentration of acids was observed to be lower under basic oxidation conditions. This observation was expected since under basic ozone oxidation conditions, the mode of oxidation is via hydroxyl radicals and is known to attack indiscriminately and thus decreasing the concentrations of both the acids and phenol (Wu *et al, 2000*; Munter, 2001; and Yiacoumi and Vithayaveroj, 2001). Under acidic conditions more organic acids were produced due to the degradation of phenol via direct ozone attack. The produced acids are known to react very slowly with ozone and thus their concentration tends to be slightly higher (von Gunten, 2003; Wu *et al, 2000*; Munter, 2001; and Yiacoumi and Vithayaveroj, 2001).

4.3 Combined GC and COD analysis

The GC-MS analysis indicated the presence of phenol and organic acids in the sample. The quantification and identification of organic acids and phenol was conducted by using HPLC (these results were discussed previously) and GC, respectively.

Following the recommendations from the study conducted by Zhu *et al* on the oxidation of phenol using iron (III) catalyzed ozonation COD concentration was used to quantify and to identify the trends during the oxidation of phenol (Zhu *et al*, 2004). Therefore the COD data was used for the interpretation of the data and the observed trends during the ozone oxidation of the Merisol effluent under both acid and basic conditions. Furthermore, the data obtained on the analysis of the phenol content of the samples was also correlated with the COD data. The results obtained are graphically presented in Figures 11 and 12 for acidic and basic conditions, respectively.

The normalized COD and phenol results obtained under both acidic and basic oxidation conditions are shown in Figures 11 and 12, respectively. These results are also tabulated in Table 9 and are also related to the results discussed previously in Figures 5 and 6.

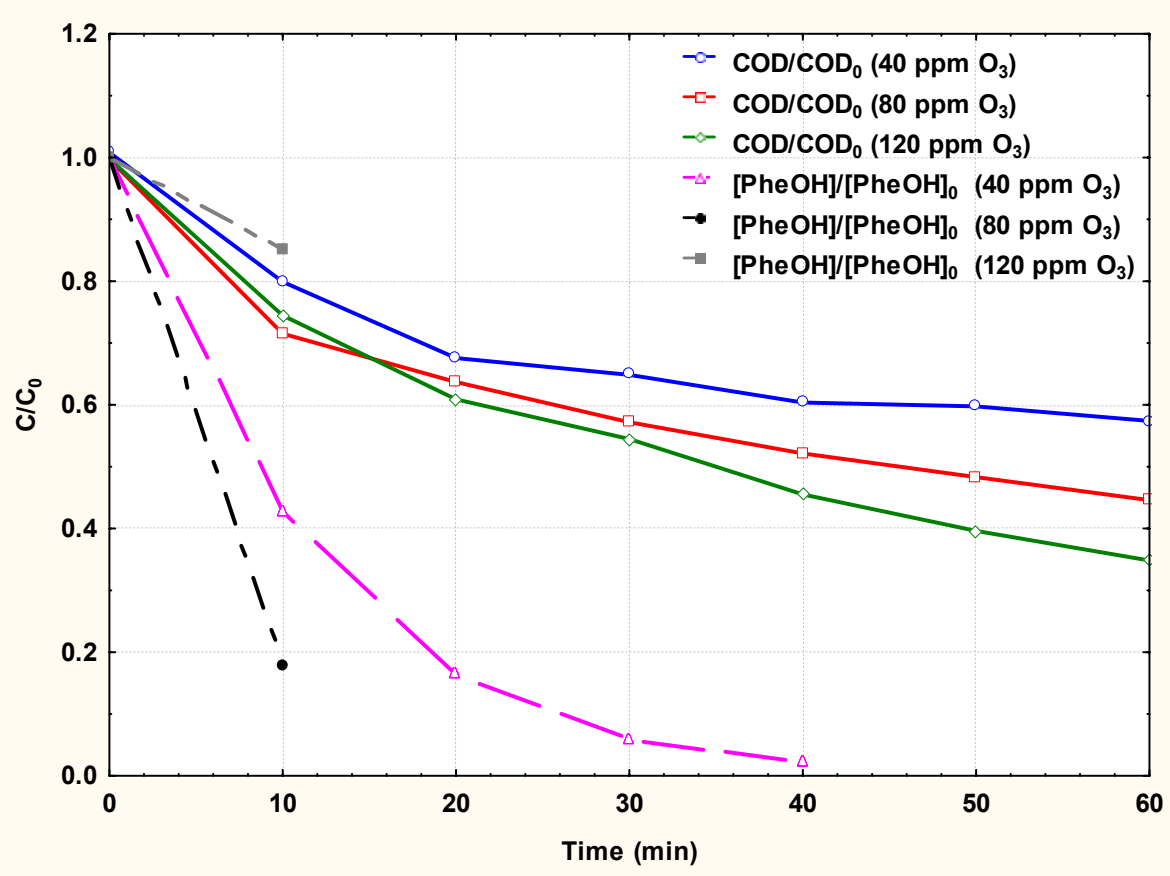


Figure 11: Normalized phenol concentrations with time under varying ozone concentrations (acidic conditions)

The results in Figures 11 and 12 as well as in Table 9 indicate that in general there was a decrease in the measured COD and phenol concentrations with increasing oxidation time. This observation was true for both acid and basic oxidation conditions.

The results in Table 9 and Figure 11 indicate that the average phenol concentration decreased to below detection levels within 40 min of oxidation. In addition the results also show that increasing ozone concentrations had a direct

impact on the removal of the phenol. The removal of phenol followed this order 120 ppm O_3 > 80 ppm O_3 > 40 ppm O_3 and this was expected. This trend was also observed for the decrease in the COD concentration of the effluent as seen in Figure 11.

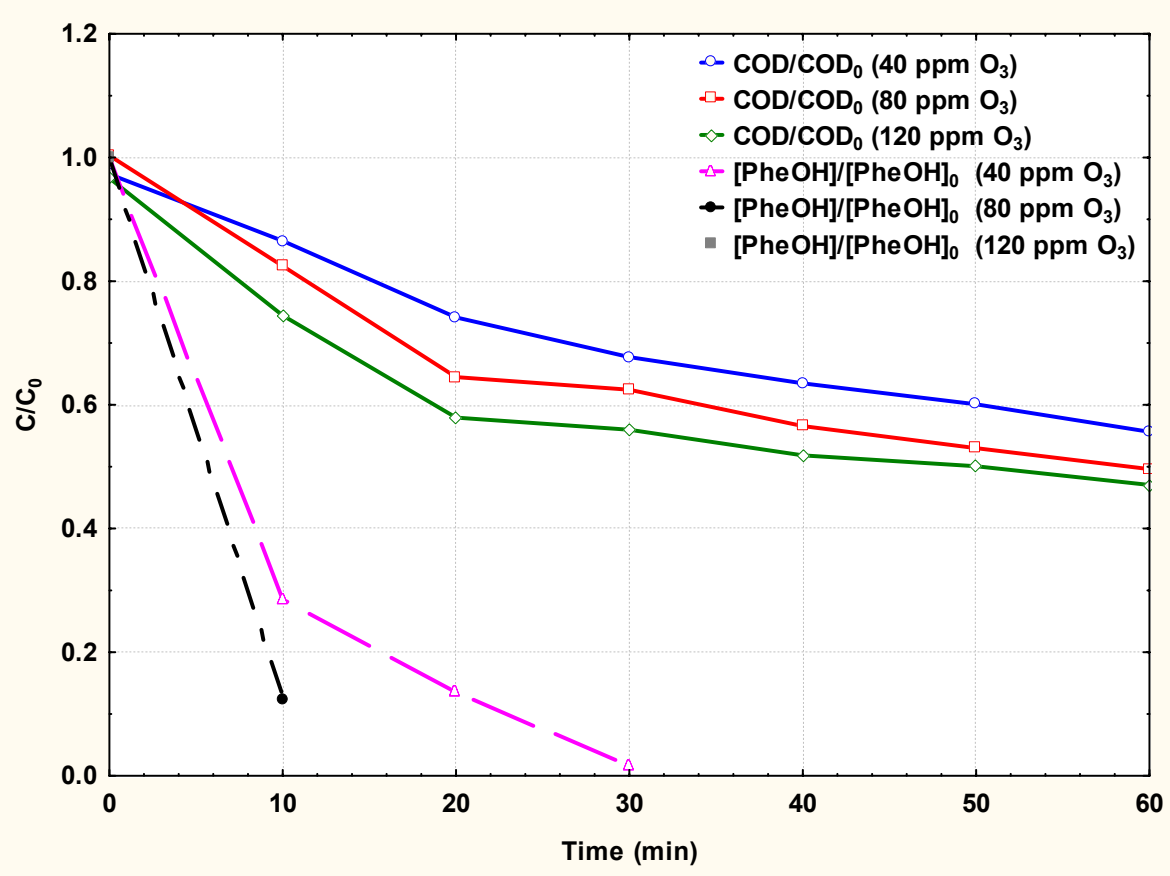


Figure 12: Normalized phenol concentrations with time under varying ozone concentrations (basic conditions)

The results in Figure 12 also indicate that the average phenol and COD concentrations decreased with increased oxidation time. Furthermore the results also indicate that a similar trend observed previously in Figure 10 was followed where phenol removal was in this order: 120 ppm O_3 > 80 ppm O_3 > 40 ppm O_3. This trend was also observed for the COD concentrations as seen in Figure 11.

It is important to note that the results in Table 9 and Figures 11 and 12 indicate that in general the removal of phenol in solution was observed to be more quicker under basic oxidation conditions (i.e. basic>acidic) . This observation could be

explained by the fact that under basic conditions ozone rapidly decomposes to form hydroxyl radicals (Wu *et al*, 2000 and Munter, 2001). The reaction kinetics of the hydroxyl radicals with organic molecules are known to be extremely fast. For an example the rate constant for benzene oxidation under ambient conditions is 2 M^{-1}•$s^{-}1$ for direct ozonation and 7.9 $X10^{9}$ M^{-1}•$s^{-}1$ for indirect ozonation (von Gunten, 2003).

Table 9: Results on the phenol qualification under acidic and basic oxidation conditions

Ozone (40 ppm)							
	Acidic						
Time (min)	**0**	**10**	**20**	**30**	**40**	**50**	**60**
Ave.	293	133	46	17	7	N.D	N.D
Std. dev	82.2	80.0	11.3	2.1	6.2	N.A	N.A
%RSD	28	60	25	12	89	N.A	N.A
	Basic						
Ave.	331	94	46	N.D	N.D	N.D	N.D
Std. dev	49.2	16.0	26.3	N.A	N.A	N.A	N.A
%RSD	15	17	57	N.A	N.A	N.A	N.A
Ozone (80 ppm)							
	Acidic						
Time (min)	**0**	**10**	**20**	**30**	**40**	**50**	**60**
Ave.	414.9	107.6	N.D	N.D	N.D	N.D	N.D
Std. dev	90.3	50.1	N.A	N.A	N.A	N.A	N.A
%RSD	22	47	N.A	N.A	N.A	N.A	N.A
	Basic						
Ave.	365	47	N.D	N.D	N.D	N.D	N.D
Std. dev	28.2	4.2	N.A	N.A	N.A	N.A	N.A
%RSD	8	9	N.A	N.A	N.A	N.A	N.A
Ozone (120 ppm)							
	Acidic						
Time (min)	**0**	**10**	**20**	**30**	**40**	**50**	**60**
Ave.	381	315	N.D	N.D	N.D	N.D	N.D
Std. dev	18.6	24.3	N.A	N.A	N.A	N.A	N.A
%RSD	5	8	N.A	N.A	N.A	N.A	N.A
	Basic						
Ave.	341.8	N.D	N.D	N.D	N.D	N.D	N.D
Std. dev	73.59	N.A	N.A	N.A	N.A	N.A	N.A
%RSD	22	N.A	N.A	N.A	N.A	N.A	N.A

N.A = Not Available; N.D = Not detected

The results in Table 9 and Figures 11 and 12 also indicate that in general the kinetics for COD removal under basic conditions were faster when compared to the acidic conditions.

4.4 Conclusion and Recommendations

It was evident from the study that ozone oxidation technology under both acidic and basic conditions could capably treat the Merisol effluent to the required COD concentration specification.

Under acidic conditions, the effluent COD concentration was reduced from approximately 1200 mg/L to 579 mg/L at 120 ppm O_3. On the other hand, the COD concentration was reduced to 397 mg/L at 120 ppm O_3 under basic conditions. These results were well within the required 1000 mg/L COD specification level. In addition, these results indicate that oxidation under basic conditions yielded better results when compared to oxidation under the natural pH of the effluent (acidic).

Phenol and acetic acid (as well as traces of formic, butyric and propionic acids) were identified as major components in the Merisol effluent. The presence of acetic acid was due to the use of butyl acetate for phenol extraction by the Merisol Plant.

The degradation products of phenol ozone oxidation were identified as formic, butyric and propionic acids which were shown to increase during oxidation. Furthermore, the concentration of these acids decreased with increasing oxidation time

Given the possible fluctuations in the effluent pH, it is recommended that either acidic or basic oxidation processes be considered for the Merisol Plant. Implementation of this technology would increase the degree of compliance of the Merisol Plant as well as that of Sasol One site with regard to the Department of

Water Affairs and Forestry (DWAF) phenol specification under the discharge water licence conditions.

FUTURE WORK

Following promising results obtained during this study a pilot-scale study has been recommended to verify the results. In addition economic evaluation of this technology will be performed.

The high pH ozone oxidation process may also be applied to treat the combined effluents from the Sasol One site prior to entry into the Bioworks. This would result in increased BOD/COD ratios as well as a decrease in the total organic load to the Sasol One Bioworks.

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APPENDIX 1

Table A1.1 1: COD results under acidic oxidation conditions

Ozone (40 ppm)							
	Time (min)						
Run#	0	10	20	30	40	50	60
1	1218	1061	901	832	799	738	682
2	1176	1126	856	804	752	724	664
3	1161	974	952	839	769	734	687

Ozone (80 ppm)							
	Time (min)						
Run#	0	10	20	30	40	50	60
1	1190	980	734	717	654	625	579
2	1192	1023	834	791	703	656	616
3	1199	941	734	721	663	611	576

Ozone (120 ppm)							
	Time (mins)						
Run#	0	10	20	30	40	50	60
1	1230	954	703	684	665	643	570
2	1176	947	729	691	639	619	592
3	1161	846	706	690	609	586	574

Table A1.2: COD results under basic oxidation conditions

Ozone (40 ppm)							
	Time (min)						
Run#	0	10	20	30	40	50	60
1	1143	97	736	698	642	680	647
2	1138	853	807	790	724	686	654
3	1175	912	774	736	704	683	667

Ozone (80 ppm)							
	Time (min)						
Run#	0	10	20	30	40	50	60
1	1143	714	752	640	555	538	499
2	1128	951	806	733	683	578	508
3	1148	787	626	588	550	541	522

Ozone (120 ppm)							
	Time (min)						
Run#	0	10	20	30	40	50	60
1	1141	1077	801	694	558	491	407
2	1154	711	629	585	499	425	392
3	1121	761	654	586	501	440	393

APPENDIX 2

Preparation of organic acid standards

This solution was prepared by adding the organic acids in this manner (the balance was zeroed each time before addition of any component):

1. 0.11 g ± 0.008 g formic acid (let weight be W_1)
2. 0.11 g ± 0.008 g formic acid (let weight be W_2)
3. 0.11 g ± 0.008 g propionic acid (let weight be W_3)
4. 0.10 g ± 0.008 g butyric acid (let weight be W_4)
5. 0.11 g ± 0.008 g pentanoic acid (let weight be W_5)
6. Dilute to the mark with pH 2.7 water (solvent B) after tarring the balance and reweigh the flask (let weight be W_6)
7. And let the total weight be $W_T = W_1 + W_2 + W_3 + W_4 + W_5 + W_6$

Therefore the concentration of the individual organic acid could be calculated by using this formula:

(ppm) Concentration = $\frac{W_X}{W_T} X 10^6$

Where W_x = individual weight of the organic acid added and W_T is the total weight of the sample in a 100 ml flask.