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Study of byproducts from dry-mill ethanol plants

by

Shilpi Singh

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Program of Study Committee:
Maohong Fan (Co-major Professor)
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This is to certify that the master's thesis of

Shilpi Singh

has met the thesis requirements of Iowa State University

Signatures have been redacted for privacy

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STUDY OF BYPRODUCTS FROM DRY-MILL ETHANOL PLANTS

ABSTRACT

S. Singh

Volatile organic compounds (VOCs) are released during the drying of distiller's wet grains from dry-mill ethanol production plants. Almost nothing has been studied about these emissions so far including the information gaps on the types of VOCs emitted and the temperature range at which most of them are evolved. One of the two objectives of this study is to find out the temperature ranges where emission of VOCs is possible and also to investigate the main cause of VOC emissions.

Samples from ethanol plant including distiller's wet grains, distiller's dried grains with solubles, syrup, and thin stillage were tested using thermogravimetric and derivative thermogravimetric analyses (DTGA) to acquire information on the loss of volatiles as a function of temperature. The results showed weight loss events in all the samples in the temperature range of 25-100°C and are expected to be due to moisture and volatile organic compounds.

Thin stillage obtained from centrifuging the whole stillage has a very high chemical oxygen demand (COD) of 75,000 mg/L. A portion of thin stillage is recycled to the plant for reuse and remaining is sent to the evaporator to be converted into syrup which is then added to the DWG during drying operations. The other objective of this study is the treatment of thin stillage, which would help in providing cleaner recycle water to the ethanol industry and in reducing the emissions of VOCs.

Ozonation and catalytic ozonation were applied for the removal of COD from thin stillage as simple single-step unit processes. Two different catalysts Fe(II) and Fe(III) were used and both the catalysts resulted in almost the same improved COD removal rates when compared to ozonation alone.

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CHAPTER 1. INTRODUCTION

Dry-milling process is a commonly used process in the United States for ethanol production from corn. This study focuses on two of the concerns related to ethanol production from dry-milling, which are 1) to reduce emissions of volatile organic compounds (VOCs) from drying of distiller's wet grains (WDG) with solubles, and 2) to find methods to clean thin stillage in order to provide cleaner recycle water to the ethanol plant.

The thesis is organized in five chapters. Chapter 2 presents a literature review on ethanol, the ethanol production process, and a few concerns related to dry-mill ethanol production. The control and abatement of VOCs released from dry-mill ethanol production is one of the objectives of this research. This chapter briefly discusses the various kinds of VOCs, their sources, harmful effects on humans, and traditional techniques used for their monitoring and abatement. The second objective of this research is the chemical treatment of thin stillage to provide cleaner recycle water to the dry-mill ethanol plants. It reviews the various methods employed to reduce the chemical oxygen demand (COD) of wastewater.

Chapter 3 explains the thermoannalytical studies conducted on the byproduct streams from dry-mill ethanol production. It explains the materials and methods that have been used to acquire information on the loss of volatiles from different samples obtained from the dry-mill ethanol plant. It also summarizes the results obtained using thermogravimetry.

Chapter 4 summarizes the ozone treatment for COD removal of thin stillage from dry-mill ethanol plant. It includes a literature review of the published studies on ozonation and catalytic ozonation of organic compounds in wastewater. It describes the various instruments and chemicals used in this research, results of ozonation and catalytic ozonation, suggested mechanisms, and the cost evaluation.

Finally, chapter 5 concludes the results from chapter 3 and 4. It also provides a few recommendations on future research.

CHAPTER 2. LITERATURE REVIEW

2.1 INTRODUCTION

Oil and natural gas are the two primary energy sources in today's world. At present, oil accounts for almost 40% of all energy use. The current rate of consumption of non-renewable energy resources suggests that we will soon deplete all our natural energy resources. So, there is a need to look for alternatives to natural energy resources to lessen our dependence on them. For the past few decades, researchers have been focusing on developing agricultural alternatives, such as plant matter, or *biomass*, to create products and energy.

Biomass is defined as the recent organic matter derived from plants as a result of the photosynthetic conversion process, or from animals, and which is destined to be utilized as a store of chemical energy to provide heat, electricity, or transport fuels [1]. Crops and residues from agricultural production, organic waste by-products from food and fiber industry, wood from forests, etc. are some common biomass resources. The chemical energy contained in the biomass is derived from the process of photosynthesis. Biomass with its stored chemical energy has the potential to become a fuel. In the biomass derived fuel or *biofuels*, include methane, producer gas, alcohols, esters and other chemicals made from cellulosic biomass.

Biofuels have many advantages over conventional fuels. All petroleum-derived fuels are primarily compounds of carbon and hydrogen atoms. Liquid biofuels differ chemically from the conventional petroleum based fuels because they contain oxygen atoms in addition to carbon and hydrogen atoms. The presence of oxygen atoms ensures higher octane number to biofuels when compared to gasoline. Biofuels are renewable energy resources that can be used to generate energy assuming that the feedstock is produced in a sustainable fashion. Also, biofuels are environmental friendly fuels when compared to conventional fossil fuels because during the process of photosynthesis, crops take up carbon dioxide and release oxygen into the atmosphere. When burned, biofuels result in little or no net emission of carbon dioxide to the atmosphere. On the other hand, when fossil fuels are burned, there is a net increase in atmospheric carbon dioxide (CO_2) because they release carbon dioxide that was consumed millions of years ago during the process of photosynthesis.

Nowadays, bioethanol is the most widely used biofuel especially in the United States. Bioethanol or ethanol is made from crops like corn, wheat and sugar plants. The following section gives an overview of ethanol production from corn.

2.2 ETHANOL

Ethanol or ethyl alcohol (CH_3CH_2OH) is an alcohol made from grains such as corn, maize, and wheat. It is an oxygenate and can be used as high octane-fuel in vehicles [2]. Its non-toxic nature and ability to reduce harmful fuel emissions has increased the use of ethanol as an alternative to other harmful fuel additives like, methyl tertiary butyl ether (MTBE) and benzene, both of which are carcinogens [2]. Ethanol is blended into various fuel formulations called E10, E85, and E90. E10, 10% ethanol in 90% petroleum, is the most widely used and can be used in almost all automobiles without any modifications. Higher ethanol blends like, E85 is being used for specially designed vehicles called flexible fuel vehicles while E90 is still being tested for [2, 3]. In the United States the use of ethanol is increasing every year and according to the U.S. Department of Energy, the demand for ethanol will increase to 3.0 - 3.5 billion gallons per year by 2010 [4].

In the United States, nearly 95% ethanol is made from corn by using either dry or wet milling processes. Dry milling is the most commonly used because of the lower capital costs of construction and operation of dry mill ethanol plant. As shown in Figure 1.1, both the process essentially comprises the same basic steps of preparing the feedstock, fermenting sugars and recovering ethanol and the byproducts. The main difference lies in the preparation of the feedstock. In wet milling corn is presoaked and milled to produce germ, fiber and starch while in dry milling corn is milled to obtain meal.

2.3 ETHANOL PRODUCTION PROCESS OVERVIEW

In a typical dry milling process corn goes through the following steps:

Milling: The corn is ground into a fine powder called *meal* by passing it through a series of hammer mills [4].

Liquefaction: During liquefaction, corn is mixed with water and enzyme. *Alpha- amylase* is the most commonly used enzyme that helps in the further break-down of meal [4]. This mixture of corn, water and alpha-amylase is then passed through the cookers to liquefy starch into simple sugars. Cookers are maintained at temperature ranging from 250 °F to 300 °F. High temperatures in the cookers help sterilizing the bacteria in the mash.

Saccharification: The mash from the cook tanks is cooled down and then *gluco-amylase* is added to convert liquefied starch into simple sugars called dextrose [4].

Fermentation: During fermentation process yeast is added to convert simple sugars to ethanol and CO_2. The mash is passed through several fermenters in series for its complete fermentation [4]. Mash stays in one fermenter unit for 48 hours before it goes to the next unit.

Distillation: The mash after fermentation is referred to as *beer* and contains 10% alcohol. Beer contains all the solids from the original feedstock [4]. It is then transferred to the distillation unit where different constituents including ethanol are separated based on the differences in their boiling points. The residue from distillation column is called whole stillage and is pumped from the bottom of the distillation column for further processing to be used as live-stock feed.

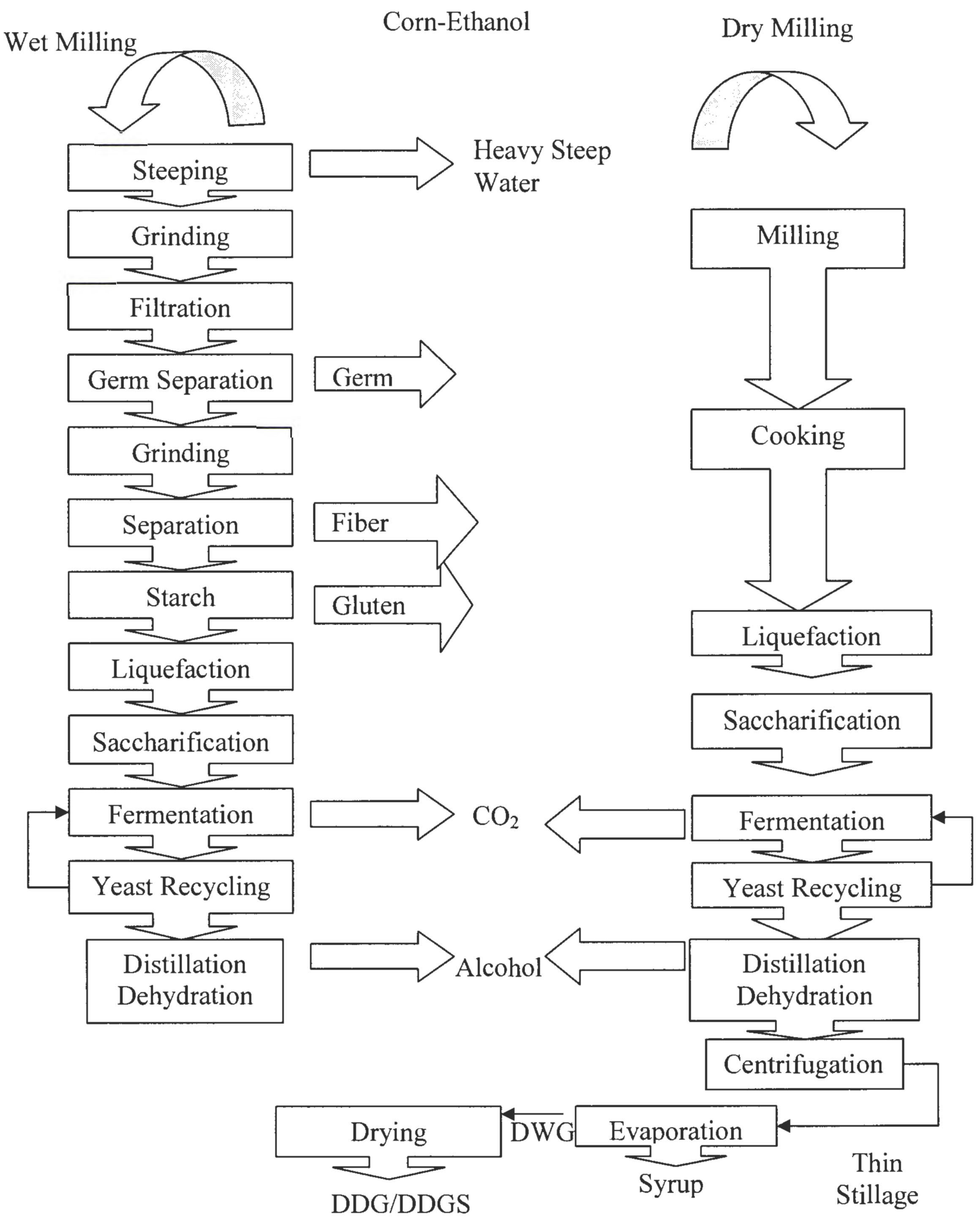

Figure 1.1. Ethanol production process overview [4].

Co-products: CO_2 and distiller's dried grains are the two main co-products from dry-milling [4]. CO_2 gas is generally collected by the plant owners and sold for carbonating beverages while distiller's dried grains are used as livestock feed.

2.4 CONCERNS RELATED TO DRY-MILLING PROCESS

There are a few concerns related to dry-mill ethanol production, two of them are 1) to reduce emissions of VOCs from drying of WDG with solubles, and 2) to find methods to clean thin stillage in order to provide cleaner recycle water to the ethanol plant.

Thin stillage is found to have a very high COD, which is expected to be due to the presence of organic acids in it. Also, since distiller's dried grains are obtained after centrifuging the whole stillage, it is expected that a few of these organic acids contributes to the VOCs emissions. The following few sections briefly discusses the various kinds of VOCs, their sources, harmful effects on humans, and traditional techniques used for their monitoring and abatement.

2.4.1 Volatile Organic Compounds

VOCs are emitted into the atmosphere from a variety of anthropogenic activities, like discharges from industrial and commercial facilities, municipal discharge, transportation activities, etc. Also, there are a few natural sources of VOCs emission. It was only recognized recently, that even grasses are significant sources of volatile organic compounds, particularly oxygenated species, and that these emissions increase significantly when the grass is cut [5]. These compounds may have harmful effects on human health [6]; hence knowledge of the levels of such materials in the ambient atmosphere and their removal is required in order to prevent the living organisms from their harmful impacts.

Definition

VOCs are organic compounds that easily vaporize at room temperature [7]. Most of the VOCs have no color, smell, or taste but some may produce odors at very low levels that are considered objectionable. VOCs include a very wide range of individual substances, such as hydrocarbons (for example benzene and toluene), halocarbons and oxygenates.

Classification

Based on the chemical composition, VOCs are classified into two main categories: (1) Halogenated VOCs, and (2) Nonhalogenated VOCs. A halogenated VOC is one onto which a halogen (fluorine, chlorine, etc.) is attached. Some of the common halogenated VOCs are listed in Table 1.1. A nonhalogenated VOC is one which does not have a halogen (e.g., fluorine, chlorine, etc.) attached to it. Table 1.2 lists some typical nonhalogenated VOCs (excluding fuels, BTEX, and gas phase contaminants).

Sources of VOCs

The four main categories of VOCs sources are the following [8]:

(1) *Point sources* are large stationary sources. They include large industrial and commercial facilities with emissions larger than specified levels. These levels vary depending where the plant is located. Point sources are chemical plants, cement manufacturers, steel mills, power plants, surface coating operations, and printing operations.

(2) *Area sources* are sources which, when viewed individually, do not have large enough emissions to warrant individual tracking, but in the aggregate may significantly contribute to emissions. They include small industrial or commercial sources, like small printing shops, small auto body collision repair shops, and gas stations. Personal activities such as, house painting and solvent use are also generalized under this category.

(3) *Mobile sources* are vehicles traveling on public roads. Cars, trucks, busses, and vans are all included in this category.

(4) *Off-road mobile sources* are vehicles and equipment, which are not normally operated on public highways. This includes construction and industrial machinery, farm equipment, railroads, lawn and garden equipment, boats, and aircraft.

Table 1.1. Some of the common halogenated VOCs [9].

1,1,1,2-Tetrachloroethane	Bromoform	Glycerol trichlorohydrin
1,1,1-Trichloroethane	Bromomethane	Hexachlorobutadiene
1,1,2,2-Tetrachloroethane	Carbon tetrachloride	Hexachlorocyclopentadiene
1,1,2-Trichloroethane	Chlorodibromomethane	Hexachloroethane
1,1-Dichloroethane	Chloroethane	Methylene chloride
1,1-Dichloroethylene	Chloroform	Neoprene
1,2,2-Trifluoroethane (Freon 113)	Chloromethane	Pentachloroethane
1,2-Dichloroethane	Chloropropane	Perchloroethylene
1,2-Dichloropropane	Cis-1,2-dichloroethylene	Propylene dichloride
1,2-Trans-dichloroethylene	Cis-1,3-dichloropropene	Trichlorotrifluoroethane
1,3-cis-dichloro-1-propene	Dibromochloropropane	Monochlorobenzene
1,3-trans-dichloropropene	Dibromomethane	Tetrachloroethylene (Perchloroethylene) (PCE)
1-chloro-2-propene	Dichlorobromomethane	Trichloroethylene (TCE)
2-butylene dichloride	Dichloromethane	Vinyl chloride
Acetylene tetrachloride	Ethylene dibromide	Vinyl trichloride
Bromodichloromethane	Fluorotrichloromethane (Freon 11)	Vinylidene chloride

Table 1.2. Some of the common nonhalogenated VOCs [9].

1-butanol	Cyclohexanone	Methyl isobutyl ketone
4-Methyl-2-pentanone	Ethanol	n-Butyl alcohol
Acetone	Ethyl acetate	Styrene
Acrolein	Ethyl ether	Tetrahydrofuran
Acrylonitrile	Isobutanol	Vinyl acetate
Aminobenzene	Methanol	
Carbon disulfide	Methyl ethyl ketone (MEK)	

Harmful Effects of VOCs

VOCs are easily absorbed by human beings through ingestion, inhalation, the digestive tract (if swallowed) and the lungs (if breathed in). Once absorbed, they move throughout the body in the blood. The acuteness of the VOCs exposure on human health depends on the amount and duration of exposure.

Some immediate effects of VOCs on health include eye irritation/watering, nose irritation, throat irritation, headaches, nausea/vomiting, dizziness, and asthma exacerbation [10]. Some chronic health effects of VOCs include cancer, liver damage, kidney damage, and central nervous system damage. Also VOCs, in combination with nitrogen oxides, are responsible for ground level ozone and smog.

Various Methods of VOCs Removal

Different techniques are used for VOCs removal from air, water and soil and are discussed below:

1. For removal of VOCs from soil*, sediment, bedrock and sludge*, the following techniques are used: bioventing, enhanced bioremediation, phytoremediation, chemical oxidation, electrokinetic remediation, fracturing, soil flushing, soil vapor extraction, solidification/stabilization, thermal treatment, biopiles, composting, land farming, chemical extraction dehalogenation, separation, incineration, pyrolysis, excavation and offsite disposal, landfill cap.

2. For removal of VOCs from *ground water, surface water and leachate*, the following techniques are used: enhanced biodegradation, natural attenuation, phytoremediation, air sparging, bioslurping, chemical oxidation, dual phase extraction, hydrofracturing enhancements, thermal treatment, in-well air stripping, bioreactors, constructed wetlands, adsorption/absorption, advanced oxidation processes, air stripping, ground water pumping, deep well injection.

3. For removal of VOCs from *air emissions/off-gas*, the following techniques are used: biofiltration, high energy destruction, membrane separation, oxidation, vapor phase carbon adsorption.

A literature review of some of the recent researches in VOC removal methods is summarized below:

Law et al. [11] made an attempt to incorporate the transition metal species with variable oxidation state into the zeolite structures and to explore there performance on VOC removal when working together with an oxidant-generating device. Zeolite NaX was used and was pretreated in an oven for removing any organic contaminants. Ion exchange between Zeolite NaX and cobalt (Co (II)) was done at different concentrations of cobalt solution. Acetone was used as a representative VOC. The experiment was conducted under five different conditions, (1) No treatment, (2) Treatment with NaX, (3) Treatment with NaX and inonizer, (4) Treatment with CoX-1 and ionizer, and (5) Treatment with CoX-1 and ionizer. The ability of zeolite to capture the pollutants was observed in all cases. It was observed that the combination of zeolite containing transition metal with the ionizer resulted in a faster rate of pollutant removal. It was believed that the octahedral coordinated cobalt (II) complexes shift to tetrahedral coordination upon entering into the pores of NaX, which then work with the reactive oxygen species released from the ionizer and catalyze the oxidation reactions of the adsorbed VOCs. The results proved the potential applications of transition metal containing zeolites in odor removal and indoor air quality control.

Scirè et al. [12] proved catalytic combustion as one of the most promising technologies for VOC removal. The major advantages of this approach are that it can operate with dilute effluent streams (<1% VOCs) and at lower temperatures than thermal oxidation. In this research catalytic combustion of some representative VOCs (2-propanol, methanol and toluene) on gold/cerium (Au/CeO_2) catalysts were investigated [12]. Gold/cerium oxide catalysts were prepared by two different techniques, (1) coprecipitation (CP), and (2) deposition–precipitation (DP). On the basis of characterization data (H2-TPR, X-ray photoelectron spectroscopy (XPS), X-ray powder diffraction (XRD), BET surface area), it was suggested that the high activity of Au/CeO_2 system was due to the capacity of gold nanoparticles to weaken the Ce–O bond. This increases the mobility/reactivity of the surface lattice oxygen, which is involved in the volatile organic compounds oxidation through a Mars-van Krevelen reaction mechanism. This effect was found to be dependent on the preparation method of gold catalysts because deposition–precipitation leads to gold nanoparticles which were preferentially located on the surface of ceria. The experimental results proved that deposition–precipitation was more suitable than coprecipitation to obtain highly active Au/CeO2 catalysts.

Navvari et al. [13] used activated carbon fibers for VOC removal. These fibers are generally made from polymer raw materials which are carbonized and activated. These materials have the advantage of quicker adsorption kinetics over powdered products. This is primarily due to the internal microscopic structure of their pore network, which is composed of micropores; mesopores; and macropores. Activated carbon fiber contains 70 % micropores, accounting for the higher specific area and hence better adsorption capacity. The aim of the research was to study activated carbon fiber materials by evaluating their performances in terms of VOC (ethyl acetate, xylene & perchlorethylene) adsorption capacity, and looking at the influence of specific area, number of layers, and gas type, velocity and concentration on this parameter. Experimental results showed that activated carbon fiber had high adsorption capacity, even with volatile gases. It may reach 54% to 10% breakthrough (In the text, breakthrough point was defined as that point where the downstream concentration of VOC was 1%, 5% or 10% of the upstream concentration) depending on the test conditions. Based on the results, it was concluded activated carbon fiber materials are extremely efficient and useful for gas cleaning applications.

Shareefdeen et al. [14] applied biofiltration to eliminate nuisance chemical odors from industrial air streams. In biofiltration, odorous chemical pollutants in the air are transported to biofilms by diffusion, solubilization and adsorption processes. Odorous pollutants are then micro-biologically oxidized into harmless and odorless products by the bacteria within the biofilms. Good adsorption property, pH buffering capacity, low pressure drop, good pore structure, very low compaction with time, and good biological properties forms the basis of biofilter media selection. The main objective of this paper was to present the developments in biofiltration technology, and to demonstrate robustness of biofilter technology in eliminating a wide variety of compounds found in industrial and municipal air streams, including VOCs such as Propylene Glycol Monomethyl Ether Acetate (PGMEA) [14]. Four different case studies dealing with different applications, biofilter configurations, media type, and airflow directions were presented. In one of the cases, biofilters were packed with inorganic synthetic media known as BIOSORBENS. This media was composed of strong, inert, and hydrophilic cores that are uniform in shape and resist compaction. In addition, the hydrophilic cores were coated with nutrient rich organic and inorganic material to provide suitable environment for bacterial growth. Superior performance for VOC abatement of this inorganic media, BIOSORBENS over organic media were observed.

VOCs from Thin Stillage

Whole stillage obtained from the distillation columns (Figure 1.2), is found to have 88% moisture content and is pumped from the bottom of the distillation column to the centrifuge to separate out the solids with a moisture content of 60-65% called *distiller's wet grains*(DWG) from the liquid called *thin stillage* (94% moisture). DWG are then sent to two or more rotary driers to finally reduce the water content to 10-12%. Also, a portion of the thin stillage is sent to the evaporator to thicken it to syrup with a moisture content of 60%. During the drying process the syrup is mixed with the DWG. It is during the drying of DWG that volatile organic compounds are released. Almost nothing has been studied about these emissions so far including the information gaps on the types of VOCs emitted and the temperature range at which most of them are evolved. All different kinds of samples from ethanol plant including distiller's wet grains, distiller's dried grains with solubles, syrup, and thin stillage are tested to find out the temperature ranges where emission of VOCs is possible and also to investigate the main cause of VOC emissions. Thermogravimetric and derivative thermogravimetric analyses were used on the samples to acquire information on the loss of volatiles as a function of temperature. Derivative thermogravimetric analyses (DTGA) was found to be more effective at separating different weight loss events in the TGA data [15].

2.4.2 Thin Stillage Treatment

Thin stillage so obtained from centrifuging the whole stillage is found to have 94% water content. High pressure liquid chromatography analyses of thin stillage showed that it contains different organic acids including oxalic acid, acetic acid, lactic acid, propionic acid, pyruvic acid, butyric acid, butanoic acid and very little concentrations of ethanol (Table 3.1). Chemical oxygen demand (COD) analysis of thin stillage revealed that it has a very high COD of 75000mg/L because of the presence of many organic compounds. A portion of thin stillage is recycled to the plant for reuse and remaining thin stillage is sent to the evaporator to convert it into syrup which is then added to the DWG during drying operations. Syrup is a low value, sticky and hard to dry substance that only adds volume to the already excessive DDGS. Since, syrup is obtained from evaporating thin stillage; it contains organic compounds, which when added to DWG while drying operations may cause VOCs' emissions. Treatment of thin stillage would help providing cleaner recycle water to the ethanol industry and would also help in reducing the content of organic compounds in thin stillage that would further help in reducing the harmful emissions.

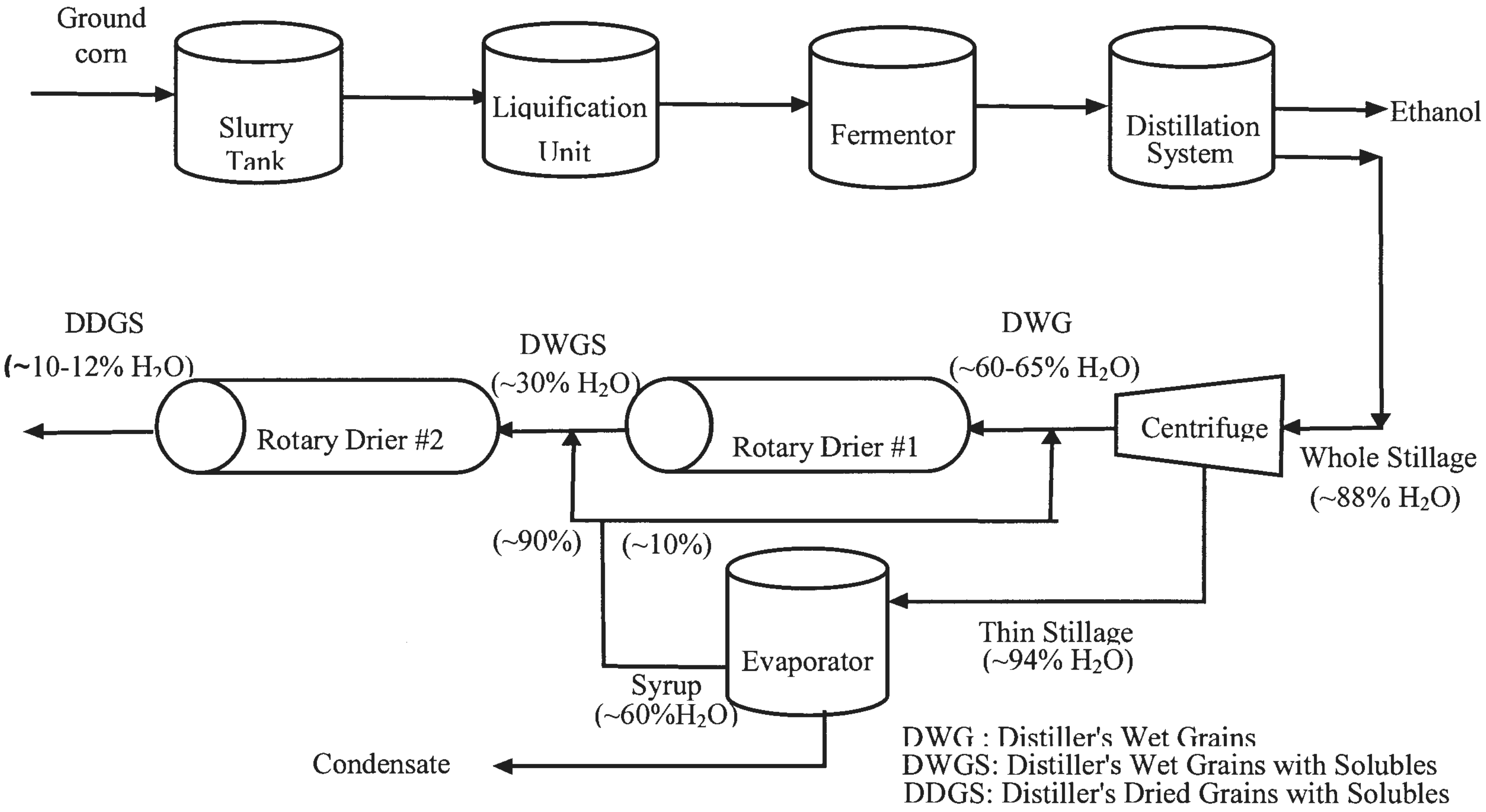

Figure 1.2. Dry mill ethanol plant lay-out, located at Lakota, Iowa and owned and operated by Midwest Grains Processor.

There are two main treatment technologies for water and wastewater, namely biological treatment and chemical treatment. Biological treatment is the most widely used process for industrial and domestic wastewater containing organic compounds. Chemical methods, more specifically chemical oxidation technologies are better suited for some of the organics that are not easily biodegradable. In this study, chemical treatment method is used for removal of organic pollutants from thin stillage. COD is used as a parameter to measure the removal efficiency of organic matter from thin stillage.

Chemical Oxygen Demand is a measure of the oxygen-consuming capacity of inorganic and organic matter present in wastewater. COD is expressed as the amount of oxygen consumed in mg/L.

The following section summarizes a few different types of chemical treatment methods being used for pollutants removal.

Chemical Coagulation

It is a two step process including destabilization and flocculation in which settling is improved by agglomeration of smaller particles into larger particles. It involves the use of some chemical aids called coagulants, which when added destabilizes the particle charge and help them form larger particles called flocs. The conventional inorganic coagulants such as aluminum sulfate, ferrous or ferric chloride, ferric sulfate, etc. perform both the functions in a single action and powdered activated carbon (PAC) and polymers work in a two-step process [16].

Electrocoagulation

This process is based on the in situ formation of the coagulant as the sacrificial anode corrodes due to an applied current, while the simultaneous evolution of hydrogen at the cathode allows for pollutant removal by flotation [17]. Aluminium and iron are the most widely used materials for the sacrificial anode. The efficiency of the process depends on the type of the electrode material, intial pH and current density. During electrocoagulation, three main processes occur synergistically to remove the pollutants: electrochemistry, coagulation and hydrodynamics. The following reaction is an example of the chemical reaction occurring in electrocoagulation at the electrodes [17]:

$$Al \rightleftarrows Al^{3+} + 3e^{-} \ (anode) \tag{1}$$

$$3H_2O + 3e^{-} \rightleftarrows \frac{3}{2}H_2 + 3OH^{-} \ (cathode) \tag{2}$$

Based on the anode potential, secondary reactions may also occur at the anode, such as direct oxidation of organic compounds and of H_2O_2 or Cl^- present in water.

Electro-Fenton Method

A combination of H_2O_2 and ferrous salt is one of the very effective and simple oxidant and is known as Fenton's reagent. The process involves the generation of hydroxyl radical by the reduction of H_2O_2 with ferrous ions. In the past, studies have been conducted to show the effectiveness of Fenton's reagent in the treatment of wastewater polluted with organic compounds [18]. One of the main handicaps of using Fenton's reagent is the large amount of $Fe(OH)_3$ sludge that is produced within the system which requires further processing for disposal. One of the improved alternatives to Fenton's reagent is the electro-fenton method. The electro-fenton method uses either ferrous ions and electrogenerated H_2O_2 that is produced by the two-electron reduction of sparged oxygen on graphite or uses H_2O_2 and electrogenerated ferrous ions produced via the reduction of ferric sulfate or ferric hydroxide sludge [18]. The main advantage of the electo-fenton method is the small amount of sludge produced when compared to the use of conventional Fenton's reagent.

Advanced Oxidation Processes (AOPs)

AOPs are mainly used for the degradation of non-biodegradable organic compounds. They are based on the generation of very reactive and oxidizing free radicals mainly hydroxyl radical ($HO^{\bullet}$). The generation of $HO^{\bullet}$ is mainly achieved by either using a single oxidant or a combination of different oxidants such as ozone, hydrogen peroxide and UV radiation [19]. A common reaction mechanism is described below for the oxidation of organic compounds by the hydroxyl radicals [20]:

$$OH^{\bullet} + RH \rightarrow H_2O + R^{\bullet} \tag{3}$$

$$R^{\bullet} + H_2O_2 \rightarrow ROH + OH^{\bullet} \tag{4}$$

$$R^{\bullet} + O_2 \rightarrow ROO^{\bullet} \tag{5}$$

$$ROO^{\bullet} + RH \rightarrow ROOH + R^{\bullet} \tag{6}$$

These techniques have been applied to different pollutants in the past and satisfactory results were reported. One of the studies showed the effectiveness of AOPs such as H_2O_2/UV photolysis and TiO_2 photocatalysis in reducing the toxicity of pharmaceuticals [21]. In another study, efforts were made to apply the UV/hydrogen peroxide system to degrade endocrine disrupting chemicals [22]. Also, a comparison was made between the effectiveness of ultraviolet (UV) radiation photolysis and the UV/hydrogen peroxide advanced oxidation process. Positive results were reported for the treatment with AOP than to UV radiation photolysis. The main advantage of AOPs is that complete demineralization of organics is possible but also the handicap lies in its high costs of energy and the use of costly reagents.

Ozonation

In this study, ozone was the choice as an oxidant because of its high oxidation potential and its ability to oxidize organic compounds partially or completely depending on the reaction conditions and the type of the pollutants. Ozone treatment does have a few disadvantages that include its relatively low solubility and stability in water and also its high production cost. Considering the high cost of production, ozone oxidation can be used as a pretreatment step to improve biodegradability or post-treatment step to remove remaining COD for the treatment of wastewaters containing refractory organic pollutants because that would have lower ozone consumption compared to complete ozone oxidation. Also, in order to provide greater ozone efficiency and to reduce the cost of ozone application, catalytic ozonation is being considered as a better alternative to ozonation in the recent years. In the past, studies have been conducted to show that the economic cost of ozone oxidation and its efficiency can be improved by using catalysts [23, 24, 25, 26, 27, 28, 29].

The ozonation and catalytic ozonation of thin stillage is a new approach. In this research, an effort has been made to investigate the effect of ozonation on the COD removal of thin stillage. Also, a comparison is made on the treatment efficiencies of O_3, O_3/Fe^{+2}, and O_3/Fe^{+3} systems for the removal of COD from thin stillage.

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CHAPTER 3. THERMOANALYTICAL STUDIES OF BYPRODUCT STREAMS FROM DRY-MILL ETHANOL PRODUCTION

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A paper submitted to Chemical Engineering and Processing

3.1 ABSTRACT

The emission of volatile organic compounds from byproduct streams during drying is a major concern in the dry-mill production of ethanol. Thermogravimetric analysis on distiller's wet grains, distiller's dried grains after the first drier, distiller's dried grains after the second drier, and syrup was conducted to acquire information on the loss of volatiles as a function of temperature. Results show that there is a weight loss in all the samples in the temperature range of 25-100°C and this weight loss is expected to be due to moisture and volatile organic compounds. It is also observed that devolatilization takes place in distiller's dried grains collected after the first and second rotary driers in between 125-220°C. This weight loss is expected to be due to volatile organic compounds.

Keywords: Volatile organic compounds, thermogravimetry, devolatilization, dry-mill ethanol production, distiller's dried grains

3.2 INTRODUCTION

Volatile organic compounds (VOCs) are present everywhere in the environment and are a risk to human health. They are released into the atmosphere from a wide variety of natural and anthropogenic sources [1, 2]. The harmful effects of VOCs on the environment [3, 4] have led the researchers to develop and investigate various methods for identification [5, 6, 7, 8] and removal [9, 10, 11] of VOCs but very limited information is available on the emission of VOCs from dry mill ethanol plants.

In the dry mill ethanol production, corn undergoes milling, liquefaction, fermentation, distillation and drying processes. It is the starch portion of the corn kernel that is converted into ethanol. The remaining nutrients in corn including fat, protein, minerals, and vitamins are concentrated and are dried to form dried distiller's grains (DDG). DDG is an important co-product of the ethanol industry and is used as livestock feed. It is during the fermentation, distillation and drying that VOCs are released from dry mill ethanol industry. Very little is known about the types and the temperatures at which these VOCs are emitted.

This paper summarizes the thermoanalytical study done on the byproduct stream from a dry mill ethanol plant. The results provided information on the loss of volatiles as a function of temperature using a thermogravimetric analyzer (TGA) [12, 13]. Specifically, derivative thermogravimetric analysis (DTGA) was used, since that approach is much more effective at separating different weight loss events in the TGA data [14]. The samples used for the research were provided by the dry mill ethanol plant in Lakota, Iowa, owned and operated by Midwest Grain Processors (MGP).

3.3 MATERIALS AND METHODS

3.3.1 Thermogravimetric Analyses

Thermogravimetry (TG) is a technique whereby the weight of a sample can be recorded over a period of time while its temperature is being changed (usually increased at a constant rate). The instrument used for TG was a Perkin-Elmer TGA 7 (Figure 2.1). TGA curves and first derivative TGA (DTGA) curves were obtained and studied from experimental runs on the various samples obtained from MGP. A TGA curve gives the variation of the weight loss as a function of temperature (or time if it is an isothermal scan) while a DTGA curve represents the rate of weight loss as a function of temperature (or time).

Figure 2.1. Thermogravimetric analyzer (Perkin Elmer TGA-7).

3.3.2 Samples Used

Figure 1.2 shows the lay-out of the dry-mill ethanol plant in Lakota, Iowa and also shows sampling points for samples collection. The samples obtained from Midwest Grain Processors (MGP) were (1) distiller's wet grains containing 60-65% moisture and collected at the first rotary dryer inlet (DWG without syrup), (2) fresh syrup containing 60% moisture and collected at the evaporator outlet, (3) distiller's grains with solubles containing 30% moisture and collected after the first rotary dryer (DDGS after first drier), (4) distiller's dried grains with solubles containing 10-12 % moisture and collected at the second rotary drier outlet (DDGS after second drier), and (5) thin stillage collected at the centrifuge outlet. All the samples obtained from MGP were stored in a refrigerator.

To clearly demonstrate what the TGA and DTGA data curves show, TGA analysis was conducted on cupric sulfate pentahydrate ($CuSO_4.5H_2O$). Figure 2.2 shows the TGA and DTGA curves for cupric sulfate pentahydrate. The sample was ground and then screened using a 50-mesh sieve. In Figure 2.2, the weight loss curve (having three plateaus) shows how the sample weight changes as a function of temperature, and shows various dehydration episodes in the sample. The DTGA curve, which is the first derivative of the TGA data, shows the *rate* of weight loss as a function of temperature. This converts TGA weight loss events into negative peaks that provide an excellent visualization of those events.

3.3.3 Sample Preparation

There are a number of sources of error in TGA that leads to inaccuracies in the recorded temperature and weight data. A few of these are buoyancy effect of the sample container, electrostatic effects on the balance mechanism, measurement of weight by balance, turbulence effects from gas flow, non-homogeneity in grain size, weight of the sample used and heating rate chosen for analysis. Figure 2.3 shows the effects of a few of the above-mentioned causes of errors in the TGA curve. This TGA run was done on the DDGS after

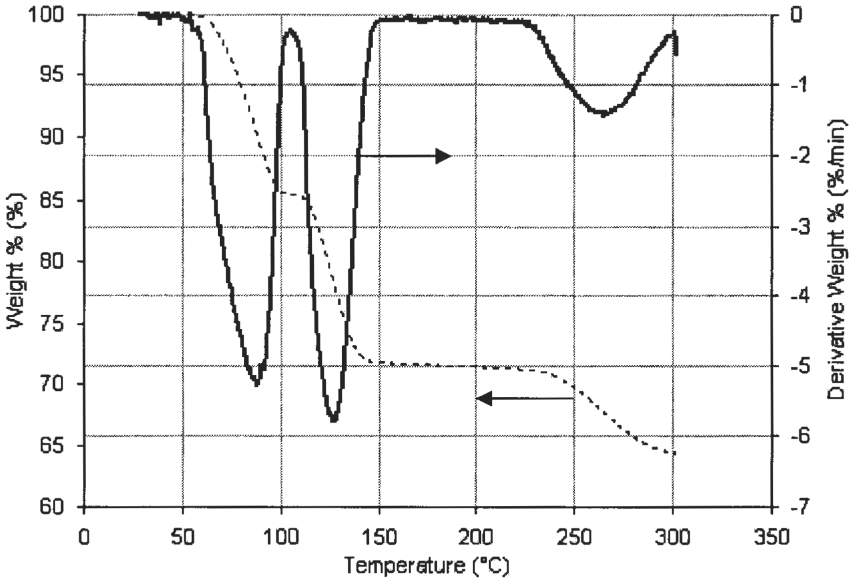

Figure 2.2. TGA run on powdered cupric sulfate ($CuSO_4.5H_2O$).

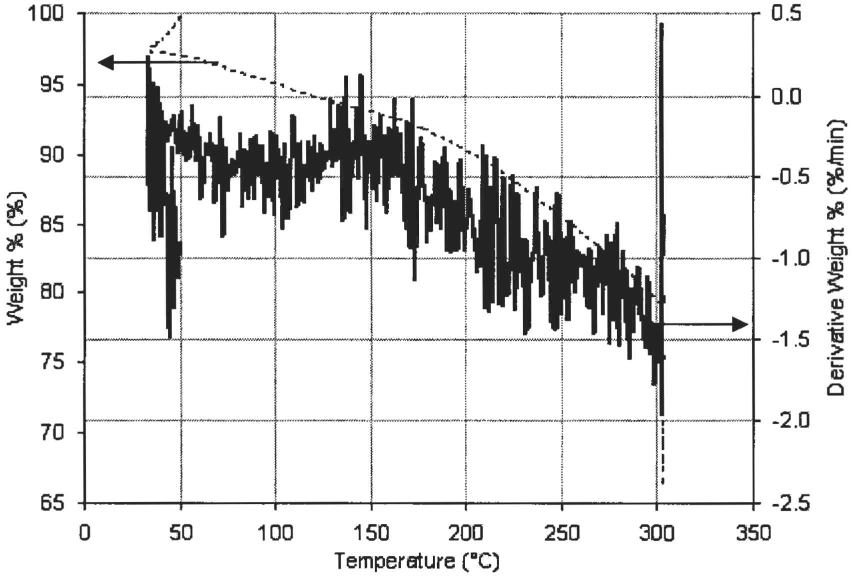

Figure 2.3. TGA run on 'Distiller's Dried Grains With Solubles' sample collected at the second rotary showing noise due to non homogeneous sample.

the second rotary drier sample. The sample grains were coarse even after grinding in a mortar and pestle and was also not mixed well before starting the run. The noise in the DTGA curve was expected due to the non-homogeneity of the sample and the bigger particle size. In order to overcome the noise in the TGA curves and to obtain clearer data, all the samples were ground to a consistent mesh size (50 mesh sieve) before the TGA run.

Distiller's Wet Grains containing 60-65% moisture (DWG without Syrup)

A distiller's wet grains without syrup sample was air-dried for 24 hours, and then particle size reduction was done by grinding in a mortar and pestle and by gently working the sample through a 50 mesh sieve. The process was repeated until the entire sample passed through the sieve. The obtained sample was mixed well and used for the TGA run.

Fresh Syrup containing 60% Moisture

Two different syrup samples were obtained from MGP. One of the samples was received a few months before starting the tests and hence was stored in the refrigerator. This old sample had a few solids (grains) in it. The solids were separated from the syrup by passing the original syrup through a 40-mesh sieve.

The filtered syrup so obtained was stored in a sample bottle and labeled "filtered syrup" for TGA runs and the syrup solids were air dried for about 24 hours. However, the resulting mass was still very viscous. The air-dried solids were about 5.5 g/L of syrup, and 0.6% of the total sample (unfiltered syrup) by weight. Next, the air-dried weight was moistened with water and then put in a freezer at about -10°C for 18 hours. However, it still remained very viscous. The "solids" still had a substantial liquid syrup component that resulted in a very viscous mixture. The viscous material was "ground" in a mortar and pestle and then allowed to air dry overnight before testing by TGA; we named this sample "syrup solids". The second fresh syrup sample obtained from MGP was not filtered because no solids were visible and this sample was called “fresh syrup”. This sample was run within a few hours of its receipt. Thus, three different kinds of samples were prepared from the syrup as described above including fresh syrup, syrup solids, and filtered syrup.

Distiller’s Dried Grains with Solubles Containing 30% Moisture (DDGS after First Drier)

A few drops of water were added to the original sample and the sample was put in a freezer at –10°C for 18 hours. Then it was ground in a mortar and pestle and was air-dried for 24 hours. It was passed through a 50-mesh sieve by gently working sample through the mesh.

Distiller’s Dried Grains with Solubles with 10-12 % Moisture (DDGS after Second Drier)

DDGS after the second drier sample was prepared in a fashion similar to the DDGS after first drier sample preparation. The only difference being that after grinding it in a mortar and pestle, the sample was air-dried for 30 hours and then was passed through 50-mesh sieve by gently working the sample through the mesh.

Thin Stillage

The thin stillage obtained from MGP was centrifuged. After centrifuging, the liquid phase was analyzed and found to contain 6630 µg/ml of lactic acid and 1740 µg/ml of acetic acid and so the solids from the centrifugation were also expected to contain small amounts of organic acids. The solids were not sticky and had the consistency of very thick mud. We named the sample “dewatered thin stillage” and analyzed it using TGA.

3.3.4 TGA Procedure

Unless otherwise noted, about 10 (±1) mg of sample was heated in a gas stream containing 7% O_2 (in a N_2 balance) flowing at 90 ml/min. The heating program consisted of increasing the temperature from 25 to 300°C at a rate of 10°C/min. A minimum of two runs was done on each sample to confirm the reproducibility of the TGA data.

3.4 RESULTS

3.4.1 DWG Without Syrup

As can be seen form Figure 2.4, the TGA curve showed a weight loss of about 3% in the temperature range of 30-100°C. This weight loss is expected to be largely due to the moisture content. The second slight dip in the DTGA curve in the range of 125-200°C can be the weight loss due to VOCs. At this small dip, the weight loss is only about a 3% that can be read from the TGA curve.

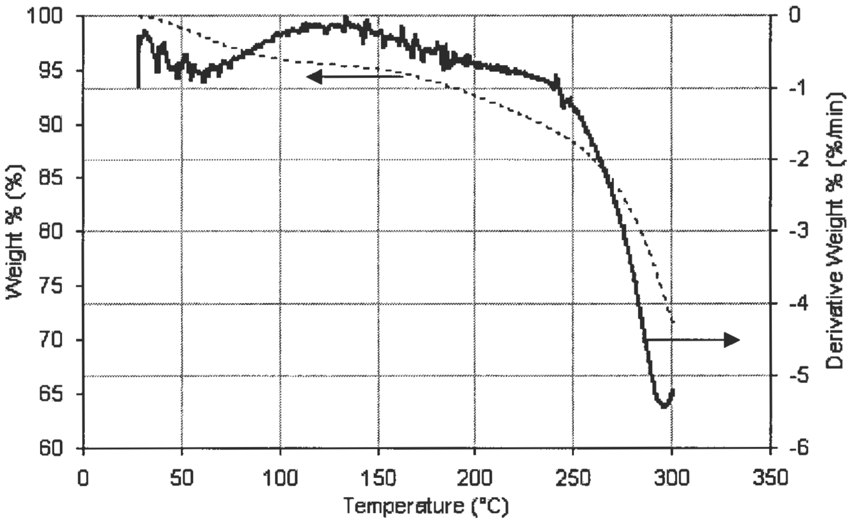

Figure 2.4. TGA run on 'Wet Grains Without Syrup' sample showing weight loss % and derivative weight loss % from the sample.

3.4.2 Fresh Syrup (60% H_2O)

As can be seen from Figure 2.5, the DTGA curve showed two negative peaks, one around 80°C and the other around 180°C. The weight loss between 30-125°C is probably due to the moisture content. The weight loss in the temperature range of 150-230°C is expected to be due to VOCs. It constitutes about a 12% loss in the sample weight.

3.4.3 Filtered Syrup

The negative peak in the DTGA data centered at 200°C, shown in Figure 2.6, was very reproducible. We were expecting that the peak might be due to oxidation and not devolatilization but this possibility was eliminated when a TGA run was done on the sample using only N_2 as the gas over the sample. The same results were obtained. Thus, this is truly devolatilization and not oxidation.

3.4.4 Syrup Solids

At around 100°C, an overlapping of peaks was observed, shown in Figure 2.7. The first negative peak in the temperature range of 25-100°C was because of moisture loss and the second overlapping negative peak in the temperature range of 100-150°C shows a weight loss of 6% that may be due to the VOC devolatilization. A third peak was observed around 200°C indicating a 16% weight loss. The cumulative weight loss that is expected to be due to VOCs from syrup solids sample equals about 22%. The syrup solids constitute only 0.6% of the syrup sample resulting in a total weight loss of only 0.13%. It can be assumed that the solids contribution to devolatilization is almost negligible.

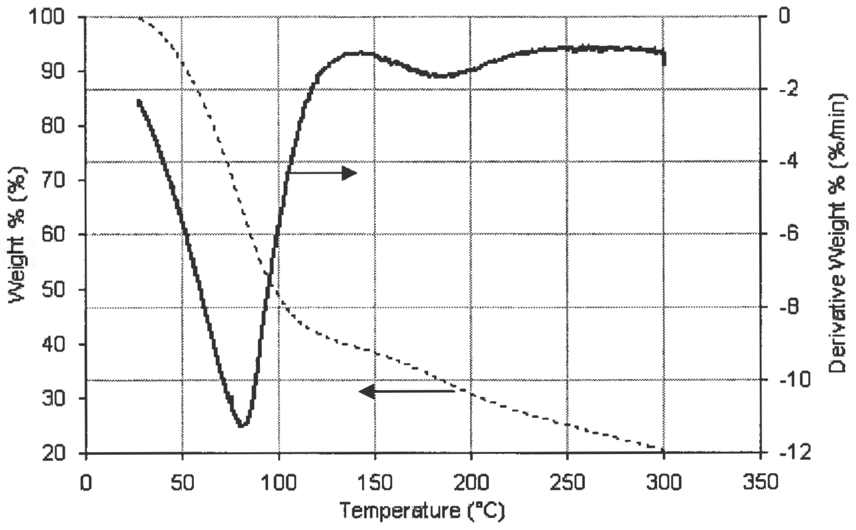

Figure 2.5. TGA run on 'Fresh Syrup' sample.

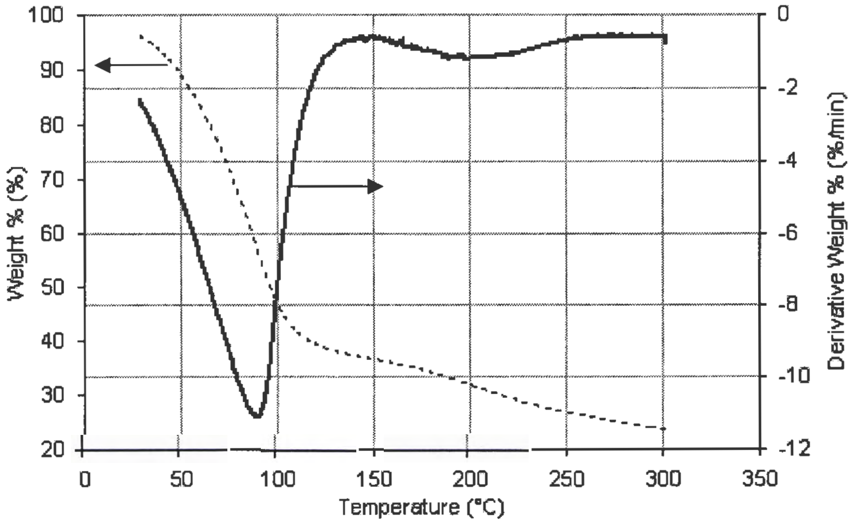

Figure 2.6. TGA run on 'Filtered Syrup' sample.

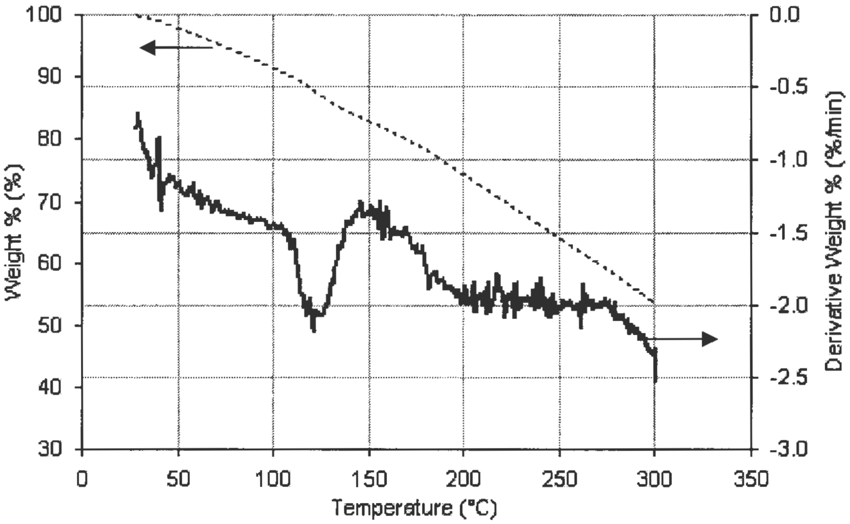

Figure 2.7. TGA run on 'Syrup Solids' sample.

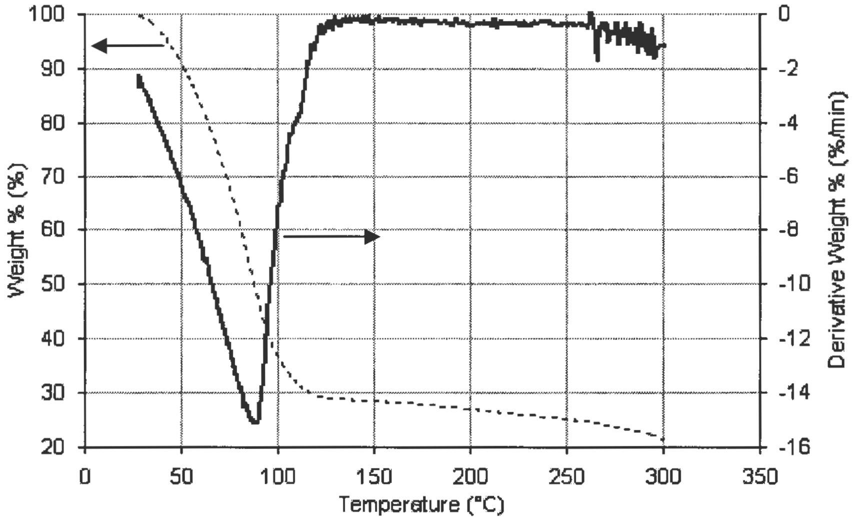

Figure 2.8. TGA run on 'Dewatered Thin Stillage' sample.

3.4.5 Dewatered Thin Stillage (Mud)

Dewatered thin stillage contained small amounts of lactic acid and acetic acid. The boiling points of those compounds are between 100°C and 120°C, which makes it difficult to distinguish from water in the TGA scans. The very small shoulder on the DTGA curve, in Figure 2.8, at about 110°C was reproducible. Lowering the heating rate to 2°C/min did not help resolve this apparent peak. Instrumental drift was suspected as the cause for this weight loss. In order to confirm it, the instrumental drift was determined by running SiO_2 under the same conditions. It was found that the instrumental drift accounted for only a 0.1% drop in weight over the temperature range of 150°C to 300°C. It is concluded that the weight loss in the dewatered thin stillage is real; in other words it is not from instrument drift.

3.4.6 DDGS After First Drier

In Figure 2.9, two minor dips can be seen in the DTGA curve, one in the temperature range of 25-100°C and the other in between 125-220°C. The first peak is expected to be due to moisture loss and represents about 4% weight loss. The second weight loss peak shows around 6% loss.

3.4.7 DDGS After Second Drier

In Figure 2.10, the first peak ranging between 25 °C and 100 °C accounts for a weight loss of about 4% and this weight loss is expected to be due to moisture. The second weight loss event of 10% was observed around 200°C; it was reproducible and is expected due to VOCs.

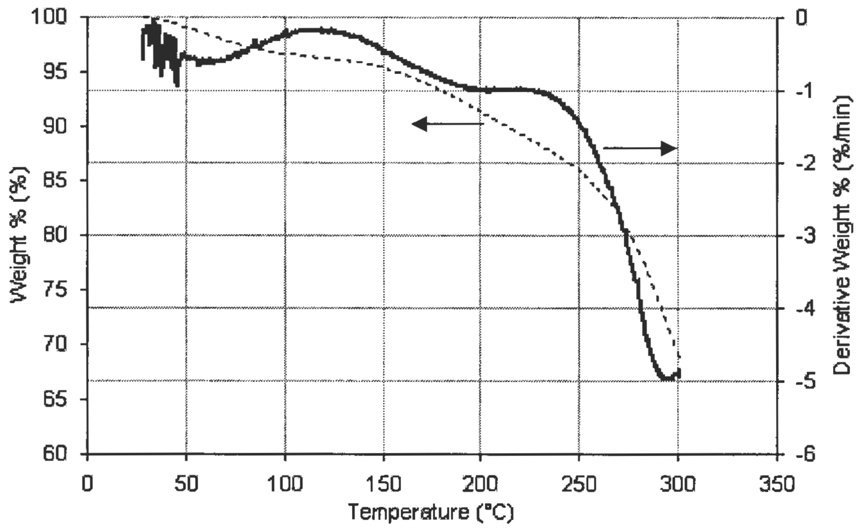

Figure 2.9. TGA run on 'Distiller's Dried Grains With Solubles' collected after the first rotary drier.

3.4.8 Isothermal Tests

A few isothermal scans were done on almost all the samples to check if the heat loss also takes place when the sample is subjected to an isothermal period after a rapid heating rate. All the experimental conditions were the same except the heating program. Samples were heated from 25 °C to 150 °C at a constant rate of 50 °C/min followed by an isothermal scan of 30 minutes. In all the runs on different samples it was found that most of the weight loss took place in the rapid heating period. Since no significant weight loss occurred during the isothermal scan, it was concluded that the weight loss event is associated with the heating period. Figures 2.11, 2.12, 2.13, 2.14, and 2.15 show the TGA curves of these isothermal scans.

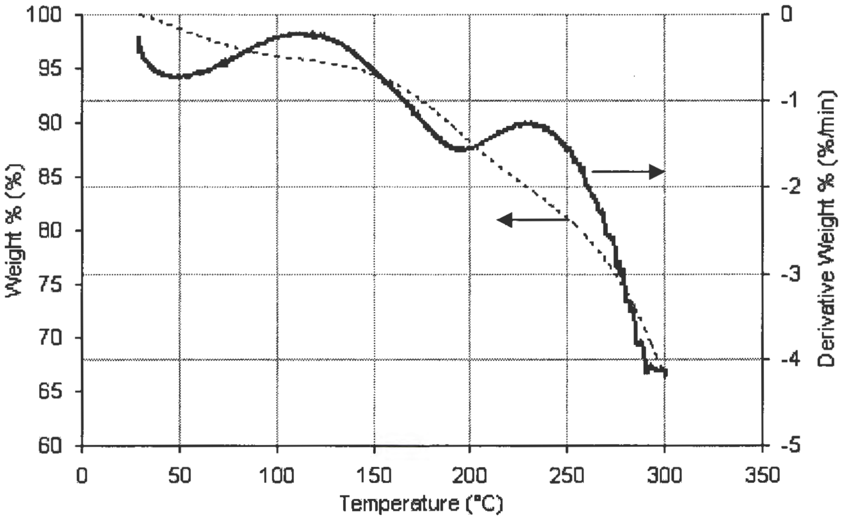

Figure 2.10. TGA run on 'Distiller's Dried Grains With Solubles' collected at the second rotary drier outlet.

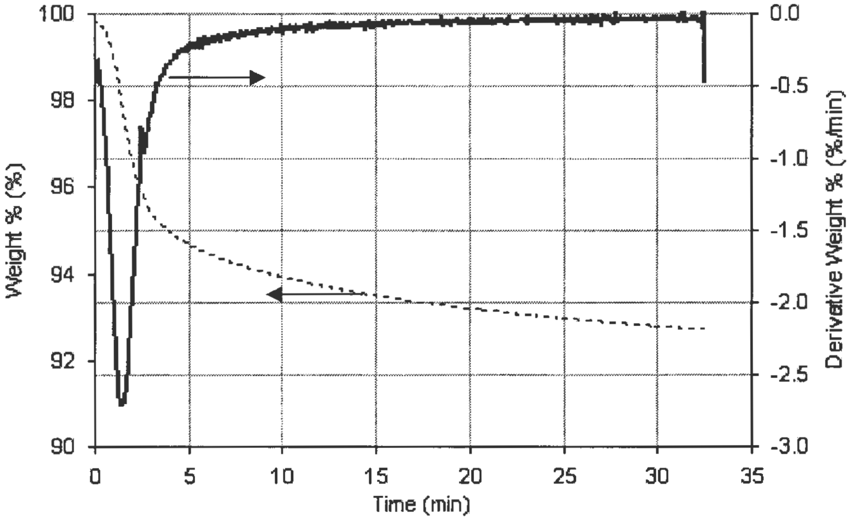

Figure 2.11. Isothermal scan on 'Distiller's Wet Grains Without Syrup' sample.

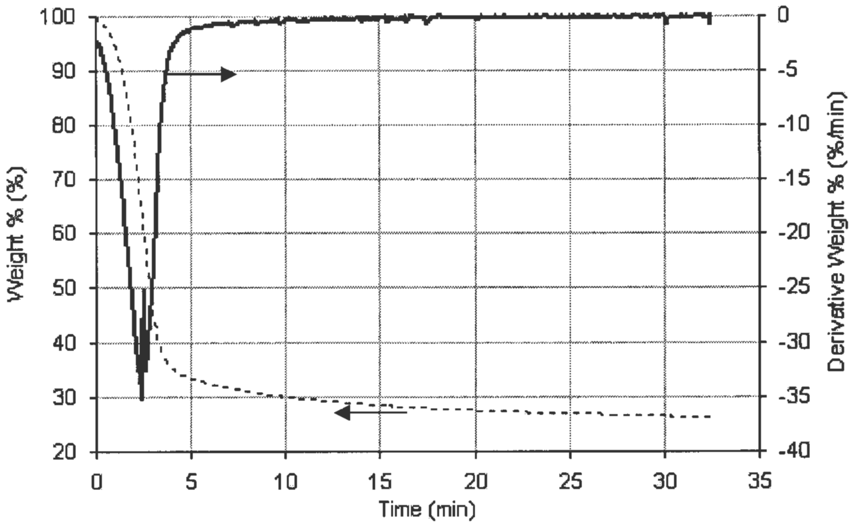

Figure 2.12. Isothermal scan on 'Filtered Syrup' sample.

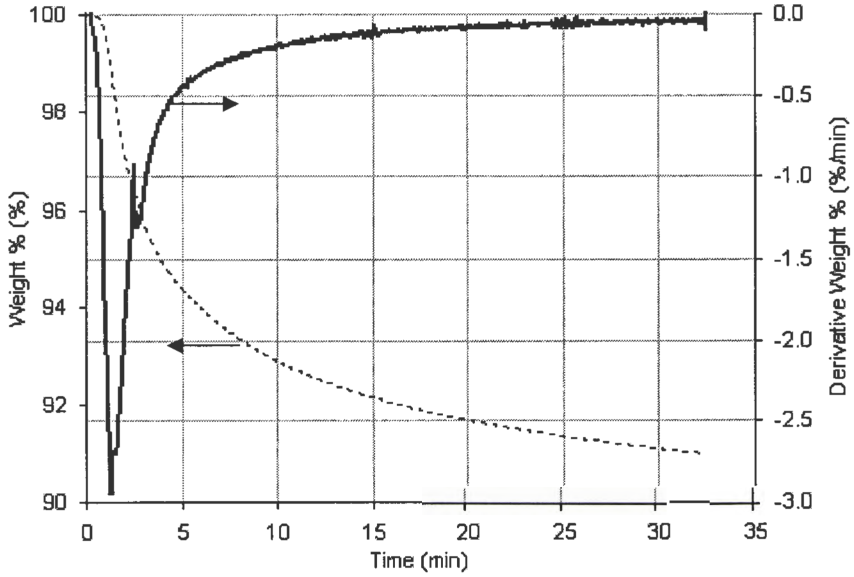

Figure 2.13. Isothermal scan on 'Distiller's Dried Grains With Solubles' collected after the first rotary drier.

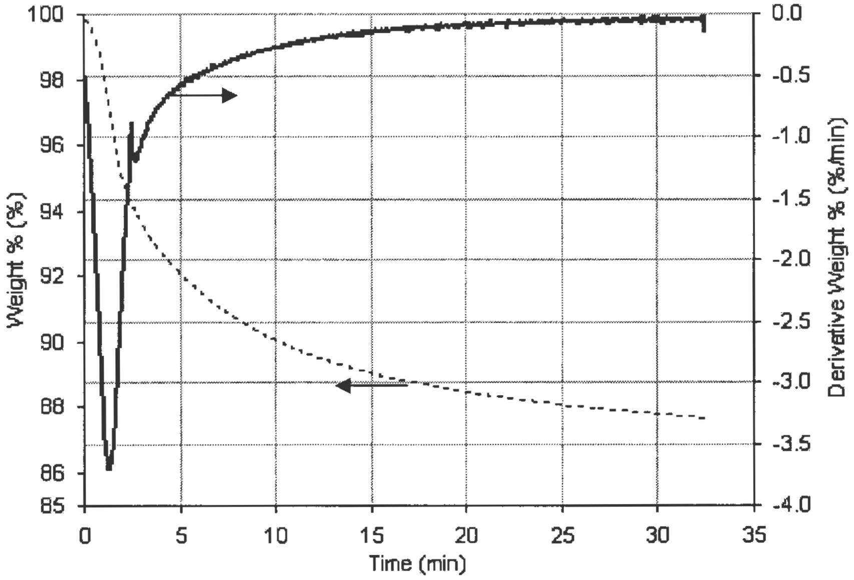

Figure 2.14. Isothermal scan on 'Distiler's Dried Grains With Solubles' collected at second the rotary drier outlet.

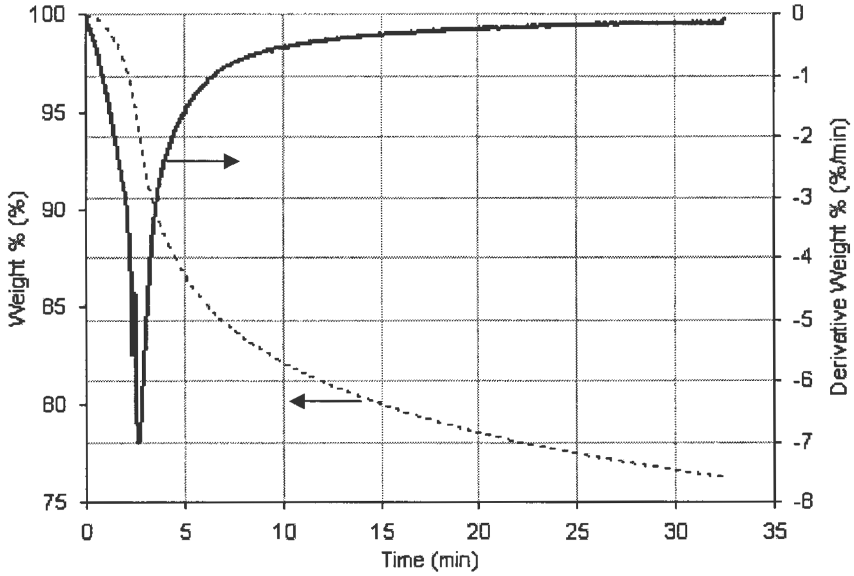

Figure 2.15. Isothermal scan on the 'Syrup Solids' sample

3.5 CONCLUSIONS

The TGA analysis shows that significant volatile fractions are released from the by-product streams from dry-mill ethanol production. The initial releases are expected to be moisture but subsequent releases are expected to be volatile organic compounds. Also, it was found that the volatile emissions are associated with the heating period and not with the isothermal period. Further, the temperature ranges of interest for each sample are obtained, i.e. those temperature ranges where devolatalization is expected. These temperature ranges will be studied further with gas chromatography to help identify the compounds being released.

3.6 ACKNOWLEDGEMENTS

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CHAPTER 4. OZONE TREATMENT FOR COD REMOVAL OF PROCESS WATER FROM DRY-MILL ETHANOL PLANT

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A paper to be submitted to Chemical Engineering Journal

4.1 ABSTRACT

Dry mill ethanol production for fuel ethanol is becoming popular. Thin stillage, the process water, is found to have a very high chemical oxygen demand (COD) of approximately 75,000mg/L. This research focuses on the removal of COD from thin stillage using ozonation as a simple single-step unit process. Also, a comparison is made between COD removals of ozonation and catalytic ozonation. Three different application rates of ozone $O_{3,1}$ = 7 mg/min, $O_{3,2}$= 21 mg/min, and $O_{3,3}$ = 33 mg/min were used for 8 hours on each of the three dilutions 20, 30, and 40 times. COD removal of 85% was observed with $O_{3,3}$ = 33 mg/min and D_3 = 40. Two different catalysts Fe(II) and Fe(III) were used and the samples were ozonated for 4 hours. Five different dosages of each of the two catalysts were used and better COD removal was observed compared to ozonation alone with all 5 dosages. COD removal rate was increased from 45% to 74% with Fe(III) and was increased to 77% with Fe(II). Both the catalysts resulted in almost the same improved COD removal rates when compared to ozonation alone.

Keywords Chemical oxygen demand, catalytic ozonation, ozonation, ozone, thin stillage, Fe(II), Fe(III), corn, fermentation, ethanol

4.2 INTRODUCTION

Ethanol is a renewable fuel made from plants. It is biodegradable, water soluble in nature and has low toxicity. It provides high octane at low cost and its use as a fuel additive reduces harmful exhaust emissions [1, 2]. Also, it can be used in all spark ignition engines without modifications. Following the above listed advantages of ethanol, the use of ethanol blended fuel is increasing in the United States. Ethanol fuel is typically a 10 percent blend of ethanol and conventional gasoline but 85 percent blend is also being used in flexible fuel vehicles and 95 percent blend is now being tested.

In the United States, ethanol is primarily made from corn. Wet milling and dry milling are the two different processes used in production of ethanol from corn. Most of the plants in the United States apply dry milling process for ethanol production because of its lower capital costs required to build and operate. In dry milling, the corn kernel is ground into fine powder, which is referred to in the industry as *meal*. The meal is mixed with water to form a "mash" and enzymes are added to it to convert the starch to dextrose, a simple sugar. Also, ammonia is added for pH control and as a nutrient to the yeast. The mash is then cooked at a high temperature to sterilize the bacteria prior to fermentation. The mash is cooled and transferred to the fermentation unit where yeast is added to convert sugar to ethanol and carbon dioxide (CO_2). After fermentation, the *beer* so produced is transferred to the distillation columns to separate the ethanol from the remaining *whole stillage*. Whole stillage is centrifuged to separate the distiller's grain from the solubles that are referred to as *thin stillage*. The distiller's grain are dried in the dryers to produce dried distillers grains with solubles (DDGS), which is a high quality and rich in nutrients livestock feed. During the fermentation process, CO_2 is released, which is collected and sold for use in carbonating beverages and the manufacture of dry ice. Some portion of the thin stillage is recycled in the ethanol plant and the rest of it is evaporated to produce syrup, which is then mixed with distiller's grains in the dryer. Thin stillage is found to have a very high chemical oxygen demand (COD) of 75000mg/L. Presence of different organic compounds including acetic acid, pyruvic acid, oxalic acid, and ethanol accounts for high COD content of thin stillage. Table 3.1 lists the concentrations of various organic acids found in thin stillage. There is a need to reduce the COD of thin stillage to provide cleaner recycle water to the ethanol industry.

Table 3.1. Characterization of filtered thin stillage, process water from dry mill ethanol plant used in this study.

Constituents	Unit	Value
Acetic acid	ppm	3500
Butyric acid	ppm	100
Lactic acid	ppm	6000
Oxalic acid	ppm	5500
Propionic acid	ppm	5000
Pyruvic acid	ppm	800

Biological treatment is the most widely used process for industrial process and wastewater containing organic compounds. Some of the organics are not easily biodegradable. In such cases, chemical oxidation technologies help oxidizing the refractory organic compounds. Ozone is a strong oxidizing agent used for both in drinking water treatment and wastewater treatment. Table 3.2 shows the physico-chemical properties of ozone [3]. Ozone treatment is specifically suitable for partial or complete oxidation of non-biodegradable components [4, 5]. Ozone oxidation can be used as a pretreatment step to improve biodegradability or post-treatment step to remove remaining COD. The disadvantage of ozone in wastewater treatment is the high energy cost required for its production. Catalytic ozonation is a good alternative to ozonation developed in the recent years. In the past, studies have been conducted to show that the economic cost of ozone oxidation and its efficiency can be improved by using catalysts [6, 7, 8, 9, 10, 11, 12, 13].

The application of ozonation and catalytic ozonation on thin stillage is a new approach. The goals of the present study are as follows:

(i) To investigate the removal of COD from thin stillage by O_3.

(ii) To compare the treatment efficiencies of O_3, O_3/Fe^{+2}, and O_3/Fe^{+3} processes for the removal of COD from thin stillage.

The results of this investigation are presented in this paper.

Table 3.2. Physico-chemical properties of ozone [3].

Property	Value
Melting point, °C	-251
Boiling point, °C	-112
Critical pressure, atm	54.62
Critical temperature, °C	-12.1
Specific gravity	1.658 higher than air 1.71 gcm^{-3} at -183 °C
Critical density, kg/m^3	436
Heat of vaporization, calmol^{-1}[a]	2,980
Heat of formation, calmol^{-1}	33,880
Free energy of formation, calmol^{-1}[b]	38,860
Oxidation potential, V[c]	2.07

[a] At the boiling temperature. [b] At 1 atm and 25 °C. [c] At pH = 0.

4.3 LITERATURE REVIEW

Ozonation

Ozone is a strong oxidizing agent. Ozone reacts directly with constituents found in solution and is also capable of forming highly reactive chemical agents that can contribute to additional oxidizing reactions. The most common of these reactive agents is the hydroxyl free radical. Molecular ozone can serve as a dipole, an electrophilic or a nucleophilic agent. Its high reactivity accounts for its high unstability in water. Ozone decomposition follows the following chain reaction [15]:

$$O_3 + H_2O \rightarrow 2HO^{\bullet} + O_2 \qquad (7)$$

$$O_3 + OH^- \rightarrow O_2^{\bullet -} + HO_2^{\bullet} \qquad (8)$$

$$O_3 + HO^{\bullet} \rightarrow O_2 + HO_2^{\bullet} \leftrightarrow O_2^{\bullet -} + H^+ \tag{9}$$

$$O_3 + HO_2^{\bullet} \rightleftarrows 2O_2 + HO^{\bullet} \tag{10}$$

$$2HO_2^{\bullet} \rightarrow O_2 + H_2O_2 \tag{11}$$

The above chain reaction clearly shows that OH^- plays a significant role in initiating the ozone decomposition process in water. Also, there are several organic compounds that can initiate (OH-, H_2O_2/HO_2^-, Fe^{2+}), propagate (R_2-CH-OH, formate, humic substances) and inhibit (CH3-COO^-, alkyl-(R), HCO_3^-/CO_3^-) the chain reaction.

Organic matter or COD removal only occurs when ozone reacts with organic compounds to produce carbon dioxide and water. Ozone can react with organic compounds in aqueous solution either directly through selective reactions with specific functional group (double bonds, nucleophilic positions) or through a radical reaction like hydroxyl radicals that are produced by the decomposition of ozone in water [16]. For instance, oxalic acid does not have the specific functional group favorable for direct ozone reaction and hence the suggested mechanism is through hydroxyl radicals.

Catalytic Ozonation

Catalytic ozonation can be of two types: homogeneous catalytic ozonation and heterogeneous catalytic ozonation. In homogeneous catalytic ozonation, ozone is activated by metals ions particularly transition metals like Fe(II), Mn(II), Co(II) while heterogeneous catalytic ozonation takes place in the presence of metals or metal oxides on supports such as Cu-Al_2O_3, Cu-TiO_2, TiO_2/Al_2O_3. The use of Fe(II) and Fe(III) in our experiments supports of it being an example of homogeneous catalytic ozonation.

4.4 MATERIALS AND METHODS

4.4.1 Thin Stillage

Thin stillage samples were obtained from a dry-mill ethanol plant in Lakota, Iowa, owned and operated by Midwest Grain Processors (MGP). The sample was refrigerated as soon as it was obtained from the dry-mill ethanol plant. Before the ozonation/catalytic ozonation experiments, thin stillage was centrifuged for 30 minutes at 4500 revolutions per minute (rpm) using laboratory scale (IEC Model K) centrifuge. After centrifuging, it was filtered through 0.22 μm pore size (Glass Microfiber Filter, Whatman) filter. COD of thin stillage was measured using standard methods 5220C [14]. Also, thin stillage was found to contain various organic acids including lactic acid, acetic acid and oxalic acid. High pressure liquid chromatography (HPLC) was conducted on thin stillage to find the concentration of the organic acids present in thin stillage, the results of which are listed in Table 3.1.

4.4.2 Ozonation

Ozone was generated using a laboratory scale ozone generator (Ozat Compact Ozone Unit, Ozonia) that produced ozone via electric discharge of oxygen from a compressed oxygen gas cylinder with a purity of 99%. The output of the ozone generator was determined by passing the ozone gas through a potassium iodide trap and titrating with standardized sodium thiosulfate as per standard method 2350 E [14]. Three different ozone dosages were used for COD determination including $O_{3,1}$ = 7 mg/min, $O_{3,2}$= 21 mg/min, and $O_{3,3}$ = 33 mg/min. Samples were collected at regular intervals corresponding to know applied ozone dosages for COD analysis.

Ozone Losses

The experiments were conducted in an open 3 L pyrex cell and certain ozone losses were expected from the pyrex cell. To calculate the actual ozone consumption, the output of the ozone generator was passed through a 200 mL volume of the 40 times diluted sample for 45 minutes. The offgas from the sample trap was passed through a 200 mL potassium iodide trap for 15 seconds. Further, the potassium iodide solution was titrated with standardized sodium thiosulfate to calculate the ozone losses. The process of passing the offgas through the potassium iodide trap was repeated every 15 minutes and total ozone loss from the system was calculated to be about 50%.

4.4.3 Catalysts

Ferric(III) chloride ($FeCl_3.6H_2O$ certified A.C.S., Fisher Scientific) and ferrous(II) chloride ($FeCl_2.4H_2O$, ARCOS organics) were used as a catalysts to speed up the oxidation process. Five different dosages of each of the two catalysts were tested including 100ppm, 200ppm, 300ppm, 400ppm, and 500ppm.

4.5 EXPERIMENTAL SECTION

All the experiments were done in a 2-liter Pyrex cell in a batch mode (Figure 3.1 and Figure 3.2) at room temperature. Ozone was bubbled into the reactor by means of a diffuser. A mixer with a mixing speed of 200 rpm was used to provide good contact between the diluted sample and ozone. Run times of 8 hours and 4 hours were used for ozonation alone and catalytic ozonation experiments respectively. In each run; a sample volume of 2L was used. Three different dilutions, $D_1 = 20$, $D_2 = 30$, and $D_3 = 40$ were investigated. Samples each of size 7 ml were taken at different time intervals for determination of COD. The collected samples were filtered through 0.45 µm filter. The collected sample was further diluted 5 times for D_1 and D_2 and 10 times for D_3 before performing the COD analysis.

Figure 3.1. Laboratory set-up of ozonation.

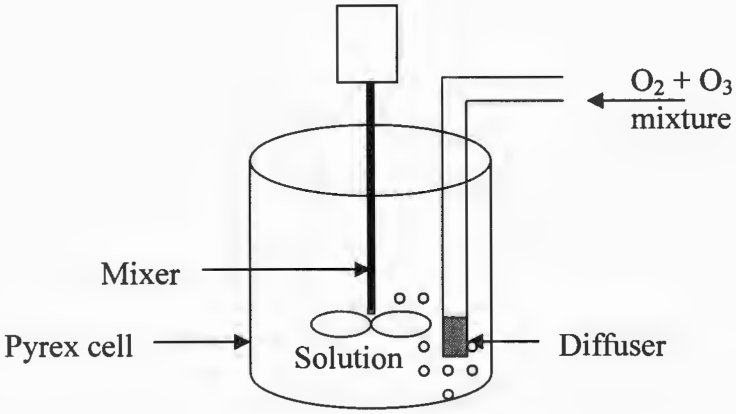

Figure 3.2. Line diagram of experimental set-up of ozonation.

4.6 RESULTS

4.6.1 Ozonation

The objective of this research was to evaluate and compare the efficiency of ozonation alone with catalytic ozonation to remove organics from thin stillage. Figures 3.3, 3.4 and 3.5 give a comparison of COD removals between three different dilutions $D_1 = 20$, $D_2 = 30$, and $D_3 = 40$ using ozone application rates of 7mg/min, 21mg/min and 33min/min respectively. All the experiments were conducted at room temperature with an ozonation time of 8 hours. For each of the three ozone application rates, it was found that the COD removal increased with the increased dilution. Also, improved COD removal was observed with the application of higher ozone dosage. For the lowest ozone application rate, $O_{3,1} = 7$ mg/min, the lowest dilution, $D_1 = 20$, and ozonation time of 8 hours, 61 percent COD removal was achieved while the maximum COD removal of 85% was observed with the highest ozone application rate, $O_{3,3} = 33$ mg/min and the highest dilution, $D_3 = 40$.

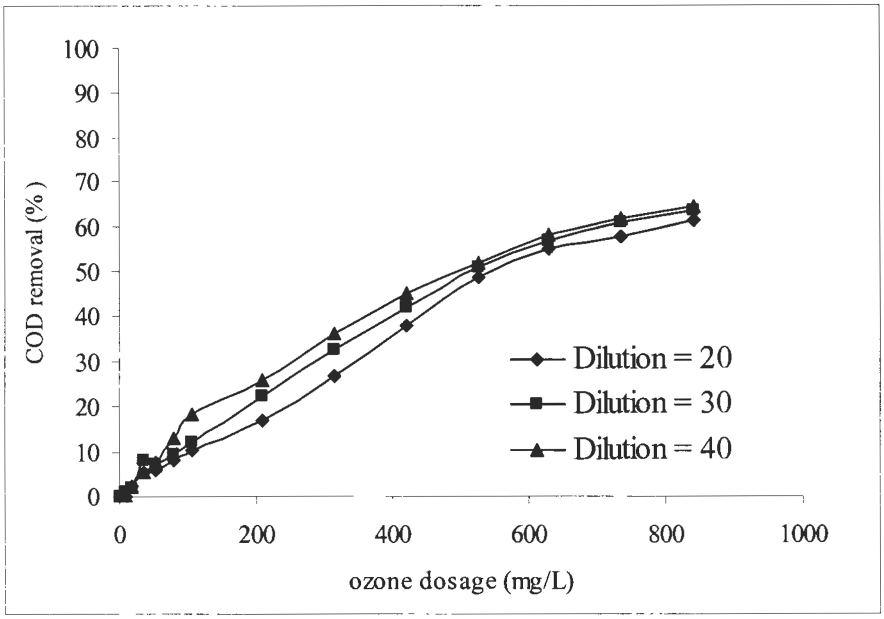

Figure 3.3. Comparison of COD removal using ozone application rate of 7mg/min on different dilutions.

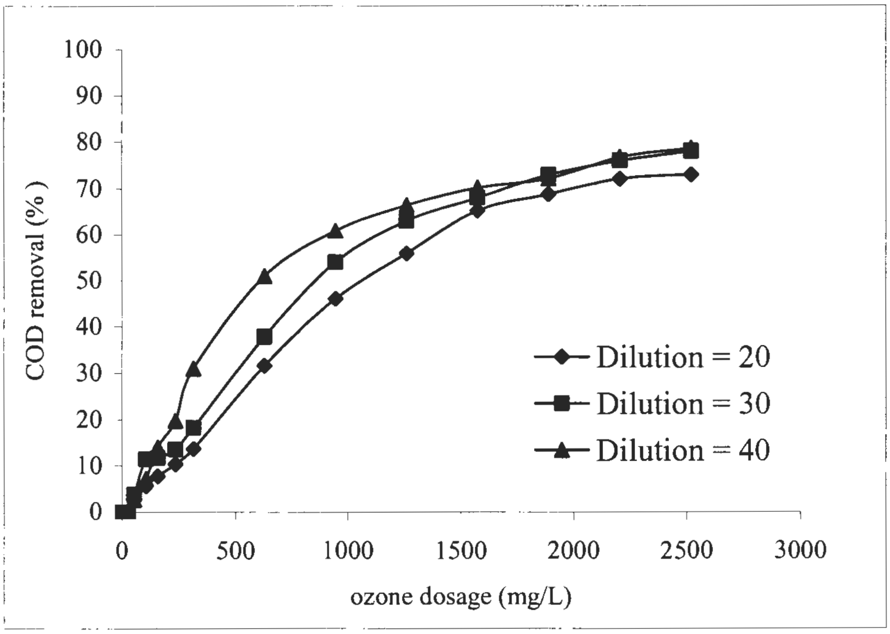

Figure 3.4. Comparison of COD removal using ozone application rate of 21mg/min on different dilutions.

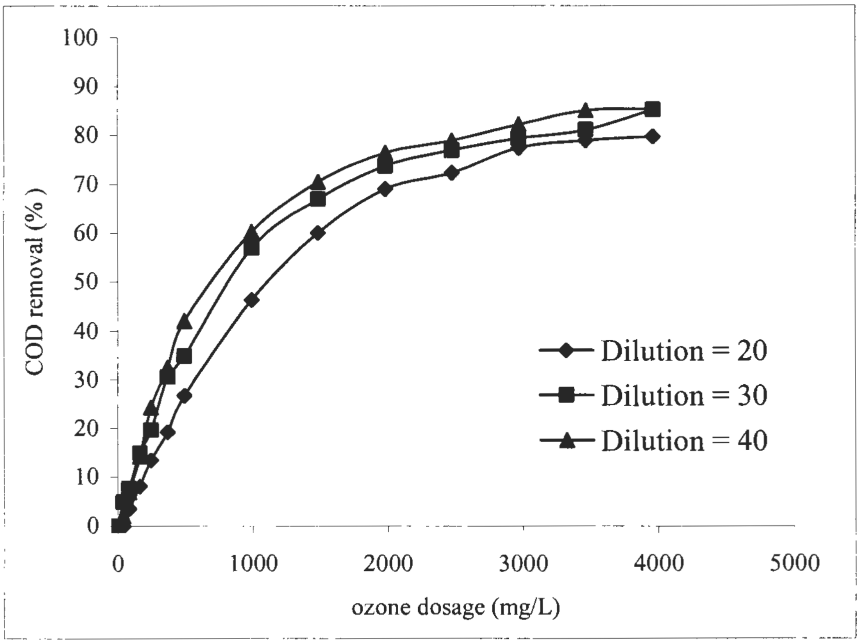

Figure 3.5. Comparison of COD removal using ozone application rate of 33mg/min on different dilutions.

4.6.2 Catalytic Ozonation

In order to quantify the catalytic effects of Fe(II) and Fe(III) when compared to ozonation alone, ozone application rate of 7 mg/min was applied to 40 times diluted sample for 4 hours.

Organic acids can also adsorb to the surface of iron. To check for the possible adsorption on the surface of the ferric chloride, separate experiments were conducted by adding the highest dose of 500ppm of ferric chloride to the 40 times diluted sample without passing any ozone. Similar experiment was done for ferrous chloride. No adsorption was observed with any of the catalysts. This showed that most of the removal in the Fe-catalyzed ozonation experiments was due to oxidation.

Figures 3.6 and 3.7 give the comparison of COD removal efficiencies for ozonation alone to Fe^{3+}/O_3 and Fe^{2+}/O_3 systems respectively. The results indicate that catalytic ozonation in the presence of Fe(II) and Fe(III) improved COD removal in comparison to the standard ozone experiments. For 500ppm of ferrous chloride added to the diluted sample, a removal efficiency of 77% was observed when compared to 45% efficiency of ozonation alone. However catalytic ozonation resulted in more than 40% improvement in the final COD removal efficiencies for each of the catalysts and their dosages when compared to ozonation alone, not a significant difference was observed between the two catalysts. Also, COD removal efficiency was only increased slightly on the application of higher catalyst dosage.

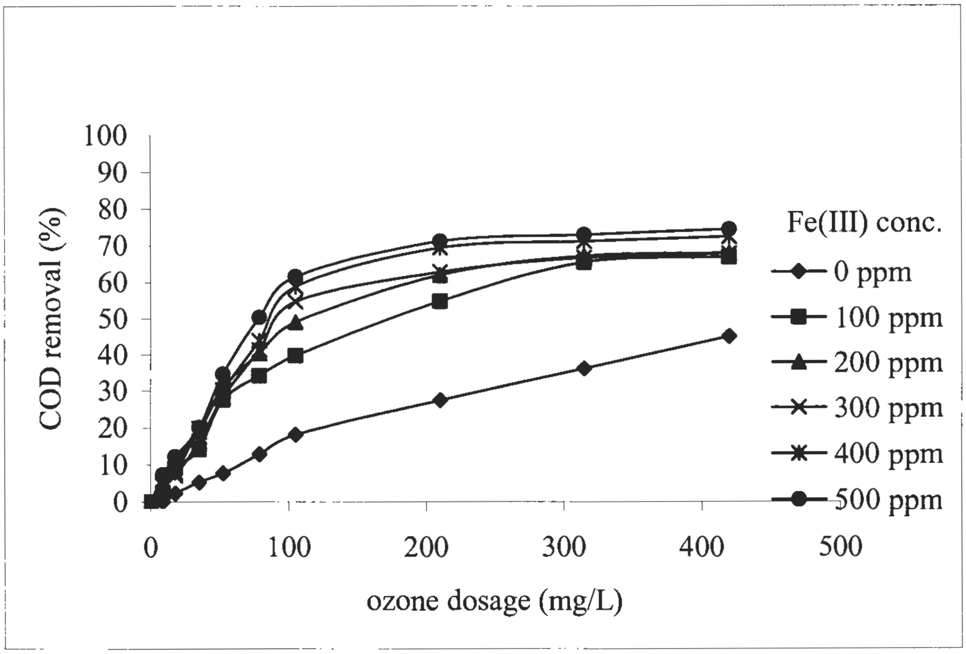

Figure 3.6. COD removal results for thin stillage from Fe(III) catalyzed ozonation experiments using the ozone application rate of 7 mg/min and 40 times dilution.

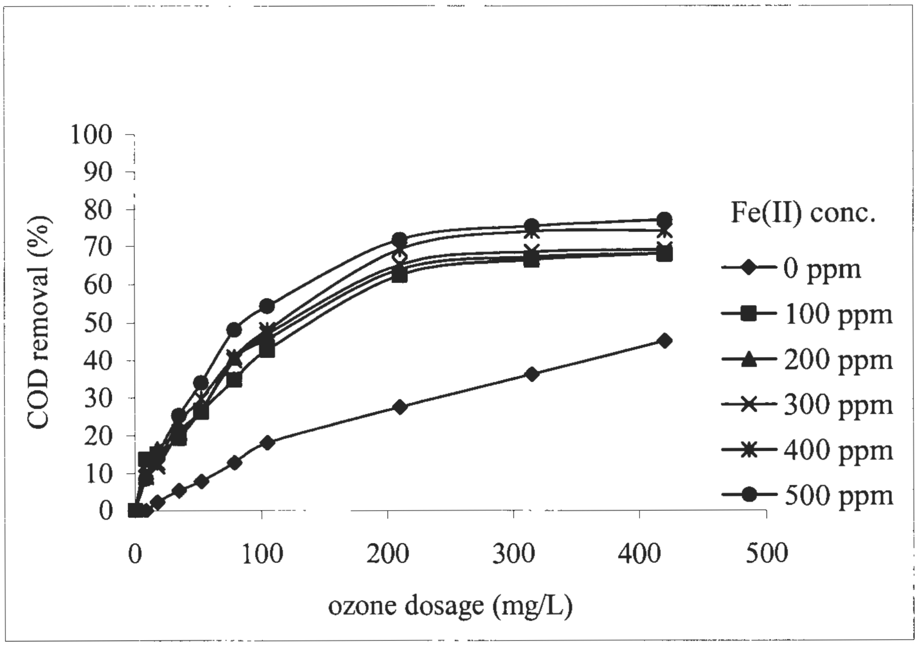

Figure 3.7. COD removal results for thin stillage from Fe(II) catalyzed ozonation experiments using the ozone application rate of 7 mg/min and 40 times dilution.

4.7 DISCUSSIONS

The mechanism of homogeneous catalytic ozonation is mainly a two step process. Ozone is decomposed by the active metal species followed by the generation of free radicals. Then complex formation takes place between catalyst and organic acids followed by final oxidation step.

Our system is slightly acidic with a pH of 5.0. For Fe^{2+}/O_3 system, the following mechanism is suggested for free radical generation in an acidic medium [12]:

$$Fe^{2+} + O_3 \rightarrow FeO^{2+} + O_2 \tag{12}$$

$$FeO^{2+} + H_2O \rightarrow Fe^{3+} + OH^{\bullet} + OH^{-} \tag{13}$$

$$FeO^{2+} + Fe^{2+} + 2H^{+} \rightarrow 2Fe^{3+} + H_2O \tag{14}$$

$$Fe^{3+} + OH^{\bullet} + H^{\bullet} \rightarrow Fe^{2+} + H_2O \tag{15}$$

Fe^{2+} reacts with ozone in the acidic medium to produce FeO^{2+}. Hydroxyl radical is generated from the reaction of FeO^{2+} with water. Hydroxyl radical thus produced helps in the oxidation of organic acids. For instance, the oxidation of oxalic acid in the $Fe(II)/O_3$ first takes place with Fe(II)-oxalate complex formation, which is then oxidized by ozone to Fe(III)-oxalate (Figure 3.8). In the second step, the decomposition of Fe(III)-complex takes place with the formation of an oxalate radical and Fe(II).

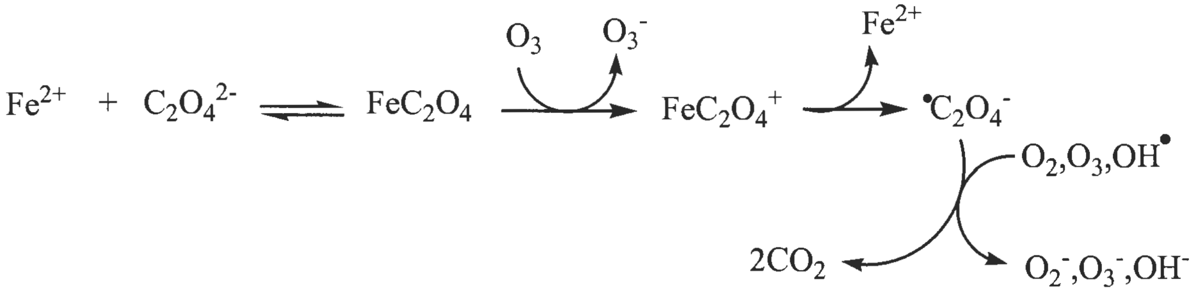

Figure 3.8. Suggested mechanism for catalytic ozonation of oxalic acid by $Fe(II)/O_3$ system [15].

For Fe^{3+}/O_3 system, the suggested mechanism for free radical generation and oxidation of organic acids is as follows [17]:

$$Fe^{3+} + O_3 + H^+ \rightarrow Fe^{2+} + OH^\bullet + O_2 \tag{16}$$

$$Fe^{3+} + OH^\bullet + H^\bullet \rightarrow Fe^{2+} + H_2O \tag{17}$$

$$Fe^{3+} + [org] \rightarrow Fe^{2+} \ldots [org] \tag{18}$$

$$Fe^{3+} \ldots + [org] \rightarrow Fe^{2+} + [org]^+ \tag{19}$$

$$Fe^{3+} + [org] \rightarrow Fe^{2+} + \text{product} \tag{20}$$

$$OH^\bullet + [org] \rightarrow \text{product} \tag{21}$$

4.8 COST EVALUATION

An efficiency index is proposed by the Photochemistry Commission of the International Union of Pure and Applied Chemistry to compare the electrical efficiencies of UV-based AOTs. Electrical efficiency is defined as the amount of electrical energy required for the degradation of contaminant by one order of magnitude in $1m^3$. We have applied this concept of electrical energy in our process also because it shares the commonality of hydroxyl radical chemistry with UV-based AOTs. Electrical efficiency in our case is more appropriately defined as the electrical energy required to generate the necessary amount of ozone that can bring about the degradation of a contaminant by one order of magnitude in $1m^3$ of water[18]. It can be calculated by using the following equation for a batch type process [18]:

$$E_{EO}\left(kWh/m^3/order\right) = \frac{P_{kgO_3}\left(kWh/kg\right)\times R_{O_3}\left(mg/\min\right)\times t\left(\min\right)\times 1000\left(L/m^3\right)}{10^6\left(mg/kg\right)\times V\left(L\right)\times \log\left(c_i/c_f\right)} = \frac{0.022\times R_{O_3}\times t}{V\times \log\left(c_i/c_f\right)} \tag{22}$$

In equation (22), R_{O_3} is the rate of ozone application (mg/min), t is the time (min), P_{kgO_3} is the electrical energy required to generate 1kg of ozone (22 kWh/kg O_3), V is the volume (L) of water in the reactor, and c_i and c_f are the initial and final concentrations of the pollutant [18]. $\$0.066\text{kWh}^{-1}$ was used as the cost of electrical energy for evaluating the cost of ozone generation [19]. All the cost evaluations are based on the actual ozone dosages applied to the system after incorporating the 50 % ozone losses from the system. Table 3.3 shows the E_{EO} for the oxidation of COD from thin stillage by ozonation and the corresponding operational treatment cost. The treatment cost is higher for lower dilutions because of lower COD removals. Table 3.4 shows the E_{EO} for the oxidation of COD from thin stillage by ozonation, catalytic ozonation and the corresponding operational treatment cost for an ozone dose of 7 mg/min, dilution factor 30. The treatment cost for catalytic ozonation for the same dilution and same ozone dosage was reduced by almost 50 percent.

Table 3.3. The EEO for the oxidation of COD from thin stillage by ozonation alone and the corresponding operational treatment cost.

Ozone rate (mg/min)	Dilution	Initial COD(%)	Remaining COD(%)	EEO (kWh/m^3/order)	Treatment cost($\$.m^{-3}$)
7	20	100	39	45.2	2.7
	30	100	37	42.8	2.6
	40	100	36	41.6	2.5
21	20	100	27	97.5	5.9
	30	100	22	84.3	5.1
	40	100	21	81.8	4.9
33	20	100	20	124.6	7.5
	30	100	15	105.7	6.4
	40	100	15	105.7	6.4

Table 3.4. The EEO for the oxidation of COD from thin stillage by ozonation and catalytic ozonation and the corresponding operational treatment cost (Catalyst dose of 300 pppm, Ozone dose of 7 mg/min and the dilution factor of 40).

Sample	Initial COD(%)	Remaining COD(%)	EEO (kWh/m^3/order)	Treatment cost($.m^{-3})
Ozonation alone	100	55	71.2	4.3
Fe(II)	100	31	36.3	2.2
Fe(III)	100	32	37.3	2.2

4.9 CONCLUSIONS

It is possible to remove most of the COD (85%) from thin stillage using ozonation alone. Addition of catalysts results in more efficient and quicker COD removal for the same experimental conditions because of the generation of hydroxyl radicals. For an ozonation time of 4 hours with $O_{3,1} = 7$ mg/min, dilution, $D_3 = 40$, COD removal efficiency was increased from 45% in case of ozonation alone to 74% in Fe(III)/O_3 system and increased to 77% in Fe(II) /O_3 system. Fe(II) and Fe(III) were found to have almost the same COD removal efficiencies. In the Fe(II) /O_3, the reaction proceeds by the oxidation of Fe(II) to Fe(III) and thus competes with the oxidation of organics, which suggests that Fe(III) is a better alternative to Fe(II). Ozonation demands are high and probably uneconomical for complete oxidation. Considering the high cost of ozone production catalytic ozonation is the preferred alternative. Also, this study provides a baseline for further study on partial oxidation with O_3 and AOPs as a pre-treatment step to improve the biodegradability or post treatment step for removing residual COD.

4.10 ACKNOWLEDGEMENTS

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CHAPTER 5. GENERAL CONCLUSIONS

5.1 GENERAL DISCUSSION

TGA results gives the temperature ranges of interests for each sample, i.e. those temperature ranges where devolatilization is expected on the samples from dry mill ethanol plant.

The results of ozonation and catalytic ozonation experiments show the effectiveness of using ozone for COD removal of thin stillage. The results of O_3/ Fe^{2+} and O_3/ Fe^{3+} systems show that the two catalysts does not result in significantly different COD removal efficiencies. The cost evaluation provides a comparison between ozonation alone and catalytic ozonation economics and provides a clear indication of catalytic ozonation being more economical over ozonation alone.

5.2 RECOMMENDATIONS FOR FUTURE RESEARCH

The TGA results only provides weight loss information on different samples and also the sample quantities tested were very small (10 mg). The information provided from TGA results can be used for large scale test in a tube furnace. The samples can be heated in the tube furnace at the temperature of interest and the emissions can be collected in Teflon gas sampling bags as per the requirements of EPA Method TO-14A for sampling and analyses of VOCs. GC-MS analyses can be performed on the collected VOC samples for the identification of the specific VOC. The identification of VOCs emitted from the dry mill ethanol plant would definitely help in designing more cost effective VOCs control and abatement technologies.

For the treatment of thin stillage, a pilot scale study is recommended for ozonation and catalytic ozonation to find out more realistic figures for ozone losses and also to obtain a better cost estimate for ozone production. Also, use of other oxidizing chemicals like Fe(VI), is suggested to make a comparison between ozonation and other chemicals in order to find the best alternative.