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High-yield Extraction Method of Humic Acids from Lignite using Ultrasonic Processing

by

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A THESIS

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Abstract

More coal power plants are retiring yearly, and more countries are phasing out these plants in hope for more sustainable future. This will free up large amounts of coals specifically low-rank coals (like lignite and subbituminous) for utilization in non-combustion routes. Therefore, it is of paramount importance that alternative, cost-effective, efficient, and sustainable routes are developed and investigated. In this study, the conversion of lignite to humic acids is investigated. Humic acids are organic fertilizers and soil conditioners that help deliver nutrients to plant, improve soil structure and help retaining water in the soil. Humic acids have a potential market growth of 14% compound annual growth rate (CAGR) over the next decade. The growth is driven by the need for more organic fertilizer and the deterioration of soil health due to climate change. Current commercial technologies for humic acids production suffer from longer extraction time and low yields. Therefore, ultrasonic processing is being introduced in this study as a novel and new technology to improve the yield and reduce the time required for the production of humic acids from lignite. Ultrasonic processing is based on cavitation phenomena where ultrasound goes through the solution to generate microbubbles that grow and eventually collapse causing high localized pressure and temperature. Chemical and physical effects happen during ultrasonic processing leading to higher rates of reactions. During the reaction, oxygen is being incorporated creating more humic substance and the alkaline media allows for higher solubilization in the solution. Several parameters have been investigated including amplitude, reaction time, initial lignite concentration, KOH amount, and the concentration of H_2O_2 . The international standard ISO19822 method was employed for product characterization. Product characterization also includes the use of FTIR, TOC, CHN analysis and TGA. The characterization confirmed the conversion of lignite to humic acids, allowed for the quantification of humic acids and gave a

picture of the chemical and physical characteristics of the products. A lump kinetics model based on power law and Arrhenius equation was built to calculate the kinetics triplets, rate constant, activation energy and pre-exponential factor.

Keywords: ultrasonic, lignite, humic acids, fulvic acids, fertilizers

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List of Symbols, Abbreviations and Nomenclature

Symbol or abbreviation	Definition
A	Pre-exponential factor
C	Concentration
C_A	Concentration of lignite after the reaction
C_{A0}	Initial concentration of carbon in lignite
CAGR	Compound Annual Growth Rate
C_B	Concentration of organics in the solution
CHN	Carbon, hydrogen, and nitrogen
E_a	Activation energy
FA	Fulvic Acid
FTIR	Fourier-transform infrared spectroscopy
GHG	Green house Gases
HA	Humic Acids
HS	Humic Substance
IC	Inorganic carbon
ISO	International Organization for Standardization
k	Rate constant
kHz	Kilohertz
Mt	Mega tonnes
n	Reaction order
R	Universal gas constant.
T	Temperature
t	Time
TC	Total carbon
TGA	Thermogravimetric Analysis
TOC	Total organic carbon

Chapter 1 Introduction

1.1. Overview

In the past decades, the demand for clean and sustainable energy and products has increased due to the increasing concern over the negative impacts of combustion of fossil fuels [1]. Therefore, technologies that have the ability to reduce the energy utilized in traditional processes or offer an alternative sustainable route have gained a strong traction. The production of fertilizers and soil conditioners is considered a large contributor to greenhouse gas (GHG) emissions and has been increasing in the past decades [2]. Increasing yield and conversion can help reduce the overall life cycle emissions of these products along with reduction in cost stemming from the energy savings. Furthermore, the world has started phasing-out coal power generation plants due to the large GHG emissions release when combusting coals [3]. This in turn will leave large amounts of coals, specifically low-rank coals (i.e., lignite and subbituminous) idle. It is, therefore, imperative to look for alternative, sustainable and economical ways for utilizing these resources.

Humic acids (HA) are polymer-like components of decayed organic matter which form a solubility class materials that are typically defined as the fraction of matter that is soluble in basic solution, and insoluble at acidic pH levels [4]. The other fraction that is soluble throughout the entire pH range are fulvic acids (FA). FA is similar to HA but has lower molecular weight. There is no defined molecular structure for humic acids, instead they can be found in a wide range of molecular weights with various combinations of carboxyl, carbonyl and hydroxyl groups [5]. There has been a lot of work done in the area of extracting humic acids from soils, coals, and other organic matter. The most reported methods of extraction involve the use of alkaline solutions, although other organic solvents have also been studied, and mixing these solutions with the source of humic acids for hours under certain temperatures [6–8]. These extraction techniques suffer from longer times,

high energy consumption and low yields. Humic acids are majorly utilized in agriculture as soil conditioners and fertilizers, but they are also used in medicine, wastewater treatment, and other applications [4,9]. Due to the existence of carboxylic and phenolic groups in HAs, HAs are negatively charged in aqueous solutions under normal environmental conditions [10,11]. HAs were reported to effectively purify metal ions and improve water quality [12]. Furthermore, HAs can be used as surfactants, flocculants, ceramic additives, battery cathode expansion agent, boiler anti-crustator, etc. [13,14]. High functionality of the surface ensures that HAs are a good adsorbent with an excellent capacity for treating the pollution caused by waste gases [15,16].

Humic acids market size is expected to grow by 14% CAGR (Compound Annual Growth Rate) by 2026 [17]. This increase is driven by increasing population and changing food consumption pattern due to health awareness. The global humic acid market share is also driven by increasing focus towards organic fertilizers over chemical fertilizers. Furthermore, the increase in environmental regulations against chemical fertilizers will have a positive influence on the humic acid market size. Agriculture seems to be the largest sector utilizing humic acids and it is forecasted to see the largest increase over the next decade (**Figure 1.1**) [18]. However, other sectors such as ecological bioremediation, horticulture, and dietary supplements are also forecasted to see an increase over the next decade.

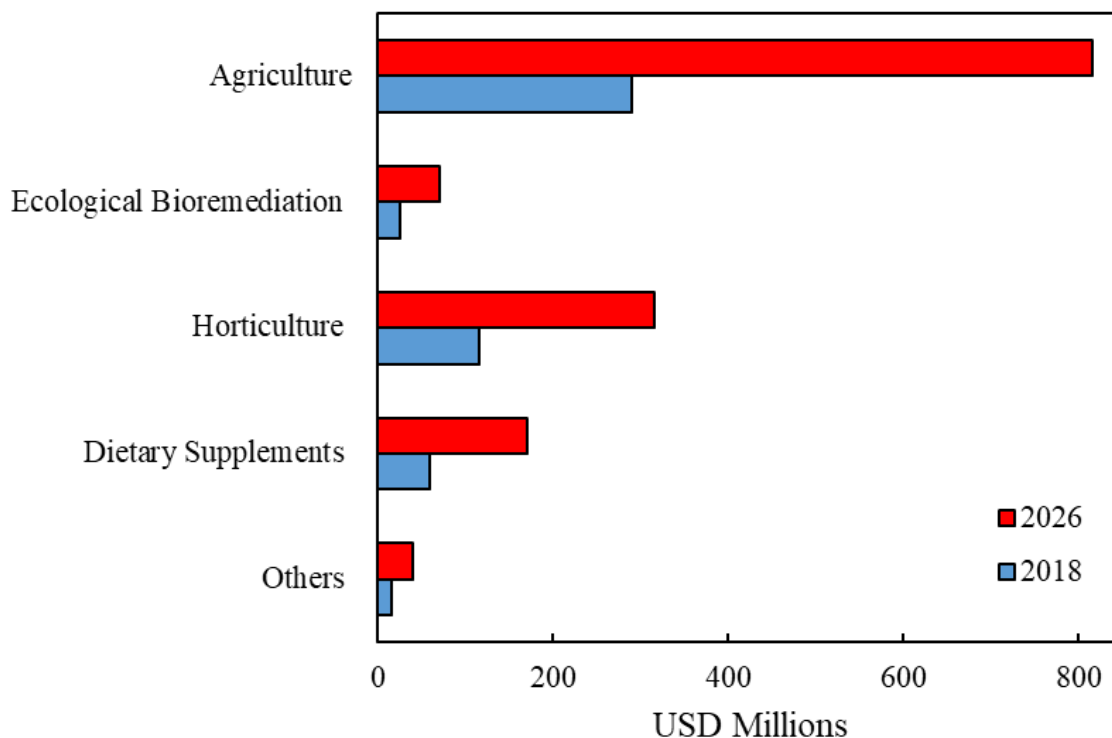


Figure 1.1: Economy sectors utilizing humic acids and potential growth [9].

Humic acids have been reported to be extracted from several sources including lignin, leonardite, compost, peat, manure and lignite [19,20]. These sources differ in availability, cost and the amount of humic acids [21]. Lignite is one of the sources where humic acids are extracted from, and its reserves account for nearly 45% of global coal reserves. Compared to humic acids from soil and peat, lignite humic acids are characterized by higher carbon content and biochemical activity, lower oxygen and nitrogen content, more aromatic moieties, and fewer carboxylic groups [22]. Humic acids from lignite are also characterized by the presence of methylene and ethylene bridges between the aromatic rings. Furthermore, they contain saturated long chain alkanolic acids with a strong predominance of even numbered homologues compared to humic acids from soil [22]. Ultrasonic processing has been utilized in enhancing and promoting chemical reactions and improving mass transfer and offers the potential for shorter reaction times, cheaper reagents, and

less extreme physical conditions [23]. It has been applied in studies of cleaning, organic synthesis, catalysis, extraction, emulsification, material processing, food processing, and wastewater treatment [24]. Ultrasonic waves traveling through solutions generate small cavities or bubbles that expand and implode, creating tremendous heat [25]. These extreme conditions provide an unusual chemical environment where chemical reactions can proceed.

In this thesis, ultrasonic processing has been utilized as a novel and new method for the production of humic acids from lignite. **Figure 1.2** shows a generalized view of converting lignite coal using ultrasonic processing with H_2O_2 and alkaline solution. This conversion results in the production of humic and fulvic acids with varying percentages based on operational parameters such as temperature, chemicals and methods utilized [26–29]. Several parameters have been tested including ultrasonic amplitude, reaction time and concentration of reactants to optimize for the highest yield of humic acids. A lump reaction kinetics model has been studied to calculate the activation energy and reaction rate constants and to get an idea of the reaction mechanism.

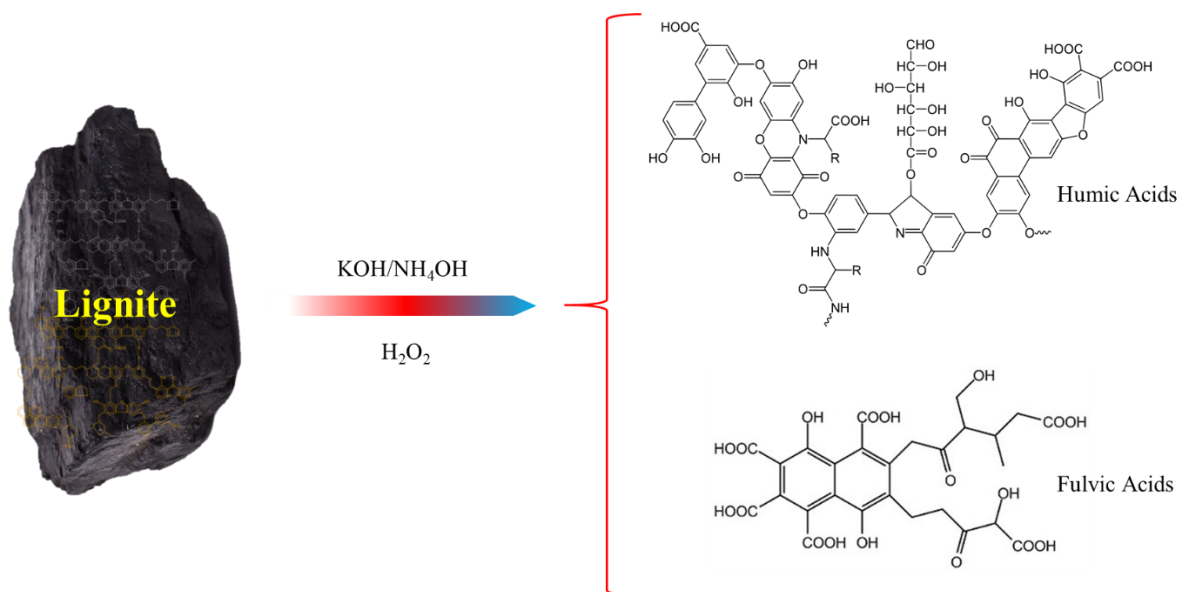


Figure 1.2: Generalized view of lignite to humic acids and fulvic acids conversion.

1.2. Thesis Objective

The major objective of the thesis is to investigate and optimize the performance of ultrasonic processing as a new and novel technique to improve the yield of humic acids from low-rank coal (lignite). This objective can be translated into the followings:

- **Build a complete setup to carry out the experimental work:** The setup consists of an apparatus to carry out the reaction. The apparatus is connected to a transducer to create sonic waves. The transducer is hooked up to a monitoring device to monitor and adjust the parameters of the experiments such as amplitude and time. To control the temperature of the reaction, a water bath is used. The water bath is also connected to a thermocouple to measure the temperature in the reaction zone.
- **Increasing the yield of humic acids:** Typical yield reported in the literature and patents ranges from 25% to 80% under high temperature and longer times. Increasing the yield while reducing the time and steps involved is very essential.
- **Optimizing the major parameters affecting the process** (i.e., amplitude, time, and concentration of reactants): The optimization goal is to find the set of parameters that can be used to obtain the highest conversion.
- **Proposing a kinetic model for the reaction:** Estimating the kinetics triplets (activation energy, reaction constant and pre-exponential factor) to describe the reaction mechanism.

1.3. Thesis Organization

The thesis is divided into five chapters as follows:

- Chapter 1: Introduction

The chapter goes over the general background information about the thesis including objectives and the organization of the thesis. The chapter offers a brief glance at what the thesis is all about regarding lignite, humic acids, and ultrasonic processing.

- Chapter 2: Literature Review

The information in this chapter includes the research and development efforts happening in the field of humic acid extraction and what other research groups are working on or had been working on. It goes over the lignite market and utilization and humic acids uses and methods of production.

- Chapter 3: Experimental Work and Methodology

The chapter presents all the information about the experimental work including materials, equipment, experimental variables, and characterization techniques. The experimental setup consists of an ultrasonic vessel and a thermocouple with a circulating bath. Experimental variables are explained, which include, ultrasonic amplitude, time, dosage of H₂O₂, and concentrations of chemicals utilized. The characterizations include Fourier-transform infrared spectroscopy, Total Organic Carbon, Thermogravimetric Analysis, Carbon Hydrogen and Nitrogen analyzer and procedure for ISO 19882 protocol.

- Chapter 4: Results and Discussion

Chapter 4 goes over the interpretation of the experimental findings and optimization of the variables and how they affect the experimental findings. Furthermore, the chapter discusses a lumped kinetic model for the reaction to calculate the activation energy, pre-exponential factor and rate constants. The chapter also goes over the interpretation of the characterization of materials.

- Chapter 5: Conclusion and Recommendations

Chapter 5 discusses the conclusion of the thesis and recommends next steps to improve and take the technology to the next level.

Chapter 2 Literature Review

2.1. Lignite and lignite utilization

2.1.1. Overview

Lignite is a low-rank coal that has the macromolecular structural features of the coal-forming plants to larger extent than higher-rank coals [30]. **Figure 2.1** shows the four major ranks of coals. Each type differs based on the amounts of carbon it contains and on the amount of heat energy it can produce. The total reserve of lignite globally is around 4 trillion tonnes which is around 40% of the world's total coal reserves [31]. The majority of lignite reserves are directly utilized as solid fuels for electric power generation and heat through combustion [32]. The disadvantages of lignite as a fuel sources are the fact that it has high moisture content, high ash yield, and low calorific value which makes it inferior from both economic and environmental points of view [33]. The high moisture content of lignite can lead to added energy consumption for desiccation and increasing transportation costs, and therefore prevents the efficient utilization of lignite [34]. Lignite is also rich in oxygen-functional groups, this can result in the increase of CO₂ emission during combustion and a strong tendency to spontaneous ignition during storage and transportation [34]. However, the high content of oxygen-functional groups offers a big advantage for lignite as it can be utilized as a potential feedstock for producing value-added oxygenated chemicals such as humic acids, short-chain aliphatic acids, and benzenepolycarboxylic acids.

Oxidation studies of lignite with different oxidants suggested that the predominant aromatic structures are benzene and phenol rings [35,36]. Hydroaromatic structures, such as tetralin fragments, can also be important part of the structure [35]. On the other hand, structures containing more than one ring are fairly rare in lignite. The studies have also suggested that polycyclic and heterocyclic ring systems are not important components of the structure [36]. Studies by the United

States' Department of Energy suggested that either dimethylene bridges or hydroaromatic structures such as 4,5-dihdropyrene are major contributors to the structure of certain types of lignite [37].



Figure 2.1: The different types of coals arranged based on rank starting with the highest rank anthracite coal.

2.1.2. Availability

China is considered the largest producer of lignite with over 235 million tonnes in 2019 which account for 27% of the total amount of lignite produced worldwide in 2019 [38]. Canada has a total of 6.6 billion tonnes of proven coal reserves [39]. Anthracite and bituminous coal amount to 3471 Mt, and subbituminous coal and lignite is around 3107 Mt (871 Mt of subbituminous coal and 2236 Mt of lignite) [40]. **Figure 2.2** shows the worldwide production of lignite with China having the highest production of lignite at 235,883 thousand tons and Canada ranking the 11th in the world [38]. **Figure 2.3** shows that most of coal reserves in Canada are located in the Western Provinces, with some reserves in Ontario, Nova Scotia and Northern Canada. Over 90% of the Canada's resources are in the Western Canada Sedimentary Basin which extends from the Canadian Shield to the Rocky Mountains through Manitoba, Saskatchewan, Alberta and British Columbia. Most of the subbituminous deposits are located in Alberta while lignite is mostly in Saskatchewan [41]. Other types of coal including bituminous coal, and semi-anthracite are

scattered all over the country. The majority of Canadian coal is mined via opencast techniques. Around 10.5 Mt of lignite is produced each year in Canada, which is mainly used for power generation [41]. Saskatchewan has three mines that produce lignite; all is used for thermal applications. Lignite is found in southern Saskatchewan, southeastern Alberta and southwestern Manitoba although currently, only the Saskatchewan deposits are being mined; at present, only the Ravenscrag Formation contains lignite deposits of economic interest. This is an extension of lignite-bearing beds distributed through North and South Dakota, Montana and Wyoming in the USA. Around 90% of all lignite produced is consumed within the province of Saskatchewan, almost all by Minemouth power plants. The remainder is exported to Ontario and Manitoba, mainly for power generation [41].

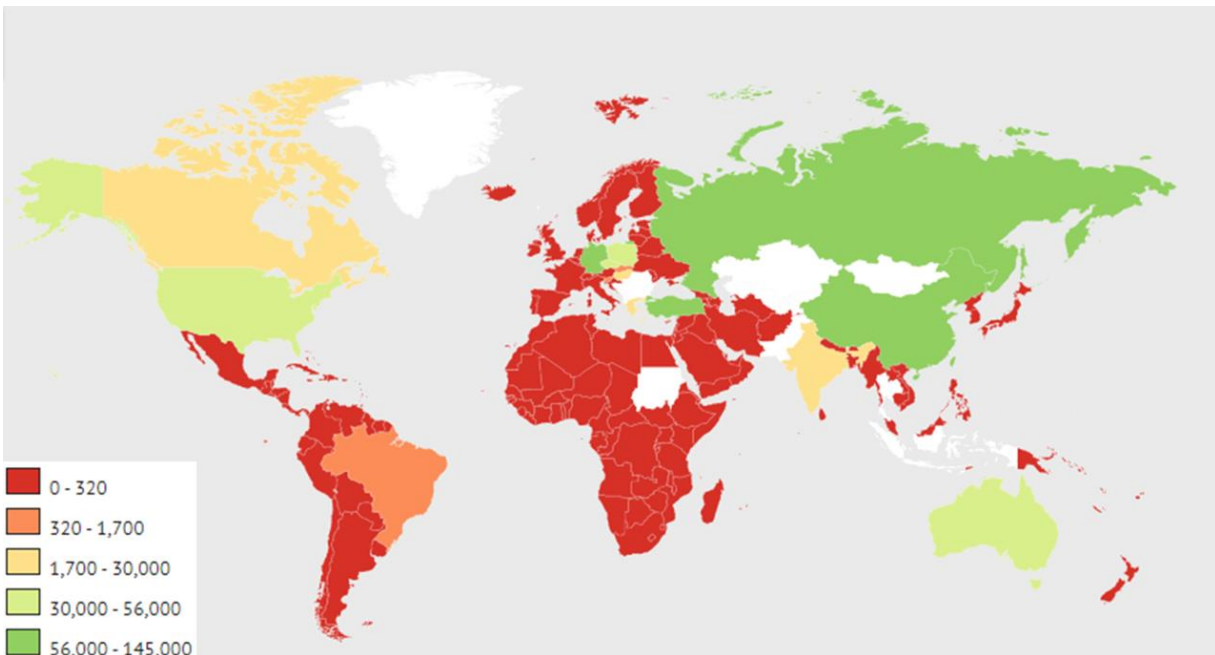


Figure 2.2: Worldwide lignite production in thousands of tonnes as of 2019. Green: the highest production, red: the lowest and white: no available data [38]

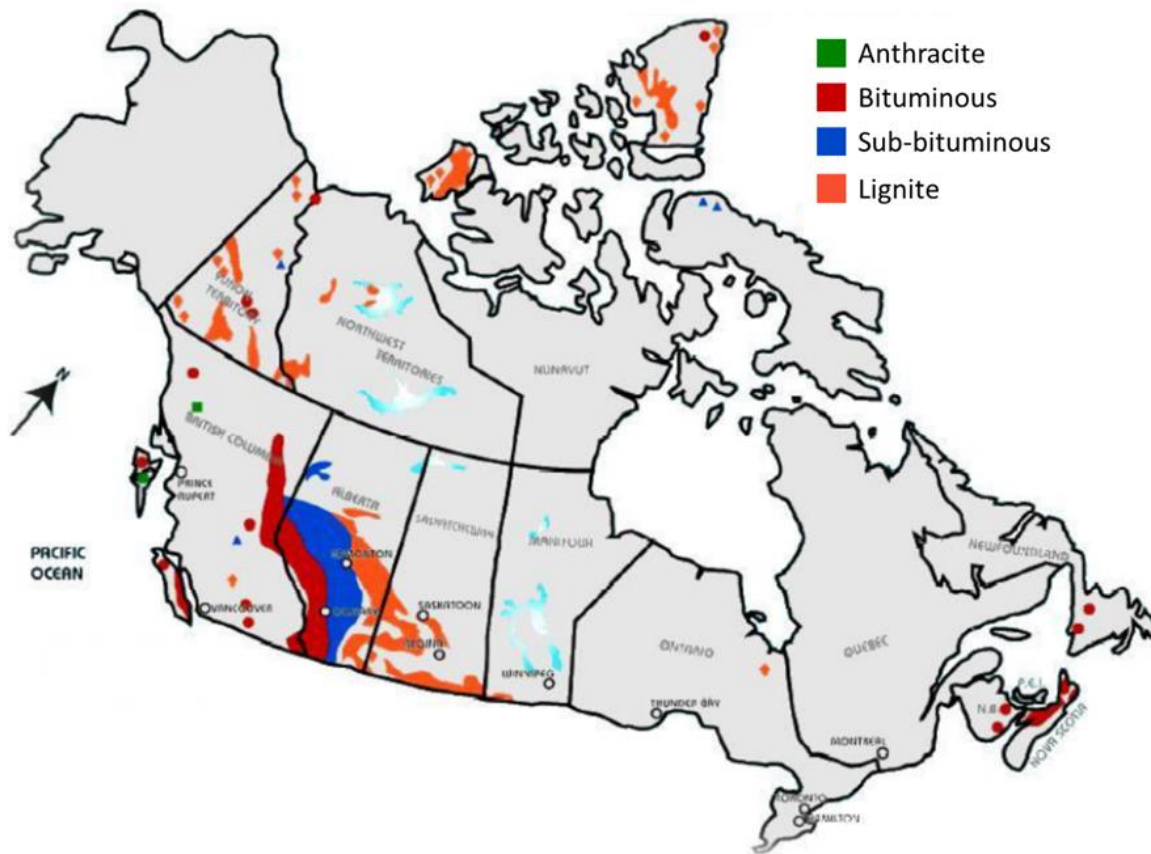


Figure 2.3: Distribution of coal types in Canada including anthracite, bituminous, sub-bituminous and lignite [42]

2.1.3. Uses of lignite

Lignite is a versatile feedstock that has been used in multiple ways, below is a summary of several major utilization routes of lignite.

2.1.1.1. Combustion of lignite

Combustion of lignite for steam generation for electric power is by far the most significant commercial application of lignite worldwide [43]. Combustion also happens at smaller scale for space heating and raising steam for industrial processing. Combustion of lignite happens in four stages starting with the removal of surface moisture at low temperatures, followed by evolution of water from organic functional groups then evolution and combustion of the volatiles, and lastly

burnout of the char [44]. Unlike other types of coals, where tar is the major volatile material, large amounts of carbon monoxide, water, and carbon dioxide are released from lignite [45]. Lignite is more reactive than bituminous coals for combustion purposes; however, for practical design purposes the reactivity advantage can be lost via the need of coarser fuel grind obtained and the lower flame temperature resulting from the high moisture content [44]. A major disadvantage of this type of technology is the large amount of emissions associated with process including NO_x and CO_2 [44]. The low heating value of lignite compared to other types of coals also considered a barrier for this technology [46]. For this reason and others, a lot of governments around the world are trying to phase-out this type of use of lignite in general [47].

2.1.1.2. Gasification of lignite

Gasification is a technology that can convert lignite to synthesis gas, a gas mixture including carbon monoxide and hydrogen, through pyrolysis and char gasification [48]. Gasification is an endothermic reaction. The heat for gasification is supplied by partially oxidizing lignite with air or oxygen. Oxygen, steam, and air are typically used as the gasifying agents. Various reactor configurations of gasifiers have been developed and others are being developed, including those with fixed beds, entrained beds, and fluidized beds and each one of them has its own distinct features [49]. However, gasification of lignite suffers from the same problems combustion suffers from including the emissions of large amounts of CO_2 [50].

2.1.1.3. Liquification of lignite

Liquification of lignite can be direct and indirect. Direct liquefaction is the conversion of lignite to a liquid product by hydrogenation [51]. Typically, lignite is slurried in a solvent medium, with no intervening process steps between the lignite and liquid. Later, liquid products go through down-stream treatment. On the other hand, indirect liquefaction is the formation of liquids from

synthesis gas produced by lignite gasification. Indirect liquefaction would employ the Fischer-Tropsch synthesis or some variant of the Fischer-Tropsch as the liquefaction step [52]. Neither the direct nor indirect liquefaction of lignite is currently commercially employed, and it does not seem likely that liquefaction will become commercial in the near future.

2.1.1.4. Combustion of lignite-water slurries

The preparation and use of lignite-water slurries is considered part of the liquefaction technologies, since the slurry is a fuel in liquid form. On the other hand, slurries represent a new technology for lignite preparation and beneficiation. Interest in slurries likewise derives from several sources: an approach to lignite drying that gives a dried product resistant to moisture re-adsorption; an alternative approach to transportation; and a liquid fuel that might be used, for example, as an energy source in boilers that had originally been designed for oil firing. In 1980's commercial interest in slurry preparation and utilization has risen dramatically. By 1990's the commercial sector's participation in slurry research, production, and use has virtually vanished. The extent to which slurries will represent a viable commercial-scale technology in the future, other than in specialized niches, is questionable.

2.1.1.5. Chemical products from lignite

The majority of lignite today is devoted to its use as a fuel in electric power generation, and to a much lesser extent its conversion to substitute natural gas. Furthermore, results of pilot-scale testing from the synfuels of the late 1970's and early 1980's suggest that lignite has significant potential as a feedstock for direct liquefaction processes [53]. However, it is important to bear in mind that with time, more coal power plants are retiring and phasing out all over the world. This will free up great quantities of lignite for non-combustion purposes. Natural gas, petroleum, and coals all are potential raw materials or feedstocks for non-combustion processes. Non-combustion

products include humic acids, fulvic acids, activated carbon, wax, direct use for wastewater treatment, charcoal, carbon nanotubes, microfibers and recovery of precious metals. In this thesis, the production of humic acids from lignite using ultrasonic is investigated as a technology for the utilization of lignite to make organic fertilizers and soil conditioners that can have very important role in improving crop yield especially with the climate change that is happening causing reduction in land fertility [13].

2.2. Humic substance

Humic substances (HS) also referred to as humus or humic matter, are supramolecular structures of heterogeneous molecules that contain molecules of sugar, fatty acids, aliphatic chains, and aromatic rings, held together by hydrophobic interactions and hydrogen bonds [54,55]. They are complex organic compounds, and their main characteristics are their intricate chemical structure, dark color, richness in redox functional moieties, and resistance to biodegradation [56]. Humification is the name typically given to the chemical, enzymatic and microbial processes that slowly degrade carbonaceous compounds leaving behind residue [56]. Several aquatic and terrestrial ecosystems can be ideal environment in which humus is formed and preserved during large periods of time, thus HS are believed to be ubiquitous in the environment [57]. Humic substance has been classified into three major components based on solubility in an acidic and alkaline medium. These components are humin, humic acids and fulvic acids. **Figure 2.4** shows the three different categories of humic substances and their major differences including solubility, molecular weight and color.

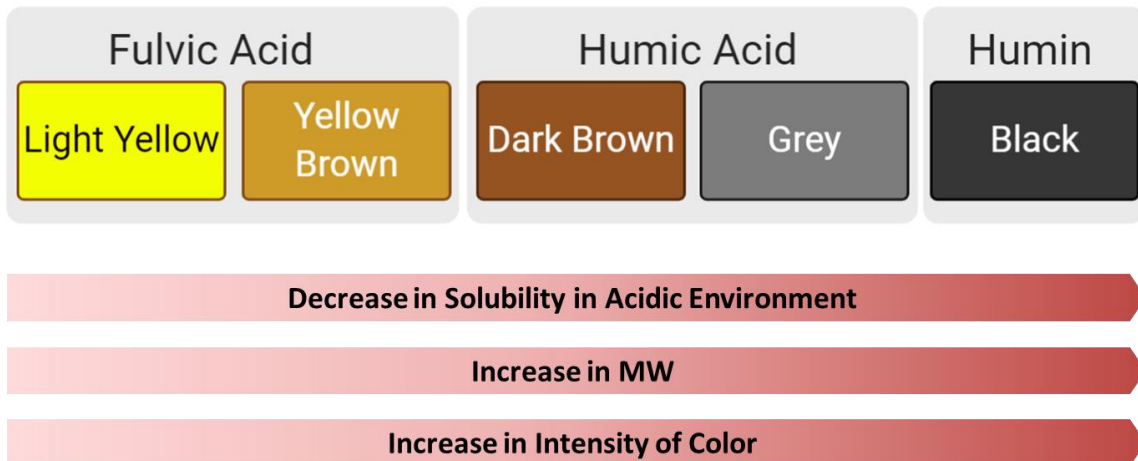


Figure 2.4: The three different components of humic substances and their major differences.

2.3. Humic acids (HA)

The upper portion of soil in a farmland is typically comprised of approximately 45% minerals, 50% air and water, 2% plant and animal remains, 2% humus and less than 1% living organisms such as bacteria and insects [58]. Humus is formed in a cycle that starts with organic matter being broken down into smaller basic components by decomposers such as fungi insects and bacteria [59]. With the decomposition of organic matter, rocks and minerals start to degrade by weathering and rock eating organisms called Lithotrophs [60]. The cycle continues with the reformation of the broken-down particles into a variety of chemical compounds typically referred to as humus. Eventually these compounds will break down into molecules that are chemically stable and resistant to further decay. These complex molecules are known as humin, fulvic acids and humic acids.

2.3.1. Humic acids in agriculture

Humic acids' high carbon content provides food for microbes improving the soil ecology but their primary benefit is their ability to chelate nutrients (a molecule's ability to hold on to ions) [61].

Molecules of humic acids are negatively charged because they have lost positively charged hydrogen ions and this creates spaces on the molecules where positively charged particles such as iron, copper, zinc and manganese can attach [62]. The root systems of plants are also negatively charged but have a more powerful charge than that of humic acids ions are drawn to the plant root [63]. The positively charged ions will leave the organic molecule to the root. The plant is then able to absorb these important micronutrients for growth and reproduction. The mineral portion of soil is comprised of various combinations of sand, silt and clay. Because clay particles have a strong negative charge, soils with large percentages of clay have a high cation exchange capacity which reduces leaching of the positively charged cations. Sandy soils have a low cation exchange capacity, so some nutrients are more likely to be washed away from the root zone [64]. Because of their ability to chelate cations, humic acids may have the ability to raise the cation exchange capacity of soil making nutrients more readily available to plants and making fertilizer applications more efficient.

2.3.2. Chemical structure of humic acids

There is no defined molecular structure for humic acids, instead there is a wide range of molecular weights with various combinations of carboxyl and hydroxyl groups. However, most of the researchers in the field reported that humic acids contain carbon, hydrogen, heteroatoms (O, N, S) and some metals (Fe, Si) [9,65,66]. **Figure 2.5** shows one of the complex humic acid models based on extensive testing and analysis done by Schulten [5,67]. **Figure 2.6** shows a simpler model of humic acids developed by Stevenson [56]. Both structures share a common characteristic such as a high degree of edge oxidation in the form of carboxyl, carbonyl, and hydroxyl functional groups and aromatic rings structures. It has been found that oxygen containing functional groups which

include carboxyl, carbonyl, alcoholic and phenolic hydroxyl, and methoxyl groups are predominant specifically carboxyl and phenolic groups [68].

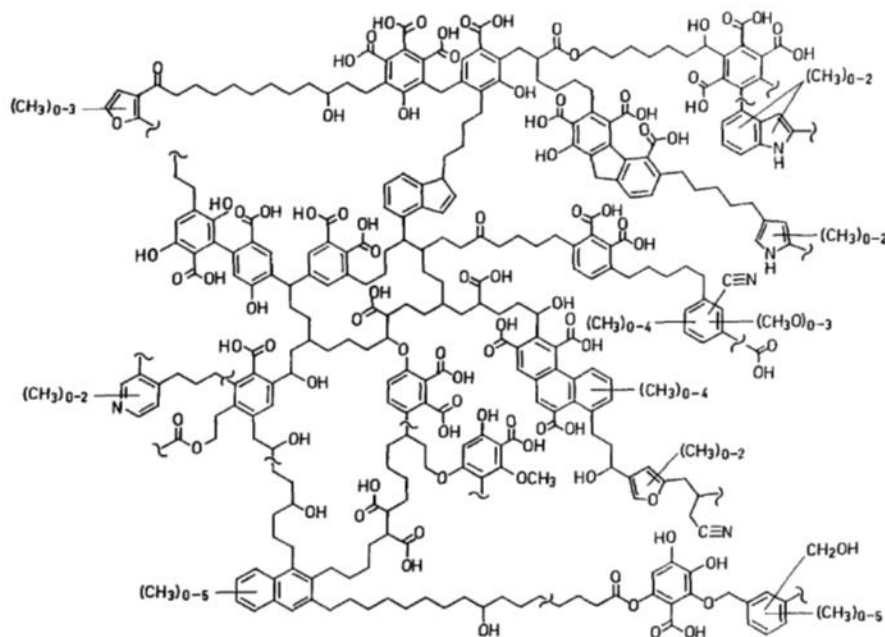


Figure 2.5: Proposed humic acids chemical structure formed by alkyl benzene moieties attached through covalent bonds [5]

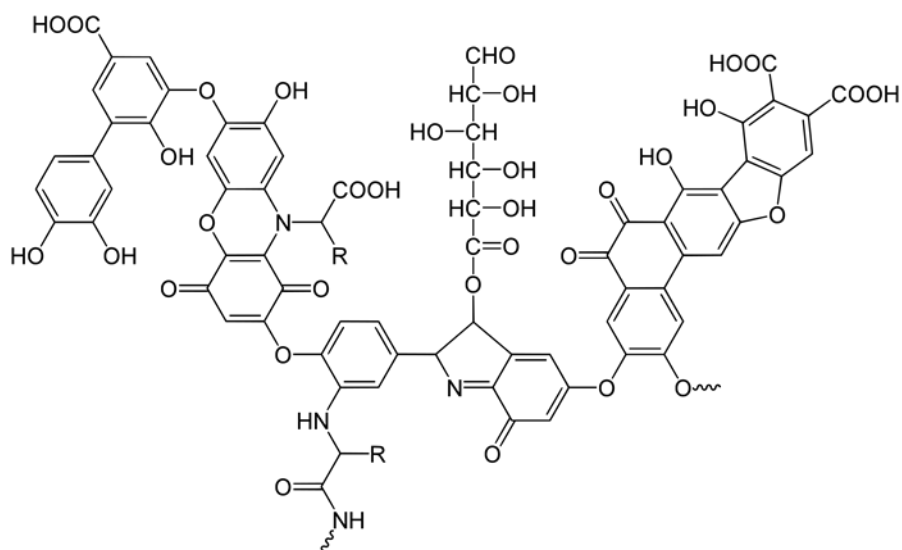


Figure 2.6: A simpler chemical structure for humic acids [42]

2.3.3. Humic acids extraction

The most common methods of humic acids extraction involve the use of bases in aqueous solutions [69–71]. However, other organic solvents have been studied as well. Humic acids produced by a single extraction step often followed by further purification based on the application. Basic solutions are used to dissolve humic and fulvic materials, allowing the separation from insoluble components. The resulting alkaline solution is then acidified to precipitate humic acids which can then be collected. Another method is solvent extraction where solvents are used to obtain HA from a precursor material. The following is detailed look at some of the extraction and production methods.

2.1.1.6. Aqueous extraction

Humic acids extraction using basic and acidic solutions is the most common method used today due to its simplicity. Comprehensive studies were assembled and published by Sprengel [72], in which alkaline and acidic solutions were utilized to extract humic acids from soil. Sprengel's method was similar to the limited work on HA extraction done previously. The extraction procedure utilizing basic and acidic solutions laid the groundwork for what would eventually become the standardized procedure of the International Humic Substance Society (IHSS) for the extraction and quantification of humic acids [73].

Later, other researchers looked at extracting humic acids from feedstocks that is not soil. Frost et al. [74] reported their findings on extraction steps of humic acids from coal and leonardite. The work used several alkalis to extract lignite slack material as well as leonardite, naturally occurring form of oxidized lignite coal. They also reported that yielded humic acids contains less ash. This work was considered the first unofficial, but widely used procedure for the extraction of HA by

alkaline solutions. IHSS standardized HA extraction procedure was published also based on this work.

In 1981, the International Humic Substance Society (IHSS) published the standardized procedure for humic acid extractions [73]. This publication contained guidelines on testing soils and coal for HA with a procedure very similar to that developed by Frost et al [72]. The procedure has NaOH as a base to extract humic materials under continuous mixing (**Figure 2.7**). After that, acidification to a pH of 1 using HCl happens to precipitate humic acids followed by centrifuging or filtration. This method is still used today as the main method for the extraction and quantification of humic for testing soils and producing humic acids commercially.

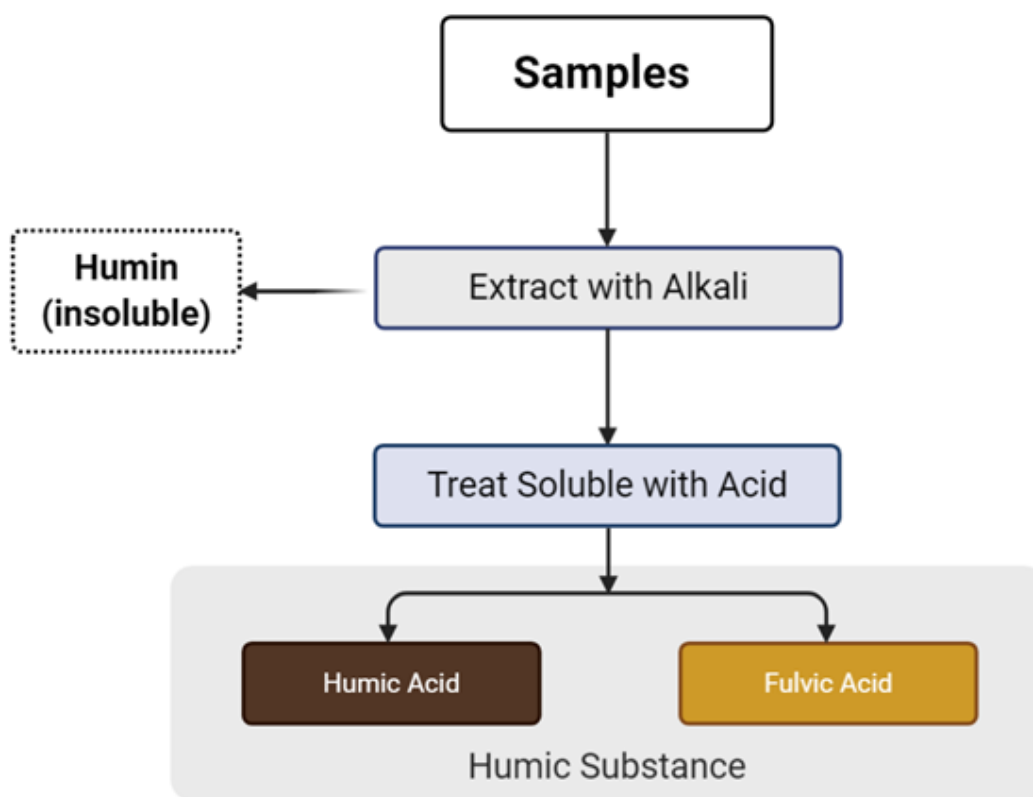


Figure 2.7: A simplified flow diagram for the IHSS method of HA extraction.

Several researchers have tried modifying the IHSS method but most of these attempts were not widely adopted. **Table 2.1** shows some of the attempts with the yield and time for the extraction.

The major disadvantages of the IHSS method are the time required for extraction which for some feedstocks can be over 25 hours and low yield of the humic acid extracted.

Table 2.1: Summary of researchers attempts to modify or replace the IHSS standardized method for HA extraction.

Raw material	Extraction technique	Extractant Type	Time, h	Yield	Ref
<i>Lignite</i>	Modified IHSS extraction	NaOH	-	32.8-48.6%	[75]
<i>Subbituminous coal</i>	Combined fungal and oxidation treatments	NaOH	24	31.1-54.2%	[76]
<i>Lignite</i>	Modified IHSS extraction	NaOH	-	51.6%	[14]
<i>Lignite</i>	Oxidation pre-treatment followed by IHSS extraction	KOH	-	13.6-24.6%	[77]
<i>Lignite</i>	Modified IHSS extraction	NaOH and Na ₄ P ₂ O ₇	-	3-11.4%	[22]
<i>Biochar</i>	Modified IHSS extraction	KOH	12	18.75%	[78]
<i>Lignite</i>	Modified IHSS extraction	Mixture of NaOH and Na ₄ P ₂ O ₇	6	-	[79]
<i>Peat</i>	Modified IHSS extraction	KOH	12	25.3-35.5%	[80]
<i>Organic Wastes</i>	Modified IHSS extraction	NaOH	-	0.98-7.3%	[81]
<i>Sub Bituminous Coals</i>	Modified IHSS extraction	KOH	-	1.5-11.1%	[82]
<i>Lignite</i>	Modified IHSS extraction	KOH	-	8.51-21.63%	[28]
<i>Lignite</i>	Modified IHSS extraction	NaOH and Anthraquinone	-	50.48-62.81%	[83]
<i>Compost</i>	Modified IHSS extraction	KOH	24	TOC: 42.3-81.3%	[84]
<i>Leonardite</i>	Modified IHSS extraction	NaOH	-	54-56%	[85]
<i>Lignite</i>	Modified IHSS extraction	KOH	-	13.67%	[86]

<i>Lignite wastes</i>	Modified IHSS extraction	NaOH	4	54.2%	[87]
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When humic acids are extracted, the proton in -COOH and -OH is replaced with K^+ or Na^+ depending on the type of base used. The hydrophobic and hydrogen bonding is then eliminated or minimized which allows the molecules, in this case as salts of Na-humic acids or K-humic acids, to be soluble. When these salts (i.e., humates) are treated with acid such as HCl, they get protonated which brings back the interaction among them and causes the precipitation. **Figure 2.8** shows the simplified mechanism where KOH is dissolved into ions in water and the exchange of ions happening with breaking of some hydrophobic interaction, hydrogen bonding, di and trivalent cations. This creates humates, in this case potassium humates, which can be separated from solution using strong acid to protonate the functional groups again.

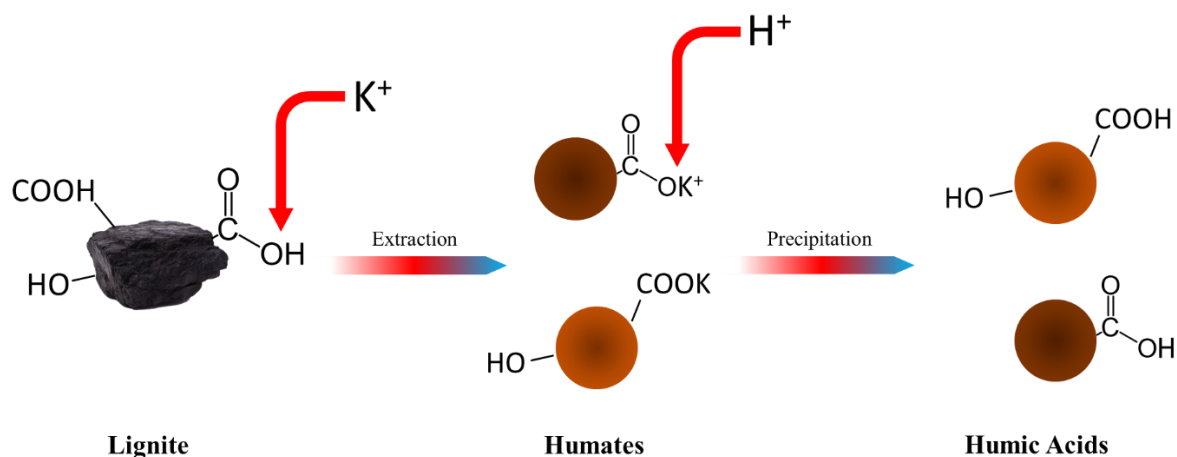


Figure 2.8: A simplified mechanism of humic acid extraction from lignite based on basic/Acidic treatment.

2.1.1.7. Organic solvent extraction

While aqueous extraction of humic acid using bases and acids is a well-established method, it has some disadvantages. Such disadvantages include the use of strong acids and bases as well as the requirement for fresh acids and bases for each extraction step. Furthermore, aqueous extraction

requires materials which can handle both high and low pH conditions, this can increase the cost of materials at large scale. These challenges and others have pushed researchers to find a suitable organic solvent for the effective extraction of HA from different sources.

Thiessen and Engelder [88] suggested the use of hot acetone as an organic solvent to extract HA from dried decayed wood. The use of acetone was to avoid altering the natural resins, lignins, and organic acids found in the wood materials, as they believed that strong alkali solutions could damage these compounds. Polansky and Kinney [89] tested over 250 different solvents and solvent combination to extract HA from coals. Their recommendation was to use 50% to 90% acetone and water as they observed the best results at these percentages. Frost et al. [74] also tested acetone to water at 3:1 ratio and found that HA can be soluble at that ratio. Youngs et al. [72] looked at the used of acetone, water and HCl mixture to extract humic acids from leonardite. The composition of the solvent that gave the best results was 80% acetone and 20% water by volume, along with 10 g of HCl per 100 g of leonardite. Other researchers tested multiple solvents including EDA, pyridine, sulpholane, DMF, and EDTA, but none performed as well as the NaOH in the IHSS extraction method [8]. For example, Piccolo et al. tested DMF and DMSO and the results showed lower yield than that extracted by alkaline procedure [90]. Humic acids extracted using organic solvents was found to be more aliphatic than those extracted by the IHSS method which are more aromatic. While several researchers showed that organic solvents can possibly be used to replace basic/acidic extractions for obtaining HA, organic solvent still suffer from lower yield, high cost, and complex extraction procedure.

2.1.1.8. Electrochemical oxidation

Multiple sources reported the use of electrochemical oxidation to achieve higher extraction rate of humic acids from lignite and coal in general [91,92]. The process starts with grinding the lignite

particles to 80-200 mesh, then adding the powder to alkali solution to prepare a slurry. The slurry is then added to an electrochemical reactor in the anode section and adding alkali solution with the same concentration to the cathode section. The slurry from the anode, after the reaction, is centrifuged and acidified using sulphuric acid to pH of 3 and collecting the solid product after settling. According to the patent, the process yielded around 70% humic acids. The major disadvantage of the process is the use of electrochemical reactors. These reactors need to be extensively washed and the anode and cathode materials will be degraded so easily with time because of the use of coal.

2.1.1.9. Ion exchange

In this method, a preoxidation using nitric acid is carried out first. Lignite is crushed to 80 mesh then 0.5 M NaOH solution is mixed with crushed lignite and for an hour and rotation speed of 150 rpm. The extracted solution is then filtered using whatman paper. The filtrate is then treated with resin cation to obtain humic acid. The idea of using resin cation is to reduce the pH from 14 to 2 through the exchange of Na⁺ ions with H⁺ ion [93]. Major disadvantages are the slow extraction speed, selection of the appropriate resin is difficult since many components of HA will destroy the resin, and the costs of maintenance and replacement of materials are high.

2.1.1.10. Thermal oxidation

Yanhong et al. [94] reported a thermal oxidation method for extracting humic acids from lignite. The process starts with washing followed by drying. The dried lignite is then subjected to temperatures in the range of 100 to 250°C under oxygen or air for 5 to 10 days. The oxidized lignite is then mixed with alkali solution and stirred under temperatures from 80 to 100°C. The resulting mixture is then treated with acid to separate the humic acid. Manasrah et al. [95–98] reported the catalytic oxy-cracking of petroleum coke to humic acids under temperatures around

200°C and pressure of 750 psi. Doskocila et al. [99] reported the use of H₂O₂ as an oxidant instead of oxygen for shorter reaction times and lower temperatures and achieved a maximum yield of 30%. Drawbacks include slow operation, multiple steps, high temperatures and low yield.

2.3.4. Fulvic acids

The fraction of humic substances that is soluble in water under all pH conditions is typically referred to as fulvic acid or fulvic fractions. They remain in solution after removal of humic acid by acidification. Fulvic acids have lower molecular weight compared to humic acids and light yellow to yellow-brown color [100]. **Figure 2.9** shows the hypothetical model structure of fulvic acids as proposed by Buffle contains both aromatic and aliphatic structures, both extensively substituted with oxygen-containing functional groups [101]. While fulvic acids are less utilized for agricultural applications, they have very important role in reducing surface tension of water, building biomass, and are considered good chelators [96].

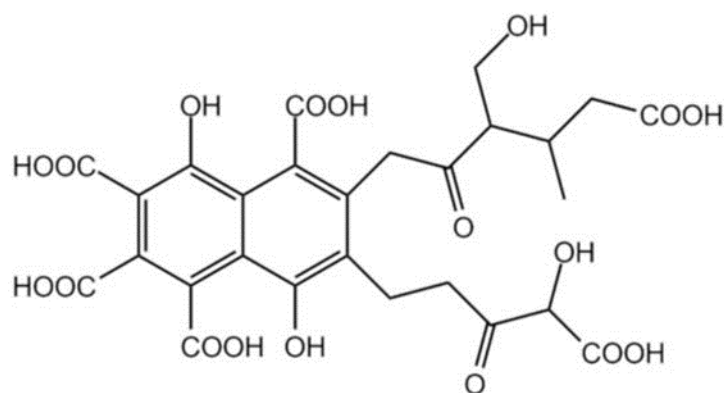


Figure 2.9: Fulvic acid structure as proposed by Buffle [78]

2.3.5. Humic

Humic is the insoluble component of soil or coals that remains after extraction of the other components that are soluble in aqueous base [102]. Typically, humin have been mostly considered

as combustible materials to supply heat for biorefineries [103]. More research is being done on the high value applications, notably the use of humin in the manufacturing of catalytic materials, plastic reinforcement and construction materials [104]. Humin can also be subjected to thermal treatments to convert it to lightweight and porous humin foams [105].

2.4. Sonochemistry

Sonochemistry refers to the chemical and physical processes happening in a solution through the energy brought by power ultrasound [106].

2.4.1. Ultrasound

The pressure waves generated from some mechanical disturbance causes sound waves. Human hearing can not go beyond about 18 kHz, sound beyond this limit is inaudible and is defined as ultrasound. Ultrasound as sound above 20 kHz and up to 100 kHz can generate greater acoustic energy and affect chemical reactivity [107].

2.4.2. Cavitation

The effects of ultrasound are caused by the cavitation phenomenon, which refers to the formation, growth and collapse of gaseous microbubbles in liquid phase (**Figure 2.10**) [108]. The microbubbles grow over the period of a few cycles to an equilibrium size at the frequency applied. The sudden collapse of those bubbles causes mechanical, thermal and chemical local effects and these effects are at the origin of all the applications of sonochemistry. An example of these effects is what happens in water, where at ultrasonic frequency of 20 kHz, each cavitation bubble collapse causes a localized hot-spot, generating temperatures of over 5,000 K and pressures higher than 1,000 bars [109].

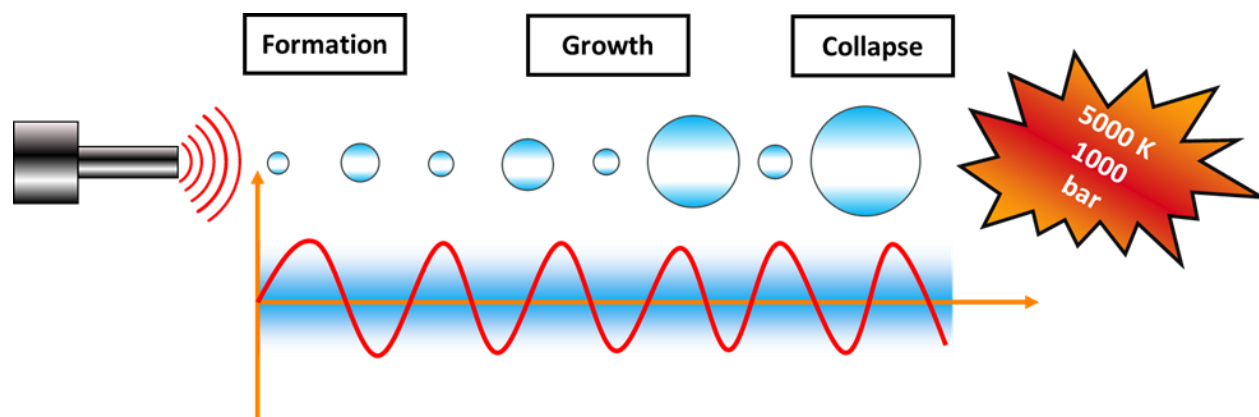


Figure 2.10: Schematic ultrasonic cavitation phenomenon

The collapsing microbubbles have both physical and chemical effects. The physical effects can enhance the reactivity or accelerate a reaction by proper mixing of reagents and improved mass transfer. On the other hand, the chemical effects can enhance reaction rates due to the formation of highly reactive radical species formed during the collapsing of microbubbles in the solution.

The first investigation of organic compounds sonolyses in aqueous solutions have focused on aromatic compounds, chlorinated aliphatic and aromatic hydrocarbons and phenols [110,111]. The mechanisms of sonolyses of organic compounds in aqueous solutions are not clearly interpreted [112,113]. Weissler et al. found that aqueous solutions of CCl_4 liberated Cl_2 upon ultrasonic processing in the absence of O_2 and accelerated the formation of I_3^- in aqueous iodide solutions [112]. In 1959, the role of free radicals in the formation of H_2O_2 by ultrasonic waves was investigated [114]. Zechmeister et al. reported the successful cleavage of the benzene ring and heterocycles using ultrasound [115–117]. Spurlock et al. reported that the irradiation of aqueous suspensions of thioethers gives mostly sulfoxides and sulfonic acids, and aldehydes give mostly carboxylic acids [113,118]. **Table 2.2** summarizes some of the research done on organic materials conversion using ultrasonic processing.

Table 2.2: Ultrasonic processing of organic compounds

Type	Reactants	Intermediates and Products	Ref.
<i>Aliphatic hydrocarbons</i>	methane	H ₂ , C ₂ H ₆ , C ₂ H ₄ , C ₃ -C ₄ hydrocarbons, CO, CO ₂ , CH ₂ O	[119]
	methane	H ₂ , C ₂ H ₂ , C ₂ H ₄ , C ₂ H ₆ , CO, C ₃ H ₈ , C ₃ H ₆	[120]
	acetylene	H ₂ , CO, CH ₄ , HCOOH, CH ₃ COOH, HCHO, CH ₃ CHO, other C ₂ -C ₈ hydrocarbons, insoluble soot, C ₆ H ₆ , styrene, naphthalene, and phenylacetylene	[121]
<i>Aromatic hydrocarbons</i>	benzene	C ₂ H ₂ , CO	[122]
	toluene	HCHO, phenolic hydroxyls, benzoic acid	[123]
	toluene	benzaldehyde, bibenzyl	[124]
	ethylbenzene	benzene, toluene, styrene, cumene propylbenzene, diphenylmethane, 1,2diphenylethane, benzaldehyde, acetophenone, phenylacetylene.	[125]
<i>Halogenated aliphatic hydrocarbons</i>	tetrachloromethane	Cl ₂ , CO ₂ , HCl, C ₂ Cl ₆ , C ₂ Cl ₄ , HOCl	[112]
	dichloromethane	Cl ⁻ , Cl ₂	[126]
	ethyl iodide	I ₂ +I ⁻	[127]
	trichloromethane	Cl ⁻ , H ₂ , CO, CO ₂ , CH ₄ , C ₂ H ₄	[128]
	trichloroethylene	Cl ⁻ , H ₂ , CO, CO ₂ , CH ₄ , C ₂ H ₄ , C ₂ HCl, C ₂ Cl ₂ , C ₄ Cl ₂ , C ₂ Cl ₄ , C ₄ HCl ₃ , C ₄ Cl ₄ , C ₄ HCl ₅ , C ₄ Cl ₆	[129]
<i>Halogenated aromatic compounds</i>	bromobenzene	Br ⁻ , C ₂ H ₂ , C ₄ H ₂	[117]
	o-dichlorobenzene	Cl ⁻	[127]
	chlorobenzene	Cl ⁻ , CO, CO ₂ , CH ₄ , C ₂ H ₂ , C ₄ H ₄ , C ₄ H ₂ , phenylacetylene, benzene, chlorophenols, non-chlorinated mono- and dicyclic hydrocarbons	[130, 131]
	iodobenzene	I ⁻ , C ₂ H ₂ , C ₄ H ₂	[117, 127]
	polychlorinated biphenyls	biphenyl, ethyl benzene, diethylbiphenyl, dibutylbiphenyl, phenol, propylphenol, di-butyl phenol, chloride	[132]
<i>Alcohols</i>	cyclohexanol	C ₂ H ₂	[133]
	methanol	H ₂ , CH ₂ O, CO, CH ₄ , C ₂ H ₄ , C ₂ H ₆ under Ar. CO ₂ , CO, HCOOH, CH ₂ O, H ₂ O ₂ , H ₂ under O ₂	[134]
	alcohol	CH ₄ , C ₂ H ₆ , C ₃ H ₆ , C ₂ H ₄ , C ₂ H ₂	[135]
	t-butanol	CH ₄ , C ₂ H ₂ , C ₂ H ₄ , C ₂ H ₆ , C ₄ H ₆	[136]
<i>Phenols</i>	phenol	hydroquinone, catechol, CO ₂ , benzoquinone	[137]
	chlorophenol	chlorohydroquinone, chlorocatechol, hydroquinone, catechol, chloride at pH 11, glyoxylic acid at pH 3, CO ₂	[138]

<i>Organic sulfur compounds</i>	iodothiophene in silver nitrate solution	AgI, Ag ₂ S, silver acetylide, and silver diacetylide	[117]
	dibutyl sulfide	(C ₄ H ₉) ₂ SO, n-butylsulfonic acid, butyric acid, CO, C ₂ H ₄ , CH ₄	[118]
	carbon disulfide	sulfate under air, amorphous carbon and monoclinic sulfur	[139]
	benzothiophene	hydroxybenzothiophenes, dihydroxybenzothiophenes, and benzothiophenedione	[140]
<i>Organic nitrogen compounds</i>	pyridine	HCN, C ₂ H ₂ , C ₄ H ₂	[116]
	pyridine	HCN, C ₂ H ₂ , C ₄ H ₂	[141]
	ethylenediamine	NH ₃	[142]
	RCH ₂ NH ₃	H ₂ , CH ₄ , NH ₃ , RCHO, RCH ₂ OH	[143]
	4-nitrophenol	4-nitrocatechol, CO ₂ , NO ₂ ⁻ , NO ₃ ⁻ , pbenzoquinone, hydroquinone	[144]
	3-chloroaniline	Cl ⁻ , NO ₂ ⁻ , NO ₃ ⁻ , CO, CO ₂	[145]
	nitrobenzene	nitrophenol, 4-nitrocatechol	[146]

2.4.3. •OH radical reactions

It was reported that water sonolysis can produce strong oxidants and reductants that can cause oxidation and reduction reactions [147,148]. Many ultrasonic oxidation products of organic compounds at the gas-liquid interface of the microbubbles or bulk liquid were reported [113,131,149–153]. Both •OH radical and H₂O₂ released were assumed to diffuse into the bulk solution and attack solutes [154].

Lamy et al. studied the ultrasonic degradation of benzene, chlorobenzene, phenol, and chlorophenol in water [130]. During the degradation of phenol and chlorophenol, hydroxylated compounds were observed but not with benzene and chlorobenzene. Serpone et al. [138] studied ultrasonic processing of three chlorophenols. The products of the decomposition were dechlorinated, and hydroxylated intermediates. In addition, they demonstrated that the reaction takes place in the bulk solution at low concentrations of chlorophenol, while at higher concentrations, the reaction occurs predominantly at the gas bubble/liquid interface. Dewulf et al.

[155] looked at the ultrasonic decomposition of trichloroethylene and chlorobenzene and found that at low concentration $\bullet\text{OH}$ radical-induced degradation becomes significant. Miura et al. [156] reported the oxidation of lignite using 30% H_2O_2 at low temperature of 60°C for 24 h. They reported 0.71 carbon conversion of lignite to water-soluble organics. Gong et al. reported the production of fulvic acids from lignite using H_2O_2 under microwave power. Studies have shown that the use of H_2O_2 in ultrasonic processing increase the $\bullet\text{OH}$ radical concentration [157–162]. The mechanism of $\bullet\text{OH}$ radical oxidation of lignite can be complex, and it could involve breakage of aromatic rings, creation of COOH , $\text{C}=\text{O}$ and OH functional groups. More on the reaction mechanism is explained in [chapter 4](#).

Chapter 3 Experimental Work and Methodology

3.1. Materials

Low-rank coal (raw lignite) was purchased from Ward's Science (Rochester, NY, United States of America). The samples are black with brownish streaks with sizes of specimens in the range of 2.54×2.54 cm to 2.54×5.08 cm. The origin of this lignite is Bowman North Dakota USA. These samples were crushed into powder (particle size ranging from 53 to 710 μm) using a grinder before the use in the reaction. In order to create alkaline media, potassium hydroxide (KOH) and ammonium hydroxide (NH_4OH) were purchased from Sigma-Aldrich (Ontario, Canada). KOH comes as pellets with purity of over 85%, while NH_4OH comes as a solution of 28.0-30.0 wt.% NH_3 basis. Hydrogen peroxide solutions of 35 wt.% obtained from VWR (Ontario, Canada) was used as an oxidant. Hydrochloric acid (HCl) was also acquired from Sigma-Aldrich (Ontario, Canada) with 37 wt.% concentration. These chemicals were diluted to desired concentration using water. Lignite has been analyzed using carbon hydrogen and nitrogen analyzer (CHN) and the results were 59.1 wt.% carbon, 4.16 wt.% hydrogen and 1.09 wt.% nitrogen and the rest can be oxygen with traces of metals and sulphur.

3.1. Ultrasonic experimental setup

To carry out the reaction, an ultrasonic vessel was used as a reactor. The setup consists of medium volume cell of 65 mL maximum volume and rated to a maximum pressure of 100 psi. The cell is fixed in place using a clamp connected to a support stand. The ultrasound waves are generated using a probe made of titanium alloy (Ti-6Al-4V). The probe tip diameter is 13 mm with 136 mm length. The probe is part of the converter. The converter also has a piezoelectric transducer. The transducer converts the electrical energy to vibrations. The converter is connected to a control

panel. The control panel allows for the modification of time, amplitude and pulses. It also registers the amount of energy supplied to the reaction vessels through the time. At the bottom of the vessel, a temperature probe is connected to monitor the temperature of the solution inside the vessel (**Figure 3.1** and **Figure 3.2**). The whole setup is enclosed in sound abating enclosure (not shown in the picture). A copper tube is wrapped around the vessel to circulate water from the water path, which allows for the cooling of the experimental apparatus.

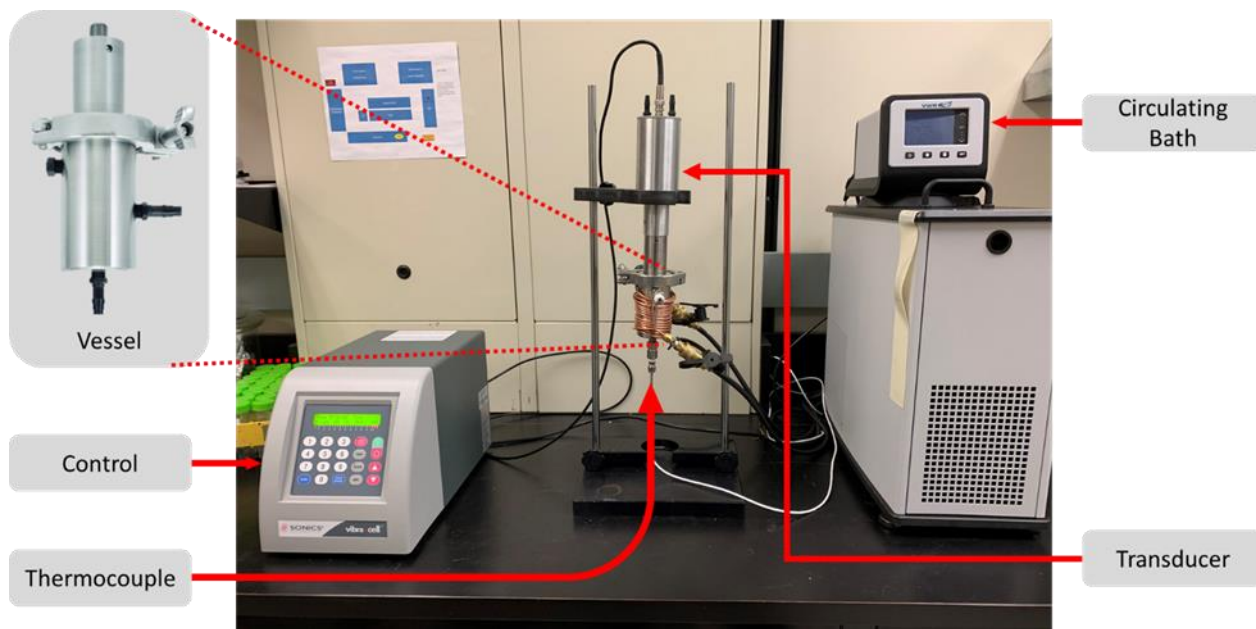


Figure 3.1: Photo of the experimental setup showing the reaction vessel, control panel, circulation bath and thermocouple.

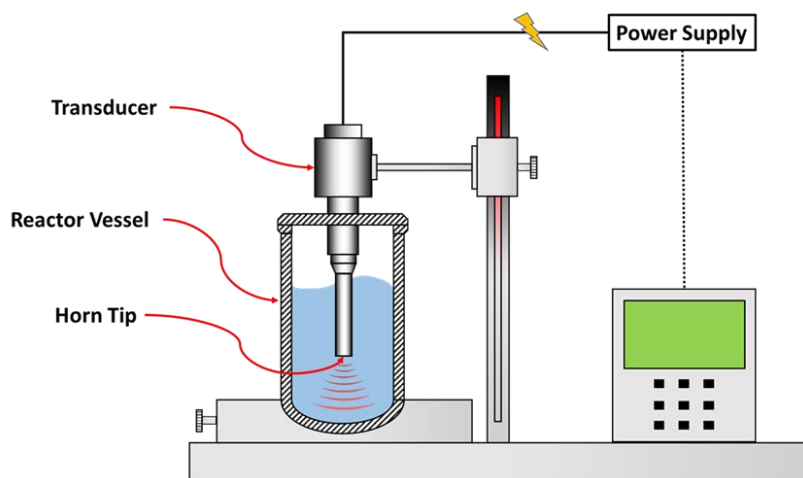


Figure 3.2: Simplified experimental drawings (not to scale)

3.2. Experimental conditions

3.1.1. Ultrasonic Amplitude

The ultrasonic probe or horn transmits ultrasonic vibrations to the liquid that is being sonicated and thus creating cavitation. The amplitude is defined as the distance between the position of the probe fully extended and fully contracted and is measured in micrometres. For each setup there is a maximum distance, and the amplitude is typically reported in percentage of that maximum. Once the amplitude is set, it stays the same for the entire duration of the reaction even if other parameters and conditions were varied. Higher amplitudes correspond to higher ultrasonic intensity and vice versa. In this work, three different amplitudes were studied namely, 40%, 30% and 20%. Some experiments also performed at 80% to verify conclusions. The maximum amplitude of 100% corresponds to 76 microns. So, at 40%, the probe vibrates up and down a distance of 30.4 microns.

3.1.2. Reaction time

Studying the effect of time on the reaction is very important. When more time passes, the amount of energy supplied to the reaction is higher consequently that leads to higher ultrasonic power.

Power is the measure of energy per unit time and is typically reported in terms of watts (W) or kilowatts (kW). The ultrasonic control panel displays the energy supplied to reaction. In this study, various time durations have been tried in the range from 1-45 min. At each time, the reaction conversion was measured to observe the trend of humic acids formation. For each time interval (1, 5, 10, 20, 30, and 45 min) various amplitudes and concentration of chemicals were tested.

3.1.3. Lignite to water ratio

Water is the medium where the reaction happens, and all humic substances released from lignite are transferred to the water. The optimum amount of lignite to water had to be found to reduce water consumption. In this work, several ratios of lignite to water have been tested to find if the water ratio has an impact on the amount of humic substances extracted. The experiments started with 20 mL water and 1 g lignite. In subsequent experiments, the amount of lignite has been increased to 1.5, 2 and 3 g while keeping the volume of water constant. At each experiment, the reaction conversion was calculated to make a conclusion for the optimum amount of lignite to water in our ultrasonic reactor. Reducing the amount of water required for each gram of lignite is going to make the process not only economical but also environmentally friendly.

3.1.4. KOH to lignite ratio

Based on the chemistry of humic substances, they need an alkaline media to be dissolved in. In this study, KOH and NH_4OH has been utilized. KOH was the major alkaline used in the majority of the experiments. Therefore, the study has focused on the optimum amount of KOH needed for the maximum amount of humic substances produced. The experiments started with a mass ratio of 1:1 of KOH to lignite and later reduced to 0.75, 0.5 and 0.1 ratios to observe the impact on the reaction conversion and yield of HA. Reducing the amount of KOH will reduce the operational cost.

3.1.5. H₂O₂ concentration

The use of an oxidant is important to increase the amount of humic acids retrieved from lignite. The oxidant role is to provide radicals and oxygenate the functional groups in lignite. Several oxidants have been tested in the literature and H₂O₂ was chosen in this study. Hydrogen peroxide was chosen since it was reported as the ultimate environmental oxidant since its by-products are not harmful [163]. Other oxidants such as HNO₃ and KMnO₄ can result in harmful gas being release and can cause corrosion to the reactor vessel. Several concentrations of H₂O₂ have been tested ranging from 1% to 5%. At each concentration, the conversion was calculated, and other parameters were changed such as amplitude to see the impact of that on the conversion.

3.1.6. Production of humic acids from lignite using ultrasonic experimental setup

Figure 3.3 represents the experimental flow diagram of the steps taken during the ultrasonic processing of lignite to humic acids. First, raw lignite is crushed to obtain powdered lignite for easy operation and to improve the mass transfer. Powdered lignite is then mixed with alkaline solution and H₂O₂ is added to the mixture. The mixture of powdered lignite, alkaline solution and H₂O₂ is then ultrasonically processed based on desired amplitude and reaction time and this is where the novelty of the work is represented. Once the reaction is done, the liquid portion and any residue left is collected. The residue is dried and weighted for characterization. The liquid portion is centrifuged to allow any suspended materials to settle. The settled materials are collected, dried and weighted. The supernatant is then mixed with HCl until the pH of the solution reaches 1 and the humic acids start to precipitate. Supernatant with the precipitated humic acids is centrifuged to get any suspended humic acids to settle. After centrifuging, fulvic fraction (the supernatant) is decanted from the humic acids. The humic acids are then dried and weighted. The details for the

process of separating humic acids from fulvic fraction is laid-out in the ISO 19822 procedure. All materials obtained were characterized using FTIR, TGA, TOC and CHN analyzer.

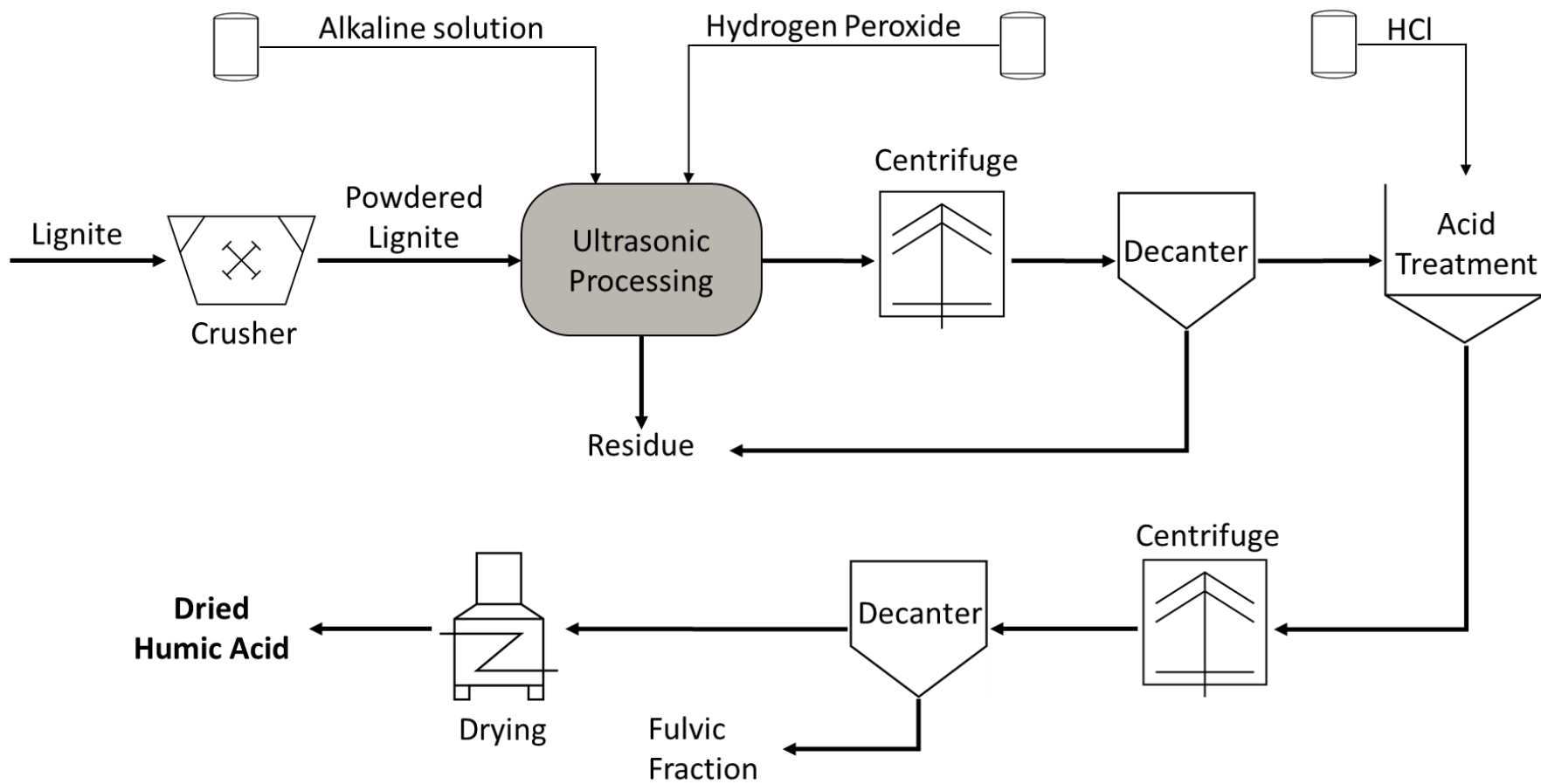


Figure 3.3: A simplified experimental flow diagram showing the major step used in the experimental work.

3.2. Characterization

3.2.1. International standardization ISO 19822 method for quantification of humic acids

ISO 19822 is an internationally recognized method for determining the concentration of humic acids in materials. **Figure 3.4** shows a simplified diagram of the ISO 19822 procedure for the determinations of humic acids contents in any sample. The quantification of humic acids is essential for the commercial applications specifically in agriculture applications for the trade and regulation of humic products. This quantification method is similar to the International Humic Substances Society (IHSS) method and the method detailed by Stevenson [6,56]. ISO 19822 defines humic acids as an alkali extracted humic substance that is insoluble in strongly acidic solutions and that precipitate in a solution of a pH of 1. The liquid remaining after precipitation is referred to as fulvic fraction.

Hydrochloric acid solution is used as a reagent. Apparatuses include analytical balance with draft guard, drying oven, centrifuge, centrifuge tubes, and pH meter. The process starts with homogenizing the liquid sample by shaking for 1 minute and weighing 5 g test portion. While stirring, 6M HCl was added to the test portion until pH reached 1 ± 0.1 . During this time, humic acids start to precipitate. The container then covered with parafilm for 1 h. After 1 h, the pH of the test portion was checked again to determine if it still at 1. If not, it was adjusted using either 6 M HCl or 0.5 M NaOH. After the pH is stabilized, the test portion was left for 4 hours undisturbed. After 4 hours ± 5 min, the solution was centrifuged for 30 min at 3900 x g (relative centrifugal force (RCF)). The supernatant was decanted (fulvic fraction). After decanting, the flocculated humic acid is centrifuged at 1500 x g for 20 to 30 mins for further separation from the liquid fulvic fraction. Then the flocculated humic acids are dried in a vacuum oven at $62 \pm 3^\circ\text{C}$ overnight up to 24 h. In this work, 24 h was ideal. Then the dried flocculated humic acids are transferred to the

TGA to determine the ash content. During these steps, the weight of containers is recorded before and after to use in the calculations.

3.2.2. Total Organic Carbon (TOC)

Shimadzu Total Organic Carbon Analyzer (TOC-L CPH/CPN, Mandel, USA) was utilized to measure the total carbon (TC), total organic carbon (TOC), and inorganic carbon (IC) in the aqueous phase obtained after the reaction. TC is all carbon in sample containing both organic and inorganic. TIC refers to carbonate, bicarbonate and any dissolved carbon dioxide. TOC is the difference between the two and it is typically organic carbon coming from decaying vegetation and metabolic activities. The TOC analyzer passes through three stages, acidification, oxidation and detection and quantification. Acidification allows the liberation of carbonates and bicarbonates to CO₂. Oxidation converts the remaining carbon in the sample to CO₂ using high temperature catalytic oxidation. For this study, the amount of TOC is very important since humic substances are organic materials. After the reaction, the sample were centrifuged to get rid of any suspended particles. 1 mL of the sample was diluted with 12 mL of water in TOC analyzer vials. Three vials were prepared for each measurement to reduce human error and confirm reproducibility. TOC measurements were done for all samples. TOC measurements were reported in a ratio of TOC to original carbon in the feedstock (C/C_0).

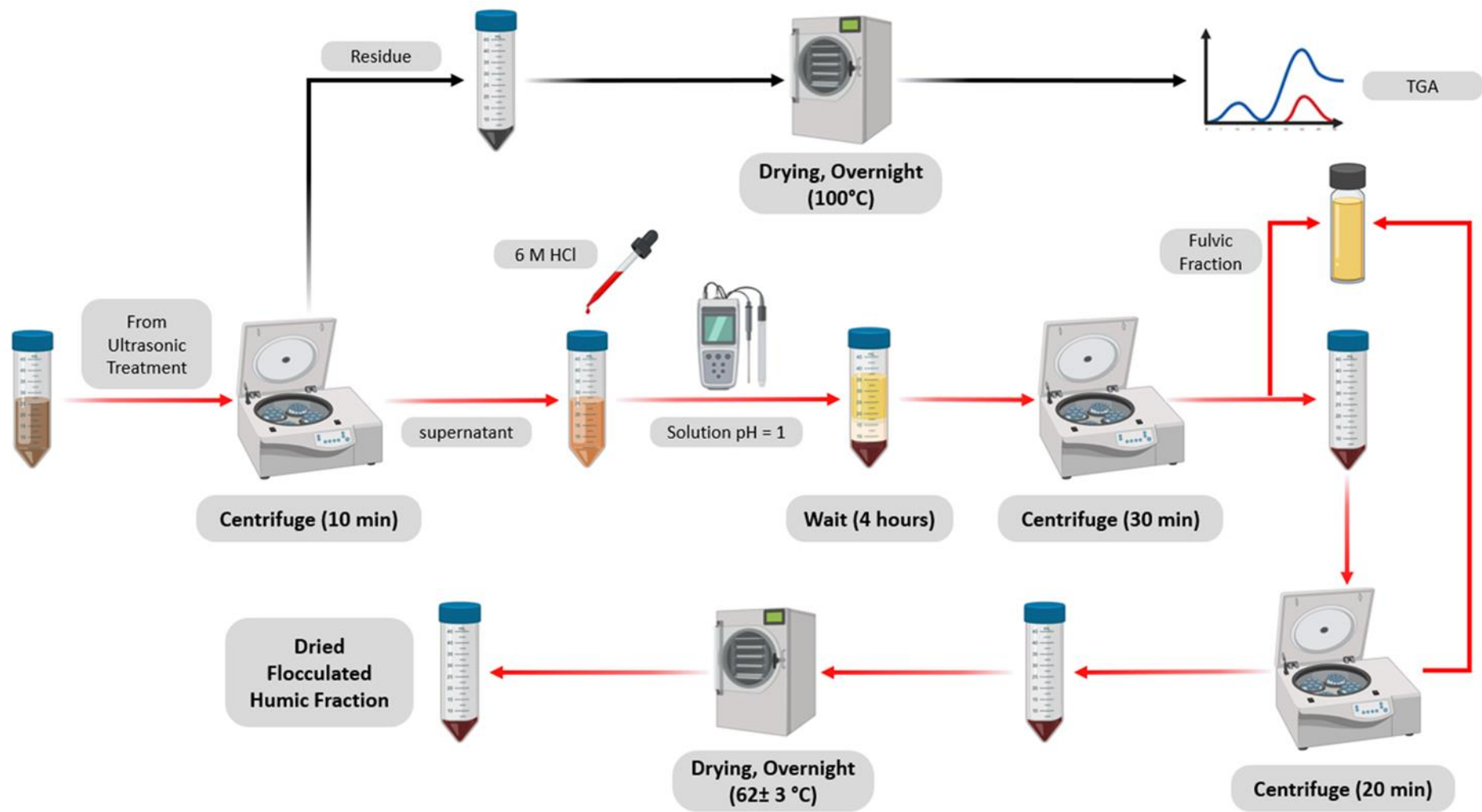


Figure 3.4: The ISO 19882 procedure to determine the amount of humic acids extracted from a certain sample

3.2.3. Fourier-transform Infrared Spectroscopy (FT-IR)

FT-IR is a technique that collects a high-resolution infrared spectrum of adsorption or emissions from a solid, liquid or gas samples. FT-IR is used to identify chemical substances and functional groups based on the fact that each molecule or functional group has a certain adsorption frequency. FT-IR is a very useful tool for the identification of humic acids in a sample through the determination of functional groups such as -COOH and -OH. In this study, IRAffinity-1S from Shimadzu Corporation (Nodel No. 3116465 Mandel, USA) was used to carry out the analysis. All tested samples were dried at 62°C in vacuum oven for 24 h. Initially KBr was used as a background and then very small amounts of humic acids, residual carbon after reaction and lignite were mixed individually with KBr and analyzed. The sample were crush to a smooth powder and added to the sample compartment. The resolution was 2 cm⁻¹ and spectra were from 400 to 4000 cm⁻¹.

3.2.4. Thermogravimetric analysis (TGA)

TGA is a technique used to measure the mass loss of a sample over time as temperature increases. The technique offers multiple information including physical and chemical phenomena including adsorption and chemical decomposition and typically referred to a proximate analysis. In this study, TGA/DSC analyzer (SDT Q600 TA Instruments, Inc., New Castle, DE) was used to test the samples of produced humic acids, residual materials and lignites. The results are used to understand how much ash is present in humic acids and the contents of carbon in the remaining residual after the reaction. The moisture content (high volatile matter), volatile matter (medium volatile matter) and fixed carbon were reported for the measurement as well. The samples were dried and placed in an open crucible made of alumina then the crucible is transferred to the sample holder in the TGA compartment. First part was pyrolysis under N₂ to measure moisture and volatiles. Then the gas is switched to air for combustion to measure fixed carbon and ash. The

procedure followed is according to ASTM E1131. The temperature was raised to 110°C and kept constant for 5 mins, then raised again to 950°C and kept constant for 15 mins. N₂ is switched to air and combustion continuous until constant weigh is achieved.

3.2.5. Elemental Analysis (CHN Analyzer)

The PerkinElmer 2400 Series II (Waltham, Massachusetts, USA) has been used to determine the concentration of carbon, hydrogen and nitrogen in humic acids, residuals and lignites. The principle behind the device is the flash combustion of the materials using the classical Pregl-Dumas method. The gases resulting from the combustion are measured and analyzed by thermal conductivity detector. The samples were dried and homogenized before utilization. The results offer a more concise measurement of carbon content in the samples. The carbon content was later used in modeling calculations. Nitrogen content is important as well to know how much nitrogen is in the product after using NH₄OH as an alkali in the extraction.

Chapter 4 Results and Discussion

This chapter presents the results obtained from the experimental work and provides explanations of the trends and reaction mechanism happening during the ultrasonic processing.

4.1. Reaction conversion and yield of humic acids

The conversion of lignite to products (humic substances) was calculated after measuring the amount of lignite reacted compared to the original amount used at the beginning of the experiment according to the following equation:

$$\%Conversion(X) = \frac{\text{Amount of reacted lignite}}{\text{Amount of original lignite}} \times 100 \quad (1)$$

The amount of lignite reacted lignite was calculated as the difference between initial amount and residual amount. **Figure 4.1** shows the conversion of lignite to products (HA) over the reaction time at 3% H₂O₂, 40% ultrasonic amplitude and 1:1 KOH to lignite ratio. As shown, the reaction time plays an important role in forming HA since the conversion is increased with the reaction time. The maximum conversion of 92% was achieved at a reaction time of 30 min. It is worth noting that the increase of conversion with time is attributed to the increase of the amount of energy supplied to the solution. This energy causes more physical and chemical effects. Physically in terms of more mixing happening because of the microjets caused by the ultrasonic waves. Chemically in terms of more •OH radicals liberated causing more oxygenation of lignite which creates more -COOH and -OH groups. The role of •OH radical in oxygenating organic molecules has been reported by Stavarache et al. [164] where the conversion of chlorobenzene to phenols and chlorophenol through radical formation during ultrasonic processing was studied. These functional groups are ideal landing sites for K⁺ which increases the solubilization of humic acids

and breakage in hydrophobic and hydrogen bonding [165–168]. Over time, more lignite particles are exposed to the •OH radicals forming, and KOH is getting attached to the functional groups in the molecules causing more solubilization in the liquid phase and less residue left over after the reaction [158–162,169]. More in this mechanism in later sections.

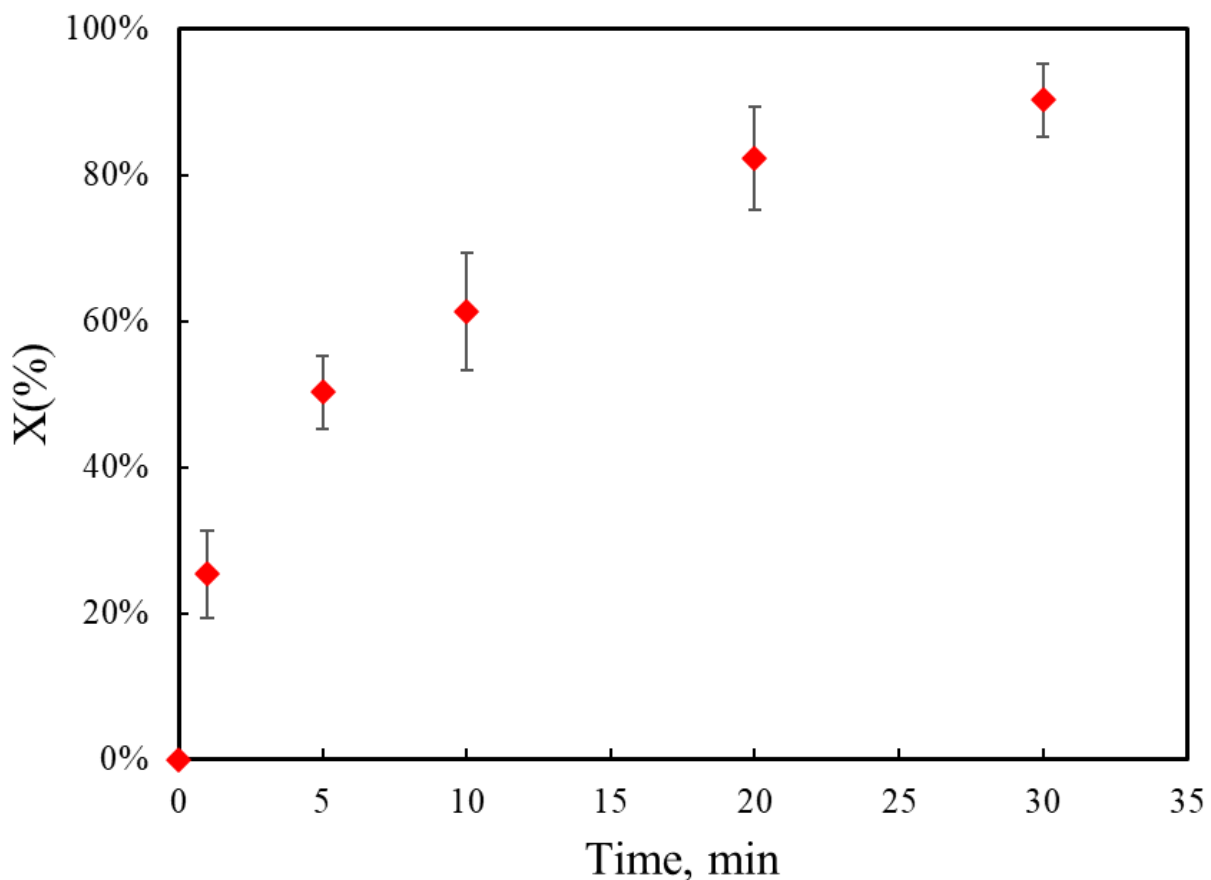


Figure 4.1: Conversion of lignite (X) against time in minutes with operational conditions of 1:1 KOH to lignite, 40% ultrasonic amplitude, and 3% H₂O₂.

The yield of forming humic acids was calculated based on the amount of ash-free humic acids formed during the reaction compared to the amount of original lignite according to the following equation:

$$\%Yield(Y) = \frac{\text{Amount of Humic Acid}}{\text{Amount of original lignite}} \times 100 \quad (2)$$

Figure 4.2 shows the yield percentage of humic acids obtained from lignite at various times at 3% H₂O₂, 40% ultrasonic amplitude, and 1:1 KOH to lignite ratio. As shown, similar to the conversion trend, the yield of HA is increased with the reaction time and the highest yield was obtained after 30 min is 72%. Fong et al. reported a maximum yield of 67% at higher temperature than this study (70°C) and higher reaction time (2 hours) [86]. Zhang et al. achieved a maximum yield of 48% of humic acids from lignite at 2 hours reactions times[170]. Syahren et al. reported a yield slightly more than 60% at 90°C [28]. **Table 2.1** shows the various attempts by researchers in the conversion of lignite and other feedstocks to humic acids. It is clear that ultrasonic processing in this study has achieved higher yields compared to the time of the reaction and temperatures used. By comparing the conversion, **Figure 4.1**, with the yield of HA, we can see that there are other forms of produced materials from lignite that can be generated other than humic acids. Such produced materials are typically fulvic acids analogs, a smaller molecule than humic acids with lighter color, which is considered part of humic substances. These materials were separated during the quantification experiments. As time increases, the intensification of the process increases causing more humic acids to break into smaller acids. These observations have been reported in the literature, for example, Doskocil et al. [99] found that humic acids can be converted into smaller acids such as malonic acid and succinic acid. Gong et al. [26] reported the production of fulvic acids from low rank coals using H₂O₂. Fulvic acids are commercially viable products used in agriculture and medicine as well.

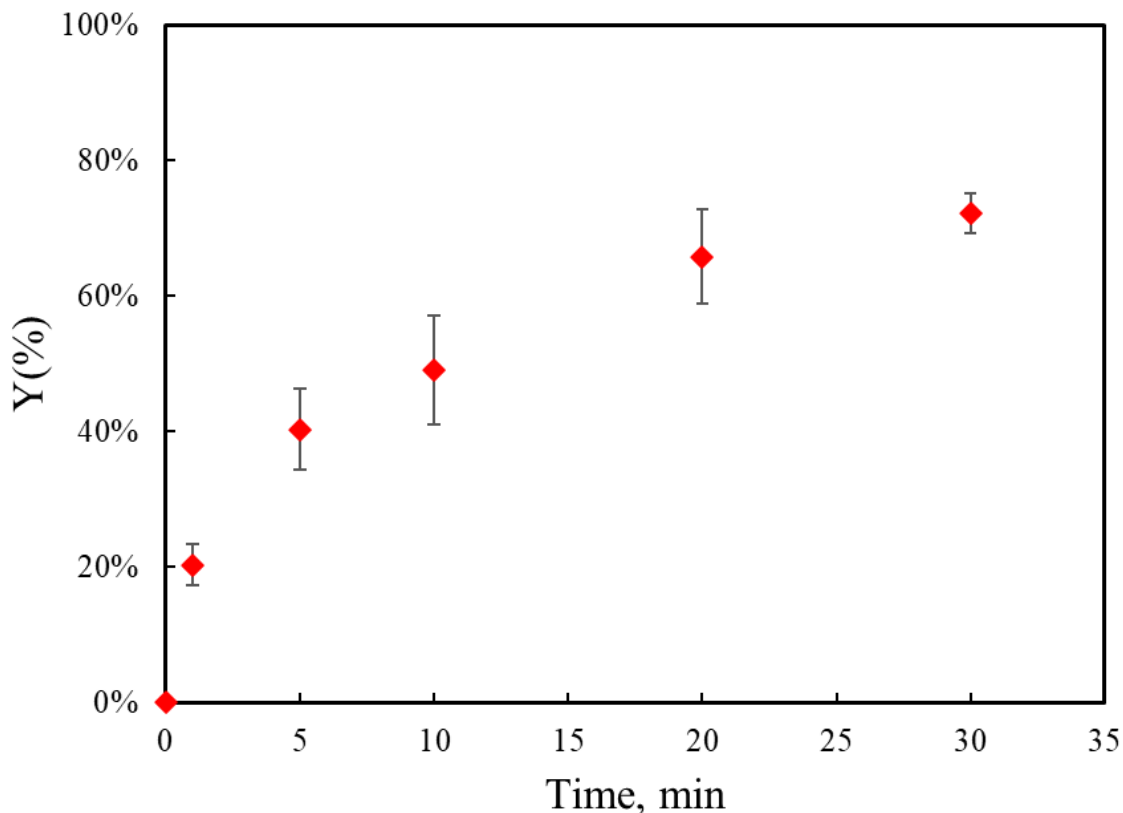


Figure 4.2: Yield of humic acids at operational conditions of 1:1 KOH to lignite, 40% amplitude, and 3% H₂O₂.

4.1. Effect of operational parameters on the production of HA

In this section, the effects of several operational parameters are discussed namely: KOH to lignite ratio, water to lignite ratio, amplitude percentage, concentration of H₂O₂ and the type of alkaline.

4.1.1. Effect of ultrasonic amplitude

Three different amplitudes ranging from 20% to 40% were considered here to investigate its effects on the solubilization of organic materials from lignite and the production HA. It should be noted that higher amplitudes (>40%) are to be avoided in this process as high emissions of CO₂ can happen due to high temperatures at these amplitudes. **Figure 4.3** shows the effect of amplitude on the ratio of C/C₀ at 3% H₂O₂, 1:1 KOH to lignite ratio where C is the amount of organic carbon

solubilized during the reaction at any time and C_o is the amount of carbon in lignite. As shown, the amount of carbon solubilized is increased with the increasing of amplitude. With the increase of amplitude more energy is being transformed to the solution resulting in higher temperature and more mixing thus increasing the contact between molecules and increasing the radical formation resulting in more solubilized materials. At higher amplitudes, lignite particles can be fragmented into smaller ones increasing the surface area and mass transfer. Oroian et al. [171] reported the effect of amplitude on the bioactive compounds extraction from propolis and observed an increased extraction rates with higher amplitude. Others have reported higher extraction yield of phenolic compounds from waste [172]. Furthermore, the effect of ultrasonic amplitude has been studied on various aspects such as morphology of nanocrystals, particle size of coal and reagent consumption in froth flotation with favourable results [173–175].

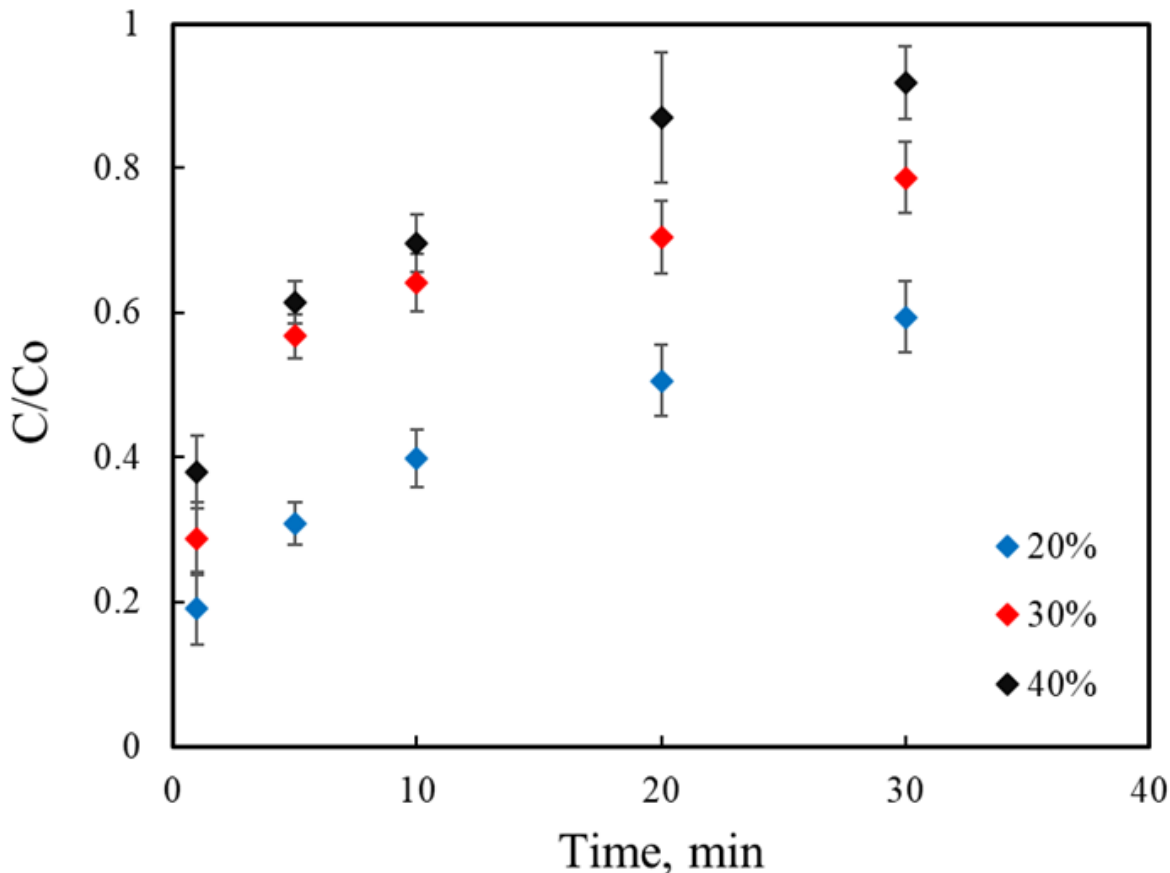


Figure 4.3: Effect of ultrasonic amplitude on the amount of solubilized carbon in the liquid portion after the reaction compared to original carbon found in lignite, operational conditions are: 3% H_2O_2 , 1:1 KOH to lignite and 05:01 seconds pulses. C: amount of organic carbon dissolved, C_o : amount of original carbon in lignite.

4.1.2. Effect of H_2O_2 concentration

H_2O_2 was used as an oxidizing agent to generate $\bullet OH$ radicals that can attack the lignite molecule thus increasing the content of oxygenated functionalities such as carboxylic and phenolic functional groups. Under ultrasonic processing, H_2O_2 disassociates to radicals that attack certain landing spots on the lignite molecules. Increasing the concentration of H_2O_2 can result in better solubilization and more humic acids as more $\bullet OH$ radicals are available for the reaction. However, lower amounts are better for economical purposes since part of the cost of humic acids will be attributed to the chemical utilized in the production. **Figure 4.4** shows the effect of H_2O_2

concentration on the ratio of the total amount of organic carbon dissolved in the solution to the original carbon. As can be seen, increasing the concentration results in more solubilization. This can be attributed to radical formations which creates more -COOH and -OH functional groups. These functional groups can be an ideal landing sites for K^+ coming from KOH which in turn can result in more solubilization. It is also not advisable to increase the concentration of H_2O_2 to high levels since this could create an acidic environment. An acidic environment will reduce the solubilization of humic acids in the solution causing it to precipitate with the residue. This has been confirmed after doing experiments at 5% H_2O_2 in this study. 5% H_2O_2 not only resulted in less solubilization but also difficulty in the operations where a lot of foaming started that can be attributed to the release of oxygen. Therefore, higher than 3% H_2O_2 was avoided in this study.

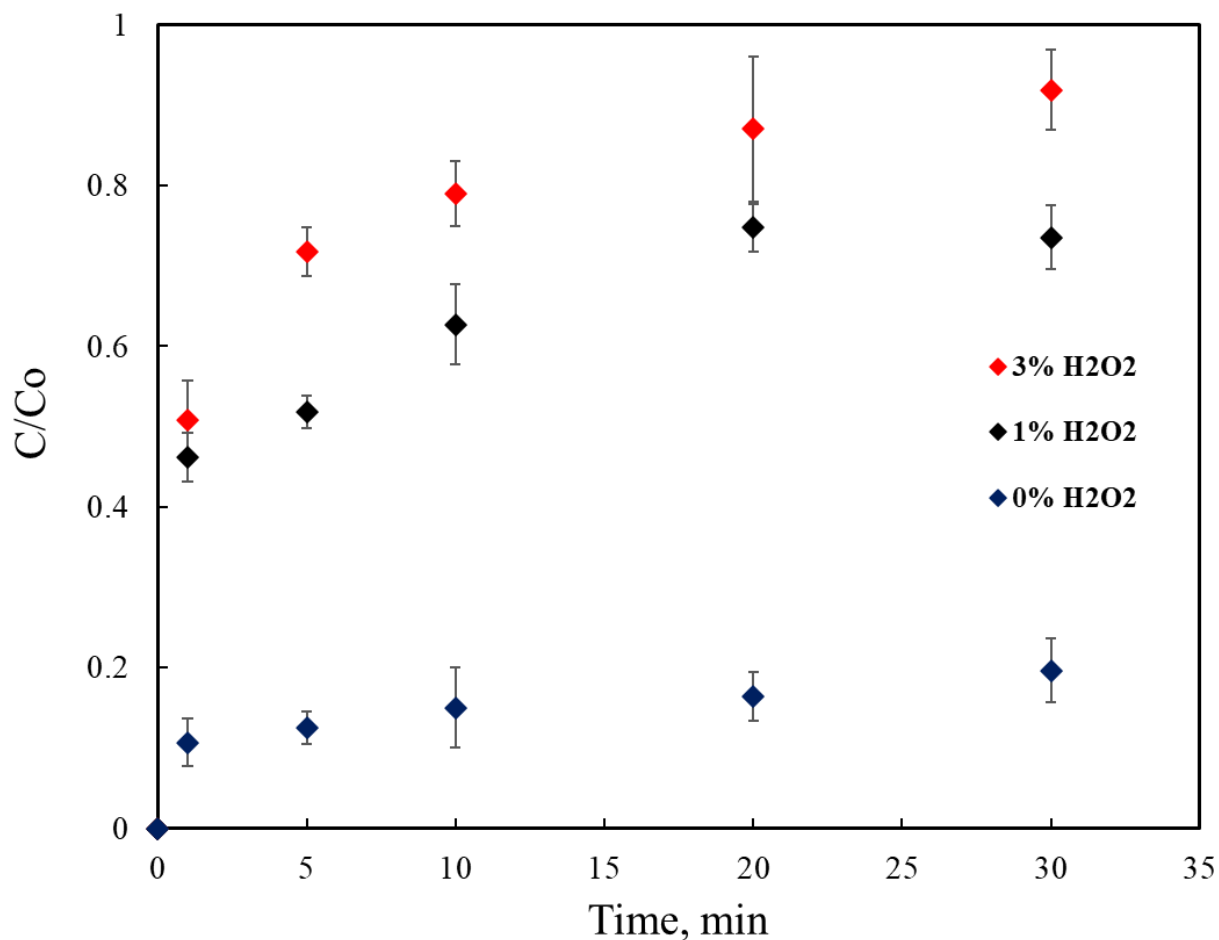
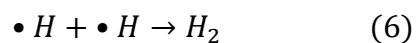
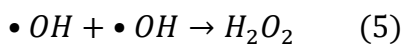
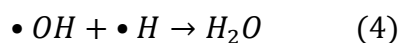
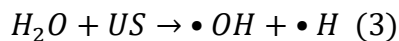


Figure 4.4: Effect of H₂O₂ concentration on the solubilization of carbon in the solution. Conditions are: 1:1 KOH to lignite, 40% amplitude. C: amount of organic carbon dissolved, C₀: amount of carbon in the original lignite

During ultrasonic processing, sonication results in radical formation, because of the very high temperatures (thousands K) and pressures (hundreds atmospheres) of collapsing gas bubbles lead to the thermal dissociation and radical formation [176,177]. The reaction chains that happen are as follows (US: ultrasonic):



When ultrasonic is coupled with H₂O₂, radical formations increase resulting in more •OH attacks on the lignite molecule. The coupling of the ultrasonic and H₂O₂ resulted in reduction in the dosage of H₂O₂ utilized in this study. Mae et al. reported the use of H₂O₂ to obtain valuable chemicals from low rank coals [169]. They were using 30% dosages compared to 3% used in this study. Fong et al. also reported higher dosages of H₂O₂ as optimum for extraction of humic acids from low rank coals when used individually [178]. Using ultrasonic and H₂O₂ has been deemed successful by multiple researchers [179–181]. The decomposition of H₂O₂ under ultrasonic can follow the following equation [157,182,183]:

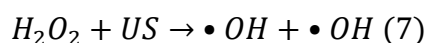


Figure 4.5 shows the proposed mechanism of the formed •OH radicals formed under ultrasonic processing from H₂O₂ and how they attack several sites on the lignite molecule. As shown, the •OH radicals simultaneously broke the weak bonds and introduced -COOH and -OH groups into the molecules. The introduction of these groups has been confirmed using FTIR characterization in the next section. Mae et al. investigated the breakage of some weak covalent bonds and the introduction of oxygen functional groups during the treatment of coals with H₂O₂ [184,185]. They reported that the amounts of COOH, O-aliphatic (including R-OH), and aliphatic carbon increased.

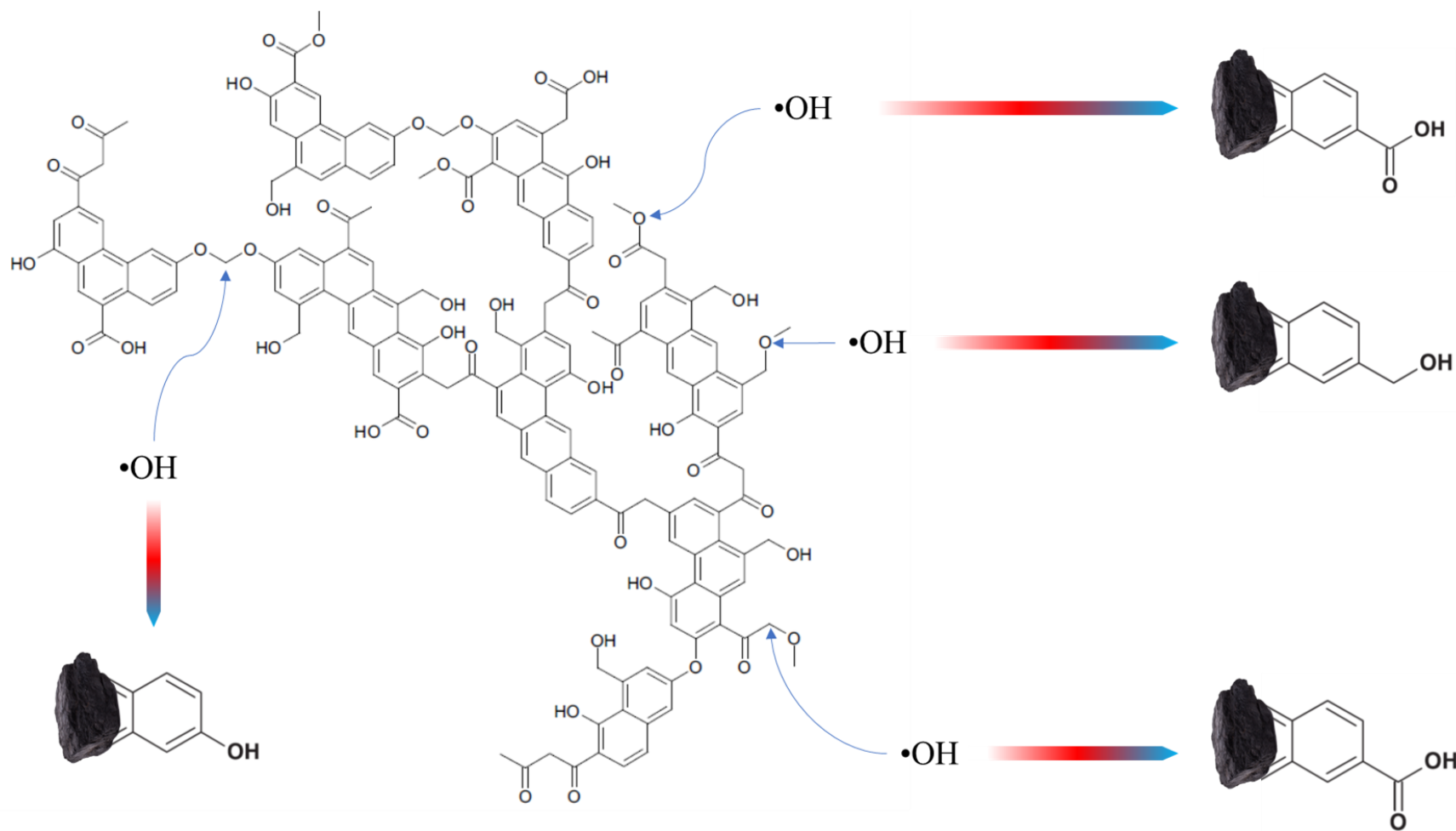


Figure 4.5: Proposed mechanism of the $\bullet\text{OH}$ radical attack on the lignite molecule (molecular model [186]) causing the formation of carboxylic and $-\text{OH}$ function groups.

4.1.3. Effect of KOH to lignite ratio and alkaline type

KOH plays an important role in solubilizing the humic substance from lignite. In order for humic substance to solubilize, an alkaline medium has to be achieved by adding any type of base. This can help protecting the intermediates and products by neutralizing the formed acids, therefore pulling these acids into the water [187–189]. In that sense, KOH allows for the protection of humic acids from deep oxidation to carbon dioxide. Kapo et al. [190] realized that increasing the concentration of NaOH resulted in reduction of CO₂ released during the production of organic acid from coal. KOH can also cause saponification reaction were certain functional groups such as esters can be cleaved to carboxylic and alcohol groups [171]. Adding a base can further help with reducing corrosion in the vessels during the reaction. Several researchers utilized different types of bases at different ratios [70,191]. Here, we reported the following ratios of KOH to lignite: 1:1, 0.7:1, 0.5:1 and 0.1:1 on mass basis. **Figure 4.6** shows the trend of C/C₀ ratio at different amounts of KOH with reaction time of 20 min, 40% amplitude, 3% H₂O₂. It does seem that lower than 0.7:1 ratio, the amount of solubilization decreased. At lower than 0.7:1, not enough K⁺ are generated for the solubilization of humic acid to happen [7,28,71,190]. Worth noting here that reducing the amount of KOH used is important from economical point of view and that higher amounts of KOH can cause salting-out which can reduce the diffusion rate of the humic acids formed on the lignite surface into the water phase [190,192]. However, the potassium coming from the KOH is beneficial in the final products since it is one of the nutrients required for plants if the produced humic acids used as fertilizers.

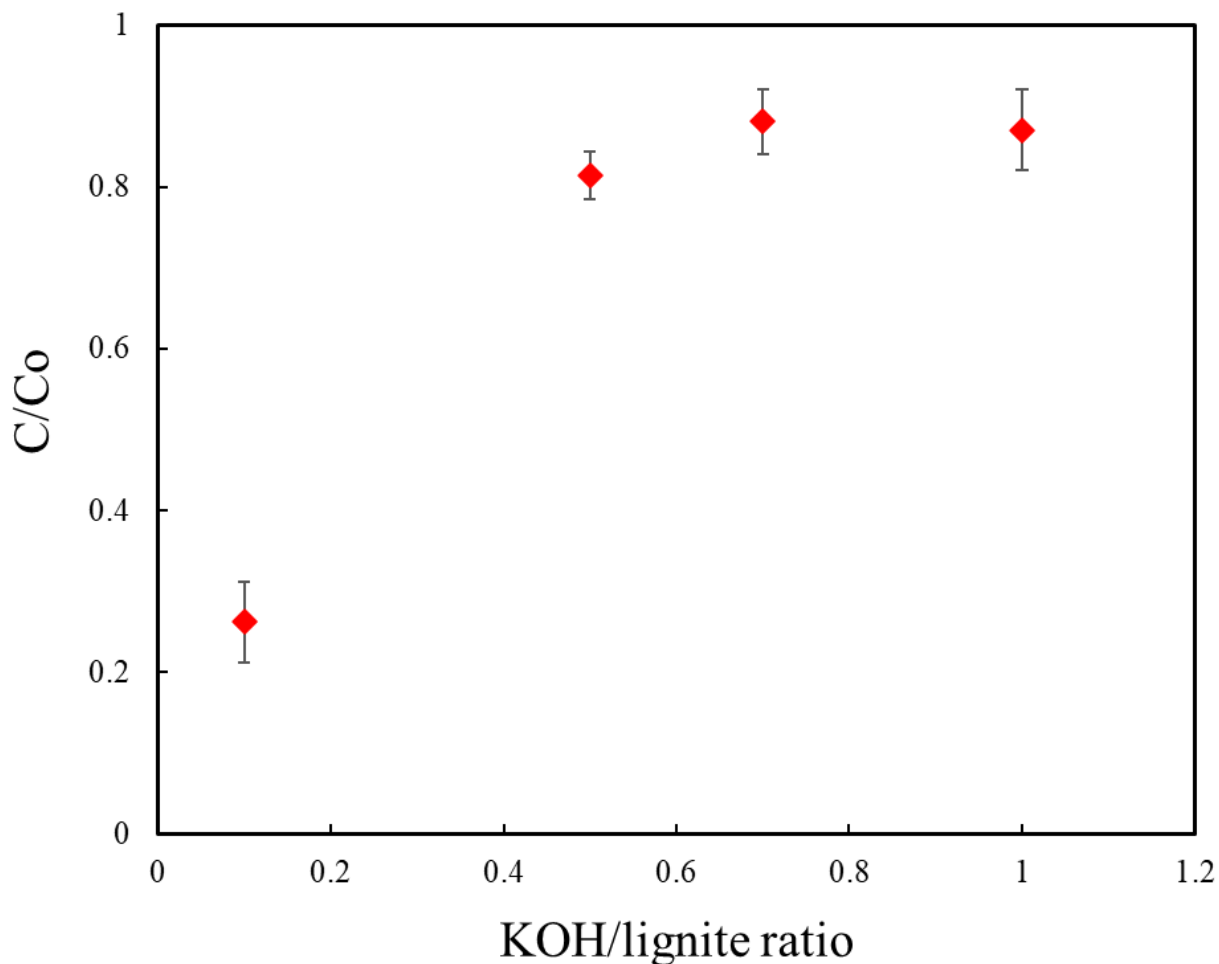


Figure 4.6: Effect of the KOH to lignite ratio on the solubilization of carbon in the solution. Conditions are: 20min time, 40% amplitude, 3% H₂O₂. C: amount of organic carbon dissolved, Co: amount of carbon in the original lignite.

Various bases have been used in the literature and commercially. For that reason, NH₄OH has been tested specifically to incorporate the nitrogen in the final products (humic acids) since nitrogen is one of the most important nutrients given to plants. First, NH₄OH was used to replace KOH and then a mixture of both was utilized. The degree of solubilization and the amount of nitrogen in the final product was investigated. **Figure 4.7** shows the effect of the type of alkaline on the solubilization and the nitrogen content. The amount of solubilized carbon decreased from over 80% to 60% when using NH₄OH as a replacement to KOH. This can be attributed to the fact that

NH₄OH is a weak base. The exchange between NH⁴⁺ and H⁺ in -COOH and -OH is weaker, resulting in more NH⁴⁺ stable in the solution with less deprotonation [27,193]. When looking at solubilization and amount of nitrogen, it seems that using 50:50 (based on molarity) is favourable as it did not impact the solubilization and increase the amount of nitrogen from less than 1% to over 7%.

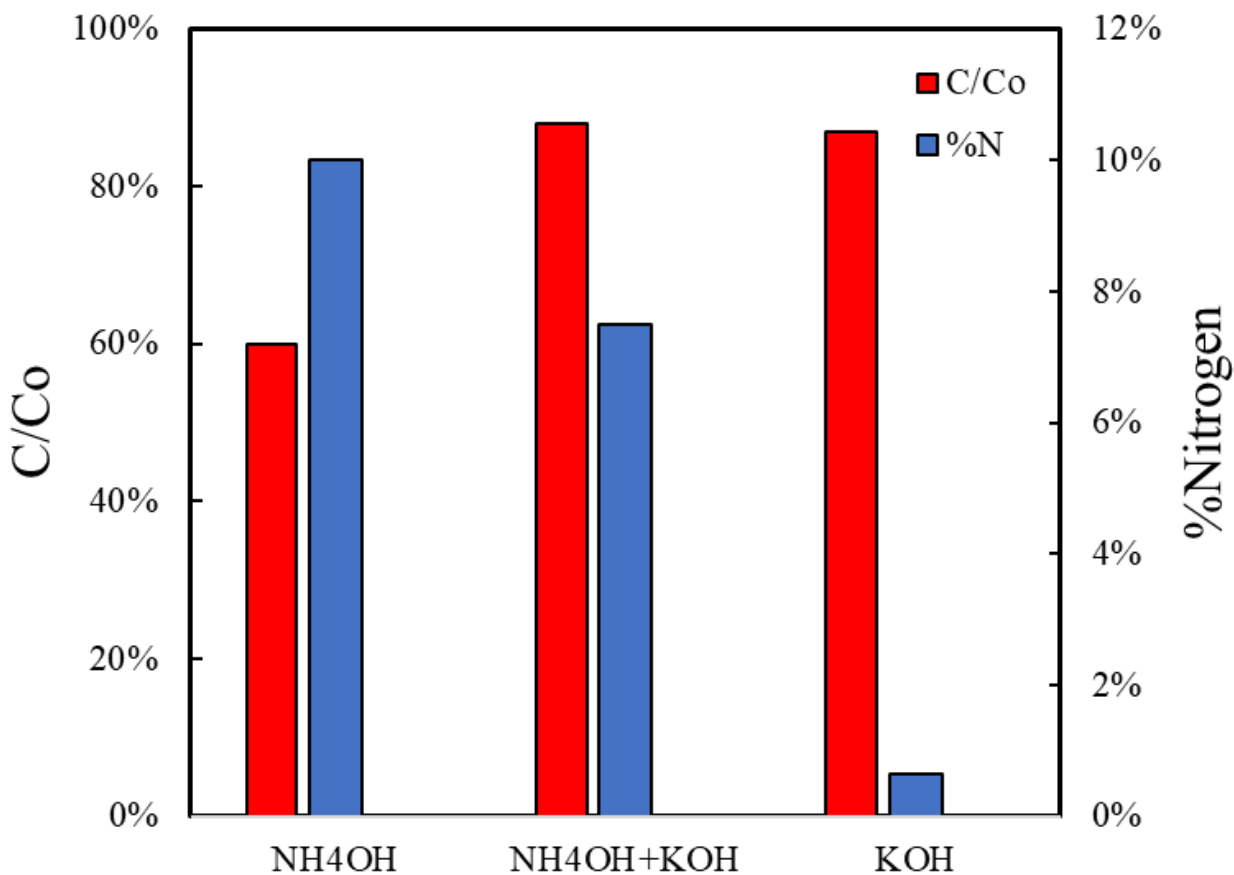


Figure 4.7: Effect of using NH₄OH on the amount of carbon solubilized and amount of nitrogen incorporated in the final products. Conditions are: Amplitude:40%, time:20 min, 3% H₂O₂. C: amount of organic carbon dissolved, C_o: amount of carbon in the original lignite.

4.1.4. Effect of water to lignite ratio

In order to reduce the quantity of water used in the process, we have tested various initial concentrations of lignite: 1, 1.3, 1.5, 2 and 3 g in 20 mL of water to examine the impact on the solubilization of organic carbon. **Figure 4.8** shows the effect of the initial concentration of lignite

on the solubilization of carbon in water keeping water content constant at 20 mL while varying the lignite amount. Other parameters were constant at 40% amplitude, 3% H₂O₂ and 1:1 KOH/lignite ratio based on the optimization in this study. There is a trend of reduction specifically above 2 g lignite to 20 mL of water. This can be attributed to the saturation of water with lignite and KOH where no more carbon can be release to water after this ratio. It is typically referred to as salting-out effects. Schnitzer et al. reported the salting out effect during humic acid extraction from soils and Kapo and Wang from lignite and coals [190,194,195].

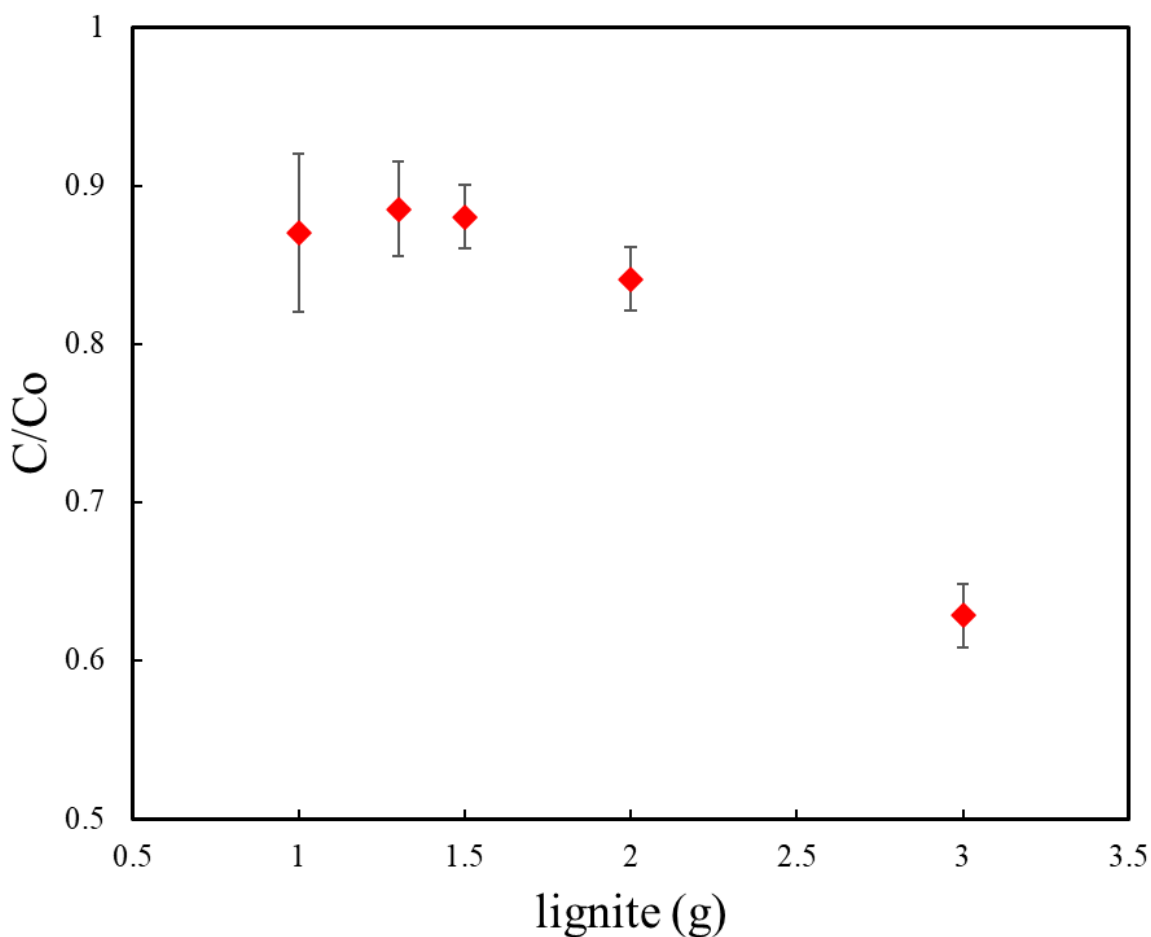


Figure 4.8: The effect of the amount of lignite in 20 mL water on the solubilization of carbon. Conditions are: 40% amplitude, 20 min, 1:1 KOH to lignite ratio, 3% H₂O₂. C: amount of organic carbon dissolved, C_o: amount of carbon in the original lignite.

4.2. Characterization of materials

In this section, detailed characterization of lignite, humic acids, and the residue left after the reaction is performed. These include FTIR, TGA and elemental analysis.

4.2.1. FTIR of lignite, humic acids and residues

Fourier-transform infrared spectroscopy is the most reported method used in the literature to analyze humic acids. FTIR was used to determine the functional groups that might exist specifically oxygen containing functional groups. **Figure 4.9** shows the spectra for lignite obtained from Ward's Science as is without treatment, residue (non-soluble part left after the reaction) and humic acids obtained from lignite after 20 min reaction time, 40% amplitude, 3% H₂O₂ and 1:1 lignite to KOH ratio. As shown in the region of 3600 to 2750 cm⁻¹, the humic acids spectra have strong and broad absorption bands compared to the residue and lignite. This band can be attributed to the hydrogen bond-associated with –OH stretching or –NH stretching vibration absorption peaks in phenolic and carboxylic acid structures [22,196]. This band appears in the three spectra of lignite, humic acids, and residue; however, they are stronger in the humic acids' spectra. Manasrah et al. [189] have obtained similar bands from oxy-cracking petroleum coke to humic acids. Similar results have been found on lignite humic acids by Wang et al. [170]. The bands from 2000 to 1000 cm⁻¹ range can be attributed to the oxygen-containing functional groups in the humic acids. The band at 1700 cm⁻¹ represented the sharp C=O stretching vibration band of carboxylic acids, aldehydes, and ketones [97,197]. The band is clearly stronger in the humic acids' spectra than in the lignite and the residue. The small band at around 1570 cm⁻¹ can be attributed to COO⁻ symmetric stretching that appears in the lignite and the residue but not the humic acids' spectra [198]. This could be an indication of the protonation happening in the humic acids [199]. Absorption near 1400 cm⁻¹ is probably due to OH deformation and C-O stretching of phenolic OH

groups, or to C-H deformation of CH₂ and CH₃ groups [96,198–200]. The band observed at 1200 cm⁻¹ can be assigned to the –COO ester group, C-O stretching of phenols and ethers, C-OH deformation [196,201]. Overall, there is a clear difference between the spectra of humic acids and lignite which indicates that there is a larger incorporation of oxygen containing functional groups such as -COOH and -OH and minor amounts of aldehyde, ketones and esters are formed during the ultrasonic processing of lignite. These functional groups are a clear indication of humic acids formation as reported by multiple studies analyzing humic acids from various sources [22,83,97,202–204]. On the other hand, the residue left after the reaction exhibit similar spectra of lignite.

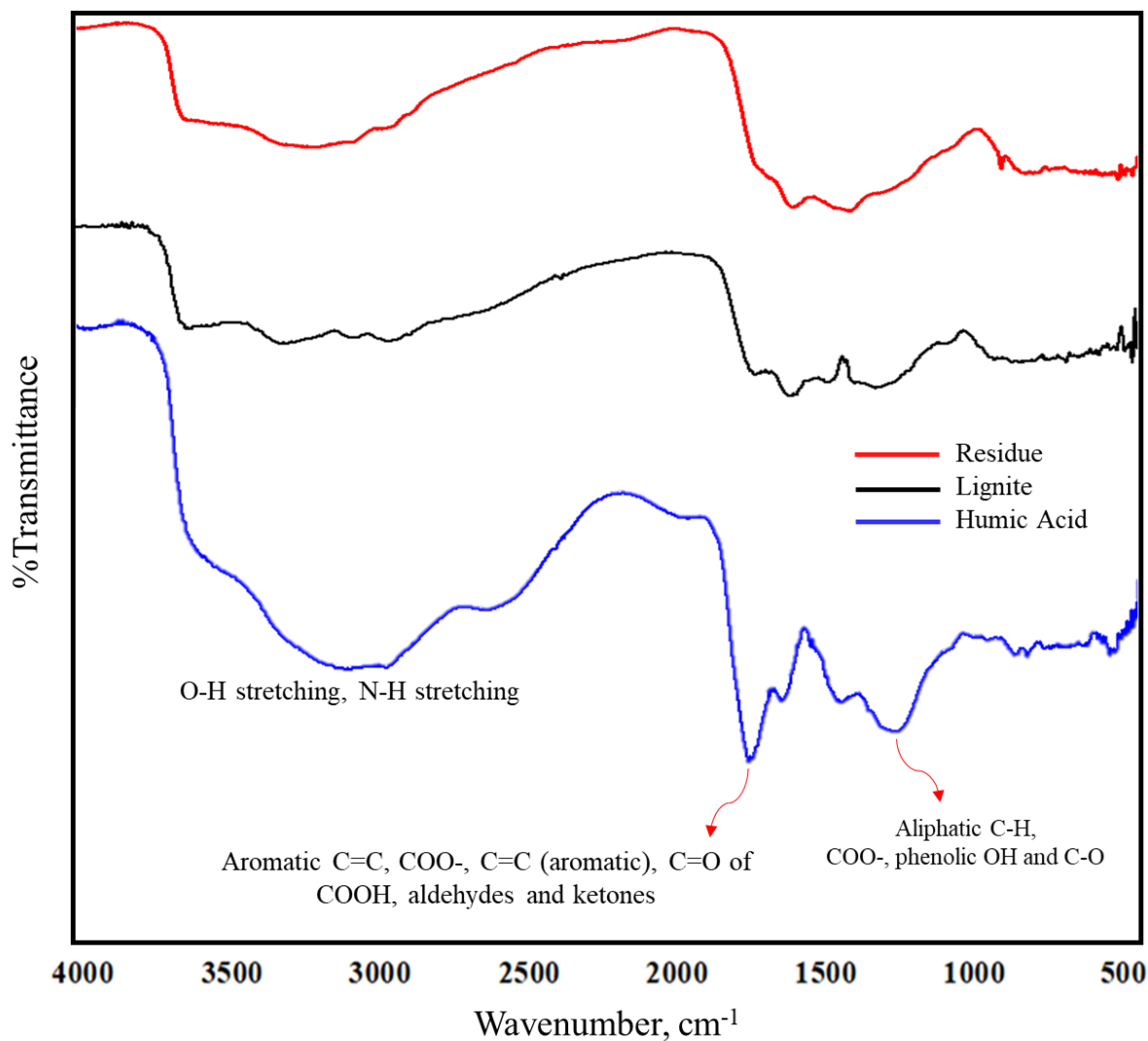


Figure 4.9: FTIR spectra of raw and untreated lignite, humic acids and residue obtained from ultrasonic conversion under the following conditions: 40% amplitude, 20 mins reaction time, 1:1 KOH ration and 3% H₂O₂.

Furthermore, we looked at the difference and intensity in spectra of humic acid extracted using KOH versus the one extracted using NH₄OH. **Figure 4.10** shows the two spectra of humic acids extracted using KOH (humic acids K) and humic acids extracted using NH₄OH (humic acids N). The two spectra share similar bands such as -OH stretching around 3300 cm⁻¹ and carboxylic -COOH at 1700 cm⁻¹. However, the intensity at 1700 cm⁻¹ is higher on humic acid K compared to humic acids N as an indication of more carboxylic groups -COOH in the humic acids extracted

using KOH. This can be an indication of less carboxylation when using NH_4OH as was seen also from the low solubility in the TOC results in this study. The intensity of the band around 2100 cm^{-1} is higher in humic acids N compared to humic acids K which could be an indication of $-\text{N}=\text{C}=\text{O}$, $-\text{N}=\text{C}=\text{N}-$, or $-\text{N}_3$. The strong peak around 1400 cm^{-1} can be assigned to NO_2 stretch [205,206]. Overall, this shows incorporation of nitrogen in the structure of humic acids as was also confirmed using CNH analyzer in this study. However, it is also noticed that the nitration and incorporating of nitrogen in humic acids can result at the expense of carboxylic groups. It is nevertheless important to incorporate nitrogen in the humic acids structure since nitrogen is an essential nutrient for plants [207].

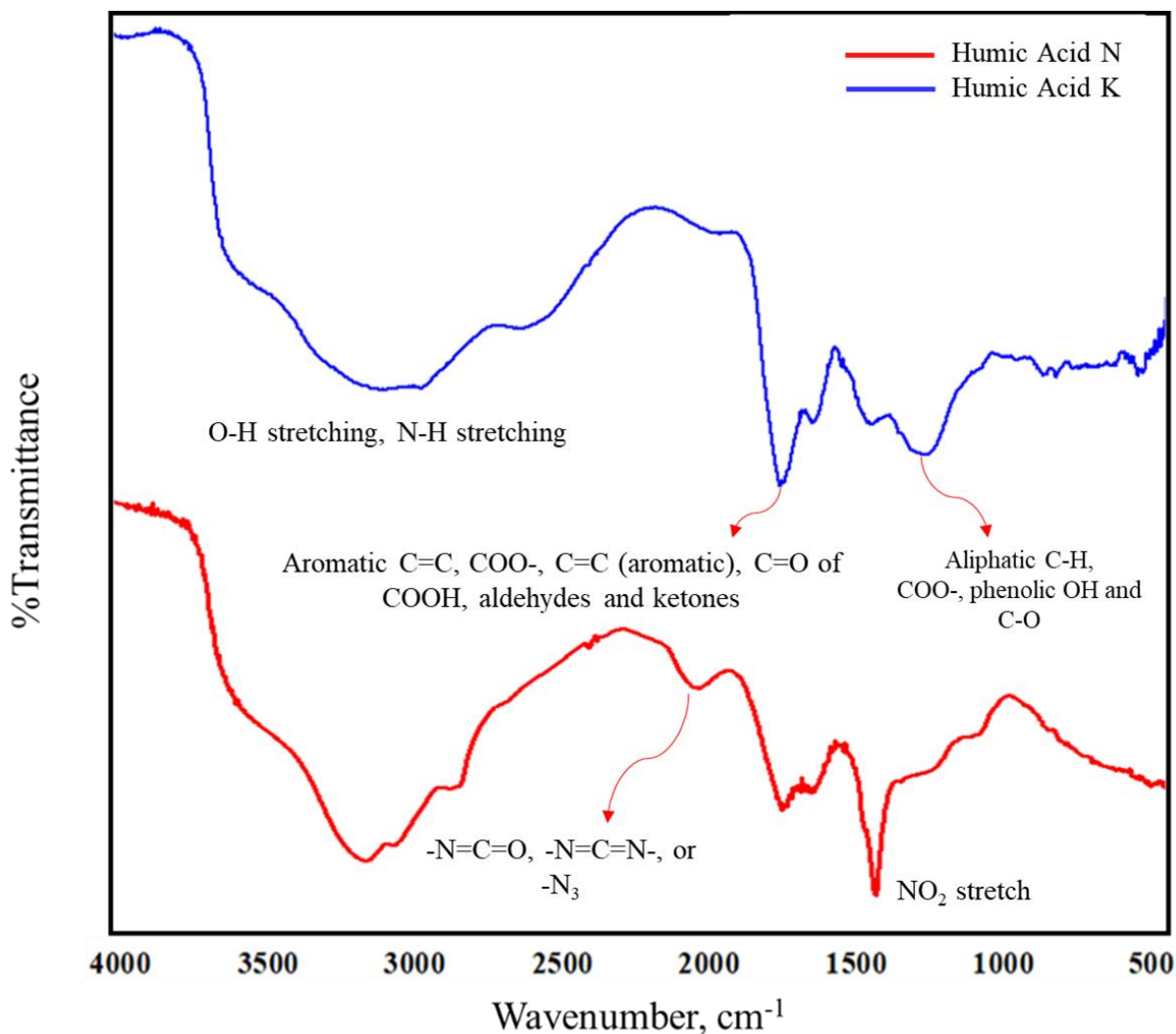


Figure 4.10: Two spectra of humic acids. Humic acids K is the one where KOH is used for extraction under ultrasonic amplitude of 40%, 20 min reaction time, 1:1 KOH to lignite ratio, 3% H₂O₂ and Humic acid N is where NH₄OH is used for extraction under ultrasonic amplitude of 40%, 20 min reaction time and 3% H₂O₂.

4.2.2. Thermogravimetric Analysis (TGA)

TGA was used to examine the physical characteristic of formed humic acids, lignite and residual lignite according to ASTM E1131 Standards. This analysis typically referred to as proximate analysis for the determination of (1) high volatile matter, including moisture, plasticizers and other low boiling components. This step is achieved through heating to 110°C and holding for 10 minutes under N₂. (2) medium volatile matter, which consists of gases and vapors released during

the pyrolysis. Step 2 is achieved through heating from 110°C to 950°C and holding isothermally to drive off all volatile components. (3) fixed carbon, the non-volatile fraction of the material. Here, the gas is shifted to air and temperature is held at 950°C until no change in weight is observed. (4) ash, the inorganic residue remaining after combustion. **Figure 4.11** shows an example of TGA analysis of formed humic acids. Humic acids are referred to as hygroscopic materials that like to adsorb moisture a lot. Therefore, extreme care was taken to reduce the exposure time of humic acids to air. Ash was determined to calculate the ash-free weight of humic acids as required by the standard quantification method (ISO 19822). It should be noted that the ash in humic acid most likely consists mainly of potassium which is a nutrient required for plants. The ISO 19822 requires the removal of ash since some extraction techniques utilize NaOH or other bases that do not contribute to the soil and plant health. **Figure 4.12** and **Figure 4.13** show the thermograms for the residue obtained after the reaction and the original lignite respectively. The high volatiles, medium volatiles, fixed carbon and ash was obtained from these thermograms and reported in **Table 4.1**. The amount of ash is clearly higher in produced humic acids compared to lignite, this attributed to the potassium coming from the KOH used in the reaction. The first stage up to 110°C corresponds to the evaporation of water incorporated in or adsorbed onto the formed humic acid, residue, and lignite. The loss, thereafter, under N₂ can be attributed to the loss of aliphatic moieties and polar functional groups in humic acid. Schnitzer et al. showed that phenolic OH and COOH groups were eliminated at 250°C and 400°C [208]. Campanella et al. found that decarboxylation and unsaturation losses occur at about 280°C for humic substances [209]. Fixed carbon was observed to be lower in produced humic acids than raw lignite. This can be attributed to higher alkyl-aromatic, and poly-aromatic compounds [210].

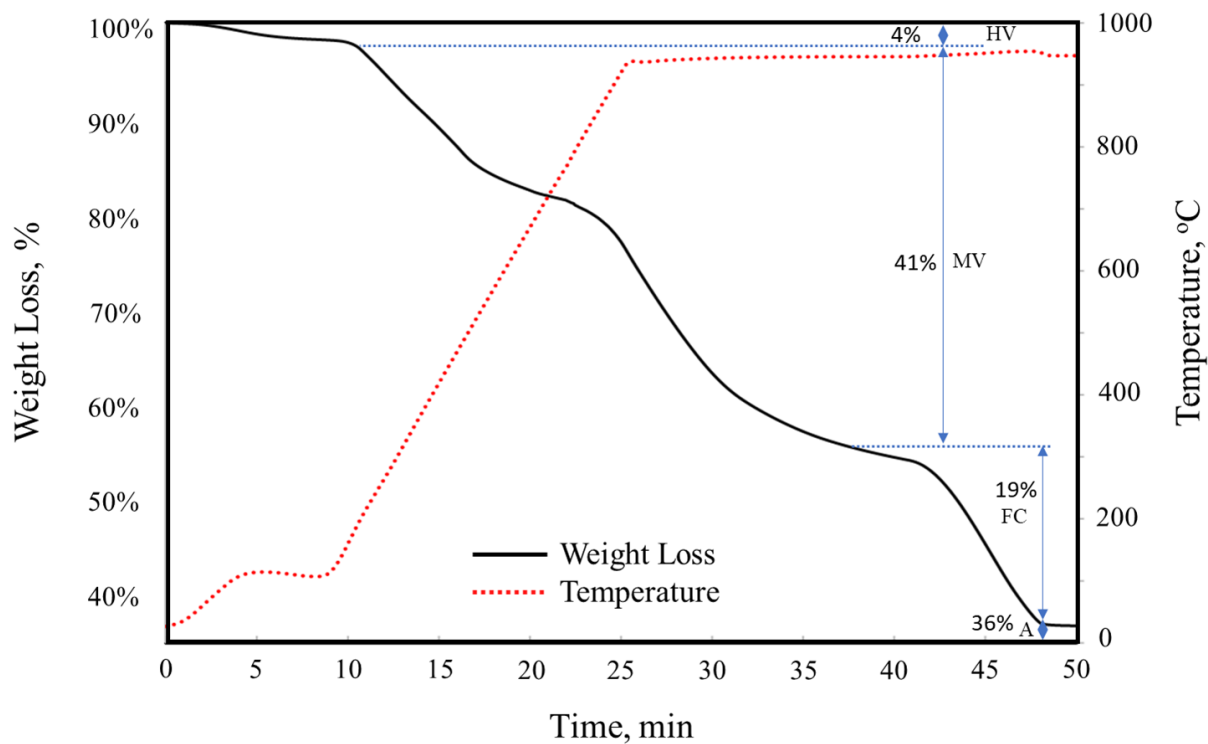


Figure 4.11: Thermogravimetric analysis of a humic acids sample obtained at 3% H₂O₂, reaction time of 20 min, amplitude of 40% and 1:1 KOH to lignite ratio. Heating rate from 10°C/min to 50°C/min and flow rate of 100 mL/min. HV: high volatiles, MV: medium volatiles, FC: fixed carbon, A: ash.

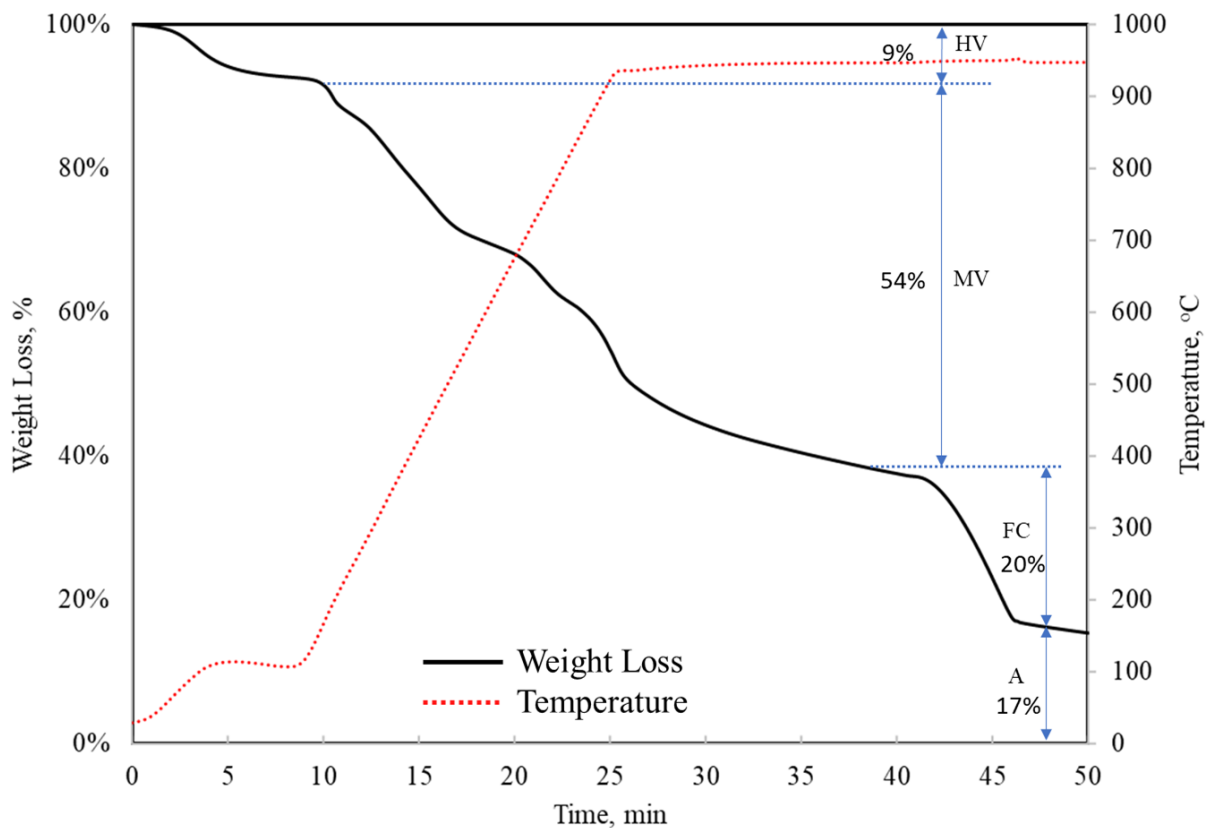


Figure 4.12: Thermogravimetric analysis of the residue obtained at 3% H₂O₂, reaction time of 20 min, amplitude of 40% and 1:1 KOH to lignite ratio. Heating rate from 10°C/min to 50°C/min and flow rate of 100 mL/min. HV: high volatiles, MV: medium volatiles, FC: fixed carbon, A: ash.

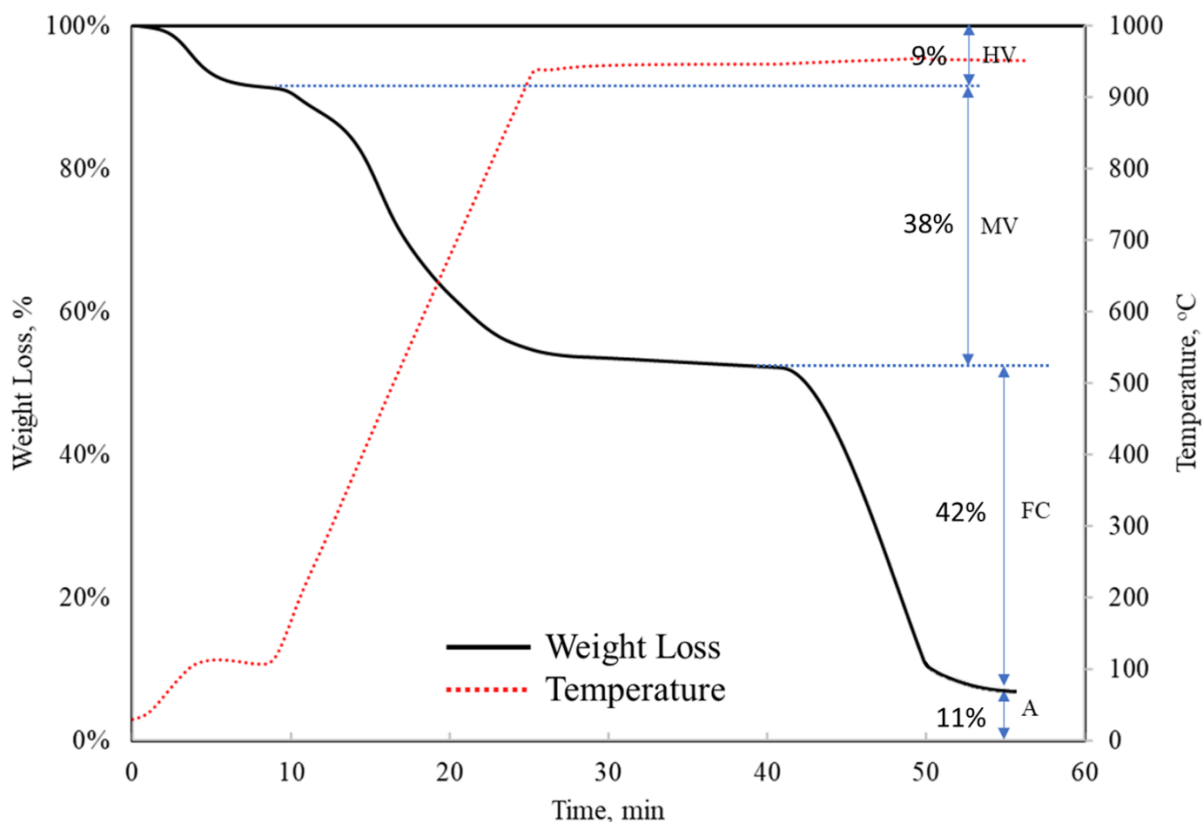


Figure 4.13: Thermogravimetric analysis of original lignite. Heating rate from 10°C/min to 50°C/min and flow rate of 100 mL/min. HV: high volatiles, MV: medium volatiles, FC: fixed carbon, A: ash.

The mass loss happens first in two stages dehydration and pyrolysis in N₂ atmosphere. These losses are related to moisture and volatile matter. Last stage is the decomposition happening in an air atmosphere and carried forward until only inorganics are left.

Table 4.1: Proximate Analysis of two sample of humic acids, lignite, and residue as percentage (Conditions: 20 mins reaction time, (Humic acid 1:3% H₂O₂, Humic acid 2: 1% H₂O₂), 40% amplitude, 1:1 KOH to lignite ratio)

<i>Materials</i>	<i>High Volatile matter</i>	<i>Medium Volatiles Materials</i>	<i>Fixed Carbon</i>	<i>Ash</i>
<i>Lignite</i>	9%	38%	42%	11%
<i>Humic acid 1</i>	4%	41%	19%	36%
<i>Humic Acid 2</i>	9%	35%	22%	34%
<i>Residue</i>	9%	54%	20%	17%

4.2.3. Elemental Analysis

Elemental analysis is used to determine carbon, hydrogen and nitrogen contents. The results were used for the kinetics modeling. Table 4 shows the %carbon, %hydrogen and %nitrogen of two humic acids samples and two residue samples obtained after 20 min reaction time, 1:1 KOH/lignite ratio, 40% amplitude with 3% and 1% H₂O₂ respectively. It is clear that the amount of hydrogen in humic acids is low indicating that these are more aromatic in nature. It has been found that samples exhibit a low H/C ratio also exhibit a high aromatic content and vice versa [211]. Less hydrogen can also be an indication of more oxygen been incorporated into the humic acids structure.

Table 4.2: Elemental analysis for selected humic acids samples and residual samples as well (Conditions: 20 mins reaction time, (Humic acid 1:3% H₂O₂, Humic acid 2: 1% H₂O₂), 40% amplitude, 1:1 KOH to lignite ratio)

<i>Materials</i>	<i>%C</i>	<i>%H</i>	<i>%N</i>
<i>Humic acids 1</i>	31	2.1	0.54
<i>Humic acids 2</i>	29	1.9	0.65
<i>Residue 1</i>	40	3.1	0.53
<i>Residue 2</i>	32	2.2	0.57

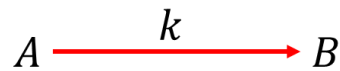
4.3. Modeling of ultrasonic reaction

This section presents the results obtained after modeling the reaction using the power law and Arrhenius equation. The objective of the kinetics model is to understand the concentration profiles under various temperatures and later the results will be used to build a continuous reactor setup.

4.3.1. Reaction kinetic model

During the ultrasonic processing of lignite, H₂O₂ decomposes into •OH radicals. These radicals attack the lignite molecule. The ultrasonic processing results in more radicals formed as has been investigated before [153,156,157,182]. The radicals formed attack the lignite molecule on various sites creating more carboxylic and phenolic functional groups and breaking some of the bridges

between aromatic clusters and aliphatic cross links. This results in forming acids (desired products) namely humic acids. The characterization of these materials in this study confirmed the formation of humic acids. The humic acids were solubilized in water with the help of KOH. This solubilization minimize the further oxidation of humic acids into CO₂. With humic acids, fulvic acids and other smaller acids may be also part of the solubilized materials. All solubilized materials were measured using TOC, and the TOC measurements were used to represent the organic solubilized materials. It is important to note that lignite molecule is too complex and there might be multiple steps of reactions involved, however, the following lumped kinetics model can serve as a first step into understanding the complex nature of the reactions involved. The concentration profiles were plotted against time for three average temperatures of 310 K, 315 K, and 322 K. The following model was used to explain the reaction happening during the process at the three specified temperatures as the concentrations change with time. Lignite (A) is converted to soluble materials (B). At operating temperatures lower than 333 K, it is assumed that none to minimal CO₂ is formed during the reaction. The kinetics model will allow for the observation of the effect of temperature and time on the degree of solubilization and conversion. The following lumped generalized kinetic model for reaction was adopted:



The kinetics rate equation are as follows:

$$\frac{dC_A}{dt} = -r_A = kC_A^n \quad (8)$$

$$\frac{dC_B}{dt} = r_B = kC_A^n \quad (9)$$

where C_A is the concentration of lignite at a certain time, t , C_B is the concentration of dissolved carbon at certain time, t , measuring using TOC. k is rate constant and n is the reaction order. The concentration of lignite at a certain time, t , was calculated using the following equations:

$$C_A = (1 - X)C_{A0} \quad (10)$$

$$X = \frac{C_{A0} - C_R}{C_{A0}} \quad (11)$$

where C_{A0} is the carbon concentration of raw lignite before the reaction, C_R is the residual carbon concentration (unreacted lignite) that remains after the reaction. To solve the differential equations, initial conditions must be set as the following: at $t = 0$, $C_A = C_{A0}$ and $C_B = 0$. C_{A0} is taken as the amount of carbon originally in lignite. The equations were solved to minimize the sum of square of errors and from each temperature, a k value was obtained. Using the k values, the activation energy and pre-exponential factor can be determined graphically using Arrhenius equation as follows, the calculation are included in the appendix:

$$k_i = A_i e^{\frac{E_{ai}}{RT_i}} \quad (12)$$

where A is the pre-exponential or frequency factor, E_a is the activation energy, R is the ideal gas constant, and T is the average temperature in Kelvin.

The kinetics experimental data were collected at three different temperatures of 310, 315, and 322 K and reaction times varying from 0 to 45 mins. The concentration profiles of C_A and C_B were plotted against time at three different temperatures. The model has been fitted and k values were calculated from each temperature profile (**Figure 4.14**, **Figure 4.15** and **Figure 4.16**). The reaction temperature is a key parameter in the ultrasonic processing. At higher temperature (higher

ultrasonic amplitude), the solubilization of organic acids in water is increased and achieved the maximum concentration faster than at lower temperatures.

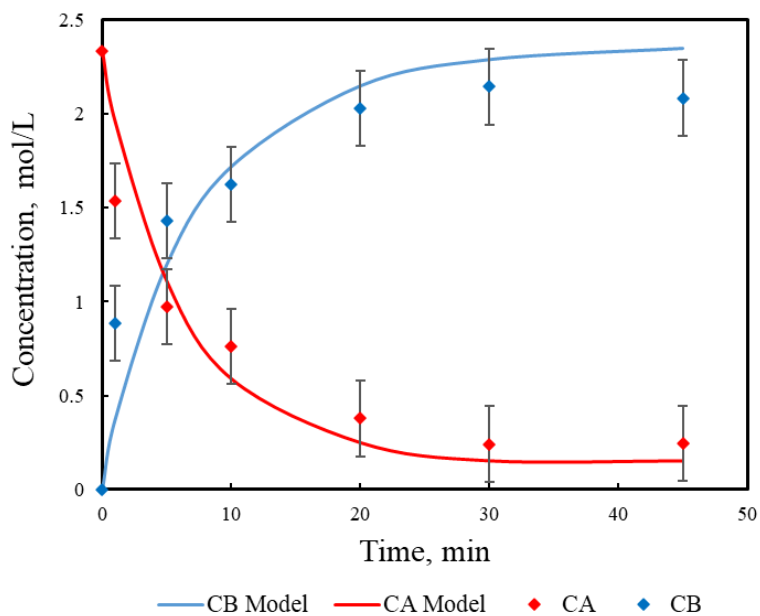


Figure 4.14: Concentration profiles for A and B with the model fit at T=322 K

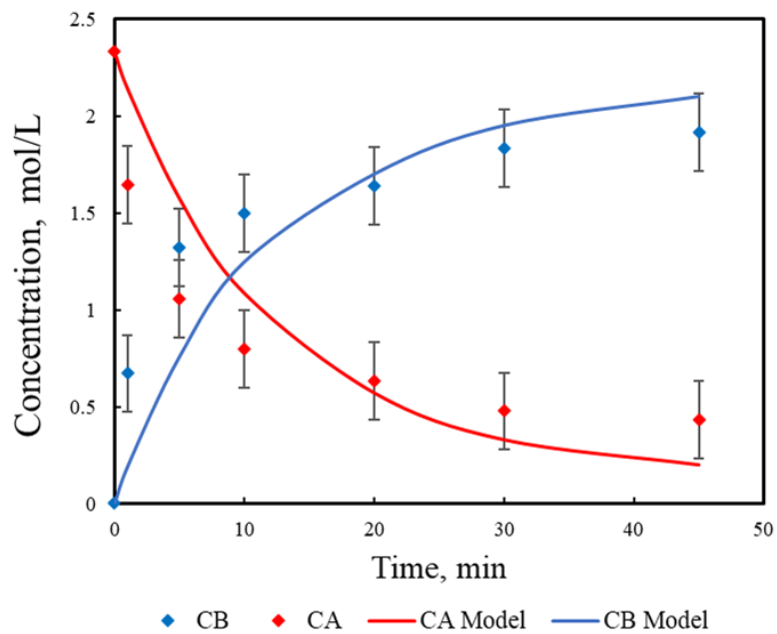


Figure 4.15: Concentration profiles for A and B with the model fit at T=315 K

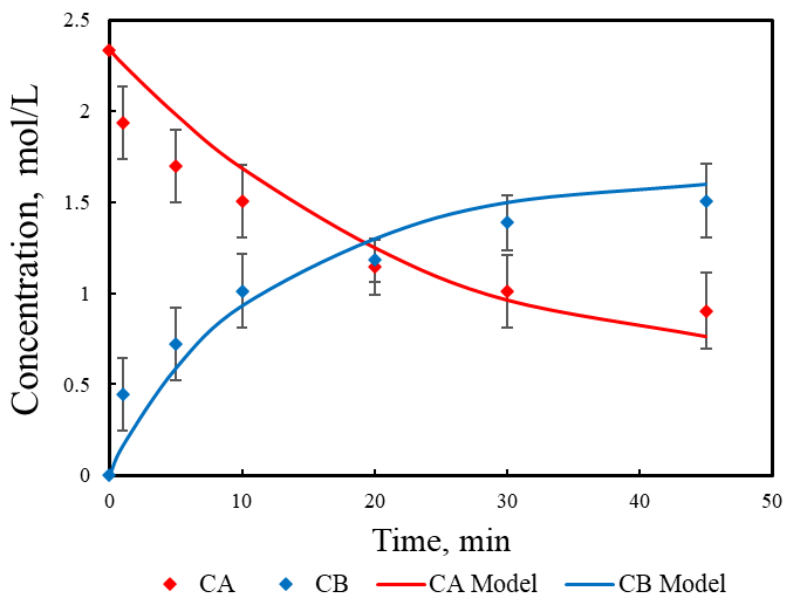


Figure 4.16: Concentration profiles for A and B with the model fit at T=310 K

The reaction order was determined based on the experimental values to be 1. **Figure 4.17** represents the Arrhenius plot of lignite ultrasonic reaction at three different reaction temperatures. Plotting $\ln(k)$ against $1/T$ gave a good fit between Arrhenius equation and the experimental data, indicated by R^2 value of 0.99. From the slope and intercept of the best-fit-line, the values of activation energy and frequency factors of were calculated and summarized in **Table 4.3**. Multiple authors reported the conversion of lignite and coals to organic acids under mild temperatures but there is lack of data on the influence of ultrasonic processing on the reaction. Kelemen et al. reported the mild oxidation of coal having an activation energy of 48 kJ/mol and this is not far from what is reported in this study (54 kJ/mol) [212]. Lee et al. reported activation energies ranging from 9 to 66 kJ/mol [213]. The differences can be attributed to the type of coal utilized in the study and the use of ultrasonic processing. Ultrasonic processing can result in higher mass transfer which in turn can increase the rate of reaction [214–217].

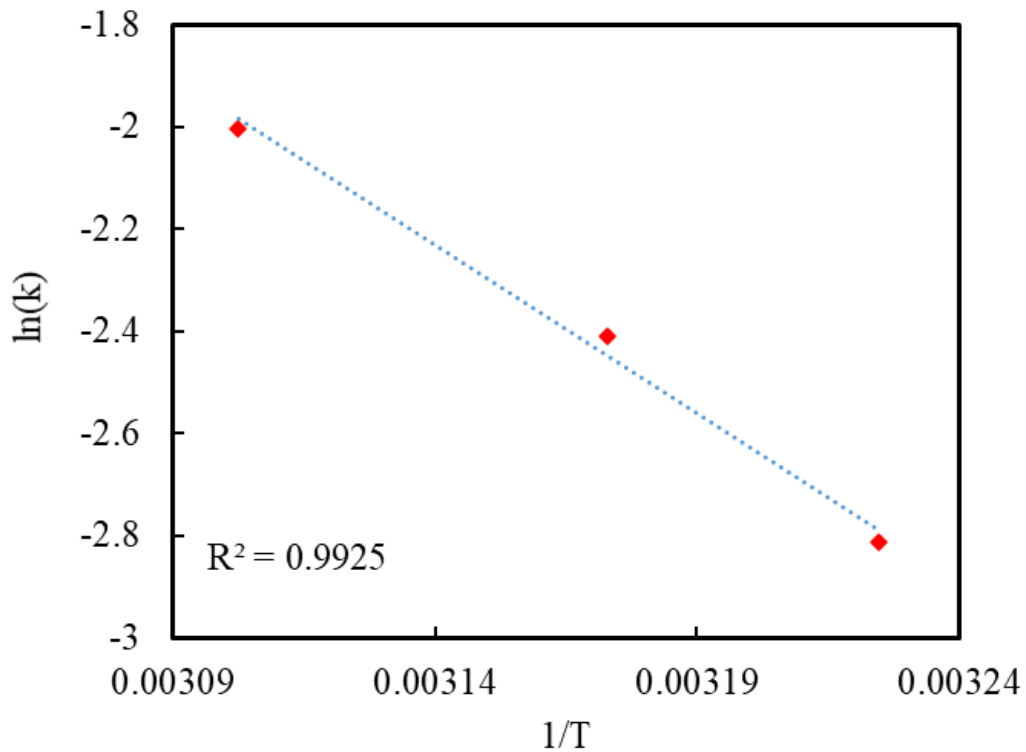


Figure 4.17: Arrhenius plots for model developed plotting natural log of reaction constants against the reciprocal of temperature in kelvin

Table 4.3: Kinetics parameters obtained from the modeling.

k (s^{-1})	Temperature (K)	E_a (kJ/mol)	A (s^{-1})
6.173×10^{-2}	310	54.7	6.5×10^7
9.237×10^{-2}	315		
13.53×10^{-2}	322		

Chapter 5 Conclusion and Recommendations

5.1. Conclusion

In this study, ultrasonic processing was investigated as a novel technology to improve the yield and reduce the time of converting low-rank coal (lignite) to humic substance (both humic acids and fulvic acids). The work investigated the process experimentally and theoretically through kinetics modeling. Experimentally, several parameters were studied including ultrasonic amplitude, reaction time, alkaline concentration and type, initial concentration of lignite and the dosage of H_2O_2 . The ultrasonic processing was carried out on samples of lignite weighing 1 to 3 g in 20 mL water. Reaction time was varied from 1 to 45 mins. Dosage of H_2O_2 was tested at 0% to 3%. Alkaline amount from 0.1 to 1 were tested with two bases, potassium hydroxide and ammonium hydroxide. After each experiment, residual materials were collected, and total organic carbon was measured for liquid portion. Humic acids were then extracted from liquid portion and analyzed with FTIR, elemental analysis and TGA. Residual materials were also analyzed using FTIR, elemental analysis and TGA. It was observed that as the reaction time increases, the reaction conversion and yield of HA increase as well. The same trend was observed with H_2O_2 concentration and the ultrasonic amplitude. The optimum parameters for the highest yield of humic acids from lignite were: 40% ultrasonic amplitude, 1:1 KOH to lignite ratio, 30 mins reaction time, and 3% H_2O_2 . Strong bases such as KOH are more favourable, however, mixing two bases such as KOH and NH_4OH has been deemed beneficial because it increased the amount of nitrogen in the final products as nitrogen is an important nutrient for plants in case the humic acids were to be used as a fertilizer. The technology has achieved a solubilization of carbon of above 90% and yield of ash-free humic acids of 72%. Compared to current technologies, the ultrasonic processing achieved higher conversion and yield for lower temperatures and reaction times. The

internationally recognized method (ISO 19822) was used for the quantification of humic acids to calculate the yield. The characterization of the produced humic acids showed successful incorporation of oxygen functional groups specifically COOH and OH into the final products. Reaction kinetics modeling was done to investigate how concentration profiles change with temperature and time and to calculate the kinetics parameters, reaction constants, activation energy and pre-exponential factor. Three temperatures were used 310, 315, and 322 K. The reaction constant values were, 6.173×10^{-2} , 9.237×10^{-2} , 13.53×10^{-2} (s^{-1}). Activation energy and pre-exponential factor were calculated to be: 54.7 (kJ/mol.) and 6.5×10^7 (s^{-1}) respectively. It was determined experimentally that the reaction is first order reaction. The kinetics modeling helped with constructing a reaction mechanism scheme where $\bullet\text{OH}$ radicals produced through ultrasonic attack the lignite molecule at various sites breaking weak bonds and creating -OH and -COOH functional groups. The kinetics model will be used in developing a continuous process in later stages. The main objective of this thesis was successfully achieved using the ultrasonic processing in reducing time and improving yield of humic acids from low-rank coals through increasing radical formation and improving mass transfer.

5.1. Recommendations

The groundwork for ultrasonic processing of lignite to humic acids has been established as a new and novel method. However, there is still more to be done to build a robust technology with the potential for scale up and commercialization. The following is recommended for next stages:

- Build a continuous reactor setup to process more lignite to humic acids and study the same parameters utilized on this study on the continuous setup.
- Improve the kinetics model to investigate more complex models with the potential inclusion of CO₂ release during the process.

- Complete the ISO 19822 assessments by measuring the fulvic acid fractions which has major application in multiple fields.
- Incorporating more nutrients such as Mg in the final product of humic acids through the utilization of other types of alkaline such as MgOH.
- Complete a comprehensive study on the impact of humic acids produced on the growth of plants and soil health.
- Build a comprehensive study to screen various materials for extraction and conversion such as different oxidizing agents and bases.
- Investigate the potential use of ultrasonic processing to obtain other materials from various feedstocks.

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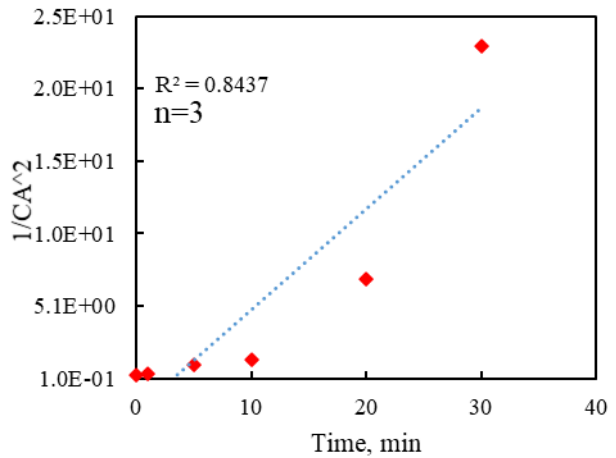
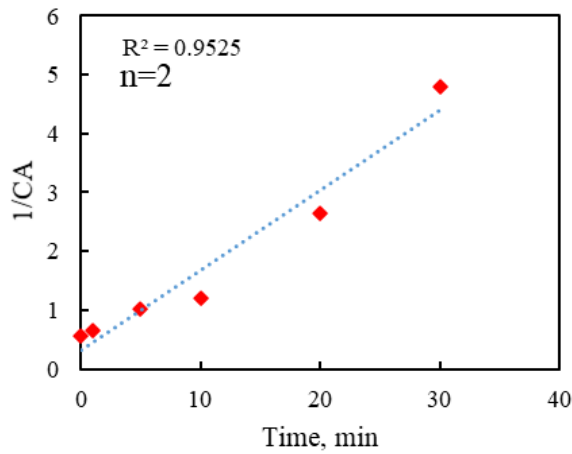
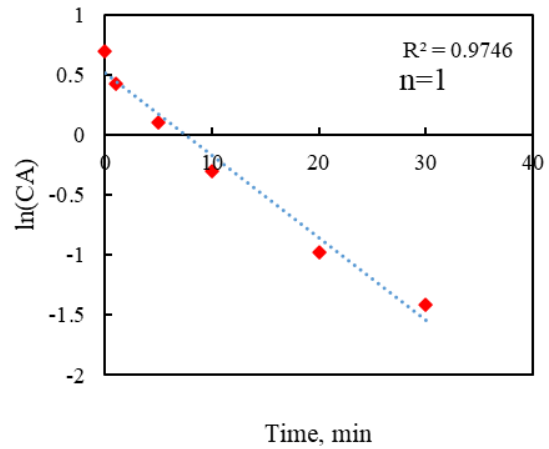
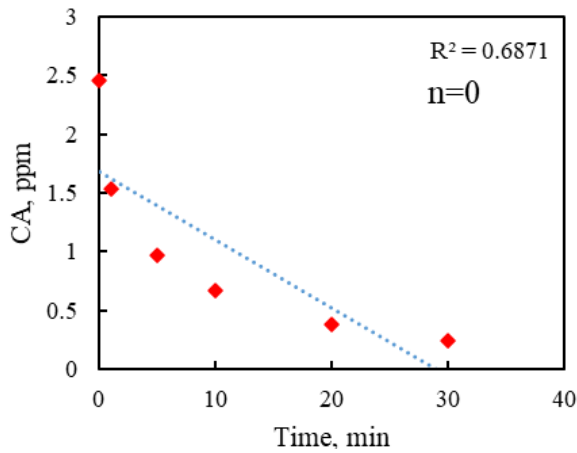
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Appendix

Kinetics calculation

The order of the reaction was found experimentally using the following graphical method, where C_A , $\ln(C_A)$, $1/C_A$, and $1/C_A^2$ were plotted against time to see which one results in a linear fitting.



The fitting for first order reaction resulted in more linear trend, indicating the reaction can be assumed to be first order. The following equation can now be solved simultaneously using MATLAB to minimize the error:

$$\frac{dC_A}{dt} = -r_A = kC_A^1 \quad (13)$$

$$\frac{dC_B}{dt} = r_B = kC_A^1 \quad (14)$$

Equation 8 becomes:

$$dC_A = -r_A = kC_A^1 * dt \quad (10)$$

Integration happens from $t=0$ to $t=45$ and $C_{A0}=2.3$. The same thing would happen for equation 9 for C_B .

Error bars

The error bars reported in the graphs with experimental values were obtained using the standard deviation. After performing multiple measurements from the same experiments, the average is calculated. The standard deviation is then calculated using the following formula:

$$\sigma = \sqrt{\frac{\sum (X - \bar{X})^2}{n - 1}}$$

Where:

σ = Lower case sigma is the symbol for standard deviation

X = Each individual value in the data set

\bar{x} = The arithmetic mean (known as “x-bar”)

n = The number of data points in the set

The reported values are then shown as follows:

$$\text{Value (i. e. yield, conversion ...)} = \text{Average value} \pm \sigma$$