

2018-04-13

Chemical Characterization of Humic and Fulvic Acid Analogs Obtained from Wet Air Oxidation (WAO) at Different Severities

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Ahmed, F. (2018). Chemical Characterization of Humic and Fulvic Acid Analogs Obtained from Wet Air Oxidation (WAO) at Different Severities (Master's thesis, University of Calgary, Calgary, Canada). Retrieved from <https://prism.ucalgary.ca>. doi:10.11575/PRISM/31802

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Chemical Characterization of Humic and Fulvic Acid Analogs Obtained from Wet Air Oxidation
(WAO) at Different severities

by

Farouq Ahmed

A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES
IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE
DEGREE OF MASTER OF ENGINEERING

GRADUATE PROGRAM IN CHEMICAL AND PETROLEUM ENGINEERING

CALGARY, ALBERTA

April, 2018

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ABSTRACT

Due to depletion of conventional oil resources and the increasing energy demand, the role of heavy oils is significantly increasing. The heaviest portions of heavy oils are asphaltenes, which create tremendous problems in transportation and upgrading processes. Removal of asphaltenes from heavy oil improves the quality of oil and makes it easier to process. The oil industry is challenged to explore new alternatives that allow converting asphaltenes into valuable products by economical feasible routes. Wet Air Oxidation (WAO) is one proposed alternative, being herein examined together with fundamental aspects on hydrocarbon oxidation for its proper framing. The solubilization of asphaltenes in water has recently received attention due to the ease of mobilization and high level of dispersion. The WAO of asphaltenes rapidly produces both water-soluble and water insoluble oxygen rich species. The intermediate product of asphaltenes oxy-cracking reaction is Water Soluble Asphaltenes (WSA), and the final product is CO₂. At low severities WSA had characteristics similar to humic analogs whereas at high severities, products aromaticity increased and lower molecular weight components (fulvic analogs) were formed. Processed asphaltenes were found to have oxygen functionalities like carboxylic acids and their salts, ketones, sulphoxides and sulphones, responsible for their aqueous solubilization. The effect of pH (base) on oxidation of asphaltene was determined using different experimental conditions. It was found that the concentration of chemical base used as acidic corrosion prevention and as catalysts are the most influential parameter for the solubilization of asphaltene, to achieve high conversion at low temperature. The humic/fulvic acids field of knowledge was identified as key for proper understanding of HC oxidation and other feasible industrial applications, like in agriculture.

ACKNOWLEDGEMENTS

Though only my name appears on the cover of this dissertation, a great many people have contributed to its production. I owe my gratitude to all those people who have made this dissertation possible and because of whom my graduate experience has been one that I will cherish forever. It has been a period of intense learning for me, not only in the scientific arena, but also on a personal level. Writing this thesis has had a big impact on me. I would like to reflect on the people who have supported and helped me so much throughout this period.

My sincere appreciations to my supervisor Dr. Pedro Pereira-Almao. This amazing journey is the result of his vision and his trust in me, and therefore I will always be indebted. Many thanks to NSERC/CNOOC-Nexen/AIEES, and the Chemical and Petroleum Engineering Department at the University of Calgary for the financial support.

My appreciation goes to all members of the Catalysis for Bitumen Upgrading group. In particular, thanks to Dr. Lante Carbognani-Ortega for his guidance and advice throughout this project. I would like to acknowledge Dr. Ursula Ehrmann and Dr. Azfar Hassan, Dr. Gerardo Vitale, Dr. Carlos Scott, Mr. Nedal Marei and Jodi David for helping me in every stage of this research. Many friends have helped me stay sane through these difficult years. Their support and care helped me overcome setbacks and stay focused on my graduate study. I greatly value their friendship and I deeply appreciate their belief in me.

Most importantly, none of this would have been possible without the love and patience of my family. My immediate family, to whom this dissertation is dedicated to, has been a constant source of love, concern, support and strength all these years. I would like to express my heart-felt gratitude to my family.

Thank you very much, everyone!!!

DEDICATION

I would like to dedicate my thesis to my respected parents, for all their years of love and encouragement. I am extremely grateful and thankful for all they provided me in the past and continue to provide me today. Although their type of involvement has gone through many phases, one thing has never changed; their commitments to assisting me become the best person I can.

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List of Symbols, Abbreviations and Nomenclature

Symbol	Definition
CBU	Catalysis for Bitumen Upgrading group
C _{gas}	Mass of carbon in the gas stream
C _{initial}	Mass of carbon initially present in the feedstock
C _{liquid}	Mass of carbon in the liquid stream
C (t)	Total organic carbon concentration at time t
C/Co	Normalized total organic carbon concentration
D	Reactor diameter
D _p	Particle diameter
FA	Fulvic Acid
FTIR	Fourier Transform Infrared spectrophotometry
GC	Gas Chromatography
HA	Humic Acid
H/C	Hydrogen-to-carbon atomic ratio
HCK	Hydrocracking
IC	Inorganic Carbon
ICP	Inductively Coupled Plasma
L	Reactor length
nC ₅	n-pentane
nC ₇	n-heptane
N/C	Nitrogen-to-carbon atomic ratio

O/C	Oxygen-to-carbon atomic ratio
P	Pressure
SOP	Standard Operating Procedure
std	Standard
t	Time
T	Temperature
TC	Total Carbon
TGA	Thermal Gravimetric Analysis
TOC	Total Organic Carbon
Wt	Weight
WAO	Wet Air Oxidation
WSA	Water Soluble Asphaltenes
WISA	Water Insoluble Asphaltenes
X	Conversion
Y	Yield

SUMMARY OF THE STUDY

Maximizing the yields of valuable liquid products from upgrading processes and residue valorization is very important. Therefore, the demand for high value petroleum products such as middle distillate, gasoline and lube oil is increasing while the demand for low value products such as fuel oil or residue-based products is decreasing. Additionally, in recent years environmental concerns captured great attention. So, it is a great importance to the oil industry to converting heavy oil bottom of the barrel components like asphaltenes to lighter and valuable clean products.

Wet Air Oxidation (WAO) is one proposed alternative, being herein addressed together with fundamental aspects on HC oxidation for its proper framing. In this study, asphaltenes are turned into water-soluble asphaltenes (WSA) via oxidation reactions carried out in a batch reactor under elevated O₂ pressure in the presence of alkaline solution (pH 4~13). Main factors influencing the degree of oxidation of asphaltenes and reaction product yields are: intensity of stirring for the reaction mixture, reaction temperature, alkali concentration, oxygen partial pressure and lengths of oxidation.

It is observed by GC-MS and FTIR spectroscopy that during oxidation a complex mixture of compounds containing oxygen is formed, mostly including acids and their salts, ketones and sulphoxides. WSA products were separated into acid insoluble/soluble portions found to resemble natural Humic Acids (HA) and Fulvic Acids (FA), with potential use in agriculture applications. Abundance of FA was found to increase with increasing WAO reaction severity. It was established that pH (concentration of base) is the most influential parameter for the WAO

reaction to achieve high conversion of asphaltene at low set up temperature. Focusing on maximizing the amount of HA analogs at reasonable operating conditions, the results showed that lower reaction temperature and low residence time would work better for this purpose. A significant proportion (79%) of asphaltenes was solubilized in water during the process of WAO reaction at 150°C-2h-1000psi at high pH. The pH (using excess of KOH) has very significant importance in alkyl chain survival under WAO processing at high temperature. From the metal analysis it was observed that at basic high pH, metal concentration in WAO products reduced significantly compared to the results obtained using acidic low pH, this high base concentration contributes to the precipitation of native metals in the oil concept that could be used for residuals selective demetallization, additional to the initial purpose of reduced metal corrosion by the humid acids produced.

CHAPTER 1: INTRODUCTION

1.1 Background

Asphaltenes are high molecular weight hydrocarbons having a chemical structure that contains organized sheets of aromatic compounds, being the most polar components of heavy oils and bitumen.^{1, 2} Generally asphaltenes are the most polar crude oil element, which is insoluble in light paraffins but soluble in light aromatics.³ When phase separation occurs, these molecules initiate several problems in the whole petroleum price fixing process. Well bore, equipment and pipeline plugging, catalyst fouling and a tendency to coke formation occur from the presence of these solid materials.³ However, asphaltenes might epitomize a prospect if suitable processes are applied to obtain valuable products.

Alternative processes for better utilization of these materials are necessary because massive quantities of asphaltenes are produced within the province of Alberta, Canada, as a consequence of oil sands production and upgrading activities.⁴ Carbognani et al, reported via SARA analysis that heptane-precipitated asphaltenes constitute up to 12.5% of Canadian Athabasca bitumen and around 18-25% of Athabasca bitumen vacuum residue.⁵ If bitumen proved reserves in Alberta are approximately 1841 billion barrels, vast quantities of available asphaltenes are anticipated within the province.⁶ These statistics encourage investigating economically viable paths that yield cost-effective products utilizing bitumen's most polar fractions.

Asphaltenes cannot be feasible for use as fuel oil, unless solvents are added to reduce their very high viscosity so that they can be transported through pipelines. Over the past decades different methods have been studied for extracting valuable products by treating highly viscous

asphaltenes. Hydro-treatment, catalytic steam gasification, cracking and adsorption of these heavy molecules and similar carbonaceous materials, among other treatments, are some of the prospects that have been investigated.⁷⁻¹² Due to their high molecular weight asphaltenes are found within the least volatile fraction from distillation of crude oil. Conventionally, the large molecular weight hydrocarbons produced during refining processes are either rejected or broken down into lower molecular weight hydrocarbons using a process generally known as cracking. This cracking process can be used to derive value from high molecular weight hydrocarbons, but it is usually expensive due to high-energy demand and the cost of capital equipment and catalysts. In addition, conventional cracking processes typically are ineffective at breaking down large asphaltene molecules and often result in the precipitation of such molecules or in the production of petroleum coke. CNOOC-Nexen's patented technology Or Crude™-Long Lake upgrader project- is a recent industrial application where asphaltenes are removed prior to thermal cracking, and then gasified to produce synthetic gas (Alberta Energy Resources Conservation Board, 2013).⁶

Treatment of solid-state asphaltenes has several complications at different processing stages. One way to overcome these difficulties is to design an effective methodology to solubilize precipitated asphaltenes in water. Among the possibilities oxycracking or wet air oxidation of asphaltenes (WAO) is of interest because of its ability to yield further information on the chemical structure of complicated asphaltene fractions; it has the potential to convert these refractory materials to more valuable products and finally, potential cost reduction and simplicity. A new alternative oriented to creating more economic value from asphaltenes towards light products is through the combination of two reactions carried out in aqueous medium:

oxidation and cracking (oxy-cracking).

WAO was initially conceived as a destructive technology based on the oxidation of wastes at high temperature and high pressure in liquid phase. The oxidation process depends on the solubility of oxygen at high temperature and high pressure.^{13, 14} Via oxy-cracking, solid asphaltenes are converted to products like carboxylic and naphthenic acids and their corresponding salts among other products, through a controlled oxidation reaction in basic media; the reaction occurs at moderate temperatures (150-320 °C), pressures (300-1000 psi), with pH ranging from 4-12. The products from oxy-cracking can be used as raw material for organic synthesis and petrochemical processes. By maximizing solubilization, the selectivity to other products (mainly CO₂) is reduced considerably and as a result; the process could be considered environmentally friendly if the huminic products were not combusted. Processed products obtained in aqueous phase decrease challenges regarding asphaltenes clogging and transportation.

This process involves total oxidation of all hydrocarbons into very low molecular weight products, such as carbon dioxide. This is a safe, efficient and economical technique for destroying organic materials without performing expensive evaporation or desiccation.¹⁵ The concept proposed in this work is that by controllably oxidizing asphaltene particles in water, the inter-core links between asphaltene molecules can be broken and simultaneously partial oxidation (oxycracking) can release small molecular weight oxidized molecules while decreasing the size of aromatic associations. This new procedure, combined with further processing of water-soluble asphaltenes (WSAs) might provide feasible economic benefits for dealing with

waste hydrocarbons.

To provide better utilization of residual fractions and yield valuable light products, a two stage process of oxidation and separation of water-soluble asphaltenes is studied in this work. Feasible explanations for the water solubilization of large molecular weight organics like coals and petroleum asphaltenes are: 1. Molecular breaking into low MW mixtures, 2. Molecules covered with water-soluble oxygen functions, 3. Blending of the former two, and 4. Synthetic production of water-soluble HA and FA analogs like those naturally found in soils and water bodies. One possible route to increase revenues from such mixtures is to produce valuable HCs from the dissolved materials and, hydro-processing or hot compressed water processing have been presented as feasible alternatives for such purpose. From the preceding discussed processes, the research on asphaltenes oxy-cracking can lead to potential new technologies for producing valuable petrochemicals like fulvic and humic analogs which can have industrial applications as will be presented in the ensuing pages.

Most of the available literature using WAO process focused on wastewater treatment.¹⁶ A recent example of this diverging from our work direction is the work of Goulin et al.,¹⁷ who studied the catalytic wet air oxidation on wastewater management. It was shown that base metal oxide catalysts are more desirable than noble metals in terms of cost and resistance to poisoning by halogen-containing substance, though their activities are still lower than noble metals. Nevertheless, F. Charest et al.¹⁸ have published work on wet oxidation of active carbon. Probably the most interesting document was found about the use of WAO to obtain some metals concentrated in asphaltenes. In addition Senesi and Miano proposed that Humic acids (HAs)

occur not only in soils, natural waters, rivers, lakes, sea sediment plants, peat, and other chemically and biologically transformed materials but also in lignite and oxidized bituminous coal.¹⁹ Humic substances are a mixture of weak-acid polyelectrolytes having varying molecular weight moieties and functional groups.²⁰⁻²¹ The range of molecular weight of humic substances is from several hundred to several hundred thousand Daltons (Da). HAs are a principal component of humic substances, which are the major organic constituents of soil (humus), peat, coal, and ocean water. Fulvic acids (FAs) are Humic acids (HAs) of lower molecular weight and relatively higher oxygen content than other HAs, commonly used as a soil supplement in agriculture. For definition, the insoluble fraction in acidified solution (i.e. the fraction of higher molecular weight) is HAs and the soluble fraction in acidified solution (i.e. the fraction of lower molecular weight) is FAs.²⁰ It is known that there are differences in the structural features, acidities and metal ion bindings between HAs and FAs.²¹ The HAs have a more aliphatic structure and a higher surface potential than the FAs, while the acidic group contents and metal binding capacities of FAs are higher than those of HAs. Because of Fulvic Acids molecular structure, they provide numerous benefits to crop production. They help break up clay and compacted soils, assist in transferring micronutrients from the soil to plants, enhance water retention, increase seed germination rates and penetration, and stimulate the development of microflora populations in soils.¹⁹

To date, as of our knowledge, there is very limited published work on WAO of asphaltenes as source from where we can isolate and characterize HAs and FAs analogs. In the last five years a new alternative oriented to creating more economic value from asphaltenes towards light products has been investigated in our research group (Dr. Pereira's group). The

reaction was carried out through the combination of two reactions; oxidation and cracking (oxy-cracking) processes carried out in aqueous alkaline media. The present work will focus on detailed composition of selected products.²² Here via oxycracking, solid asphaltenes are converted to products like carboxylic and naphthenic acids and their corresponding salts among others products, through a controlled oxidation reaction on basic media; the reaction occurs at moderate temperatures (150-220 °C), pressures (1000 psi), with the pH range from 4-13. The out coming products from oxycracking can be used as raw material for organic synthesis and petrochemical processes. By maximizing solubilization, the selectivity to other products such as CO₂ is reduced considerably and as a result, the process could be considered environmentally friendly. Processed products obtained in aqueous phase decrease challenges regarding asphaltenes clogging and transportation.

Very recently Dr. Pereira's group has revealed a good number of findings on wet air oxidation. Ashtari et al.²³, studied reaction kinetics and possible reaction mechanism of asphaltenes oxy-cracking in water under alkali conditions. The influence of adding alkali (NaOH) in oxy-cracking reaction was examined and kinetic modeling of C₅ asphaltenes was discussed. It was shown that during the reaction-oxidized functionalities like -COOH, their salts, CH₃-O-CH₃ and esters, sulfur-oxidized, phenolics, were formed as the most significant fractions soluble in water. Ashtari et al.²⁴ also investigates the production of humic fractions using the above oxycracking process. The influence of operating parameters such as temperature, residence time, different bases, pressure, asphaltenes different masses and mixing rate on the selectivity and conversion of the reaction, was investigated. Moreover separation of humic and fulvic analogs from water solubilized asphaltene was described and distribution of humic

fractions under different reaction conditions were investigated. Abdallah et al.²⁵ examine WAO of asphaltenes using above oxy-cracking technique, where temperature, oxygen pressure, reaction time, particle size and mixing rate to optimize the solubility and selectivity of oxy-cracked products were considered. The results showed that the temperature and the residence time are the two major important parameters that affect the reaction conversion and selectivity. Reaction kinetics indicated that WAO of asphaltenes undergoes a parallel-consecutive reaction in which an oxidative decomposition took place in the first step producing different oxidized intermediates. Moreover, the elemental analysis showed that most of the metals remained in the residue.

Haghighat et al.,²⁶ went farther now attempting to further process the oxy-cracked or solubilized material. They examined the catalytic hydroprocessing of solubilized asphaltene conducted in a batch reactor in presence of alkali (NaOH) in water. It was found that at 240 °C and 2 hr residence time the asphaltenes conversion reached 80% with 50% yield to hydrogenated water soluble asphaltene (WSA). The characterization of WSA revealed that it still contains a wide range of carboxylic acids with various alkyl tails. Furthermore, Haghighat et al.,²⁷ studied kinetic study of preoxidized asphaltene hydroprocessing in aqueous phase. Hydroprocessing experiments were carried out in a batch reactor within the temperature range of 280–320 °C in the presence of presulfided NiMo/ γ -Al₂O₃ catalyst. The hydroprocessing results at different severities shows that higher oxidation temperature produces the lighter liquid hydrocarbons, which suggests the oxy-cracking of asphaltene through wet air oxidation. Increasing the reaction temperature affected the quality of products; that is, liquid hydrocarbons with lower boiling point distribution were obtained at higher reaction temperatures.

1.2 Objectives of the study

The ultimate goal of the present study is to investigate the detail conditions of the wet air oxidation and isolation of oxidized product, a concept believed to provide an alternative route for heavy oil upgrading. There are three different products from oxycracking reactions carried out with asphaltenes such as gas phase components, water insoluble asphaltenes (WISA) and water soluble asphaltenes (WSA). Among the three different fractions, WSA is the topic of our main interest, as this fraction comprises the entire HAs and FAs analogs. The objective of the present work was to maximize the amount of water solubilized asphaltenes (WSA) during oxy-cracking reaction in alkaline water. Oxycracking targets both solubilizing asphaltene and reducing the molecular weight of these molecules dissolved in water. The idea behind using this method is that by oxidizing asphaltene particles in water, inter-core links between asphaltene molecules can be broken via controlled oxidation, decreasing the size of aromatic islands. It is observed from the above preceding studies that comparatively high temperature has been used (240 to 320 °C) which is not suitable for the maximum conversion of asphaltenes to WSA, however, operation under moderate temperatures and pressures in aqueous alkaline conditions has not been reported in the open literature. Therefore, in this present study a very low to moderate and economically viable temperature range has been chosen considering the maximum conversion of valuable WSA. The particular objectives of this work are:

1. To produce water-soluble asphaltenes solutions at suitable experimental conditions, such as low temperature - high pressure as well as validate the previous experimental findings of Dr. Pereira's group which suggesting a potential oxycracking process in aqueous phase.

- To determine a suitable separation techniques for the separation of HA and FA analogs from the WSA which can be used as fertilizers and benchmark previous methodology.
- To select the appropriate characterization techniques that confirm the existence of the HA and FA analogs in WSA. Moreover, developing detailed products characterization of the asphaltene oxy-cracking process to preliminarily assess options for post-processing of this material (to be performed in other individual theses in this research program) and determining resemblances with existing oxidized hydrocarbons. These aspirations were sufficiently advanced throughout the years of development of Dr. Pereira's research group and the author considers the following chapters of this manuscript constitute evidence and credit for a final M.Eng (thesis) degree. Work outline of this study is presented in Figure 1.1.

Methodology of Wet Air Oxidation (WAO)

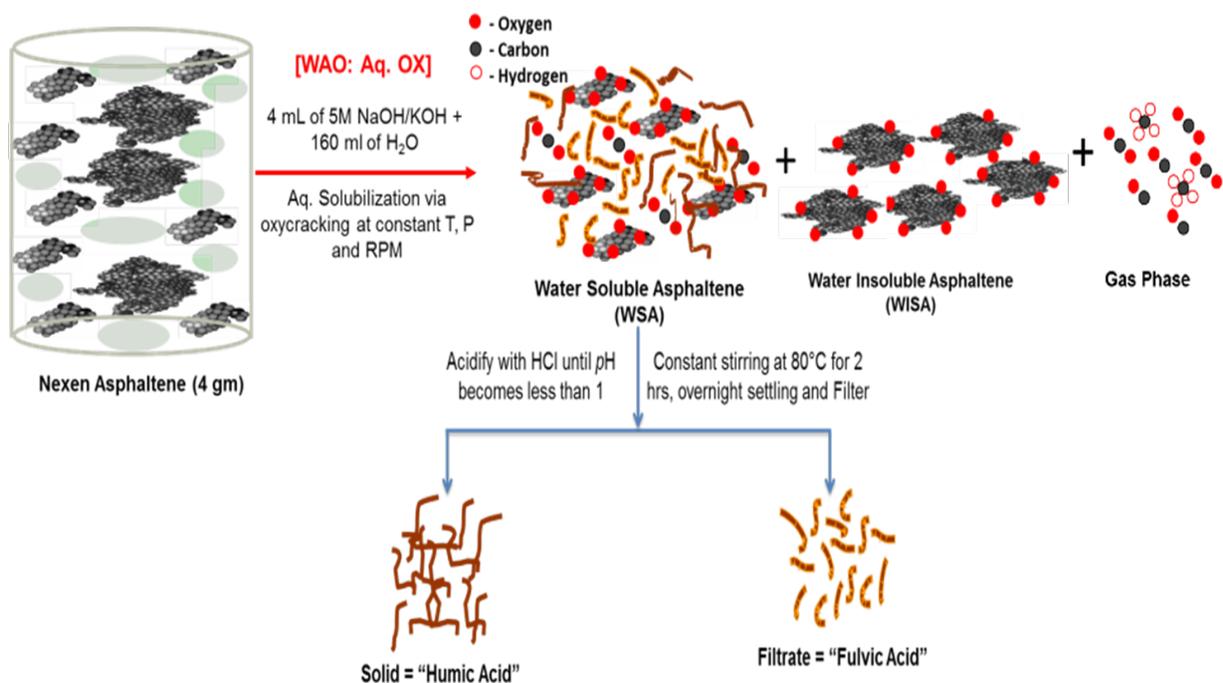


Figure 1. 1 Water-soluble asphaltene production and separation schematic

1.3 Thesis Organization

The present work is divided into six chapters where each one has the specific objectives presented on Figure 1.2. The first chapter explains the contextual, aims and determination for this research. The second chapter presents the literature review where relevant terminology, fundamental concepts and relevant processes are examined. Chapter three contains a detailed description of the materials and methodology of wet air oxidation of asphaltenes and the effect of some variables on the WSA solution. In Chapter four, wet air oxidation of asphaltene at different severities is addressed. Chapter five refers the low temperature wet air oxidation of asphaltene at high concentration of KOH. Chapter six presents findings and global conclusions from this work.

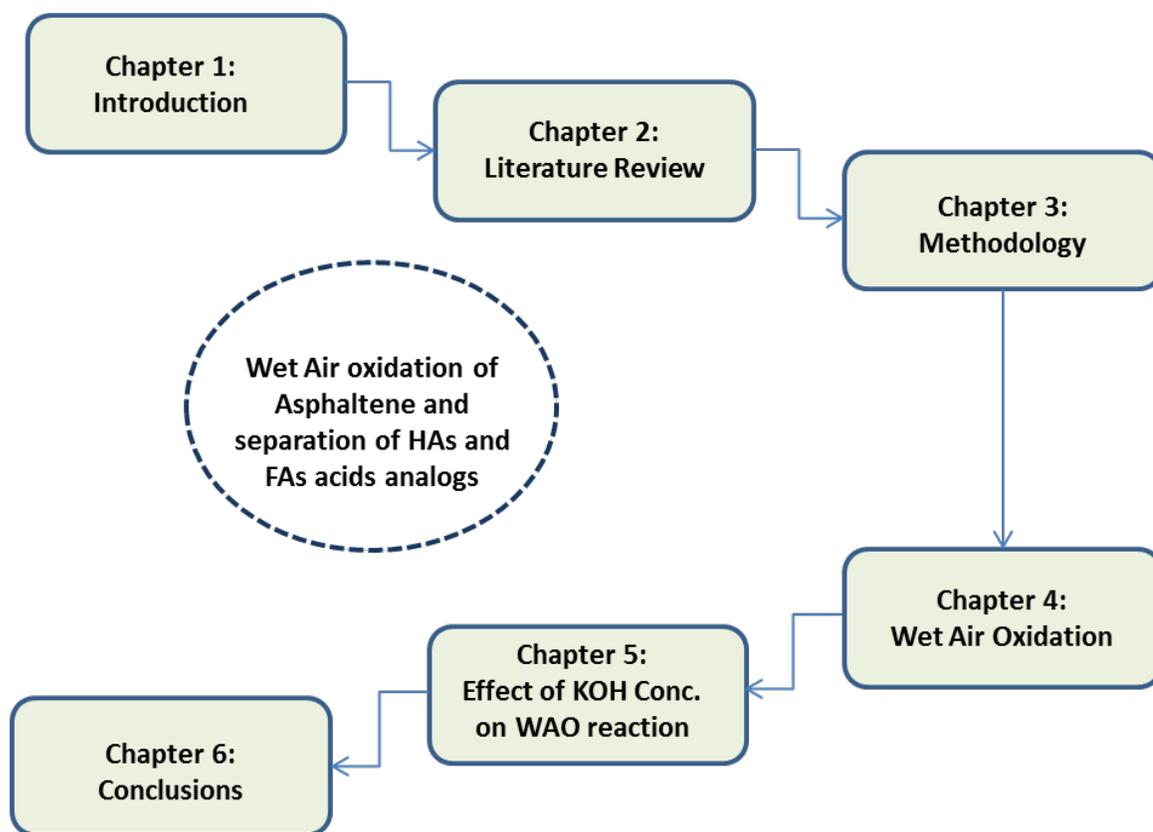


Figure 1. 2 Schematic organization of the report and topics covered in each chapter

CHAPTER 2. INTRODUCTION TO PETROLEUM ASPHALTENE

Most relevant features published in the literature are analyzed in this section related to research topics. Features of humic substances such as HA and FA chemistry are reviewed aiming to enrich subsequent discussions within this document. Details of asphaltenes and water-soluble asphaltenes characteristics were also discussed at the very beginning.

2.1 Asphaltenes

Asphaltenes are high molecular weight oil components insoluble in light alkanes such as propane, n-pentane, iso-pentane and n-heptane but soluble in liquids with a surface tension above 25 dyne/cm, such as pyridine, carbon disulfide, carbon tetra chloride and benzene.²⁸ It has no definite melting point²⁸ and it has wide range of molecular weight²⁹, from 700 to 2,000 Daltons. Asphaltene structure contains complex aromatic rings bearing heteroatoms (O, N, S, Ni, V, Fe), linked to aliphatic chains with variable lengths.³ Asphaltene molecular structure proposed for Athabasca bitumen was shown in Figure 2.1. Proposed average asphaltene structures from a +510 Venezuelan residue asphaltene in 2 and 3 dimensions were shown in Figure 2.2. Dr. Gerardo Vitale drew the 3D structure using Materials Studio Visualizer, and the optimization of the structure was done with DMol³ program. Asphaltenes can combine, prompting precipitation inside the pores of rock formations, wellheads and surface processing equipment.²⁹ Asphaltenes can impair the catalytic activity in several ways such as by adsorbing on catalyst active sites, by clogging the pores of catalyst and by promoting deposition of coke on the catalyst surface.

To avoid these difficulties a physical extraction process was implemented to separate asphaltenes from the oil to be converted. Solvent deasphalting is a physical carbon rejection

process that typically uses three to ten volumes of solvent per volume of oil phase, and then the solvent is recovered under conditions that are as economical as possible.³⁰ Propane deasphalting process is a preferred practice in refineries while n-pentane and n-heptane are commonly used in laboratory scale.³¹

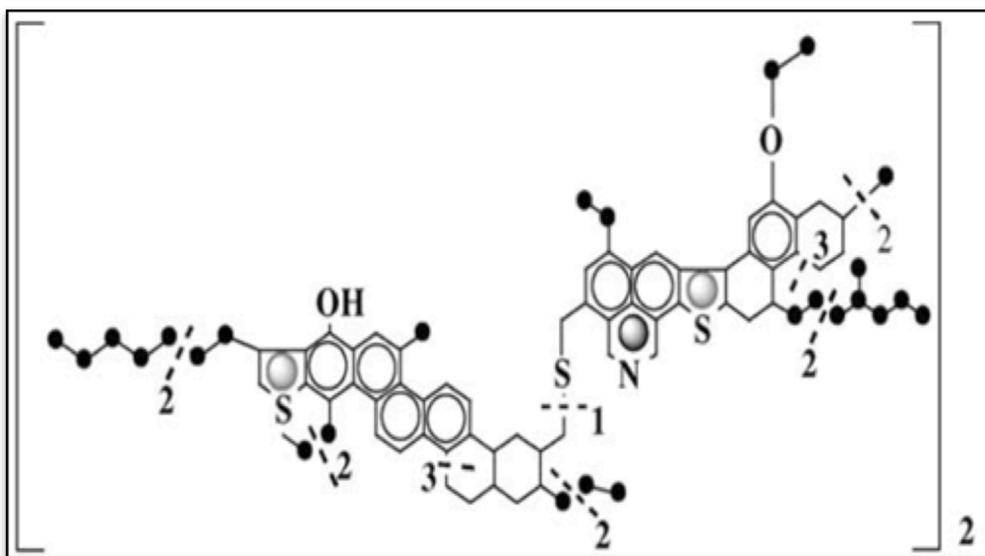


Figure 2. 1 Hypothetical asphaltenes structure from Athabasca bitumen (Suzuki et al, 1982).³²

The typical bond scission reaction separation is presented in the Figure.

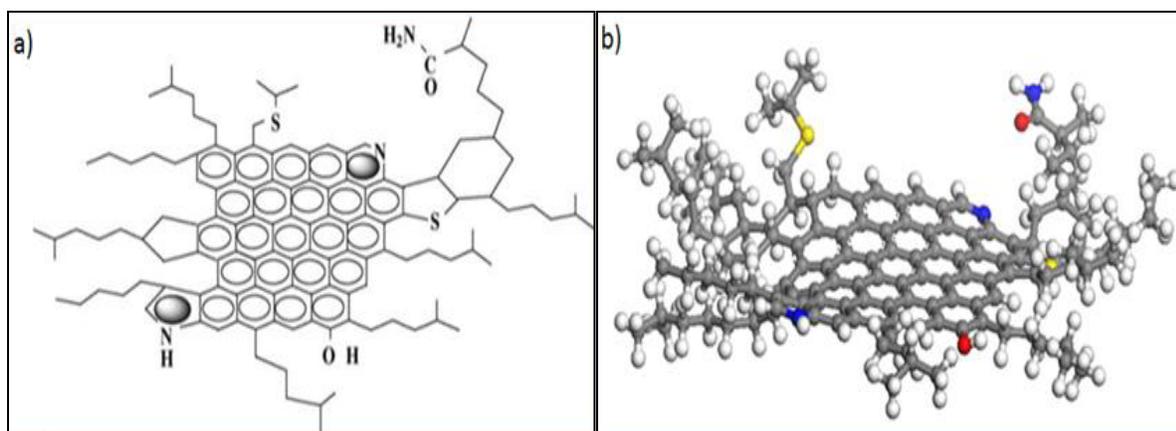


Figure 2. 2 Hypothetical asphaltenes structure a) original 2D model, and b) Gerardo Vitale's optimized 3D model. (Carbon atoms are represented in gray, nitrogen atoms in blue, sulfur atoms in yellow, oxygen atoms in red and hydrogen atoms in white).

Solvent of choice is responsible for the quantity and composition of the precipitate. It is typical to indicate n-pentane (or nC5) and n-heptane (or nC7) asphaltenes in order to specify the precipitating medium. The nC7 asphaltenes have a higher degree of aromaticity, in other words nC7 asphaltenes have a lower hydrogen-to-carbon atomic ratio than the n-pentane precipitate. Similarly, nitrogen-to-carbon, oxygen-to-carbon, and sulfur-to-carbon ratios are generally higher in the n-heptane precipitate.²⁸

2.2 Oxidation of asphaltenes and production of water-soluble hydrocarbons

At present, the Catalysis for Bitumen Upgrading group is developing a methodology to produce WSA via wet air oxidation in alkaline media. WSA production is the main focus of the research; it is worth citing a few aspects since these constitute the basis for this project.

2.2.1 *Wet Air Oxidation (WAO PROCESS)*

In the past decades partial oxidation has been studied widely as a route to solubilize high molecular weight hydrocarbon into water. Mild operating conditions (partial oxidation) result in highly oxygenated compounds, soluble in water whereas severe oxidation leads to CO₂ production and water. Oxidation of organic and inorganic substances in an aqueous solution in presence of oxygen or air at elevated temperatures and pressures either in the presence or absence of catalysts is called WAO process. Both catalytic and non-catalytic processes have been used to oxidize asphaltenes, lignin, and coal, among others, using reagents such as air, oxygen, ozone, potassium permanganate, nitric acid, etc. Catalytic oxidation studies using Thallium, Copper/Cobalt, Ruthenium and metal oxides have been previously published, as well as mechanistic features of this process (Carbognani, 2012 and references therein).⁴

The key reactions in WAO processing are similar to incineration, and any material that can be incinerated can be oxidized in water. The WAO process was first used for the destruction of paper-mill sludge and for the production of artificial vanilla flavoring (Zimmermann et al, 1943, 1945).^{33, 34} Nowadays, WAO process is successfully used in most industrial wastes destruction. The WAO process is therefore ideal for treating sludge where the organic matter is very high in concentration compared to water, waste liquors and slurries. Moreover the WAO process is capable of up to 99% conversion of toxic organics to harmless end products. An oxidizing agent is introduced into the organic materials dispersed in water to initiate WAO processing. Suitable oxidizing agents includes permanganate compounds, cerium compounds, chromate compounds, dichromate compounds, peroxides, ozone, tetroxides, nitrates, nitrites, persulfates, peroxy acids, and derivatives and combinations thereof. Usually oxidation takes

place at high temperatures and pressures. The primary raw material and reaction products undergo continuous conversion with a change in physical and chemical properties of all components formed. Intensity of stirring, reaction temperatures, alkali concentration, lengths of oxidation, and O₂ pressure are the key factors that impact the degree of oxidation and reaction product yields.³⁵

Two main stages of wet air oxidation have been identified: a physical stage followed by a chemical step. The first stage suggests transfer of oxygen from the gas phase to the liquid phase, where the only significant resistance is located at the gas/liquid interface. The chemical stage involves reaction between the transferred oxygen and the organic compounds. Typical operating conditions for complete oxidation are 150°C-320°C, 300-1000 psi, 2-6 hour of residence time and with pH ranging from 4-13. High pressures are required to keep water in liquid state and increase the concentration of dissolved oxygen in water.³⁶

2.2.2 Characterization of water-soluble hydrocarbons

For many decades scientists have made efforts to investigate oxidized and water soluble hydrocarbons. For example ozonolysis of asphaltenes was studied by Filimonova et al,³⁷ obtaining a product soluble in water, and a fraction soluble in acetone and alcohol but insoluble in benzene, aliphatic and chlorinated hydrocarbons. It was also observed that the water-soluble portion was a mixture of carboxylic acids, examined via Infrared IR Spectrophotometry. Elemental analysis also showed an increase in the H/C ratio, and oxygen content (O/C) compared to the initial asphaltenes. Similar trend was also reported by Moschopedis,³⁸ in water-soluble oxidized asphaltenes.

Curtis et al.,³⁹ extracted nC5-asphaltenes from oxidized asphalt at different levels of oxidation, and examined their adsorption performance on silica, alumina, sandstone and limestone. They showed significant increase in ketone and sulfoxide absorbance of oxidized n-C5 asphaltenes by using infrared analysis (IR). Similarly, infrared analysis also revealed the formation of carboxyl and phenolic hydroxyl groups on water-solubilized asphaltenes.³⁸

It is worth pointing out the size of water-soluble hydrocarbons. It was claimed by Marathon Oil Canada Corporation that oxidized asphaltenes have an average molecular weight in the range from approximately 5% to 75% of the average molecular weight of the initial asphaltenes fraction.⁴⁰ Catalytic oxidation performed at relatively mild temperature (25°C-95°C) and pressures near ambient, leads to breaking from around 2% to 50% of the aromatic rings in the original asphaltenes.

An oxidation process of heavy hydrocarbons using ozone and supercritical fluids proposed the structure for asphaltenes displayed in Figure 2.3, was patented by Hong.⁴¹ Using ozone and a liquid solvent carrier such as CO₂, N₂O, NH₃, ethane, lower alkanes and combinations or mixtures at supercritical conditions, associated products and reaction sequence were identified within his claims.

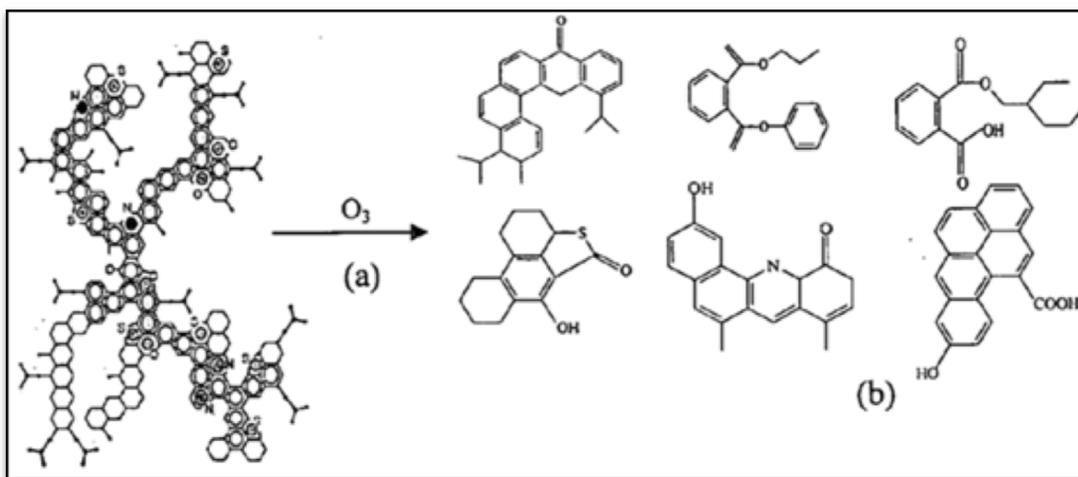


Figure 2. 3 Asphaltenes and oxidation products from heavy hydrocarbons fragmentation upgrading process (Hong, 2006).⁴¹

2.3 Humic Substance

Asphaltenes oxy-cracking reaction under mild operating conditions solubilizes asphaltenes in water giving origin to smaller molecular weight compounds than the parent asphaltenes, which can be considered as analogs of humic substances based on the determined properties.

Humic substances are organic materials naturally produced by oxidative decomposition of complex organic molecules.⁴² These materials play a critical role in the global carbon cycle. Because of their large molecular weight carbon structures, these components could help in transferring nutrients to plants and increasing water retention in soils. Furthermore, they could have other industrial applications such as additives for controlling the settling rate of concrete, dyes for leather preparation, agents in the woodworking industry, additives for increasing mechanical strength of ceramics and also medical and environmental applications.⁴³

Humic substances have been classified based on their solubility in water at different pH, into three separate fractions: fulvic acids (alkali and acid soluble), humic acids (alkali soluble and acid insoluble), and humin (alkali and acid insoluble).⁴³⁻⁴⁶ The elemental analysis of different fulvic acids and humic acids shows that their major components are C, H, O, N, and S and the structure of humic substances comprise aromatic rings attached to aliphatic chains.⁴³⁻⁴⁴ Past researches addressed the production of humic substances from coal and lignites. Treating coal with 5% and 10% H₂O₂ in a water recirculating bath for 2 hrs at 70 °C was reported. The mixture was filtered, washed and dried and then treated with 10 ml (5N) KOH at 70 °C for 2 hrs. The supernatant was filtered and washed with distilled water and then acidified with H₂SO₄ to precipitate humic acids. The experiments were repeated using other oxidizing agents like KMNO₄ and HNO₃. The results showed that HNO₃ produced the best yield in humic acids production with a wide variety of acidic functional groups in comparison with other oxidizing agents.⁴⁷ The production of humic acids using nitric acid was studied by others; however, nitric acid was found expensive compared to the obtained products and the process required long reaction times for coal particles larger than 100 µm.⁴⁸

The production of humic substances from coal was investigated industrially using oxidative processes. Coal conversion to humic acids by pre-oxidizing the coal and then treating with the aqueous solution of formaldehyde and alkali bisulfate or with an aqueous solution of ammonia and formaldehyde with the addition of sulfur dioxide at 100 °C to form water soluble products was reported. The water-solubilized sulfur-methylated product was applicable as tanning agent, additive to control flow properties of drilling muds, fertilizer component, and graphite production.⁴⁹

In another patent, coal was bio-oxidized in water using thermophilic aerobic cultures for about 48 hours at a temperature of 60 °C to produce humic acid, alcohols, methane and light fatty acids. The bacteria concentration was 1-20 wt% of the mixture of coal, water, and bacteria. The concentration of coal was between 0.01 to 50 wt% with up to 95% of the coal converted to humic acids, other products were methane, light alcohols, and fatty acids. Although coal bio-oxidation was proposed in several patents, this process is expensive and also produces significant amounts of metabolic by-products.⁵⁰

In another set of patents and articles, humic acid was produced using dry oxidation of bituminous or sub-bituminous coals or lignites. The process was carried out in fluidized bed reactors at temperatures between 150°C to 300 °C, pressures between 1.1 to 10 atm and contact times between 30-600 mins. According to these works, oxidation of coal occurred almost exclusively over the aliphatic structures.^{48, 51-52}

2.3.1 Humic acids

Natural Humic acids remarkably resemble to WSAs obtained by wet air oxidation. To provide a broader understanding of the chemistry and strategies used with these substances properties and characterization of humic matter are addressed here deemed useful for the water-soluble asphaltene studies.

Humic substances, such as humic acids, fulvic acids and humin, are the largest components of soil and a sizeable part of the planet carbon pool (Humic Consortium for Carbon Sequestration, 2008).⁵³ These substances are distinguished based on their solubility in basic and acidic

solutions. Humic acids are the major fraction of humic substances, comprised of carboxylic, phenolic, aliphatic, enolic-OH and carbonyl functional groups (Humic Consortium for Carbon Sequestration, 2008).⁵³ These substances have very high molecular weight ranging from several hundreds to thousands of daltons⁵⁴ and are prone to aggregation.⁵⁵⁻⁵⁶ The major elements in Humic Acids composition are carbon, hydrogen, oxygen, nitrogen and sulfur regardless of origin, country or continent.⁵⁷ Elemental composition of Humic acid historical data was summarized by Tan et al.⁵⁴ revealing carbon contents of 53.8% to 58.7 wt%, hydrogen contents between 3.2% and 6.2 wt%, oxygen contents ranging from 33.6% to 43.5 wt% and nitrogen contents spanning from 1.2% to 5 wt%.

To formulate the molecular structure for humic substances, computer modeling is the most recent tool. For instance, the 3D structure of the lowest energy conformation for the Temple-Northeastern-Birmingham (TNB) Humic Acid building block $-C_{36}H_{30}N_2O_{15} \cdot xH_2O-$ is shown in Figure 2.4; conversely, Stevenson (1982) developed a humic acid 2D model structure, depicted in Figure 2.5.

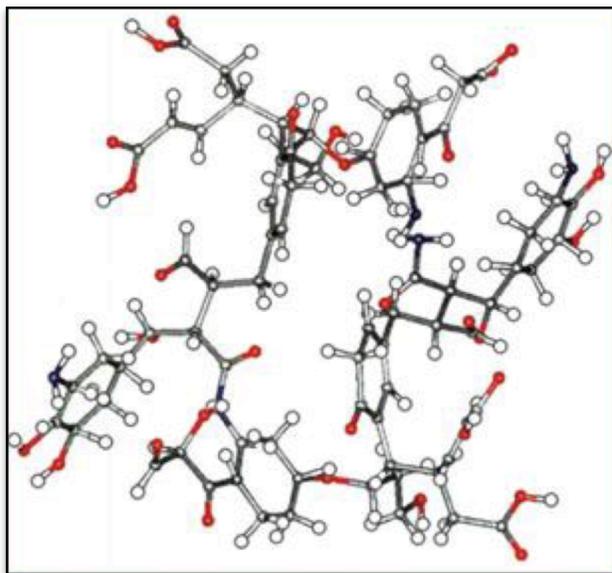


Figure 2. 4 Temple-Northeastern-Birmingham (TNB) Humic Acid building block structure. C atoms are represented in gray, O atoms in red and H atoms in white (Davies et al, 1997).⁵⁵

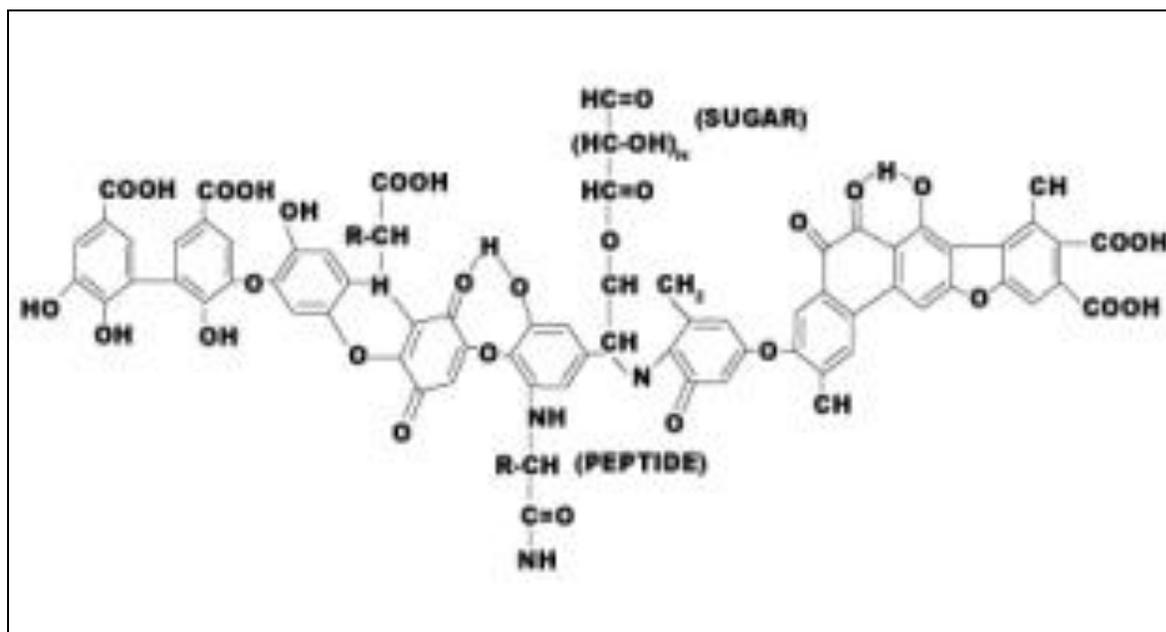


Figure 2. 5 Model structure of humic acid. R can be alkyl, aryl or aralkyl (Stevenson, 1982).⁵⁷

2.3.2 Fulvic acid

Fulvic acid is one of nature's most powerful electrolytes.⁵⁸ Fulvic acids are the yellowish to brown fractions soluble in water; humic acids are the black fractions soluble in alkali that precipitate in acid, whereas humins are insoluble in alkali, acid and aqueous media.⁵⁴ As it contains a variety of beneficial nutrients, Fulvic acid is considered one of the most chemically active compounds in soil. Fulvic acid mixtures contain an assortment of hormones, fatty acids, ketones, flavonoids, vitamins and minerals.

Fulvic acid has been discovered to be one of the most important natural miracles related to life itself. It is an acid⁵⁹ created in extremely small amounts by the action of millions of beneficial microbes, working on decaying plant matter in a soil environment with adequate oxygen.⁵⁹ Fulvic acid is part of the humic structure in rich composting soil. Fulvic acids contain a vast amount of naturally occurring bio-chemicals, free-radical scavengers, super oxide dismutases ("SOD"), nutrients, enzymes, hormones, amino acids, natural antibiotics, natural antivirals, and natural fungicides. It is of low molecular weight⁶⁰ and is biologically very active. Because of its low molecular weight, it has the necessity and ability to readily bond minerals and elements into its molecular structure causing them to dissolve and become mobilized fulvic complexes. Fulvic acid from humic (or humate) deposits usually carries 60 or more minerals and trace elements dissolved into its molecular complexes. These are then in ideal natural form to be absorbed and interact with living cells.⁶¹ Plants roots and cells readily absorb high amounts of fulvic acid, and maintain it in their structure.⁶⁰ In fact it has been discovered that these FA complexes are absolutely essential for plants to be healthy.⁶²

Humic and fulvic acids, (the later of lower molecular weight and higher oxygen content) are commonly used as a soil supplement in agriculture, and less commonly as a human nutritional supplement. As a nutrition supplement, fulvic acid can be found in a liquid form as a component of mineral colloids. Fulvic acids are poly-electrolytes and are unique colloids that diffuse easily through membranes whereas all other colloids do not. The Sizes of FA are smaller (and of lower molecular weight) than that of humic acids, with molecular weights, which range from approximately 1500 or less. Fulvic acid is an organic natural electrolyte that can balance and energize biological properties it comes into contact with.⁶³ An electrolyte is a substance that is soluble in water or other appropriate medium that is capable of conducting electrical current .⁶⁴

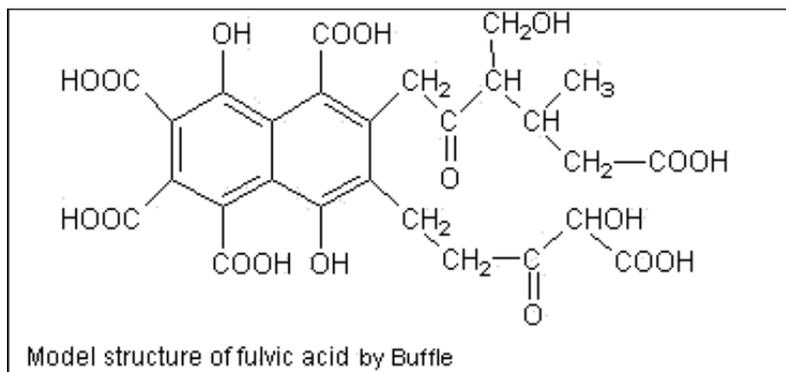


Figure 2. 6 Model structure of Fulvic acid (Buffle et al.1977)⁶⁵

2.4 Corrosion

Corrosion is a natural process, which converts a refined metal to a more stable form, such as its oxide, hydroxide, or sulfide. It is the gradual destruction of materials by chemical reaction with their environment. A corrosive substance is one that will destroy and damage other substances with which it comes into contact. It may attack a great variety of materials,

including metals and various organic compound but people are mostly concerned with its effects on living tissue: it causes chemical burns on contact.

In the most common use of the word, corrosion means electrochemical oxidation of metal in reaction with an oxidant such as oxygen or sulfur. Rusting, the formation of iron oxides is a well-known example of electrochemical corrosion. This type of damage typically produces oxides or salts of the original metal, and results in a distinctive orange coloration. Corrosion can also occur in materials other than metals, such as ceramics or polymers, although in this context, the term "degradation" is more common. Corrosion degrades the useful properties of materials and structures including strength, appearance and permeability to liquids and gases.

Many structural alloys corrode merely from exposure to moisture in air, but the process can be strongly affected by exposure to certain substances. Corrosion can be concentrated locally to form a pit or crack, or it can extend across a wide area more or less uniformly corroding the surface. Because corrosion is a diffusion-controlled process, it occurs on exposed surfaces. As a result, methods to reduce the activity of the exposed surface, such as passivation and chromate covering, can increase a material's corrosion resistance. However, some corrosion mechanisms are less visible and less predictable.

CHAPTER 3. MATERIALS, EXPERIMENTAL AND METHODOLOGY

3.1 Materials

NEXEN pitch, KOH flakes Sigma- Aldrich (purity $\geq 90\%$), and water were used as initial materials for the experiments. Ultra-high purity grade oxygen (99.993%, purchased from Praxair) was selected as the oxidation reagent. A 5N KOH solution in water from Sigma Aldrich was used to neutralize the acidity produced during the oxidation process, aiming to prevent reactors severe corrosion and to increase asphaltenes solubility in water.³⁵

3.2 Characterization of the oxidized product

3.2.1 Gas Chromatography

A gas chromatograph (SRI model 8610C) equipped with a 60/80 carboxen-1000 carbon molecular sieve column (Supelco 15 ft \times 1/8 in.) eluted with helium as the carrier gas, was used to determine gas composition. The gas was taken directly from the Batch reactor headspace. The GC was provided with four detectors: two thermal conductivity detectors (TCD), one flame ionization detector (FID) and one flame photometric detector (FPD). Due to its high thermal conductivity and safety, helium carrier is mostly used with TCDs. TCD1 used helium as a carrier gas allowing the detection of multiple hydrocarbon compounds, carbon monoxide, carbon dioxide, and hydrogen at high concentrations. TCD2 used argon to detect hydrogen at low concentrations. Praxair gas mixture certified standards were used to calibrate all the detectors of the GC. Peak Simple software version v3.72 by SRI Instruments was used for GC control, data acquisition, processing and analysis. In this work the GC column temperature was kept at 40 °C for 15 minutes, then ramped at 20°C/minute up to 210°C and finally kept for 25 minutes at that temperature. Sample injection to the GC was done online by means of a six-port injection valve

(can control pressure from 125 to 15000 psi) having 100- μ L sample loops. All measurements were at least taken in triplicate to ensure precision achieving a standard deviation of around 5%.

3.2.2 Total organic carbon (TOC) analysis of WSA

As asphaltenes are the only source of carbon during the oxidation process the Total Carbon (TC) technique was chosen to quantify the amount of asphaltenes dissolved in water. However, other oxidation products like CO₂ may solubilize in the WSA solution and also contribute to its carbon content. Therefore, a distinction between Total Organic Carbon (TOC) and Inorganic Carbon (IC) is made in order to quantify asphaltenes concentration in the aqueous stream. The TC content corresponds to the sum of TOC and IC contributions. TC, TOC and IC measurements were made in a TOC-CPH analyzer from Shimadzu. An auto sampler is used for sample injection and ultra-zero air was used for samples combustion. The liquid products were centrifuged at 6000 rpm and then filtered using a 0.45- μ m filter, to remove any suspended particles, before determining the TOC. For TC analysis, the sample is heated to 680°C in presence of an oxidation catalyst, transforming all carbon components to carbon dioxide. CO₂ is monitored by a non-dispersive infrared gas analyzer and peak areas are related to the TC concentration of the sample. IC quantification is made by injecting HCl to the sample to release CO₂ from carbonates (if present); in this case the analysis does not include CO₂ released from carbonates/bicarbonates. TOC content is determined by subtracting the IC concentration from the TC concentration. The TOC apparatus is configured to inject every sample three times into the combustion tube and to calculate an average value, providing results with more precision in relation to the TC, IC and TOC content.

3.2.3 Elemental analysis

Elemental analyses of Nexen asphaltenes, WISA and dried WSA products were carried out in a LECO 628 CHN elemental analyzer for carbon, hydrogen and nitrogen determination. In this equipment, samples are introduced into a combustion chamber where CO₂, NO₂, and water are produced and monitored with thermal conductivity detectors. By means of calibration curves, water, CO₂ and NO₂ signals are matched to the hydrogen, carbon and nitrogen content in the sample, respectively. The equipment is able to provide results with a precision of around 5% of relative error. % Oxygen (O) was calculated by subtracting (%C + %H + %N + %S) from 100%. The elemental compositions are expressed as H/C, O/C, and O/H atomic ratios, to clarify the stoichiometric relationships between the elements.

Sulfur contents were determined with an Antek 9000 SN Elemental Analyzer. After injecting samples into the combustion chamber, SO₂ was detected by an UV-fluorescent detector, which matched signals with calibration curves that were created with reference standards and reference bitumen samples. The apparatus, which is able to detect concentrations down to ppb (European Virtual Institute for Speciation Analysis, 2010),⁶⁶ provided sulfur content with relative errors below 5%.

3.2.4 Metal analysis

Metals quantification procedure consists of two steps: a) sample digestion and b) analysis by Inductively Coupled Plasma spectroscopy (ICP). Digestion was carried out in a Microwave Accelerated Reaction System (MARS) from CEM Corporation following a methodology developed by the CBU group, in which 0.5 grams of sample (weighed to the nearest 0.1

milligram) are placed in vessels and mixed with 10 mL of a 70 wt% HNO₃ solution, 1 mL of an 85 wt% H₃PO₄ solution and 23 mg of a 1,000 ppm cobalt standard solution. Next, vessels are introduced in the MARS apparatus; temperature was increased to 210°C and the system dwelled for 50 minutes. Then, vessels were cooled down to room temperature and their contents were diluted to 25 mL using deionized water. Afterwards, digested samples were analyzed in an ICP-atomic emission spectroscopy apparatus (IRIS Intrepid II XDL, from Thermo-Instruments Canada Inc.), in which the prepared dilution is injected to the nebulization chamber, converted in aerosol or vapor and ionized inside the plasma. Metal contents were quantified using calibration curves with standard wavelengths selected for each element and known standard solutions.

3.2.5 GC-MS analysis of organic extractable compounds

Samples extracted with methylene chloride (DCM) were analyzed using a Shimadzu GCMS-QP-5000/QP5050A equipped with electron impact ionization source (70 eV) kept at 250 °C. A GC column Ublon HR-1 fused silica capillary 0.25 mm X 50 m with film thickness 0.25 µm was used for the analysis. Five data points (standard dichloromethane (CH₂Cl₂) solutions at 0.005, 0.05, 0.5, 2.0, and 10 µg/mL and a blank) were prepared for calibration in such a way that the concentration of samples fell within the spanned range. Aliquots of solutions were diluted with dichloromethane to different concentrations so that the compound concentration fell within the calibration range. The injector and GC–MS interface were kept at constant temperatures of 280 and 250 °C, respectively. The column was kept at an initial temperature of 40° C for 2 min before ramping up to 250 °C at a rate of 5 °C/min and the column was then left at 250 °C for a total of 8 min. Ultra-pure helium (1 ppm impurities) was used as carrier gas at a flowrate of 1.2 mL/min. Compounds were ionized at 69.9 eV electron impact conditions (nominal 70 ev) and

analyzed over a mass per charge (m/z) range of 50–550. The compounds were identified by comparing the mass spectra with the NIST library.

3.2.6 Fourier transform infrared spectrophotometry (FTIR)

Fourier Transform Infrared spectrophotometry (FTIR) analyses were used to characterize parent asphaltenes and their oxidized products. The infrared technique relies on infrared light absorption causing vibrational excitation of chemical bonds, each one at a characteristic frequency; hence, absorption bands at determined frequencies can be used to identify specific functionalities. A Nicolet 6700 FTIR-28IR spectrometer from Thermo Electron Corporation, equipped with a diffuse reflectance cell for KBr dispersed solid samples and a transmission cell for liquid samples, was used to study the infrared region of the WISA, WSA, Humic and Fulvic acids analogs and investigate their molecular bonds and functional groups distribution. 5 mg of each sample was mixed with 500 mg of KBr and the ground mixture was spreaded over the DRIFTS sample holder. The obtained spectra are the average of 128 scans that was taken for each sample in a range from 400 to 4000 cm^{-1} with a resolution of 2 cm^{-1} .

3.3 Methodology

3.3.1 Production of water soluble asphaltene

The primary raw material and its reaction products undergo continuous conversion with a change in physical and chemical properties of all components formed. The following methodology is the basis of the procedure utilized to: a) produce WSA as feedstock for different characterization tests, and b) to examine the influence of temperature on WSA quality; variables such as stirring speed, quality and quantities of the reagents described below, remained

unchanged for all experiments performed to produce WSA. Stirring intensity of reaction mixture, temperatures, alkali concentration, lengths of oxidation, and O₂ pressure are the key factors that impact the degree of oxidation of asphaltenes and reaction product yields.³⁵ Usually, oxidation takes place at high temperatures and pressures. In this study pure oxygen at 1000 psi was used as oxidizing gas. It was also observed that the amount of oxygen consumed increases with the amount of asphaltene used, even though it is not in direct proportion to the mass. The consumed oxygen is not utilized only in converting the asphaltenes to carbon dioxide and water; a good portion of it is converted to water-soluble material and/or incorporated into mildly oxidized organics that are not water-soluble.

4 g of crushed Nexen asphaltenes, 160 mL of water and 4mL of KOH solution were poured into a 540 mL stainless steel batch reactor model 4848 from Parr instruments (see Figure 2). 1000 psig of oxygen was introduced into the reactor and stirring speed was set to 1000 rpm. The system was heated up to the target temperature and reaction took place for a period of time with constant temperature. Afterwards, the reactor was cooled down to room temperature using an in-house fabricated copper water coil cooler. Produced gases were injected into the described Gas Chromatograph (see section 3.2.1) for mass balance and yield calculations. The resulting WSA solution was filtered and unconverted solids were dried overnight and weighed for mass balances and conversion calculations. In our experiments various asphaltene particle sizes were tested, such as controlled mesh size (355 um) or random mesh sizes' asphaltenes. Different agitation speeds (500 and 1000 RPM) were also tested at fixed reaction conditions. Higher RPM such as 500 and 1000 do not produce a significant impact on WSA; however, lower RPM (250) seems to affect mass transfer control.

In each experiment, it takes about 80-90 minutes for the feed to reach the set point temperature, and then the reaction occurred at set up conditions for a constant period of time. After the reaction, the reactor was cooled down and GC measurement was performed on the gaseous products. Gaseous species (CO_2 , CO and CH_4 etc.), water and hydrocarbons were analyzed under these conditions. In the next step the liquid WSA effluent was filtered to recover insoluble-non-reacted solids and provide WSA, which is the main focus of the study. Total Organic Carbon (TOC) was measured to determine the aqueous carbon amount in WSA. The mass balance, selectivity, yield and conversion were calculated based on the amount of carbon in the WSA fractions (carbon mass balance). FTIR spectroscopies of different fractions of WAO reaction were carried out to determine the presence of distinctive functional groups before and after WAO reaction.

In this work, preliminary experiments were done using one batch stainless steel Parr reactor, (Model 4848 Parr reactor, 540 ml) with the possibility of controlling temperature, pressure and stirring rate. The experimental setup is presented in Figure 3.1. The reactor length was 16.76 cm, the diameter was 6.35 cm. In all experiments, the asphaltenes mass was fixed at 4 g and the water mass was 160 g. 4 mL (5M) alkaline solutions (KOH) were added in order to neutralize the final liquid product and to avoid metal corrosion of the reactor. During the reaction highly acidic compound has been generated which causes corrosion of the Parr reactor. To neutralize the acidic media during reaction 4 mL of 5M alkaline solutions (KOH) has been added. For heating the feed, temperature, mixing rate and pressure parameters were controlled using the systems built in controllers. In our experiments various asphaltenes particle sizes were tested and different agitation speeds were also tested at fixed reaction conditions.



Figure 3. 1 Model 4848 Parr reactor

CHAPTER 4. CHEMICAL CHARACTERIZATION OF HUMIC AND FULVIC ACIDS ANALOGS OBTAINED FROM WAO OF ASPHALTENES AT DIFFERENT SEVERITIES

In this chapter we analyzed the results of wet air oxidation at different severities. The oxidation reactions were carried out at using same amount of 5N KOH (i.e. initial pH will be constant for different severities) with variable residence time and reaction temperature.

4.1 Results and discussion

4.1.1 Separation of different fractions and their quantitative analysis

The oxidation of asphaltenes rapidly produces both water-soluble and water insoluble oxygen rich species. Experiments were carried out with random and controlled sizes asphaltenes (355 μm). The results indicated almost the same conversion of asphaltenes. It was observed that particle sizes do not remarkably affect the solubilization of asphaltenes or their conversion to CO_2 ; indicating mass transfer has a relatively insignificant impact within the range of studied conditions. Moreover different agitation speeds (500 and 1000 RPM) were also tested for different reaction conditions. Higher RPM such as 500 and 1000 do not produce a significant impact on WSA but lower RPM (250) seem to affect mass transfer control.

Different reaction parameters have been used at initial stage of our experiment to check the suitability of the parameters. Initially temperature was varied between 200-220°C, keeping other parameters unchanged. The pressure was set to 1000 psi, to maintain the water in the subcritical state; residence time was 2 hr and mixing rate was 1000 rpm to prevent increasing

mass transfer resistance and the effect of temperature on selectivity and conversion was examined. It was observed that at low RPM (below 250) the asphaltenes conversion was very low. It is observed that temperature is the key parameter in oxy-cracking of asphaltenes. As the temperature increased, organic functionalities dissolved more in water, but the organic compounds further decomposed and converted to gases like CO₂. Therefore, it is necessary to find out an optimum temperature for maximizing asphaltenes water solubilization while keeping CO₂ production minimum. It is also observed that as the temperature increased, the conversion to WSA and CO₂ increased; but the selectivity to WSA decreased, and selectivity to CO₂ increased.

Pressure was altered between 500-1000 psi to examine the effect of pressure on the production of WSA, keeping the temperature and residence time constant (200 °C, and 2 hr). One fundamental characteristic for the subcritical liquid water oxy-cracking is guaranteeing that water is in the liquid form. For having water in liquid form at temperatures spanning between 200-220 °C, working pressure should be higher than the equilibrium water vapor pressure. This investigation conclude that the asphaltene conversion increased, reaching desired values ~85, whereas selectivity to WSA did not change significantly with increasing the pressure; however, i.e. high selectivity to WSA, high conversion and low selectivity to CO₂. Therefore, it is considered that optimum reaction conditions for maximizing WSA production were identified.

The effect of base on the WSA production has been studied. It is found very crucial to carried out the reaction in basic medium as the WSA solutions become highly acidic during the reaction (pH ~ 1-2) in absence of base, which is the cause of damaging the stainless steel 316 Parr reactor vessel (holes produced through the walls). A blank reaction without oxygen was

performed at 200°C using 4 ml NaOH (5N) in an inert gas (He) for 2 hours to determine whether or not base employs additional effects over the oxy-cracking process other than acids neutralization. No change in asphaltene mass and pH of the liquid (pH=12.3) was observed after the reaction completion. However, the aqueous phase showed a bright yellow color and the TOC analysis showed total carbon content remain almost intact, which indicates that only small amounts (about 2%) of asphaltene were able to dissolve in the liquid phase. Therefore, it is concluded from the preceding that base in the absence of oxygen is not solubilizing sufficient amounts of asphaltene, because the content of oxygen functionalities in naturally occurring asphaltene is very low for compensating their large carbon backbones. Combined presence of O₂ and base generated the oxygen functions and their Na-salts that can provide the right balance (carbon functions/ polar functions) able to produce asphaltene solubilization in water.

The effect of different bases (NaOH and KOH) on the WSA production has been also examined. 4 mL 5N base was added to 160 mL water and 4 g asphaltene in each experiment. Initially, NaOH was added to prevent corrosion produced by the high acidity generated during the oxy-cracking process; but further experiments were conducted to determine whether or not metal cations from different hydroxides impact the result of the reaction. The better performance was obtained for KOH over NaOH in terms of improving the asphaltene solubilization. Here KOH increased the asphaltene conversion, as well as selectivity to WSA, more than NaOH. From these findings, it is suggested that metals from basic hydroxides can have catalytic effects on WSA production. One of our recent findings through mass spectrometry analysis of high converted materials derived from asphaltene oxy-cracking using KOH showed that solubilized materials contained in average 8 oxygen/ 20 carbon atoms per molecule,²² whereas virgin

asphaltenes contained about 0.5 oxygen/40 carbon atoms per average molecule, calculated from their elemental analysis. The preceding findings suggest that asphaltenes oxygen incorporation could have a dramatic effect over their aqueous solubilization.

Figure 4.1 schematically shows the three different products obtained from WAO reaction such as gas phase products, WSA and WISA. To isolate HAs and FAs analogs from the WSA solution the pH of the WSA solution was reduced by acidifying until $\text{pH} \leq 1$. The pH was measured using the pH meter. Adding concentrated 37% HCl drop wise precipitated the HAs analogs. Afterwards the precipitated solution was heated at 80°C for 2 hrs and follow up constant stirring to ensure maximum precipitation of HAs analogs. Filtration of the product was carried out using Millipore filters (type HVLP, $0.45\mu\text{m}$) providing a liquid phase (fulvic analogs) and a solid phase (humic analogs). By definition [soil science], the insoluble fraction in acidified solution (i.e. the fraction of higher molecular weight) is HAs and the soluble fraction in acidified solution (i.e. the fraction of lower molecular weight) is FAs. FAs are HAs analogs of lower molecular weight and relative higher oxygen content than other HAs analogs, commonly used as a soil supplement in agriculture. All the products were analyzed individually to determine the conversion of asphaltenes and close the mass balance.

Methodology of Wet Air Oxidation (WAO)

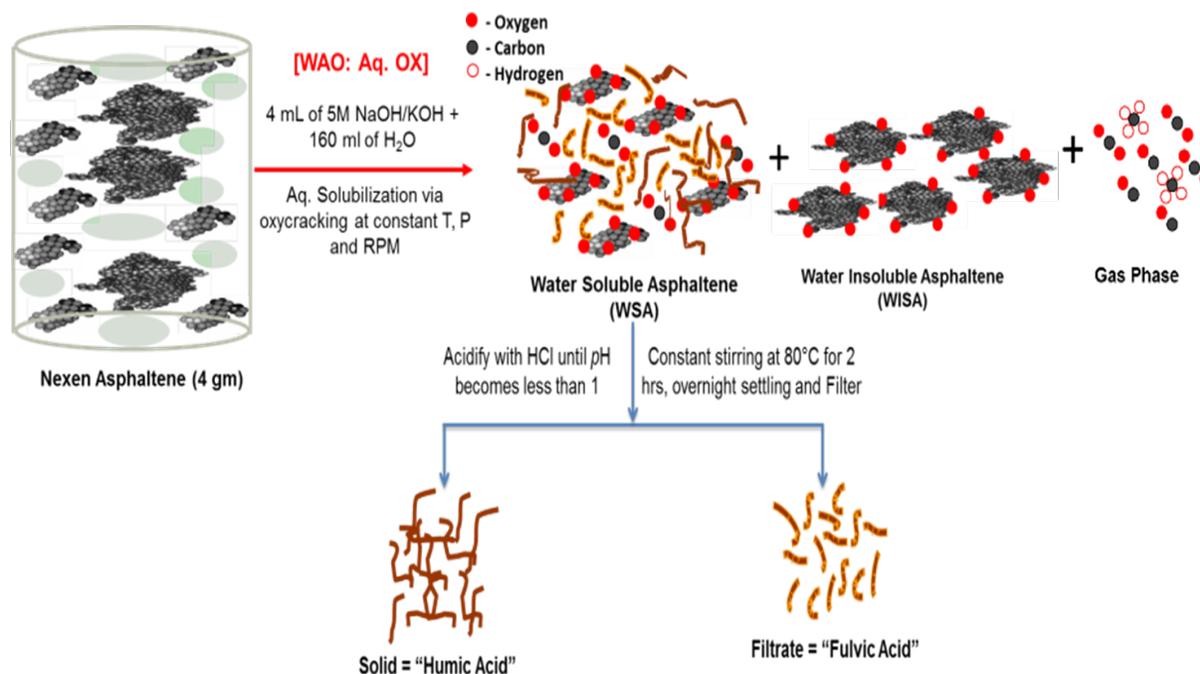


Figure 4. 1 Water-soluble asphaltenes processing

4.1.2 Separation of WSA from WISA

This section explains results from different batches of produced WSA at different temperatures exploring changes in TOC, IC and TC content. Generated gases were analyzed by gas chromatography and liquid samples were filtered and characterized in the TOC apparatus. The experimental plan consisted on performing wet air oxidation of asphaltenes following the methodology described in a previous section, quantifying unconverted solids and assessing gas and liquid streams qualities. Stirring speed was set to 1000 rpm, and asphaltenes (4 grams), water (160 grams), KOH 5N (4 mL) and ultra-high purity oxygen (1000 psig) quantities remained

unchanged for all the experiments.

Each set of experiments was repeated 2 times to ensure reproducibility with an overall carbon mass balance of $96 \pm 2\%$. Lower than 100% recoveries are attributed to experimental errors since the volume of reactor (540 mL) is very large in comparison to the amount of asphaltenes to oxidize (4 grams). Even though the reactor was cleaned between each test, asphaltenes might have been trapped in any of the joints between the reactor and the pressure gauge, the impeller and/or the thermo well. As asphaltenes initial quantity is not large, every 0.1 grams represents 2.5% of the total solids to be handled, thus, the smallest amount of lost powder contributes to the experimental error.

The entire amount of WSA and WISA from the unit was collected by washing and cleaning the reactor and agitator at least three times. Three of the experiments showed $96 \pm 2\%$ mass recovery (products) of initial reactants after the WAO reaction. Afterwards the WISA was separated from WSA by filtering the total recovered products using glass microfiber filters (934 AHTM 47 mm). Mass of WISA was determined after evaporating water and drying. By measuring the carbon contents dried WISA the percentage of asphaltenes conversion in each individual experiment was determined. The total volume of WSA was quantified with a graduated cylinder, used for calculation of carbon mass balance.

Equation (1) demonstrates how the conversion is determined.

$$\text{Conversion}(\%) = \frac{\text{Amount of C in virgin asphaltene taken} - (\text{amount of C in WISA})}{\text{Amount of C in virgin asphaltene taken}} * 100 \quad (1)$$

The liquid selectivities are determined by Equation (2-3).

$$\text{Selectivity to WSA (\%)} = \frac{\text{Amount of carbon in WSA}}{(\text{Amount of carbon in WSA} + \text{Amount of carbon in CO}_2)} * 100 \quad (2)$$

$$\text{Selectivity to CO}_2 \text{ (\%)} = \frac{\text{Amount of carbon in CO}_2}{(\text{Amount of carbon in WSA} + \text{Amount of carbon in CO}_2)} * 100 \quad (3)$$

Table 4.1 shows details of asphaltenes conversion, initial and final pH of the reaction, and oxygen consumption during reaction in three different experiments. From Table 4.1 we can conclude that as the temperature and residence time increase, pH of the products in WAO reaction become more acidic, O₂ consumption increases, conversion of asphaltenes increases. At lower temperatures (200 °C), the excess of free KOH results in high pH (>6). However, at higher temperatures (220°C), more acidic functions were produced, and the pH decreased from neutralization reactions. Amount of base was calculated from preliminary works to avoid reaching acidic pH even at high conversion. Residence time effects were also evaluated by varying this parameter 2-4 hrs under a constant temperature of 200 °C. As the residence time increased, conversion of asphaltenes to CO₂ and WSA increased, but selectivity to WSA decreased. It has been observed that the optimum residence time for high selectivity and conversion to WSA was 2 hours. The effect of residence time on selectivity to WSA was similar to temperature effect.

The pH of WSA was investigated as a function of residence times. Results displayed in Table 4.1 shown that as the residence time increased, pH decreased. It was concluded that more

acidic compounds were produced with increasing of residence time. Moreover it is observed that by increasing residence time beyond 2 hours, the hydrogen to carbon ratio decreased from 1.21 to 1.06, i.e, oxygen cracks more asphaltene molecules and detaches the aliphatic moieties from their structures. These findings confirm that by increasing the severity of the oxy-cracking reaction, alkyl moieties disappear, being substituted with oxygen functions (evidence in this direction is provided by FTIR, discussed later in this article).

Table 4. 1 Details of initial reaction conditions and conversions

Exp. Condition	Initial pH	Final pH	Pressure (psia) loss after reaction (At ambient T° C)	% C Conversion
200° C, 2 hr	12.30	6.20	41	35
200° C, 4 hr	12.30	5.50	52	36
220° C, 2 hr	12.30	4.60	65	51

4.1.3 Gas analysis by Gas Chromatography (GC)

The aim of the selection of chromatographic conditions is to achieve a proper separation of the gas components. It is also required for both the qualitative analysis and also for the proper quantification. To do so, well-resolved peaks and not distorted ones, good relation signal-noise and horizontal base line with absence of drift, must be obtained for each one of the components. For the development and selection of stationary phases, it must be considered, among other things, the thermal and chemical stability of the column, the selectivity in the separation of the components, the lining or coating surface, the diameter of the column, as well as the incorporation of more specific components to the stationary phase, or the use of different technologies to optimize the phase available to the specific regions of analyses that require better resolution. WAO reaction produced different quantities of gas under different experimental

conditions. In order to find out the type of generated gases and the amount of individual gas produced gas analysis was carried out using calibrated GC. The amount of CO₂, O₂, CO, CH₄ and other hydrocarbons, which exist in gas effluents after reaction, were thus measured. When the reaction finished and the reactor was cooled down to the initial temperature, the produced gases were evaluated by GC. Finally, The Ideal Gas Law was used for gas phase calculations. Results from the gas analysis and determination of the carbon contents help to close the carbon mass balance of the reaction. Summarized results of gas phase analysis were used for closing the carbon mass balance and showed in Table 4.2.

4.1.4 Total Carbon Analysis

Total carbon analyses were carried out for all the WSA fractions obtained from different experiments. The TOC analyzer was used to find the amount of soluble carbon in water after the reaction. The liquid products were filtered and the solution later analyzed by TOC. The mass balance, selectivity, yield and conversion are all calculated based on the amount of carbon in the system. Percentages of carbon contents in all WSA samples were shown in Table 4.2.

4.1.5 Carbon Mass Balance

Carbon mass balance was calculated by accumulating the amount of carbon contents in three different fractions such as gas phase, WISA and WSA, respectively. Table 4.2 presents the values of carbon contents in these three different fractions of WAO reactions. Figure 4.2 plots the carbon mass balances for different WAO reactions, indicating that the carbon mass balance is about $92 \pm 2\%$. We were not able to reach mass balances up to 100% due to mechanical and handling limitations.

Table 4. 2 Carbon concentration in different fractions from WAO reaction

Exp. Condition	% Conversion	% C in WISA	% C in WSA	% C in gas
200° C, 2hr	35	65.0	25.0	2.8
200° C, 4hr	36	66.0	20.0	7.9
220° C, 2hr	51	52.0	27.0	12.3

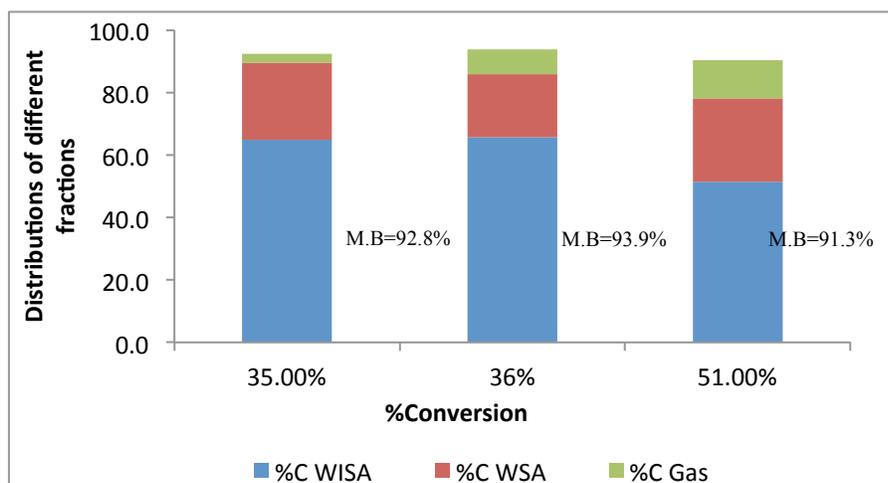


Figure 4. 2 Carbon mass balances at different experimental conditions.

4.1.6 Nature of Solids produced after asphaltene WAO reaction

Two different types of solids were obtained from the wet oxidation of asphaltenes. Solids formation are of practical importance in latter process application, so in this section an explanation will be advanced about their origin and how their formation is related to the reaction conditions. After an experiment is finished a mixture of non-reacted asphaltenes (WISA) and soluble “materials” in the liquid phase (WSA) was obtained. By evaporating the water from WSA solution, we obtained the total amount of solid contents in WSA fractions. Figure 4.3 shows how WSA amounts increased with conversion. In this regard it is important to remember

that KOH was added to the reaction components as neutralizing agent. It has been found that in order to have a neutral liquid at the end of reaction it is necessary to add 1ml of potassium hydroxide (5N) for each 1g of asphaltene used. Therefore it is clear that elemental potassium, probably as a potassium salt, will remain in the filtrate and consequently in WSA.

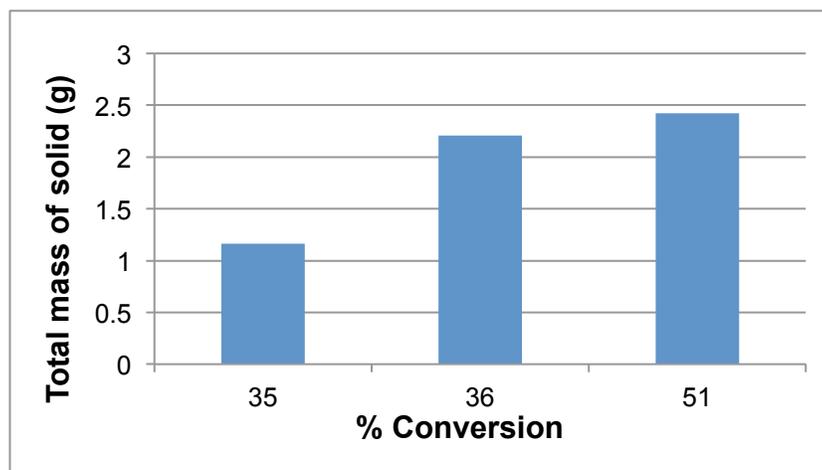


Figure 4. 3 Total mass of WSA (solid) as a function of time

4.1.7 Determination of Selectivity to WSA and CO₂

In an industrial WAO process, conditions must be selected as a compromise between highest conversion and highest selectivity to WSA and lowest selectivity to CO₂. As the conversion increases, selectivity to CO₂ increases whereas selectivity to WSA decreases. Targeting maximum production of WSA reactions at moderate or low temperatures were carried out. From Figure 4.4 we can conclude that lower severities i.e., lower temperatures and residence times are suitable for high selectivity to WSA and low selectivity to CO₂.

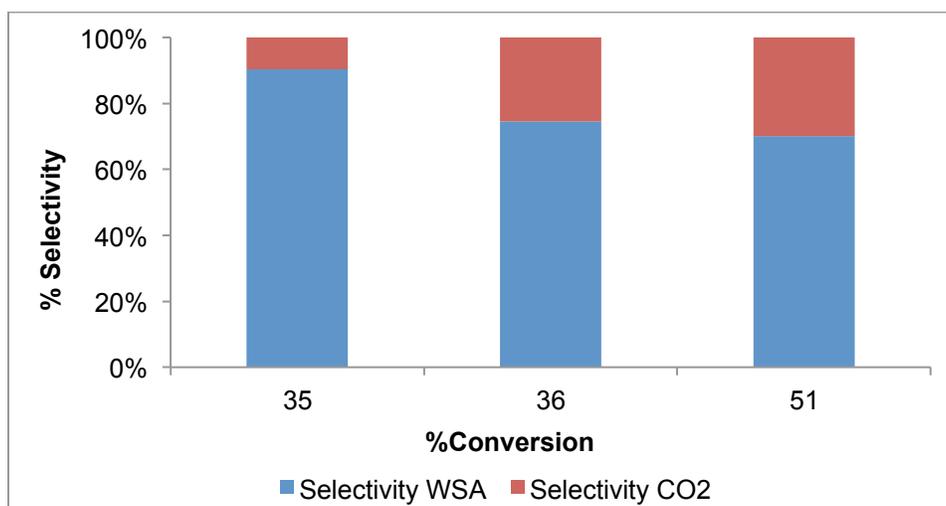


Figure 4. 4 Selectivity to WSA and Selectivity to CO₂

4.1.8 Distribution of Humic and Fulvic acids analogs

The amounts of HAs and FAs analogs produced from different experimental conditions were compared. Table 4.3 shows the variations in amounts of HAs and FAs analogs with reaction conditions. It can be concluded that as the temperature and residence time increases the amount of FA analogs increases and HA analogs decreases. Moreover, we have observed that even though conversions are almost the same for the first two experiments (35% and 36%), the amount of FAs is much higher for the second experiment (36%) suggesting that not only the temperature has effect on FAs formation but also residence time has large effects. Reported values on Table 3 correspond to organic fractions from which weights of KOH were subtracted. It is very important to confirm the selectivity to HAs and FAs analogs as it will decide the suitable reaction conditions for WAO reaction. Figure 4.5 demonstrates that as the conversion increases selectivity to HA analogs decreases and FA analogs increases.

Table 4. 3 Amount of Humic and Fulvic acids analogs from different reaction conditions

Exp. Condition	%Conversion	“Humic Acid” (g)	“Fulvic Acid” (g)	% Selectivity to HA (a)	% Selectivity to FA (a)
200° C, 2hr	35	0.59	0.22	73	27
200° C, 4hr	36	0.36	1.32	21	79
220° C, 2hr	51	0.25	1.52	14	86

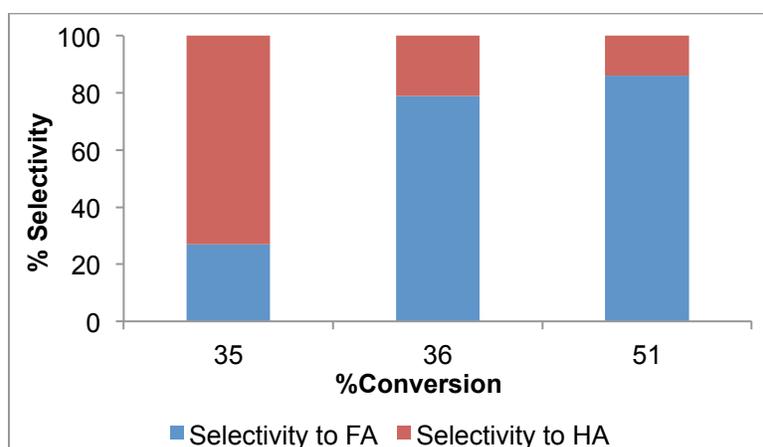


Figure 4. 5 Selectivity to HAs and FAs analogs with conversion

4.1.9 GC-MS determination of organic extractable compounds

Liquid-liquid extraction was carried out to isolate the organic extractable compounds from WSA solution, further analyzed by GC-MS (Figure 4.6). In low severity produced fractions (200°C-2h) mainly carboxylic acids were identified. The three studied cases showed that independent from the set up temperature, analyzed compounds mostly belong to two families of compounds: 1. Acids and 2. Ketones. These are typical oxidation products for petroleum, being only small molecular weight components found in the CS₂ extracts; probably large molecular mass polar components are not soluble in CS₂.

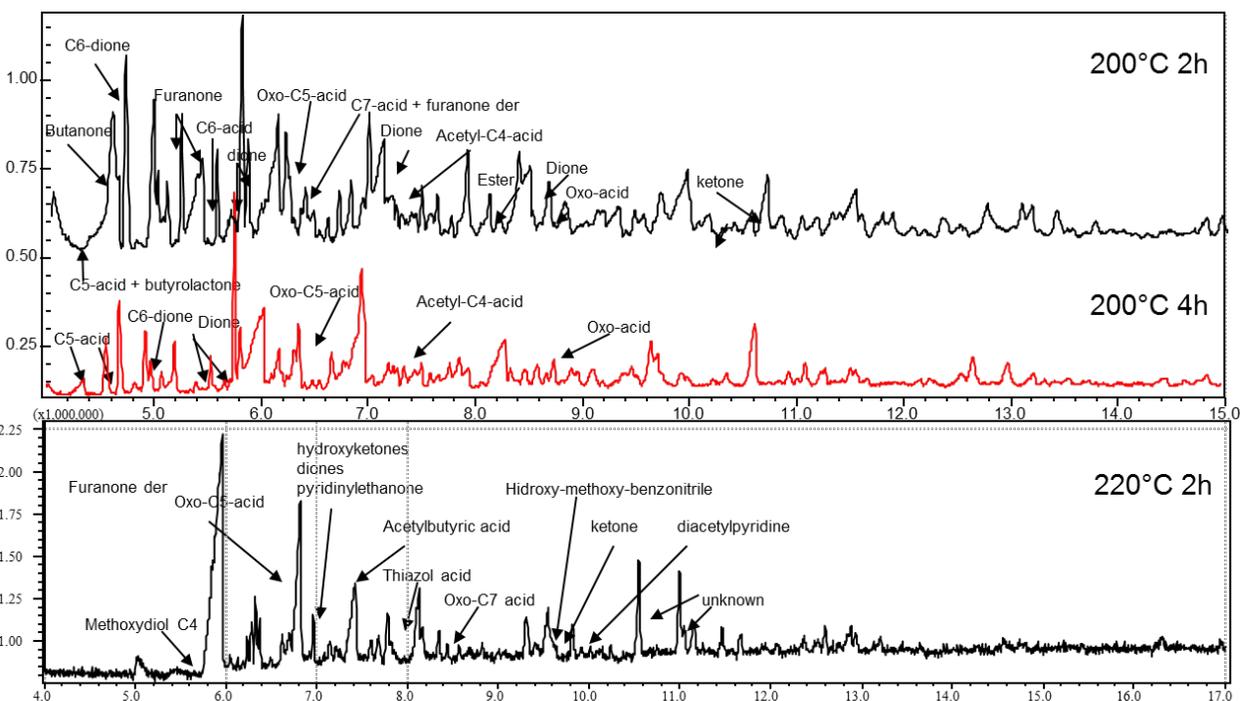


Figure 4. 6 GC-MS spectrums for organic extractable produced under different severities

4.1.10 FTIR spectroscopy

4.1.10.1 Comparison of virgin asphaltene and WISA, Humic and Fulvic Acids analogs by FTIR

Substantial amounts of oxygen and potassium are transferred to the WSA solution. In particular, oxygen increased substantially and obviously, major changes in the soluble asphaltenes structure are expected. FTIR spectrophotometry analyses were performed to identify how the oxygen is anchored in the WSA structures.

FTIR is widely used as analytical technique for characterization of oxidized hydrocarbons. In Figure 4.7 the IR spectra of virgin asphaltenes, water-soluble asphaltenes (WSA) and one sample of commercial Humic acid (Aldrich) were compared. This comparison is

carried out to find the resemblances of functional groups of commercial Humic acids with virgin asphaltenes and WSA. From the figure it can be easily found out that the IR spectrum of WSA resembles the IR spectrum of commercial Humic acid (Aldrich), being both samples enriched in oxygen functionalities and depleted in hydrocarbon signals (paraffins and aromatics) previously existing in the original virgin asphaltene. The preceding resemblance was one of the criteria selected for considering WSA fractions as analogs of humic substances, leading to a separative schematic conceived for studying humic acid and fulvic acids analogs compounding WSA fractions.

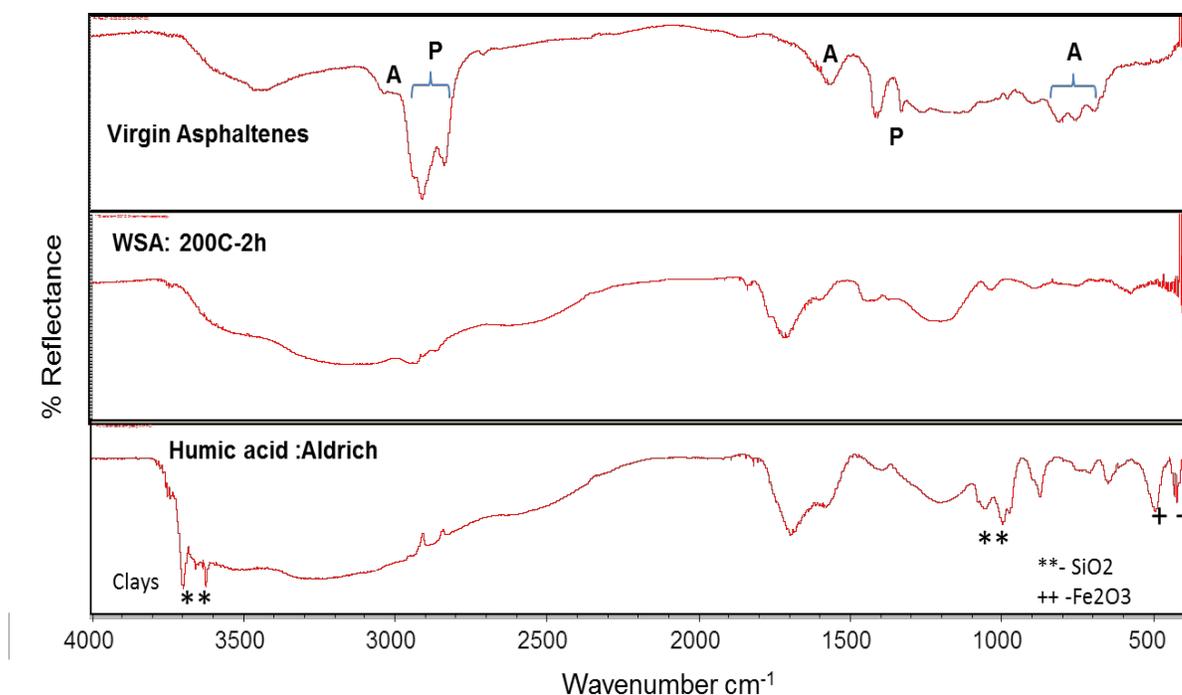


Figure 4. 7 Comparison of FTIR spectra for virgin asphaltenes, WSA obtained at 200°C-2hr (P: Paraffinic functionalities) psi and commercial HA (A: Aromatic functionalities)

Figure 4.8 illustrates the comparison between spectra of virgin asphaltenes with WISA, humic and fulvic acids analogs obtained at 200°C-2h-1000 psi. The first spectrum shows IR signals of virgin asphaltenes. Comparison of IR spectra of virgin asphaltene with IR spectra for WISA showed reduction in the alkyl bonds (C-H vibrations at 2924-2852.9 cm^{-1}) and at the same time an increase of the O-H, and O=S=O bonds (vibrations at 3200-3454 and 1138 cm^{-1} , respectively). The highlighted signal at 1700 cm^{-1} can be interpreted as C=O from acids. WISA retains some of the C-H vibration signals present in the original asphaltenes, which suggests that this solid still possesses a similar structure to the virgin asphaltenes. The third spectrum shows the IR signal of Humic acid analogs obtained at the set up conditions. We can observe that under the set-up of operational conditions Humic acid analogs still have alkyl bonds (C-H vibrations at 2924-2852.9 cm^{-1}) and acidic groups increase significantly. We can also observe that the presence of aromatic groups is significant (1600 cm^{-1}). The fourth spectrum for Fulvic acid analogs mostly contains O functional groups such as sulphonic and carboxylics. From the comparison of virgin asphaltene with WISA, humic and fulvic acids, we can conclude that aliphatics disappear, aromatics still stay in the samples, carboxylic acids increase and fulvic acid analogs mostly contains O functions.

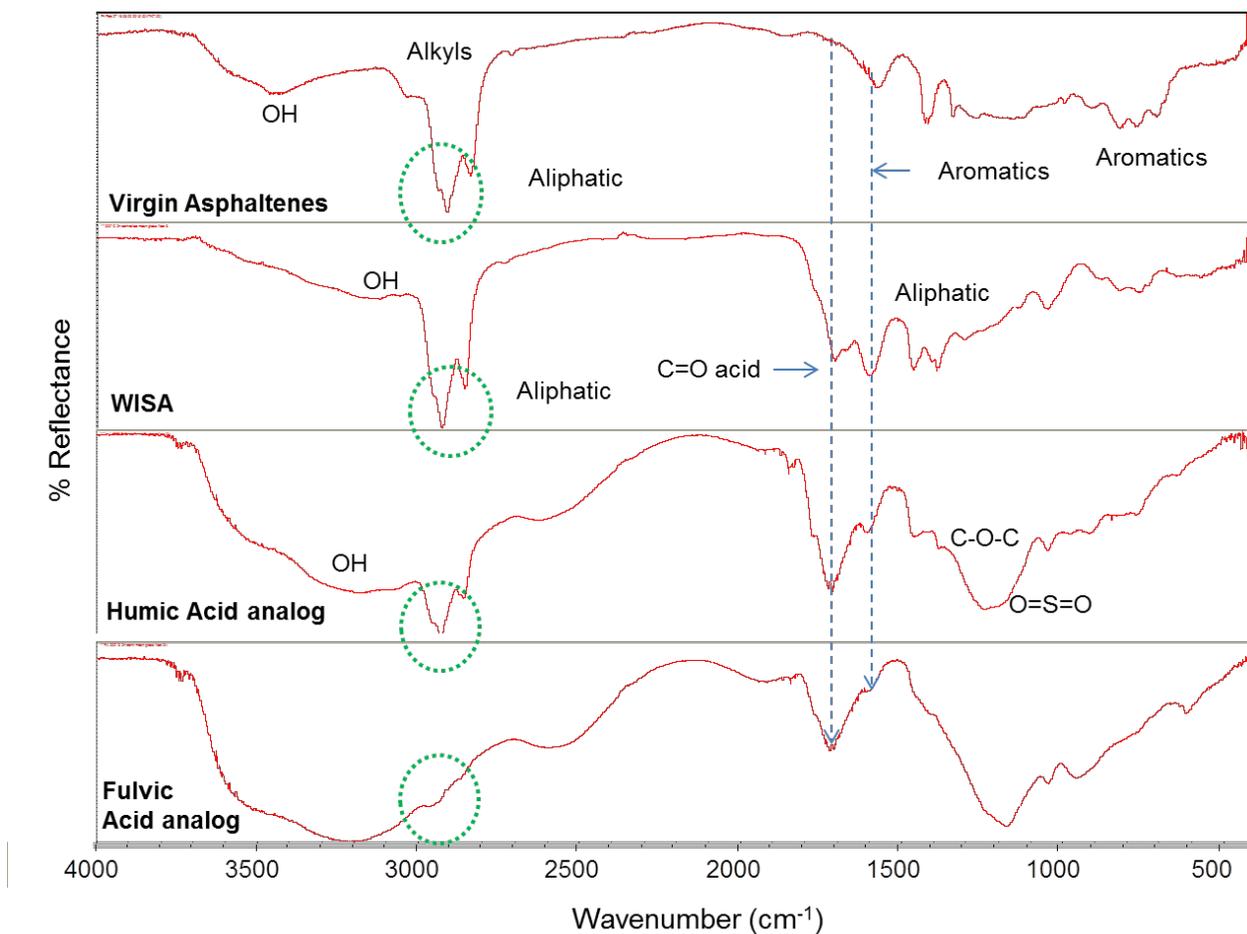


Figure 4. 8 Comparison of virgin asphaltenes and oxidation products obtained at 200°C-2hr

4.1.10.2 IR spectroscopy comparison of virgin asphaltene and WISA produced under different conditions

Figure 4.9 shows a comparison between spectra of virgin asphaltene with three different WISA obtained under three different experimental conditions. The first spectrum shows IR signals of virgin asphaltenes. The IR spectra of the WISA at different conditions show important contributions from alkyl bonds (C-H vibrations at 2924 - 2852.9 cm^{-1}) and at the same time an increase of the carboxylic (C=O) bonds (vibrations at 1700 cm^{-1}). In other words, the oxidation

has transformed the asphaltenes to mixtures containing important amounts of carboxylic acids. However, all WISA retains many of the C-H vibration signals present in the original asphaltenes, which suggests that these three solids (WISA) still have similar structures to the virgin asphaltenes but with some oxidation (may be at the surface). The presence of aromatic groups (1600 cm^{-1}) is also significant in the three-studied WISA. From the present comparison it can be concluded that OH and C=O increase, and aliphatics are approximately constant in WISA fractions.

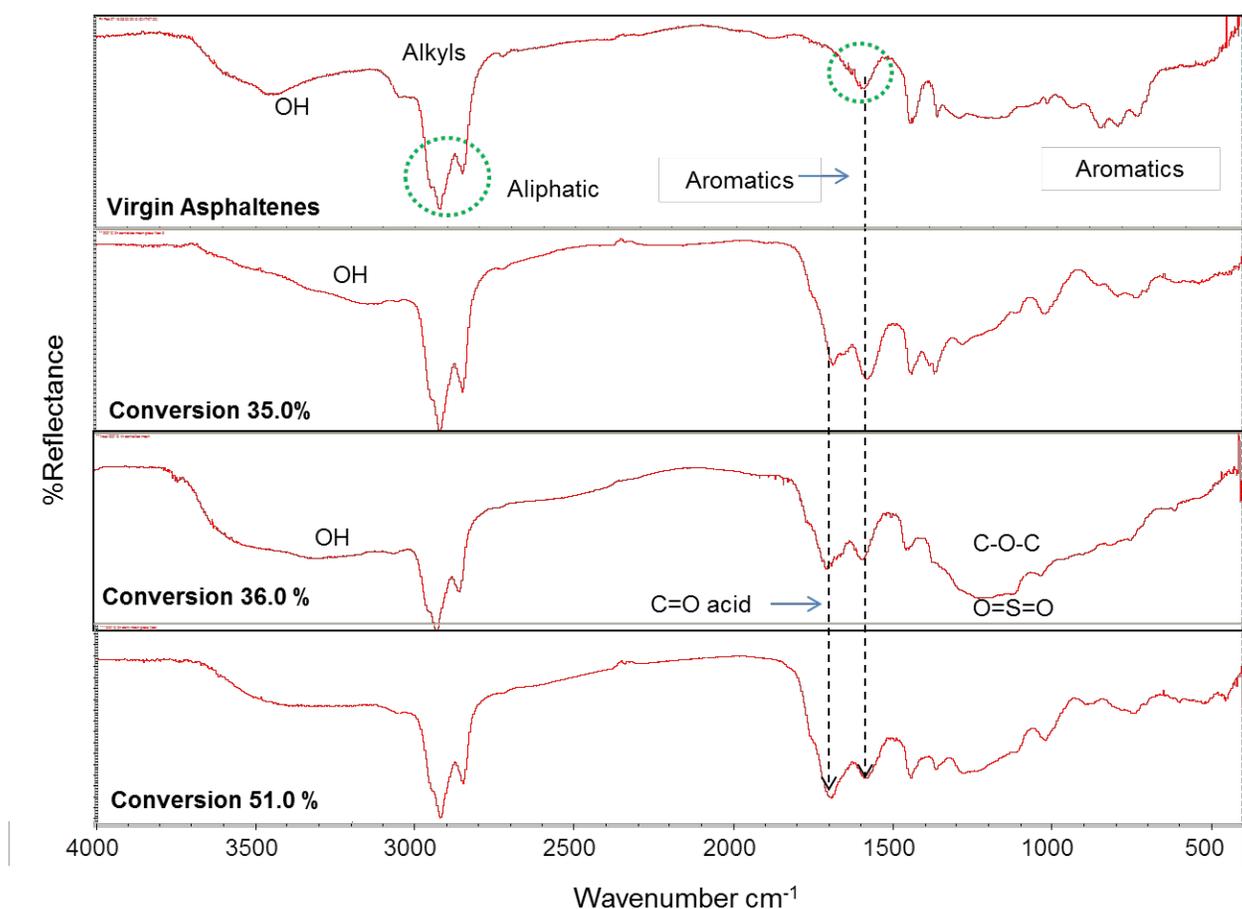


Figure 4. 9 Comparison of virgin asphaltene with three different WISA obtained at three different severities.

4.1.10.3 Comparison of Humic Acid analogs produced at different conditions vs commercial Humic acid (Aldrich)

Humic substances have been frequently studied by FTIR spectroscopy. Figure 4.10 presents a comparison between commercial humic acids (Aldrich) with three spectra of humic acid analogs obtained at three different conditions. The first spectrum shows IR signals of HA analogs produced at low conversion level (35%). IR spectra of the HA analogs obtained at this conversion show a presence the alky bonds (C-H vibrations at $2924-2852.9\text{ cm}^{-1}$), but alkyl bonds totally disappear in case of higher conversions such as 36.0% (about same as 35%) and 51%. For high conversion and high residence time experiments, no alkyl bonds were found, like in the case of commercial Humic acid; at the same time an increase in the O-H, and O=S=O bonds (vibrations at $3200-3454$ and 1138 cm^{-1} , respectively) was observed from both commercial and produced HA analogs at 51% conversion, mostly O functions are present.

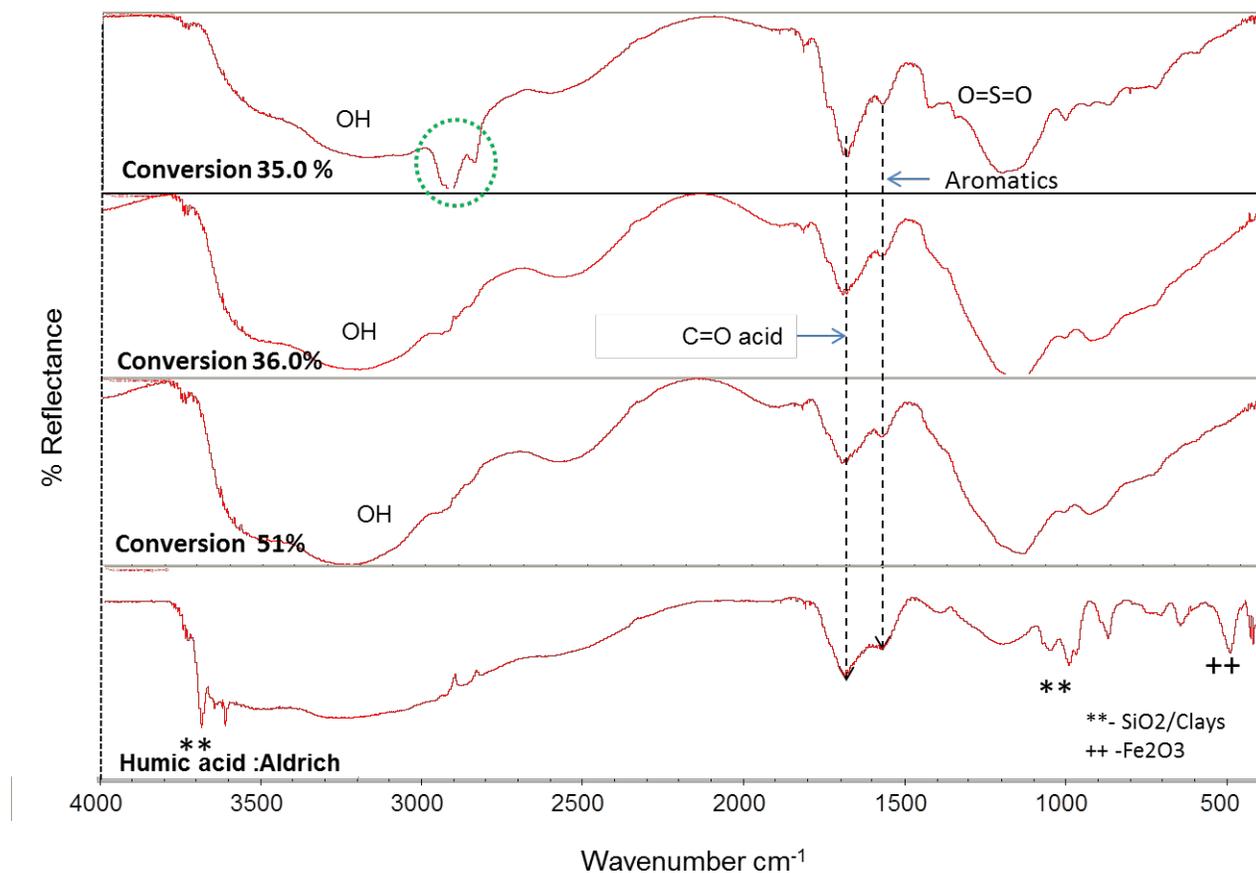


Figure 4. 10 Comparison of Humic acid analogs produced at three different conditions and one commercial HA

4.1.10.4 Comparison of Fulvic Acid analogs produced under different conditions

Figure 4.11 shows a comparison between three spectra of Fulvic acid analogs obtained at different experimental conditions. Comparison of the three different spectra shows that there is no basic difference between them, mostly O functions are visible. O functions mostly comprised hydroxyls, sulphonics and C=O groups. We also found from these spectra that aliphatics disappeared and aromatic functions survived the oxy-cracking process (1600 cm^{-1}).

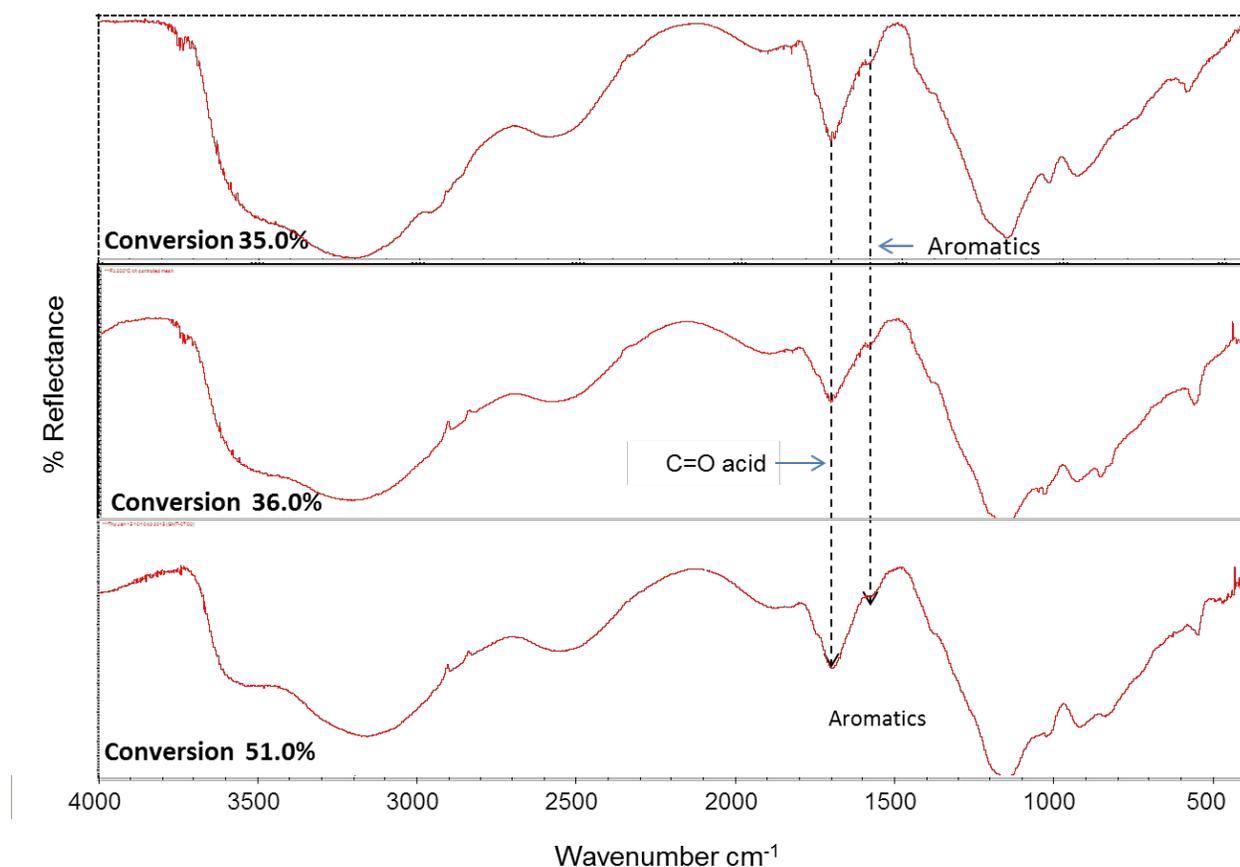


Figure 4. 11 Comparison of Fulvic acids produced at three different conditions

Above FTIR spectra for humin/ humic/fulvic analogs (Figures 4.7-4.11) concluded that, oxygen functionalities steadily increased for all fractions as a function of oxy-cracking temperature and alkyl functionalities disappeared as the temperature increased. The decreasing trend followed the decreasing order: humin > humic > fulvic analogs. In all cases, aromatic functionalities were observed to survive the oxy-cracking processing, mostly for the humin analogs. The same oxygenated functionalities were found to increase for all the studied fractions (humin / humic / fulvic analogs): -OH/ C=O (acids), esters/ lactones C=O, sulfones O=S=O. Only for the fulvic fractions, the phenolic -OH bands were observed.

4.1.11 Elemental analyses of solids obtained from WSA and WISA

The elemental compositions give further insight in to the general features of the reaction. C, H, N, O, S contents were determined for the Virgin asphaltenes and several non-soluble unconverted solids (WISA) and WSA materials using the elemental analysis technique described in section 3.2.3. The outstanding feature is the rapid and massive uptake of oxygen accompanied by a concomitant decrease in the carbon content in the oxidized products. In this stage of the reaction there are interesting differences between the solids obtained from water-soluble asphaltenes and corresponding water insoluble solids, the former being markedly higher in oxygen content, especially when long reaction times are reached. This may be interpreted in terms of a more polar water-soluble fraction enriched in oxygen. There are two main aspects worth noting from Table 4.4: the hydrogen-to-carbon atomic ratio and oxygen concentration.

The three elements (C, H, and N) are observed to decrease for all the processed samples compared to the Virgin asphaltenes. The WISA were found to have more of the three elements, compared to WSA materials. The H/C ratio decreased in the oxidized asphaltenes products (WISA and WSA), most probably due to cracking of small chains from the original structure, and consequently increasing the aromaticity of water-soluble asphaltenes. Conversely the water insoluble fraction can be regarded as the more aromatic portion, more resistant to degradative oxidation and higher, therefore, in molecular weight. Because of the complications, which were likely, to arise from highly carboxylated, highly associated mixtures, no attempt was made to measure the molecular weights of these oxidized fractions.

Table 4. 4 Elemental Analysis different components (O determined by difference)

Sample	%C	%H	%N	%O	%S	H/C
Virgin	82	8.4	1.0	3.3	5.3	1.23
WISA	69	6.2	1.0	18.2	5.6	1.08
WSA	40	4.0	1.0	39.4	5.6	1.19

4.1.12 Comparison of metal concentrations before and after WAO reaction

In Figure 4.12 ICP metal analysis compares the metal contents in asphaltene before and after WAO reaction. We could observe from the metal analysis of three different studied experiments that the amount of total Ni concentration in WISA and WSA are higher than that of virgin asphaltene in every incident. Similarly it was also found that iron (Fe) concentration increased extensively after WAO reaction compared to Fe contents in virgin asphaltenes. We are assuming that Ni and Fe is coming from the corrosion of the Parr reactor, due to acidic media existing after reaction, despite inclusion of base at the beginning of the process (As Parr reactor stainless steel 316 contains 15% of Ni and about 70% of Fe). On the other hand, vanadium (V) recovery was found lower after oxidation compared to before oxidation. However, sulfur (S) recovery after WAO was found much closer to S concentration before WAO reaction. Results indicate that Vanadium partitioned more into WSA fractions, contrary to what was observed for Ni, Fe and S.

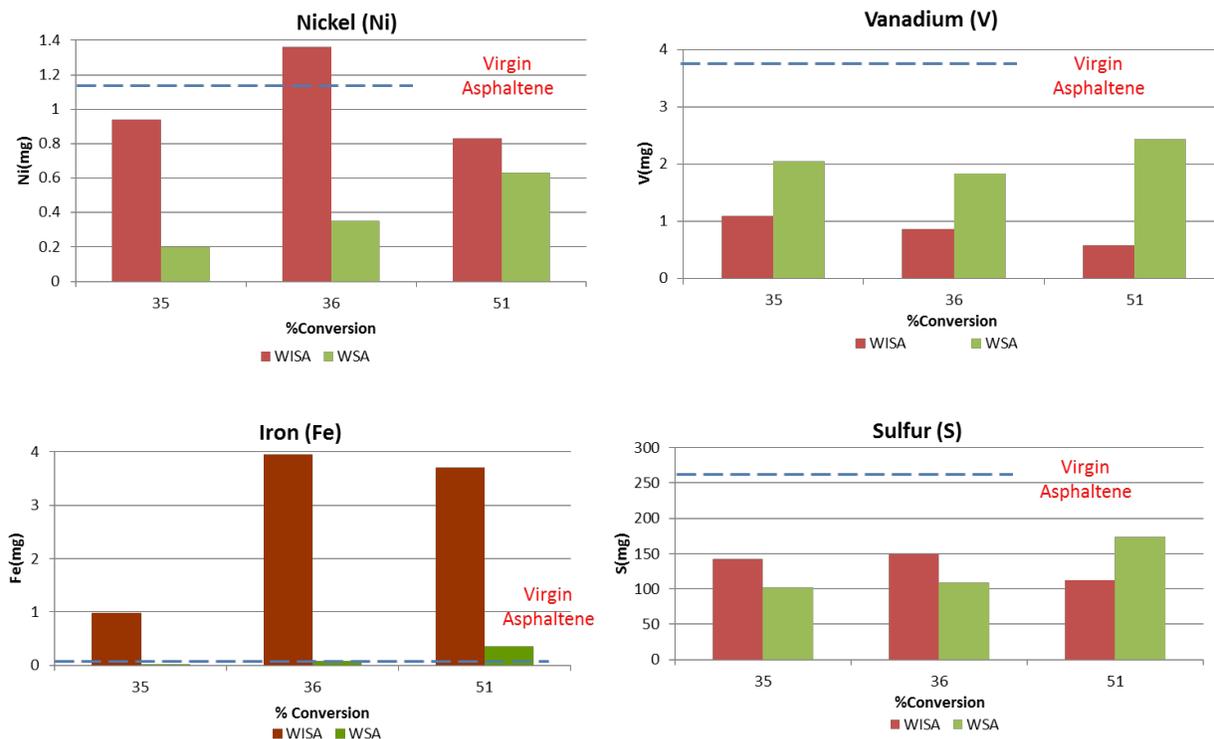


Figure 4. 12 Comparison of metal and Sulfur contents before and after WAO reaction

4.2 Conclusions

Reactions carried out at 200C-2hr-1000psi, 200C-4hr-1000psi and 220C-2hr-1000psi indicated that high severity conditions provided higher amounts of WSA + CO₂. Temperature and residence time were found to be the most important factors for optimizing oxy-cracking reactions. For having a closer look to temperature and residence time combined effects on selectivity and conversion of asphaltene oxycracking, these parameters were investigated at temperatures between 200-220 °C and residence times of 2-4 hrs. Asphaltene particle sizes did not affect this solubilization, indicating that mass transfer has a relatively insignificant impact within the range of studied conditions. Different agitation speeds were also tested at fixed reaction conditions. Higher RPM such as 500 and 1000 did not produce a significant impact on

WSA but lower RPM (250) seem to affect mass transfer control. Pressure increment could increase reaction conversion, but it does not affect selectivity considerably. To confirm proper oxidation of asphaltene molecules and asphaltene particles/ droplets mass transfer limitations in oxy-cracking, mixing rates 1000 rpm and water to asphaltene ratio equal or greater than 20 would be preferred.

The amount of oxygen consumed increases with the amount of asphaltene used, even though it is not in direct proportion to the mass. The consumed oxygen was not utilized only in converting the asphaltene to carbon dioxide and water; a good portion was converted to WSA. WSA formation implies breakage and progressive oxidation of alkane chains which disappear already above ~30% conversion with formation of oxygen functionalities. Carboxyl, carbonyl and phenolics were the main functionalities generated in WSA. To preserve alkyl chains, conversion should be kept below 30% and fast withdrawal of WSA from the reactor should be implemented. As the conversion increases, the relative amount of Fulvic acid analogs was found to increase and Humic acid analogs to decrease. The following formation pathway for WSA and derived humic and fulvic analogs is proposed based on the results discussed. Asphaltene cracked to solubilize humic and fulvic analogs in the presence of oxygen. At low severity, unconverted species and humic analogs were more abundant than the fulvic analogs. At high severity, humic analogs further cracked to form fulvic analogs, which have smaller molecular weights. CO₂ gas has been produced in every step of the reaction; this is a confirmation for oxy-cracking reactions implying initial formation of oxygenated species, which then decarboxylate. Distribution of humic and fulvic analogs comprised the presence of potassium salts (humates and fulvates), believed responsible for solubilization of these materials in water.

CHAPTER 5. EFFECT OF BASE (KOH) ON SOLUBILIZATION OF ASHPHALTENES

5.1 Introduction

In our first set of analysis we carried out WAO reaction setting up variable temperature and residence time with constant oxygen pressure (1000 psi) and comparatively fixed low pH (using 4 mL KOH). We also carried out experiments with and without using KOH, which shows alkaline solution could enhance the asphaltene solubilization. ICP metal analysis confirmed that rate of metal corrosion depends on pH of the reaction mixture. Significant amount of metals, especially Fe was found in metal analysis results, coming out from the Parr reactor, caused by high acidity of product mixtures after reaction. Our study on previous sections discovered that pH has significant effects on solubilization of asphaltenes. Since constant volume of KOH in every experiment was used it is difficult to determine the actual effects of base KOH or pH on the solubilization of asphaltenes. Moreover one of the major demerits using the previous conditions is we did not obtain sufficient amount of WSA from the first set of analysis, which was assumed to be the mixture of HA and FA acids analogs. Moreover we did not reach our goal to get sufficient amount of WSA at low and moderate temperature.

In this present set of analysis we carried out WAO reaction in different experimental conditions by varying the initial pH by using different concentration of base (KOH) and temperature. Usually oxidation takes place at high temperatures and pressures. The primary raw material and reaction products undergo continuous conversion with a change in physical and chemical properties of all components formed. The aim of this part of the study is to analyze the effect of pH on WAO of asphaltenes. The main objective is to

1) Find out suitable experimental conditions at low temperature

2) Establish reaction conditions from where the maximum amount of WSA is achieved, containing substantial amounts of HAs and FAs analogs and

3) Determine the actual effect of KOH on the solubilization and how it can reduce the metal corrosion.

Below Figure 5.1 illustrate the reaction parameters fixed or varied for this part of study.

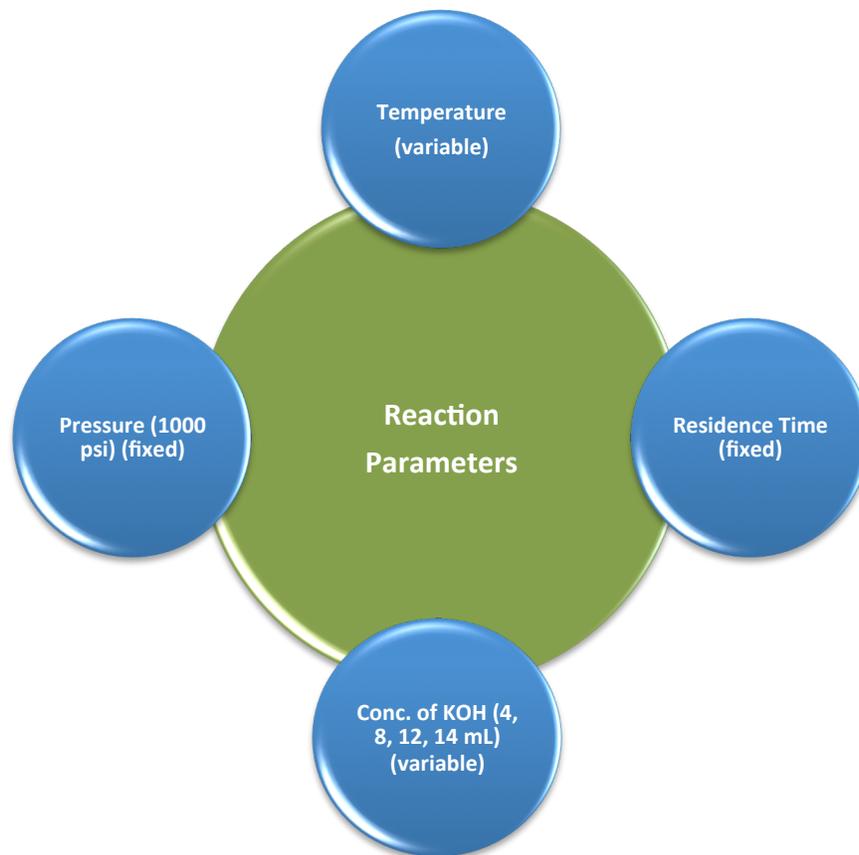


Figure 5. 1 Reaction parameters: fixed and varied for this phase of the study

5.2 Results and Discussion

5.2.1 Different experimental conditions and effects on solubilization of asphaltenes

Table 5.1 shows details of asphaltene conversion, initial and final pH of the reaction, and oxygen consumption during reactions of ten different experiments (seven new + three old experiments). From Table 5.1 we can conclude that as the temperature and residence time increase, pH of the products in WAO reaction become more acidic, O₂ consumption increases, and conversion of asphaltenes increases. Table 5.1 shows the effects of pH on the asphaltene conversion through WAO reaction. In this table we have compared the asphaltene conversion using different amount of KOH. Here we have introduced previous results so that we can easily compare the effects of pH (KOH) on the conversion of asphaltenes. It was easily observed from Table 5.1 that as the pH increased, the asphaltene conversion increases considerably. That means conversion of asphaltene not only depends on temperature, pressure and residence time but also significantly depends on pH. One of our major goals of the study was to develop WAO method, which accelerates high conversion of asphaltene at suitable low temperature.

Table 5. 1 Details of experimental condition, initial, final pH and conversions

Exp. Cond.	KOH (mL)	Initial pH	Final pH	O ₂ consumed (psia)	% C Conversion
150° C, 2 hr	14	13.2	9.2	74	77
170° C, 2 hr	14	13.2	7.5	96	81
180° C, 2 hr	4	12.7	9.0	40	35
180° C, 2 hr	14	13.2	7.0	99	92
190° C, 2 hr	14	13.2	6.6	113	97
200° C, 2 hr	4	12.5	6.2	41	36
200° C, 2 hr	8	12.7	6.2	106	92
200° C, 2 hr	12	13.0	6.5	115	99
220° C, 2 hr	4	12.3	4.6	65	51
220° C, 2 hr	12	13.0	6.6	139	97

5.2.2 Carbon mass balances

Summarized results of gas phase analysis were shown in Table 5.2, used for closing the carbon mass balance. Total carbon (TC) analyses were carried out for all the WSA fractions obtained from different experiments. The TOC analyzer was used to find the amount of soluble carbon in water after the reaction. Both organic and inorganic carbon contents were analyzed as shown in Table 5.2. It represents the values of carbon contents in three different fractions of WAO reaction separated through chemical and gas chromatography analysis. Figure 5.2 plots the carbon mass balances for different WAO reactions, indicating that the carbon mass balance is about $96\pm 2\%$. It is worth mentioning that we were not able to reach mass balance up to 100% due to mechanical and some handling limitations.

Table 5. 2 Details of carbon contents in the three fractions (WISA, WSA, & Gas phase) obtained from reactions carried out under different conditions

Exp. Condition	% Conversion	Vol of WSA (ml)	TC mg/L	Total C in 4 g of Asphaltenes	%C in WISA	% C In WSA		% Total C in Gas Phase	% C Mass Balance
						TOC	IC		
150°C-2h-14 mL KOH	77	284	7812	3.28	18.1	67.2	8.98	5.1	99.5
170°C-2h-14 mL KOH	81	425	4776	3.28	18.7	61.5	6.28	10.4	96.8
180°C-2h-14 mL KOH	92	284	7624	3.28	7.8	65.6	4.6	20.3	98.3
190°C-2h-14 mL KOH	97	265	7435	3.28	2.7	59.9	3.7	28.3	94.6
200°C-2h-8 mL KOH	92	263	6255	3.28	8.4	50	0.5	33.8	92.7
200°C-2h-12 mL KOH	99	263	6901	3.28	1.0	55.3	2.28	36.8	95.4
220°C-2h-12 mL KOH	97	300	7187	3.28	2.9	65.8	2.56	33.3	104.5

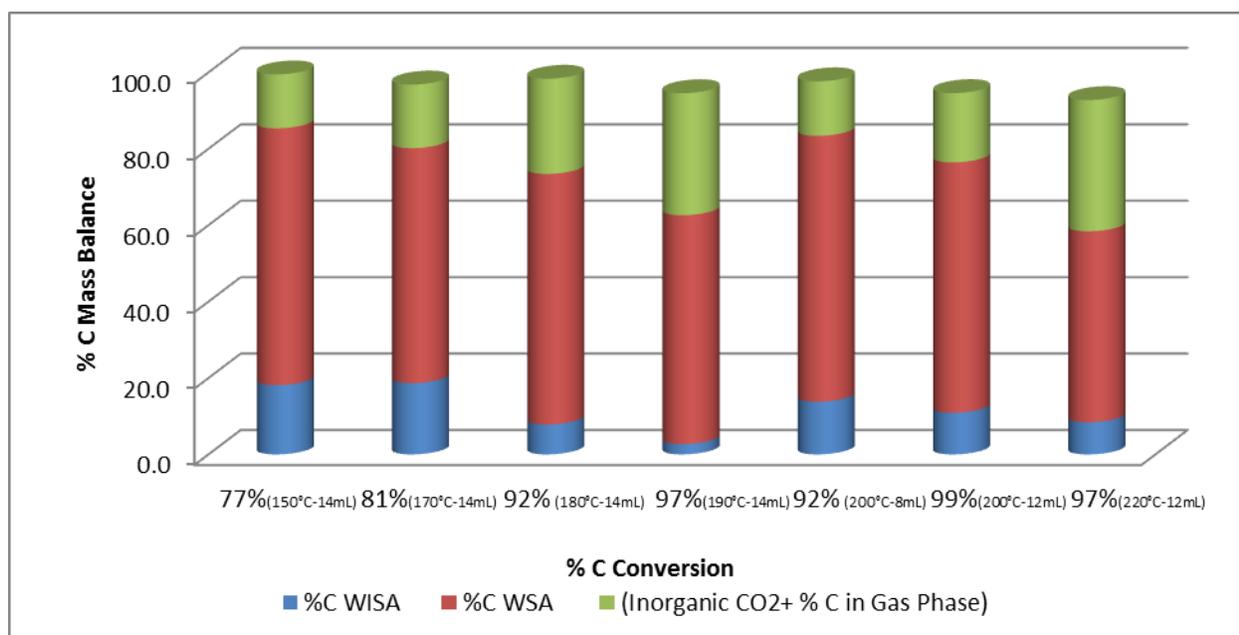


Figure 5. 2 Carbon mass balances at different experimental conditions, reaction time fixed 2h

5.2.3 Determination of total amount of solid contents in WSA

A mixture of non-reacted water insoluble asphaltenes (WISA) and soluble materials in the liquid phase (WSA) was obtained for every experiment. This liquid-solid mixture is filtered, from which a solid residue was separated (WISA) and the liquid (filtrate), which contains the above-mentioned water-soluble material we referred to as WSA. By evaporating the water from WSA solution, the total amount of solid in WSA fractions was obtained. The solid formation appears to be of practical importance in latter process application.

5.2.4 Determination of Selectivity to WSA and CO₂

In an industrial WAO process, conditions must be selected as a compromise between highest conversion and highest selectivity to WSA and lowest selectivity to CO₂. We have observed that as the conversion increases, selectivity to CO₂ increases whereas selectivity to WSA decreases. Targeting maximum production of WSA we carried out reactions at moderate or low temperatures. From Figure 5.3 we can conclude that lower severities i.e., lower temperatures and residence times are suitable for high selectivity to WSA and low selectivity to CO₂. It is concluded that as temperature and residence time increases selectivity to WSA decreases and CO₂ increases.

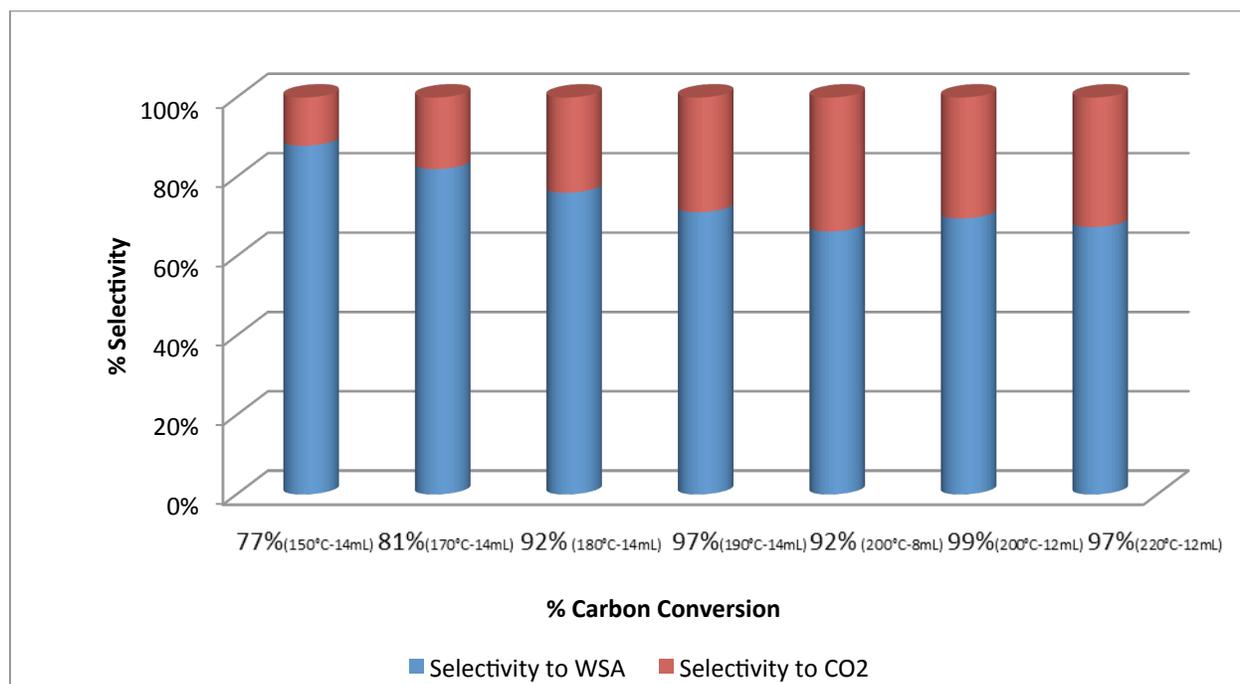


Figure 5. 3 Selectivity to WSA and selectivity to CO₂

5.2.5 Isolation and distribution of Humic and Fulvic acid analogs from WSA

Humic substances are the products derived from physical, chemical and microbiological transformation of biomolecules. Humics are divided into three main classes: Humin (alkali-insoluble), Humic acids (alkali-soluble/acid insoluble) and Fulvic acids (Alkali and acid solubles). Traditionally, fulvic and, particularly humic acids, have been considered as large molecular mass structures. As we know, HAs and FAs analogs can be water-soluble depending on the pH whereas WSA is the mixture of these two fractions. In order to separate HAs and FAs analogs from WSA solution, we followed several systematic analytical steps, which were described in section 4.1. The amounts of HAs and FAs analogs produced from different experimental conditions are shown in Table 5.3. It can be concluded from Table 5.3 that as severities (temperature and residence time of reaction) increase, the amount of FAs increase and HAs decrease. Figure 5.4 visually helps to conclude that as the conversion increases, amount of Fulvic acid analogs increase and Humic acid analogs decrease.

Table 5. 3 Amount of Humic and Fulvic analogs in different reaction conditions

Exp. Cond. (RT-2hr)	% C Conv ersion	Reactants		Products			
		KOH (g)	Asphaltene (g)	Humic K salt (g)	Fulvic K salt (g)	WISA (g)	Total CO ₂ (mg) (IC+gas phase)
150° C, 14 mL	77	3.93	4.0	2.064	5.37	0.9	10.53
170° C, 14 mL	81	3.93	4.0	1.42	6.01	0.85	14.92
180° C, 14 mL	92	3.93	4.0	1.493	5.73	0.37	20.79
190° C, 14 mL	97	3.93	4.0	0.955	6.3	0.13	26.23
200° C, 8 mL	92	2.24	4.0	0.536	5.03	0.40	25.91
200° C, 12 mL	99	3.37	4.0	0.786	5.03	0.048	27.9
220° C, 12 mL	97	3.37	4.0	0.911	5.85	0.14	29.96

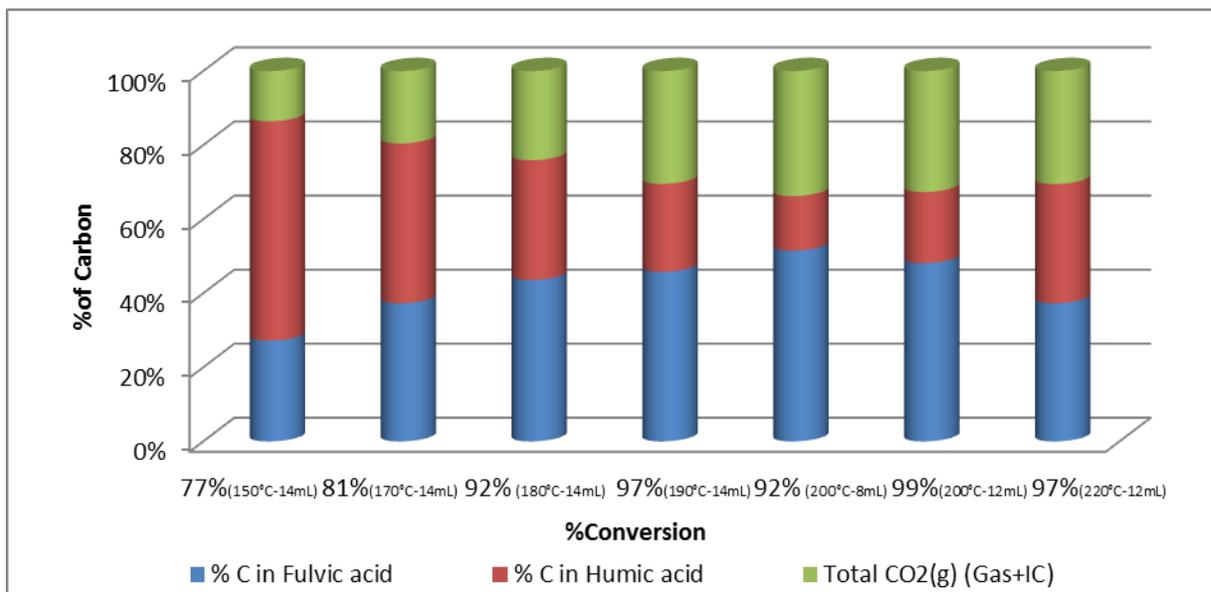


Figure 5. 4 Normalized distributions of HA and FA analogs and gas from different WAO reactions

5.2.6 IR spectroscopy comparison of virgin asphaltene and WISA at different conditions, with constant KOH (14 mL-5 N)

FTIR is the most widely used analytical technique adopted for characterization of oxidized hydrocarbons. Among the several experimental conditions, WISA obtained at three different experimental conditions (150°C-2h-1000psi-14 mL, 200°C-2h-1000psi-14 mL, 220°C-2h-1000 psi-14 mL) were analyzed. The IR spectra of the WISA at different conditions show important contributions from alkyl bonds (C-H vibrations at 2924 - 2852.9 cm^{-1}) and at the same time an increase of the C=O bonds (vibrations at 1700 cm^{-1}) and -OH centered in 3400 cm^{-1} . In other words, oxidation has introduced substantial carboxylic function over asphaltenes structures. However, all WISA retains many of the C-H vibration signals present in the original asphaltenes,

which suggests that these three solids (WISA) still display similar structures to the virgin asphaltenes (Figure 5.5). Results also suggest the significant existence of aromatic groups (1600 cm^{-1}). From the present comparison it was also observed that OH increases for lower temperature conditions whereas C=O increase for higher temperature conditions, and aliphatics were approximately constant for all experiments. Finally from the comparison of three different WISA, we can conclude that aliphatics are significant in all compound samples, aromatics still stay in the samples, carboxylic acids increase with temperature.

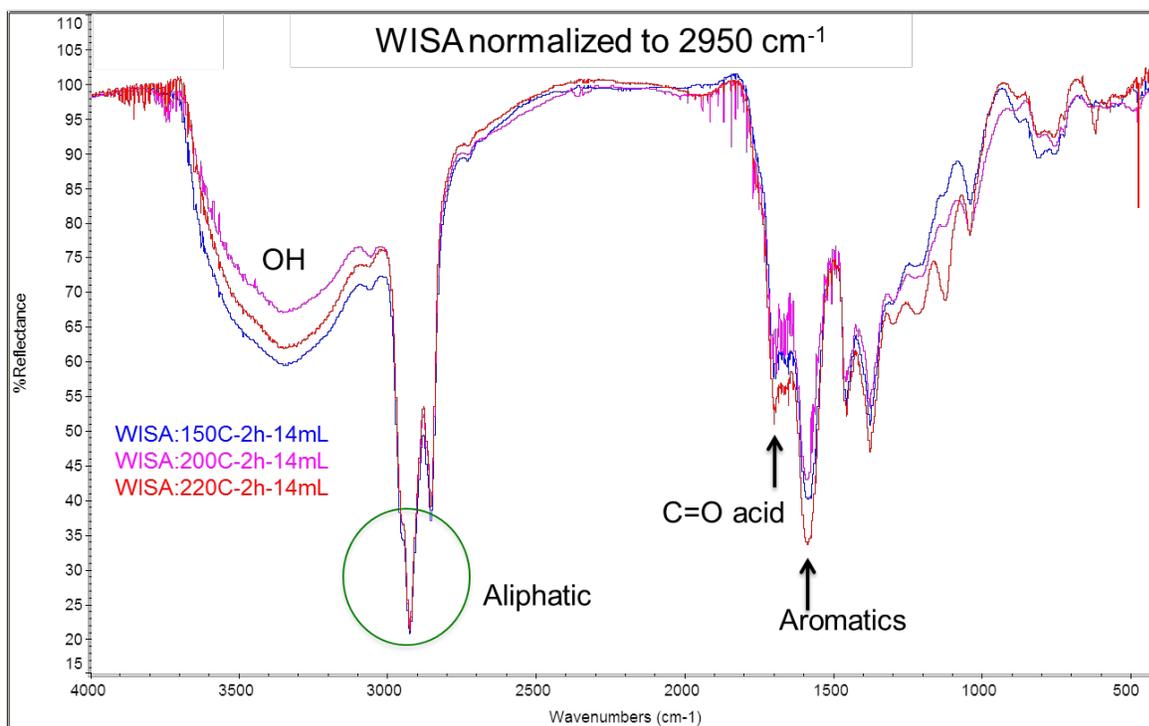


Figure 5. 5 Comparison of three different WISA obtained at three different severities

5.2.7 IR spectroscopy comparison of Humic Acid analogs obtained at different conditions, with constant KOH amount (14 mL, 5N)

Humic acid analogs obtained from different severities were studied by FTIR spectroscopy. Figure 5.6 presents the comparison between six spectra of humic acid analogs obtained at six different conditions. There were very significant differences found in the alkyl chain of HA analogs for the present set of experiments at high pH (14 mL of KOH) compared to humic acid analogs obtained under the first set of experiments at low pH (4 mL KOH). For the first set of experiments it was observed as the temperature increases alkyl bonds disappeared. But under the present experimental conditions at high pH (using a large excess of KOH), significant permanence of alkyl chains in every condition was determined. From the preceding, pH has very significant importance in alkyl chain survival under WAO processing and temperature does not affect the alkyl chain in presence of noticeable levels of the base. Aromatics were observed to contribute in all studied cases (1600 cm^{-1}). The spectra presented on Figure 5.6 shows an extra feature which is the absence of carboxylate anion bands (only those corresponding to $-\text{COOH}$ groups are present); these findings are consequence of HA analogs filtration carried out under acidic pH condition ($\text{pH}\leq 1$).

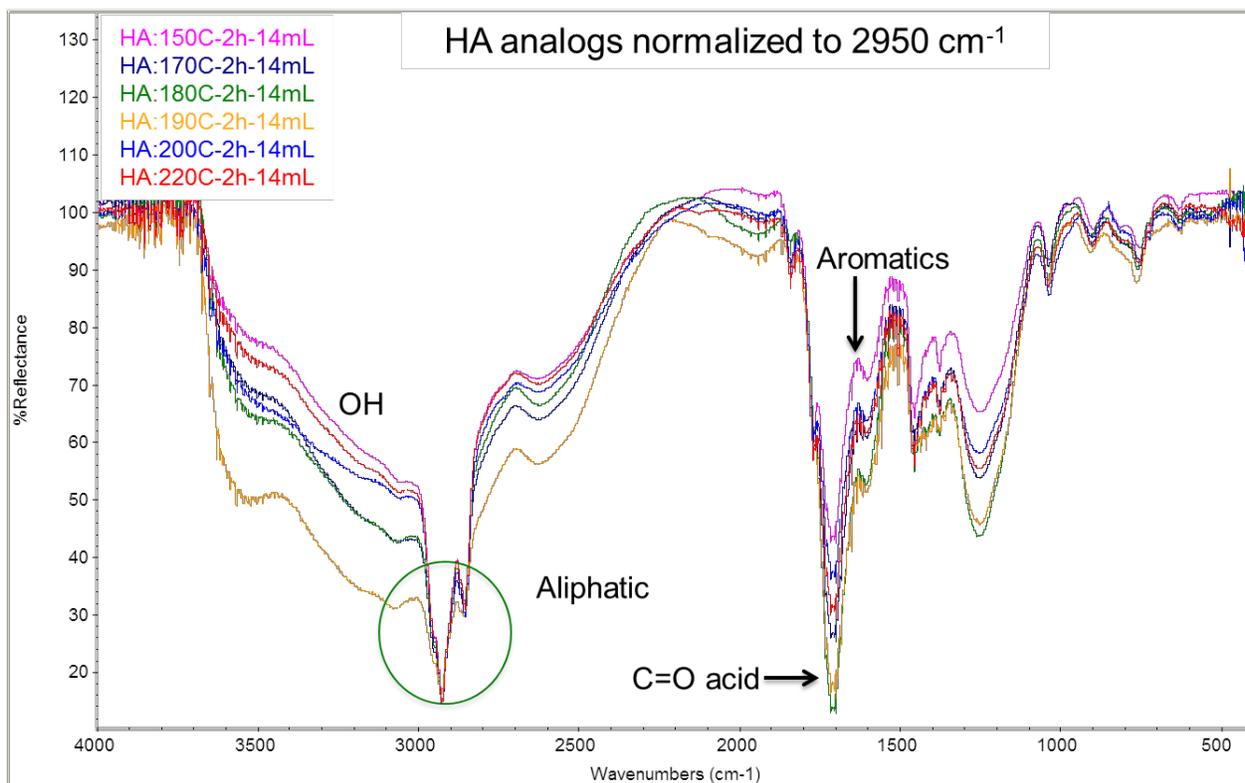


Figure 5. 6 Comparison of Humic acid analogs produced at different conditions

5.2.8 Comparison of Fulvic Acid analogs obtained at different conditions, with constant KOH amount (14 mL, 5N)

Figure 5.7 shows a comparison between spectra of Fulvic acid analogs obtained at different severities. Comparison of the different spectra shows that there was no basic difference between them. All spectra were approximately the same, mostly O functions were visible. All the spectra of fulvic acids analogs mostly contain O functions such as hydroxyls, sulphonics and C=O groups. We also found from these spectra that aliphatics totally disappeared; however, aromatic bands (1600 cm^{-1}) can be observed as shoulders to the acid C=O carbonyl (1700 cm^{-1}) in all cases after WAO reaction.

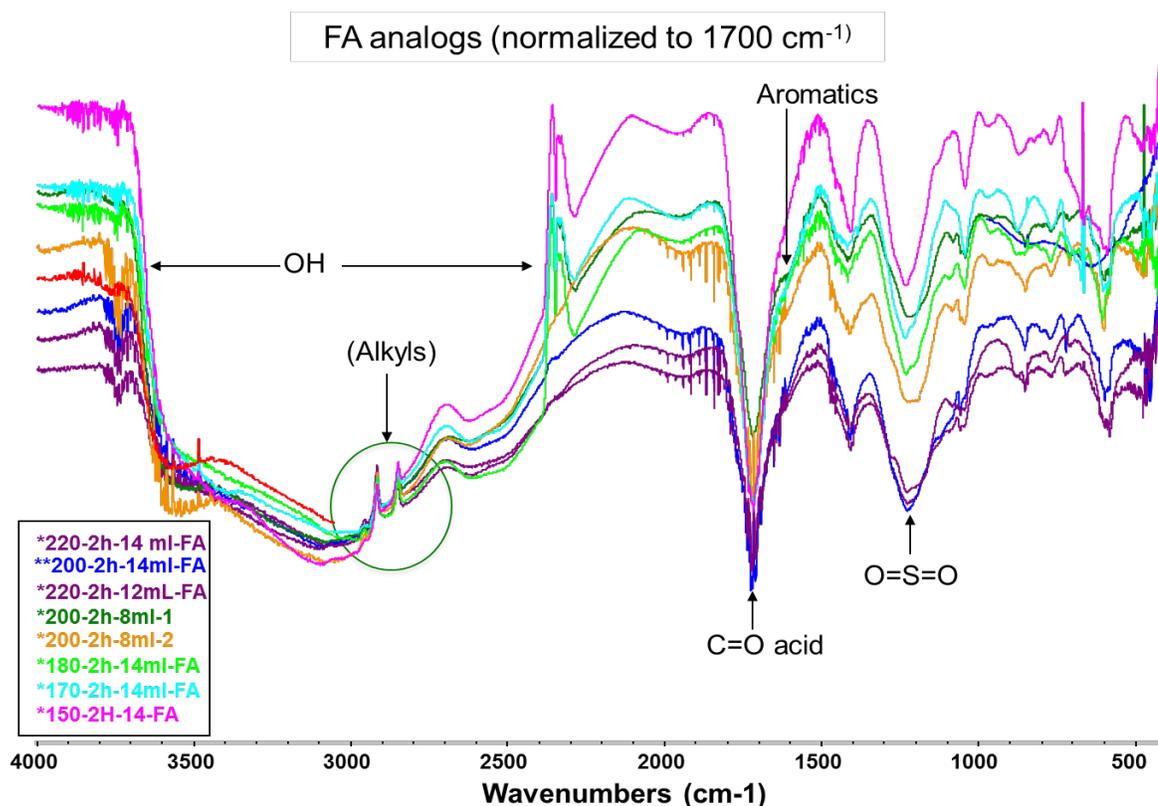


Figure 5. 7 Comparison of Fulvic acids produced at different severities

5.3 Comparison of metal concentrations before and after WAO reaction

One of the primary goals of this second set of analysis was to find out the distribution of metal components in WSA. In the first set of analysis we established that significant amount of metals (Ni, and Fe) were present in WSA solutions. Since WSA are mixtures of HA and FA analogs with feasible use as fertilizers or promoters of fertilizers, the proper presence of metal contents in these fractions is crucial for plant health and growth. To confirm the actual effects of pH on WAO reaction the metals analysis outcomes of present set of experiments at high pH (12 ml KOH), were compared with the previous set of experiments at low pH (4 ml KOH).

In the first set of experiments in Chapter 4 at low pH (4 mL KOH) we ascribed the presence of Ni and Fe excess to corrosion of the Parr reactor (As Parr reactor stainless steel 316 contains 15% of Ni and about 70% of Fe). In this present study our goal was to reduce the amount of metals in the WAO products (WSA and WISA). At high pH (using 8, 12, 14 mL KOH) was used, the excess KOH reduces the effect of acidity towards metal corrosion. Table 5.4 shows the metal concentrations analyzed by ICP for virgin asphaltenes and WAO reaction products. For the new set of experiment we have obtained that Ni concentrations selectively remained in WSA, HA and FA analogs with minimum increased levels compared to the Nickel (Ni) concentration of WAO products in first set of experiments and virgin asphaltenes. However we obtained lower levels of Fe concentrations compared to first set of experiments and virgin asphaltenes. The concentration of Fe in the first set of experiments at low pH (4 mL KOH) is more than four times greater than those derived from batch reaction at high pH (12-14 mL of KOH). Moreover, Fe concentrations were found very close to Fe in virgin asphaltenes. In addition our analysis also revealed that sulfur (S) concentration after WAO was found much closer to S concentration before WAO reaction for both cases. We were unable to compare the results for WISA at high pH (using 12 mL KOH) because of high asphaltenes conversion, which provided insufficient amount of samples for further metal analysis.

Table 5. 4 Comparison of metal contents before and after WAO reaction carried out with different amounts of base

Base Concentration	Sample	Ni (mg)	V (mg)	Fe (mg)
12 mL	Virgin Asphaltenes	0.9604	2.708	0.1592
	WISA (220°C-2h-12ml)	Insufficient amount of sample for further metal analysis because of high conversion		
	HA (220°C-2h-12ml)	0.8448	0.2616	1.225
	FA (220°C-2h-12ml) dried	0.4508	0.9982	0.0966
Total metals in the products		1.3	1.26	1.3
4 mL	Virgin Asphaltenes	0.9604	2.708	0.1592
	WISA (220°C-2h-4ml)	1.37	0.87	3.96
	WSA (220°C-2h-4ml) dried	0.37	1.83	0.0723
Total metals in the products		1.74	2.7	4.03

5.4 Conclusions

Wet air oxidation of NEXEN asphaltenes were carried out under several experimental conditions using various concentrations of KOH i.e. low to high pH (4-13). Asphaltenes are the heaviest and most polar fractions of heavy oil and bitumen having high molecular weight. In their structure, alkyl and naphthene-aromatic hydrocarbons and their sulfur and nitrogen derivatives are assembled together by covalent bonds.

Optimized operating conditions for maximizing WSA production were identified (temperature: 150-220 °C, residence time=2hr). The results showed that at less severe conditions, WSA had characteristics close to humic analogs; but with increasing reaction severity, products aromaticity increased and lower molecular weight components (fulvic analogs) were formed. In low severity oxy-cracking, organic humic type materials, inorganics and little amounts of CO₂, SO_x and NO_x are produced, but in high severity, most of the feed is converted to CO₂, SO_x and NO_x. Organic humic type materials could be carboxylic acids, ketones, phenolics and sulfonic acids. The comparison between WSA, humin, humic and fulvic analogs showed that aliphatic bands were still present in humic and humin analogs. The remaining solids after reaction resemble the virgin asphaltenes, however, these were found to contain potassium salts. In presence of KOH, these compounds converted to their salts and become soluble in water. Most inorganic compounds are acids, which are soluble in water themselves, but the primary purpose of KOH presence is to prevent corrosive destruction of the steel made reactor. Thus, acidic components convert to salts, which are soluble in water.

The effect of pH (base) on oxidation of asphaltene was determined in different experimental conditions and it was found that pH is the most influential parameter for the wet air oxidation to obtain high conversion of asphaltene at low temperature. Focusing on maximizing the amount of WSA at reasonable operating conditions, the results showed that lower reaction temperature and low residence time would work better for this purpose. An optimum set of operating conditions, under the studied range of variables, was found at 150°C-2 h (at high pH using 14 mL KOH). A significant proportion (77%) of asphaltenes was solubilized in water during the process of WAO at this condition. The results confirm that at lower temperatures

more WSA was produced and more CO₂ was formed at higher temperatures. The pH can affect the solubility of a solute in two ways. One of these is through the common ion effect. Upon the addition of KOH, for instance, the pH of the solution will increase. As the pH value increase, the interface stability of asphaltene builds up, which keep the emulsion strength. And H⁺, OH⁻ and the heteroatoms like S, N, and O in asphaltene, reacts, which makes the interfacial tension decrease. At the same time, the change of pH value can affect the ionization degree of asphaltene. This will alter the surface activity and at last influence the stability of the system. Many weakly soluble compounds have solubility, which depend on the pH of the solution. A direct example is hydroxides since the OH⁻ ion is directly involved in the equilibrium constant.

FTIR results of WISA at different severities showed important contributions from alkyl bonds (C-H vibrations at 2924-2852.9 cm⁻¹), at the same time an increase of the C=O bonds (vibrations at 1700 cm⁻¹) and -OH centered in 3400 cm⁻¹. FTIR results also suggest that WISA still display similar structures to the virgin asphaltenes. There was a very significant difference found in alkyl chains abundances of HA analogs using different pH (concentration of KOH). Under the present experimental conditions using high pH (14 mL of KOH), significant permanence of alkyl chains in every condition was determined. The pH has very significant importance in alkyl chain survival under WAO processing even at very high temperature. Comparison of the different spectra of FA analogs shows that there was no basic difference between them. All spectra were approximately the same, mostly O functions were visible. All the spectra of fulvic acids analogs mostly contain O functions such as hydroxyls, sulphonics and C=O groups. From the ICP metal analysis results it was observed that metal concentration in

WAO products obtained with high pH (12 mL KOH) reduced considerably compared to the results obtained using low pH (4 mL of KOH). These new results suggest that pH (excess amount of KOH) reduced the corrosion of the Parr reactor walls.

CHAPTER 6. FINAL REMARKS AND CONTRIBUTIONS OF THIS STUDY

Oxy-cracking of asphaltenes carried out in aqueous phase with base, forming analogs of humic substances, which can have application as co fertilizers in agriculture. A new feasible pathway for asphaltenes conversion into other chemicals such as humic and fulvic acids was explored based on oxy-cracking reaction. This research focused on a new technique endeavoring a better utilization of asphaltenes and yield valuable products such as WSA, mixture of HA and FA analogs. The intermediate product of asphaltenes oxy-cracking reaction is WISA, WSA, and the final product is CO₂. Scission reactions (cracking) were evidenced to occur leading to WSA products, which showed to have higher carbon aromaticities compared to the original feedstock. This innovative concept was assessed using different analytical techniques, changing operational conditions and analyzing various materials aiming to demonstrate the feasibility of the whole process. The conceived novel process comprised three basic steps: asphaltenes solubilization in alkaline water, separation of HA and FA analogs from the solubilized asphaltenes (WSA) and identification and quantification of the HA and FA analogs using different techniques.

Water-soluble asphaltenes were successfully produced setting up different severities. Reaction conditions and production of WSA were studied under a selected range of operating parameters. It was found that oxidation temperature; pH and residence time has pronounced effects on WSA production. Asphaltenes particle sizes within the range studied do not remarkably affect their solubilization or their conversion to CO₂, indicating mass transfer has a relatively minor impact within the range of conditions studied. Different stirring speeds were tested at fixed reaction conditions. Higher stirring rates (500 and 1000 rpm) do not produce a noticeable impact on WSA production. On the other hand, lower stirring rate (250 rpm) seems to

be affected by mass transfer control.

The effect of pH (base) on oxidation of asphaltenes was determined in different experimental conditions and it was proven that pH (concentration of base) is the most influential parameter for the wet air oxidation to achieve high conversion of asphaltene at low temperature. The quantity of WSA produced not only depends on temperature but also significantly depends on the pH (volume of base KOH) of the reaction mixture. Results showed that low to moderate temperature, high pressure and comparatively high pH increased the amount of WSA production significantly. Moreover production of oxidized functionalities like carboxylic acids, their salts, methyl ethers and esters; sulfur-oxidized forms plus phenolics were determined as the most significant fractions soluble in water. It was also established that the use of excess amount of KOH reduced the reactor's metal corrosion noticeably. Focusing on maximizing the amount of water-soluble asphaltenes (WSA) at reasonable operating conditions, the results at 150°C-2hr at high pH show that lower reaction temperature will work better for this purpose. A significant proportion (77%) of asphaltenes was solubilized in water during the process of WAO at this low severity. HA analogs were found the most abundant under low temperature conditions. It was also observed that with temperature increase HA analogs decreased whereas FA analogs increased.

FTIR results of WISA at different conditions showed important contributions from alkyl bonds (C-H vibrations at 2924-2852.9 cm^{-1}), at the same time an increase of the C=O bonds (vibrations at 1700 cm^{-1}) and -OH centered in 3400 cm^{-1} . Using 8-14 mL of KOH, significant permanence of alkyl chains in every condition was determined, findings not observed when

using 4 mL of KOH. KOH has very significant importance in alkyl chain survival under WAO processing; temperature affects alkyl chains abundance in presence of higher levels of the base to lower extents. Comparison of the different spectra of FA analogs showed that there was no basic difference between them, mostly containing O functions such as hydroxyls, sulphonics and C=O groups.

One of the main goals of this part of the study was to lower the amount of metals in WSA, which are mixtures of HAs and FAs analogs. Lowering the amount of metals in WSA is essential for plant health and growth. Metal concentrations in WSA produced with high pH i.e. 12-13 (8-14 mL of KOH) reduced significantly compared to the results obtained using pH at 4 (4 mL of KOH). These results also suggest that excess amount of KOH reduced the corrosion of the batch reactor.

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