Influence of Acid/Base Treatment on Bitumen Viscosity

by

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ABSTRACT

Canadian oil sands derived bitumen is a form of petroleum that has a high density and viscosity. One of the potential causes of the high viscosity of the oil sands bitumen is acid-base interactions. The main purpose of this project was to determine the influence of acid treatment and base treatment as potential low temperature upgrading strategies on physical properties, chemical composition and morphology of bitumen.

The working hypothesis was that bitumen viscosity could be decreased by disrupting acid-base interactions. The study was performed by treating Cold Lake bitumen with aqueous solutions of hydrochloric acid (in the range 0.0003-0.3 M), lithium hydroxide (0.003 N) and ethanolamine (0.003 N). Time and temperature were controlled parameters and were kept constant. In most experiments three product phases were observed and separated: an organic phase, an emulsion phase and an aqueous phase. The analyses of treated bitumen included measurements of viscosity, density and refractive index; determination of asphaltenes content, mass balance, Fourier Transform Infrared (FT-IR) spectroscopic analysis, ^{1}H Nuclear Magnetic Resonance (NMR) analysis and Atomic Force Microscopy analysis (AFM). The aqueous solutions were analyzed by Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) and pH analysis. Selected analyses were also performed on the emulsion phase.

Five variables in the experimental protocol were identified that had an influence on the viscosity of the treated bitumen: heating, oxidation, concentration, residual solvent (methylene chloride) and the presence of an emulsion. As part of the investigation the sample workup protocol for bitumen was revised to address the influence of these variables.

The results showed that the acid treatment and base treatment may disrupt some chemical interactions in the bitumen that also may affect physical properties such as the viscosity and density. The blank experiments (water treatment) indicated acid-base interactions may be relevant even at neutral pH. The viscosity (measured at 40 °C and corrected for residual solvent) of raw bitumen, LiOH treated bitumen and ethanolamine treated bitumen were 97.5, 15.0, and 26.4 Pa.s respectively. The extent of viscosity reduction was influenced in a similar way when a strong base (LiOH) was used compared to a strong acid (HCl), but base treatment was more prone to emulsion formation. The change of bitumen morphology after acid treatment without heating showed the disaggregation of clustered asphalthenes and other aggregating species, which correlated with the viscosity reduction. This investigation also suggested that bitumen viscosity was influenced more by acid-base interactions than hydrogen bonding.

Keywords: Oil sands bitumen, viscosity, acid treatment, base treatment, hydrochloric acid, ethanolamine, lithium hydroxide.

DEDICATION

To God. “God awards the victory to perseverance and work”
To my mother, for all her love and support.

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CHAPTER 1- INTRODUCTION TO ACID/BASE TREATMENT ON BITUMEN VISCOSITY

1.1 Background

Canada has one of the major oil sands derived bitumen deposits in the world. The majority of the Canadian oil sands are in the province of Alberta [1]. On the other hand, Venezuela has the largest reserves of heavy oil and extra heavy oil located in the Orinoco Oil Belt. The two countries' reserves account for approximately 3.6 trillion barrels of bitumen and heavy oil in place [2]. The rate of world energy consumption has increased during the last years in which the medium / light crude oil resources have continually decreased. So, oil sands derived bitumen, heavy oil and extra heavy oil are a vital source of energy. This is the feed material of interest in the present study.

The Canadian oil sands are complex multiphase systems consisting mainly of bitumen, sand, and water. Bitumen is the heaviest kind of petroleum and it is defined as an oil with a viscosity higher than 10^4 mPa·s and an American Petroleum Institute (API) gravity of less than 10 degrees, i.e. >1000 kg·m^{-3} [3]. Bitumen chemistry is very complex. The hydrocarbon portion consists of carbon (80-88 wt%), and hydrogen (8-12 wt%) with a hydrogen to carbon molar ratio (H/C) around 1.5 [4]. Therefore, the production and upgrading of oil sands bitumen involves more demanding methods for upgrading than needed for conventional crude oil [5]. This is part of the challenge addressed by this work.

Upgrading comprises the processes used by refiners to improve the quality of heavy oil and bitumen; or the heavy fraction of crude oils [6]. Heavy oil, extra-heavy oil, and bitumen have the following general properties: high density (low API gravity), high viscosity, high boiling point, high Conradson carbon residue (CCR) and ash content, low hydrogen and carbon (H/C) ratio, high heteroatom (nitrogen, oxygen, sulfur, and metals) content and high content of asphaltenes. Hence, upgrading is required to convert heavy oil and bitumen into more valuable products, or to become a suitable feedstock for a conventional oil refinery [5].

One of the main challenges in upgrading of oil sands bitumen is it poor fluidity and raw bitumen can best be described as a very viscous, viscoelastic liquid at room temperature [4]. In order to be suitable for pipeline transport, the fluidity of the bitumen must be improved so that it can be pumped easily. Two approaches are mainly employed. Firstly, dilution with a solvent reduces the bitumen viscosity. The diluents industrially used are petroleum-derived naphtha and natural gas condensates that are added to meet Canadian pipeline specifications: 0.33 Pa.s at 7.5 °C [7]. A mixture of 25:75 diluent and bitumen can be transported by pipeline, which is denominated 'dilbit', or diluted bitumen [1]. Secondly, upgrading technologies can be employed for viscosity reduction of bitumen, such as visbreaking, coking and hydroconversion [8]. The work presented follows an upgrading approach to fluidity improvement in bitumen.

1.2 Hypotheses

Recently research was carried out at the University of Alberta to study the thermal cracking behavior of oil sands bitumen by low temperature visbreaking [9]. Four temperatures were evaluated: 340 °C, 360 °C, 380 °C and 400 °C. The results showed that viscosity reduction of bitumen does not follow a regular and monotonic decrease. So, the research indicated that not only C-C bond breaking, but other interactions also influenced to the observed viscosity of bitumen [10].

It was postulated that one of the potential interactions that could affect bitumen viscosity is intermolecular acid-base interactions. This is the topic of the present study, which researched the change in viscosity of bitumen through the modification of raw bitumen by acid and base treatments. Acid treatment was performed using dilute hydrochloric acid (HCl). Two different bases were employed for the base treatment: lithium hydroxide (LiOH) and ethanolamine ($HOCH_2CH_2NH_2$). The main working hypotheses were:

- The acid treatment may disrupt chemical interactions in the bitumen that also may affect the physical properties, such as the viscosity. For instance, it is postulated that in bitumen, not all carboxyl groups are free, as some are linked with metal ions. These ions can be easily removed when washed by treating the bitumen with a low concentration aqueous solution of acid [11].

- Base treatment may be complimentary to acid treatment. If the effect of acid treatment was to disrupt just acid-base interactions, then it should in principle be possible to achieve the same by base treatment. Deactivation of acidic or basic groups can be achieved by converting them into their corresponding salts. A stronger base, LiOH, could disrupt strong acid-base interactions and the extent of Li^+ incorporation in the product would be indicative of the extent of acid-base interaction. Ethanolamine is a weaker base and would disrupt only weak acid-base interactions.
- If acid groups are primarily responsible for hydrogen bonding to cause aggregation and high viscosity, rather than acid-base interactions, then base treatment should improve viscosity more than acid treatment. Only base treatment will remove polar hydrogen through the neutralization reaction.
- Physical mechanisms or mechanisms that include weak chemical interactions could be disrupted with acid and base treatment. Such as, disaggregation of clustered asphaltenes and other aggregating species, the release of trapped material and/or a potential decrease in the boundary layer volume around the aggregates, whose effect would be the viscosity reduction [7].
- In the work-up procedure of acid/base treatment on bitumen, some variables could affect the observed viscosity values of bitumen. These variables possibly can be the following: heating, oxidation, the impact of the solvent methylene chloride and emulsion formation.
- In addition to the viscosity of bitumen, acid/base treatment could also affect other physical properties, the chemical composition of bitumen and result in morphological changes in the bitumen.

1.3 Objectives and scope of work

The main objective of this project was to investigate the response of bitumen viscosity to treatment using acid-base chemistry. In order to evaluate the working hypotheses, the scope of the work was the following:

First of all, the literature of bitumen was reviewed (Chapter 2), in this Chapter the approach was to investigate the acid and base treatments on the bitumen and factors that affect bitumen viscosity. In the first section, oil sands derived bitumen is discussed in order to know the origin of feed material that is used in this research. In the second section, the chemistry of bitumen is explained in detail with special emphasis on chemical composition and structure to understand the processes and variables could affect its chemistry. In the third and fourth sections, different publications that describe the studies of acid and base treatments of bitumen are reviewed. Finally, the last section describes the bitumen viscosity, focused the relationships between the structure and the rheological properties and the effect of water in oil (W/O) and oil in water (O/W) emulsions on viscosity.

The experimental investigation was started with influence of the acid treatment on bitumen viscosity, where chemical composition of bitumen and changes of morphology of bitumen were studied by acid treatment (Chapter 3). The impact of solvent methylene chloride and emulsion formation over bitumen after acid treatment was studied in the Chapter 4. Then, the effect of base treatment on bitumen properties, such as viscosity, was investigated in Chapter 5 and compared its effect with the acid treatment. Finally, conclusions and recommendations were described in Chapter 6.

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CHAPTER 2 – LITERATURE REVIEW ON ACID/BASE TREATMENT ON BITUMEN VISCOSITY

2.1 Oil sands derived bitumen

The major oil sands derived bitumen deposits are in Canada [1]. The Western Canadian Sedimentary Basin contains large reserves of gas, oil and bitumen. It comprises areas of the following Provinces: the Northeastern corner of British Columbia, basically all of Alberta, southern Saskatchewan and southern Manitoba. The oil sands derived bitumen deposits are all located in Alberta which are congregated into three geographic areas: Athabasca (Wabasca), Peace River and Cold Lake [2,3].

The production and upgrading involves more complex technologies and methods than needed for conventional crude oil [2]. Oil sands are complex multiphase systems consisting mainly of bitumen, sand, fines, colloids, clay organics, salts and water (Figure 2-1). The majority of oil sands are hard rocks where the unconsolidated clastic sand grains are cemented together with the bitumen. The sand collapses if the bitumen is removed by dissolution in a solvent; such as, benzene, toluene, methylene chloride, among others [3].

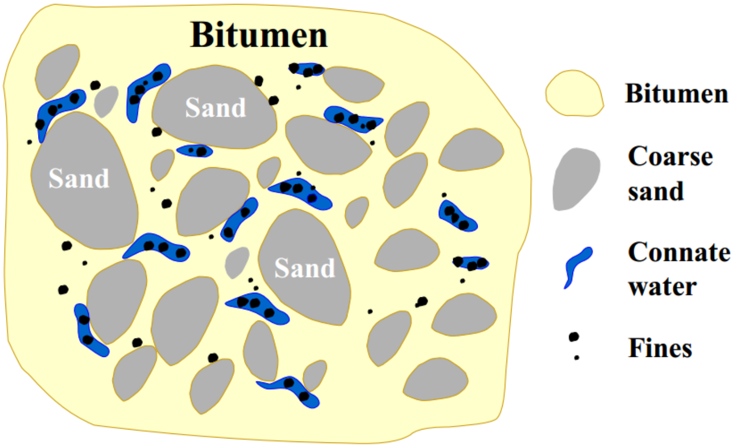


Figure 2-1: Representation of oil sands [4].

2.1.1 Extraction of bitumen from Canadian oil sands

2.1.1.1 Mining Operations

Shallow formations are produced by mining the oil sand. The mining operations in Alberta Province are unique for the production of petroleum. The profitable production of bitumen from the mineable oil sands is the product of various years of development and innovation. The operation consists of the following steps: Firstly, mining to remove the ore for processing. Secondly, extraction to remove the bitumen from the ore, it is recovered by flotation with warm water. Then, the resulting froth of bitumen, water and fine solids is cleaned after dilution with solvent to reduce the viscosity. Two principal solvents are used in processing, naphtha and paraffinic solvent such as n-hexane. Finally, the bitumen produced from the oilsands is upgraded by several technologies; for example, visbreaking, coking and hydroconversion. Figure 2-2 shows each stage and material balance for a typical mining operation [2].

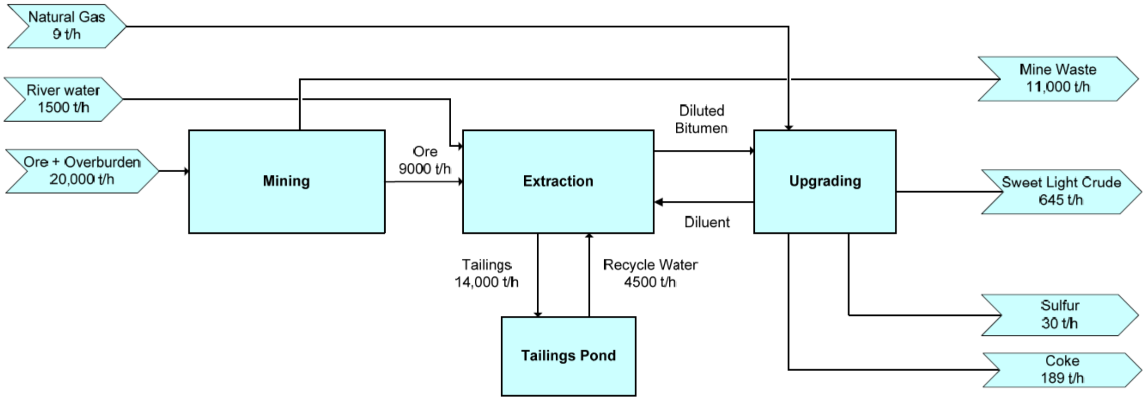


Figure 2-2: Stages and material balance for a general mining operation [2].

2.1.1.2 In Situ Production

There are several technologies of In Situ Production. Steam injection is one technology used to produce deeper formations from vertical wells or horizontal wells. It is a thermal production method because the steam injection increases the temperature of the petroleum, decreasing its viscosity. The steam assisted gravity drainage (SAGD) process is used for horizontal wells where steam is injected in the injector well into extended segments of an oilsands formation (up to 1 km long). A steam chamber is formed into the formation when steam rises from the injection well and condenses, washing warm bitumen down with condensed water. A second horizontal well (producer well) is located 3-5 m under the injection well in which the liquids are drawn off. This geometry allows gravity to drain the bitumen to the lower well where it is produced. The fluid in the producer well passes to a surface facility where the bitumen, steam condensate, produced water and gases are separated and processed [2, 4, 5]. Figure 2-3 shows SAGD process [4].

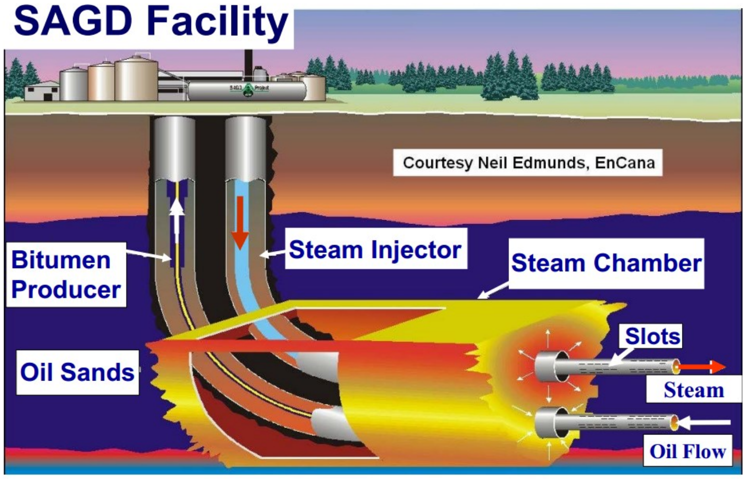


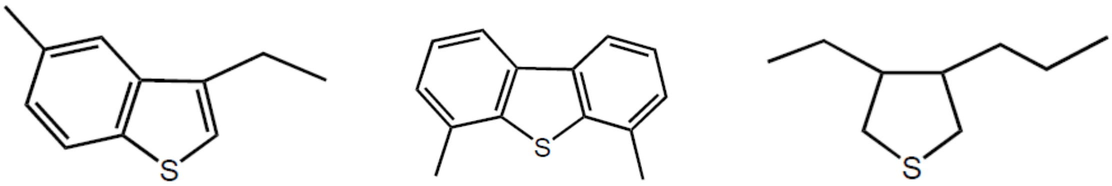
Figure 2-3: SAGD process [4].

2.2 Bitumen Chemistry

The chemistry of bitumen is very complex. When viewed as a hydrocarbon, it contains carbon (80-88 wt%) and hydrogen (8-12 wt%) with an hydrogen to carbon molar ratio (H/C) around 1.5 [6]. The chemical compounds in bitumen are supposed to be greatly degraded by bacterial action. So, the lighter boiling fractions have been removed, the remaining oil has a low concentration of alkane groups (paraffins). A lot of these groups are side chains in larger molecules [2, 3]. Furthermore, a typical oilsands derived bitumen contains 4.6 ± 0.5% sulfur, as well as lower concentrations of other heteroatoms, nitrogen (0.4 ± 0.1%) and oxygen (1.1 ± 0.3 %) [3]. Traces of metals are also found; such as, vanadium, nickel and iron [2].

2.2.1 Sulfur Compounds

Sulfur is most often encountered in two main organic classes: sulfides and thiophenes. The kinds of sulfides can either be mono-sulfides (R-S-R), or disulfides (R-S-S-R) which are cyclic and acyclic, also sulfides that are attached to aromatic rings; for example, thiaindane. In addition, the sulfides are susceptible to oxidation to sulfoxides, under oxidizing conditions sulfoxides can oxidize more and transform sulfones and sulfonic acid. On the other hand, thiophenes are aromatic compounds which contain sulfur within of the ring structure. These can be in the form of thiophene, benzothiophene, dibenzothiofene, and even more complex structures that are thiophene derivatives [2] [7]. Figure 2-4 shows the chemical structure of different sulfur compounds [2].

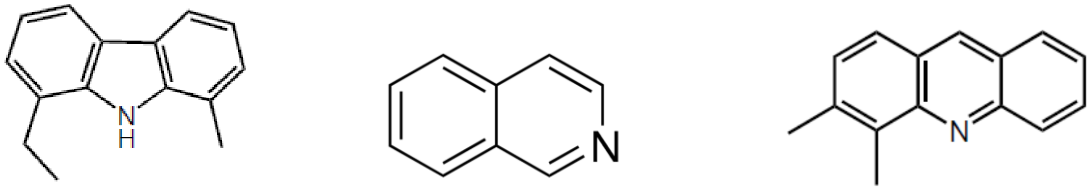


Alkyl benzothiophene Alkyl dibenzothiophene Cyclic sulfide

Figure 2-4: Chemical structure of different sulfur compounds [2].

2.2.2 Nitrogen Compounds

Nitrogen is found in two main classes; the non-basic derivatives of pyrrole, and the basic derivatives of pyridine. Both kinds of nitrogen are highly resistant to removal by hydroprocessing [2]. Pyrroles are aromatic compounds that have nitrogen as element of a five-membered ring structure and can be encountered as pyrrole, indole, carbazole, and also heavier derivatives of pyrrole. These are all neutral compounds, in spite of the N-H functionality. This is due to the lone -pair electrons on nitrogen that is delocalized in the aromatic π-electron cloud, so they are not accessible to be shared with acids. The nitrogen presents a positive charge in the majority of the resonance structures of pyrrole. On the other hand, pyridine and its derivatives such as quinoline, isoquinoline, and acridine are basic nitrogen compounds where the nitrogen is present in a six membered aromatic ring. These compounds are not desirable because inhibit conversion of acidic refining catalysts [7]. Figure 2-5 presents the chemical structure of different nitrogen compounds [2].



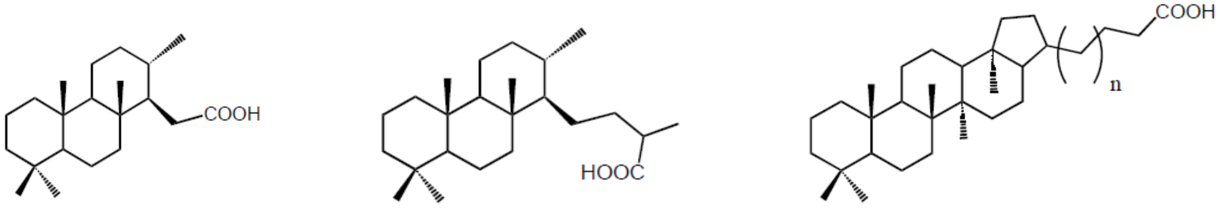
Alkyl carbazole isoquinoline Alkyl acridine

Figure 2-5: Chemical structure of different nitrogen compounds [2, 8].

2.2.3 Oxygen Compounds

According to the literature the oxygen compounds are the least studied of the main heteroatom compounds [2, 7]. The main oxygenate classes present in bitumen are carboxylic acids, esters and phenols. The most important of the oxygenate compounds are the carboxylic acids for the following reasons: abundance, their role as surfactants in extraction of the oil and the corrosion problem that they can cause when processing bitumen at elevated temperature. For example, a typical sample of Athabasca bitumen has a total acid number of approximately 5.5 mg KOH/g of oil [2].

The majority of the carboxylic acids in bitumen are naphthenic acids which comprise about 1-2% of the bitumen by weight [2]. These acids are five and six membered ring cycloalkane carboxylic acid derivatives. The naphthenic acids consist of a diversity of polycyclic structures [7]. For instance, the most important classes of naphthenic acids isolated from Athabasca bitumen are tricyclic compounds that are in the range from 20-26 carbons and pentacyclic compounds with 30-47 carbons (Figure 2-6) [2, 3].



C_{21} tricyclic terpenoid acid C_{24} tricyclic terpenoid acid Pentacyclic hopanoid acid

Figure 2-6: Naphthenic acids structures in Athabasca bitumen [2].

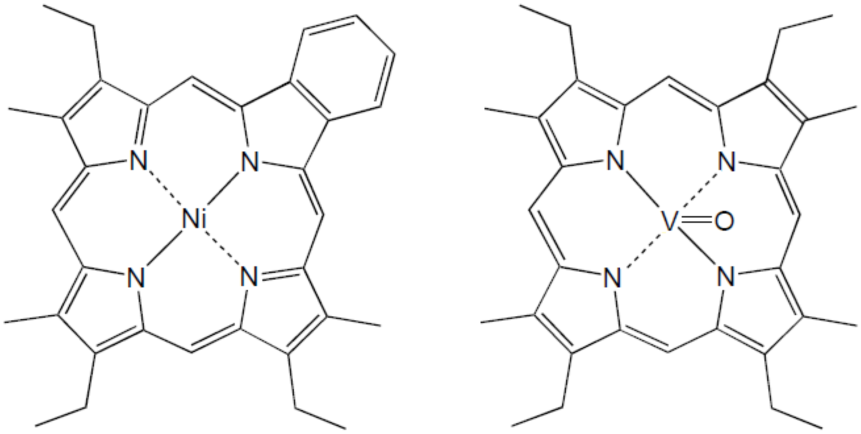
2.2.4 Metals

The main metals in bitumen are nickel (Ni) and vanadium (V) and, to a smaller extent, iron (Fe). These metals are observed in the heavier fractions and in the residue processing units of a refinery or upgrader. The vanadium and nickel are mainly trapped in molecules of the porphyrin family, which act as effective chelanting agent for ions VO^+ and Ni^{2+} (Figure 2-7) [7]. The vanadium and nickel compounds are very stable and resistant to extraction of aqueous solutions. The commercial process for their removal are catalytic hydroprocessing and precipitation. Table 2-1 shows nickel and vanadium content of bitumen vacuum residue fractions (> 524˚C normal boiling point) [2].

Table 2-1: Ni and V content of bitumen vacuum residue fractions (> 524˚C) [2].

Samples	Metals, ppm	
	Ni	V
Athabasca	150	290
Cold Lake	200	490
Lloydminster	140	190
Peace River	130	410

The carboxylic acids as naphthenic acids may act as metal carriers. For instance, alkali metals and alkali earth metals can form metals soaps, which have been involved in problems of oil production, such as, deposit and emulsion formation [7, 9]. The soaps of naphthenic acids may include iron naphthenates that are typically corrosion products. Furthermore to the metals contained in organic compounds, metals can be present in inorganic salts, the most frequent are sodium, magnesium and calcium chlorides, but sulfates and carbonates can be found too [7].



Nickel benzoporphyrin

Vanadyl petroporphyrin

Figure 2-7: Metal-containing porphyrin structure [2].

2.2.5 Saturates, Aromatics, Resins and Asphalthenes

The composition of bitumen is generally given in terms of SARA fractions which are Saturates, Aromatics, Resins and Asphaltenes. The class compositions of Alberta oil sand bitumens are found within the following limits (Table 2-2) [3]:

Table 2-2: Class composition of Alberta oil sand bitumen [3].

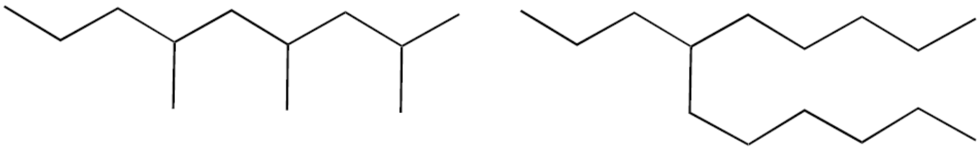
Component	Content
Saturates	15-21%
Aromatics	18-19%
Resins	44-48%
Asphaltenes	14-20%

There are several methods for SARA separation. A reference method employed for separation of bitumen is the ASTM D4124-09 [10]. The summary of this test method is described in Appendix 1.

2.2.5.1 Saturates

Saturates are constituted mainly of straight and branch chain paraffins together with alkyl naphthenes and very few alkyl-aromatics [11]. The n-alkanes can be composed 2/3 of the total light crude oil. However, biodegradation of the source crude oil totally changes this large quantity in a bitumen material. For instance, the biodegradation of Athabasca and Peace River bitumens are completely lacking of n-alkanes, however, the less degraded Cold Lake bitumen still has small amounts [3]. Figure 2-8 shows structures are found in oils that have been exposed to bacterial degradation in which the surviving paraffins are branched [2, 12].

According to reference method ASTM D4124-09, saturates are defined as "material that, on percolation in an alkane eluate, is not absorbed on calcined CG-20 alumina absorbent under the conditions specified" [10]. Saturates consist of 15 to 21% of typically Alberta oil sands bitumens [3]. They are non-polar viscous oils which are colourless or lightly coloured liquid at room temperature [11, 13]. Their H/C ratio is approximately 2, with only traces of heteroatoms. The average molecular weight is around 600 g/mol and their density at 20°C about 0.9 g/cm^3 [6, 13].



Isoprenoid T-branched alkane

Figure 2-8: Saturate structures that are found after bacterial degradation [2].

2.2.5.2 Aromatics

Aromatics, also called naphthene aromatics are described as material adsorbed on calcined CG-20 alumina with n-heptane, and desorbed by toluene, according to reference method ASTM D4124-09 [10]. Aromatic compounds from alkylbenzenes to large condensed polyaromatic and heteroatomic molecules are abundant constituents of bitumen and heavy oil. These compounds are usually alkyl- and naphthenic- substituted in the aromatic ring. It is possible to separate the aromatic fraction into monoaromatic, diaromatic, triaromatic and polyaromatic subfractions by a combination of different column chromatography methods [3].

Table 2-3 shows aromatic contents of Alberta oil sands bitumens, as can be observed the aromatic content of Athabasca bitumen has been reported to have values from 18 to 36.5 wt% depending on the method used for their isolation [3]. Other kinds of bitumen (Cold Lake, Peace River and Wabasca) have concentrations of monoaromatics and diaromatics close to those in Athabasca bitumen. In addition, the content of polyaromatics of Cold Lake, Peace River and Wabasca bitumens are sowewhat higher with respect to Athabasca bitumen [3].

Table 2-3: Aromatic contents of Alberta oil sand bitumens (wt% of bitumen) [3].

Sample	Mono-	Di-	Polyaromatics	Total	Total by Syncrude
Athabasca	8.3[a]	3.8[a]	23.8[a]	35.9[a]	18-19[b]
	8.0[c]	3.6[c]	23.9[c]	35.5[c]	18-19[b]
	>12.5[d]	7.5[d]	16.4[d]	36.5[d]	
Cold Lake	8.1[a]	3.6[a]	24.4[a]	36.1[a]	-
Peace River	8.6[a]	3.3[a]	30.2[a]	42.1[a]	-
Wabasca	7.6[a]	2.5[a]	35.1[a]	45.2[a]	-

[a] USBM API-60 separation.[b] Syncrude method of separation.[c] Silica/alumina separation.[d] Silica/alumina and FIMS/high-resolution EIMS.

2.2.5.3 Resins

Resins are also called polar aromatics. These are the material desorbed from calcined CG-20 alumina absorbent, after removal of the saturate and naphthenic aromatic fractions, using toluene:methanol (50:50, vol:vol) and trichloroethylene eluate under the conditions specified in the reference method ASTM D4124-09 [10]. So, polars are the fraction that stays back on the absorbent after elution of the saturate and aromatic fractions depending on the method of separation [3]. Resins are the most abundant constituents of a bitumen together with the aromatics with values 30-45 wt% [6].

The resin fraction is comprised of carboxylic acids as naphthenic acids, alcohols, sulfoxides, beside some sulfides, ketones, carbazoles, pyridines, quinolines, porphyrins, etc. Their components are mostly neutrals followed by acids > bases > amphoterics [3]. Koots *et al*. [14] studied the relation of petroleum resins to asphaltenes, this study shown that resins has a higher H/C ratio between 1.38 and 1.69, which presumably indicates a lower content of aromatic structures in the resins than in the asphaltenes. The structural parameters indicated that the resin molecules are much smaller than the corresponding asphaltenes. Furthermore, there is a tendency to find decreased proportions of heteroatoms in the resins relative to asphaltenes.

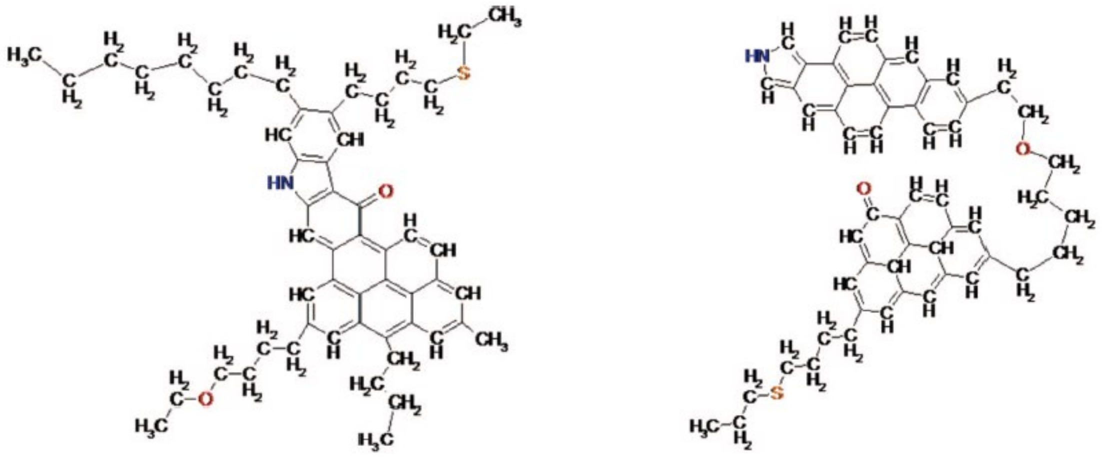
2.2.5.4 Asphaltenes

Asphaltenes are defined by their solubility characteristics as the insoluble part of a bitumen or a crude oil in n-alkane (and in some cases, branched alkanes), such as, n-heptane [15], n-pentane and iso-octane [10], but soluble in toluene or benzene [2]. The amount and features of the precipitated asphaltenes depend on the temperature, type and quantities of diluent and precipitant solvent used [3].

In general, asphaltenes have the following properties: It is the most dense fraction of petroleum with a density of approximately 1200 kg/m^3 [2]. Asphaltenes contain the largest percentage of heteroatoms (O, S, N) and organometallic constituents (Ni, V, Fe) in the crude oil [16]. The high aromatic carbon content and low hydrogen content cause asphaltenes to have a high Micro Carbon Residue (MCR) content [2]. The H/C ratio of asphaltenes is between 1.0 and 1.2 [17]. Another main characteristic of asphaltenes is their self-association in order to form aggregates, so they have the propensity to form aggregates in crude oil and in solvents such as toluene [18].

Several studies have been conducted to elucidate the molecular structures of asphaltenes. There is extensive debate with respect to structures of asphaltenes, principally with respect to the size of the aromatic groups and the form as they are linked to the other structural groups [19]. According to the literature, asphalthenes are described by two main structures: firstly, the continental (pericondensed) structure and secondly, the archipelago structure [17, 19].

The pericondensed model describes the asphaltenes structure in terms of a dominant aromatic core with several aliphatic chains in the periphery of the core (Figure 2-9) [17]. The number of fused rings consists generally of over seven rings [19]. The archipelago model describes the asphaltenes structure as smaller groups of aromatic cores linked by aliphatic bridges (Figure 2-9) [17]. Data from pyrolysis, oxidation, thermal degradation, and Small-Angle Neutron Scattering (SANS) techniques provides support the archipelago structure. During mild pyrolysis, highly condensed aromatic cores would not fragment into smaller aromatic cores [19]. Therefore, it is a point of view contrary to the pericondensed model.



Pericondensed Archipelago

Figure 2-9: Models for the asphaltenes structure [17].

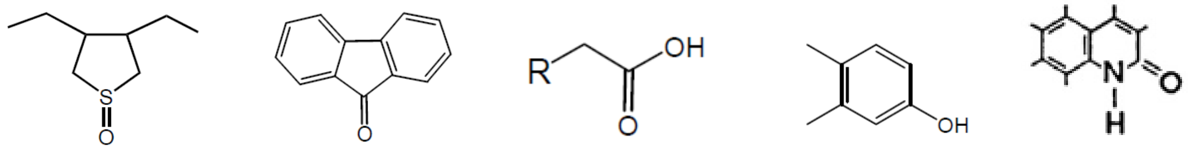
2.2.6 Ion exchange chromatography (IEC) fractions

In spite of SARA fractionation being the most common method of separation, ion exchange chromatography (IEC) provides additional information about chemistry of bitumen. With this technique the bitumen is separated into five fractions which are strong and weak acids, strong and weak bases and neutral components. These fractions are of importance when the chemistry of bitumen and its interfacial property are researched [6]. It is also of particular relevance to the present study, which investigated the acid and base treatment of bitumen.

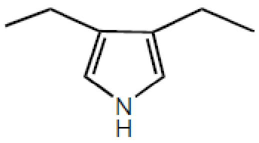
The study of bitumen components separated into IEC fractions started in 1977 with the pioneering research of Boduszynski and coworkers [6, 20, 21]. One investigation was the separation of acid and base components of maltenes only using ion exchange chromatography (IEC) through macroreticular resins, they found acidic and basic fractions in maltenes to be 7.5 wt % and 12.3 wt % respectively [20]. Another study was to prove whether or not IEC resolution of the asphaltenes could be accomplished, this research showed that IEC is effective for the removal of acid and base nitrogen constituents of asphaltenes [21].

A procedure of separation of bitumen into strong and weak acids and bases, and neutral components through IEC is the Strategic Highway Research Program (SHRP) protocol [6]. The summary of this procedure is described in Appendix 2.

A second setup was suggested by the Strategic Highway Research Program (SHRP) to separate amphoteric components [6]. This procedure is described in Appendix 3. The amphoteric fraction has appearance of a black fragile solid which is similar in appearance to asphaltenes. On the other hand, neutral fractions are liquid. Base fractions are a tacky solid that seem like resins. The chemical compositions of fractions are the following: the bases are abundant in sulfoxides and ketones. The strong acids have the majority of the carboxylic acid, phenols and 2-quinolones. Furthermore, the weak acid fraction is enriched of pyrroles. After that amphoterics are separated, they consist of high amounts of 2-quinolones. Finally, the polar groups are almost absent in the neutral fraction [6]. Figure 2-10 presents examples of functional groups of different fractions.



Cyclic sulfoxide Ketones Carboxylic acid Alkyl phenol 2-Quinolone



Alkyl pyrrole

Figure 2-10: Examples of functional groups of bases, acids and amphotherics fractions.

2.2.7 Natural surfactants in the bitumen

A tensoactive compound, or surfactant, refers to a dual polar-apolar structure, which consists of hydrophobic and hydrophilic parts. The polar part is composed of one or more polar functional groups containing heteroatoms (O, S, P or N) that are found in functional groups, such as alcohol, carboxylate, sulfate, sulfonate, phosphate, amine, amide, etc. The group apolar is a hydrocarbon chain or cyclic structure. Hence, the molecules of surfactant have a strong tendency to migrate to a surface or interface and reduce the surface or interface tension value [22, 23].

Some chemical compounds present in the bitumen have surfactant behaviour [6, 16, 24, 25]. Asphaltenes contribute to the surface activity due to the presence of polar groups, polycyclic aromatics and metal-complexes. According to the literature, asphaltenes and resins endogenous to the oil are recognized as the main components with respect to stabilization of the interface [6,16]. So, these compounds can migrate to the interface when bitumen is contacted with water, so the interfacial properties are modified. When asphaltenes are completely stabilized by the resins, these accumulate less at the interface [6]. The compound class responsible for most of the surface active behaviour is the naphthenic acids and whatever other compound classes were found to be surface active. Therefore, the bitumen holds endogenous surfactants in quantities that depend on the crude source [6].

Some evidences show the more detailed study of the native tensoactive compounds in the bitumen was performed in 1970s by F. Durrieu [6]. In the study by Durrieu the endogenous surfactants were separated using ion-exchange chromatography (IEC). Basic surfactants were isolated using a sulfonic acid column (Amberlyst A15). On the other hand, acidic surfactants were separated with a quaternary ammonium column (Amberlyst A29). The acidic surfactants showed a robust interfacial activity due to lower interfacial tension of their benzene solutions with basic water. While, the cationic surfactants exhibited a lower interfacial activity as showed by a lighter decreasing of the interfacial tension of their toluene solutions with aqueous acid. However, this interfacial tension was not close to zero as observed for the anionic surfactants [6].

The interfacial tension of an organic solution (bitumen plus solvent) and aqueous solution (basic or acidic) is reduced by the addition of surfactants. The interfacial tension decreases until the CMC (critical micelle concentration) is reached and micelles are produced. The micelles are aggregated of abundant numbers of surfactant molecules (50 or more) [26]. It suggests anionic surfactant achieves CMC to a lower interfacial tension compared to cationic surfactant.

The pH of the aqueous phase is important in bitumen-water interfaces. An acidic pH would benefit the cationic surfactants. Whereas, a basic pH would promote the anionic surface active species [6].

2.2.8 Structural model of bitumen

The structure of bitumen can be well described by the colloidal model. It consists of a colloidal dispersion of asphaltenes micelles in an oily liquid matrix (the maltenes). Where the resins, which are the polar components of the maltenes, play the role stabilizer for asphaltenes. The techniques Small Angle X-Ray Scattering (SAXS) and Small Angles Neutrons Scattering (SANS) provide evidence that asphaltenes form micelles in organic solvents, in crude oil and in bitumen. Furthermore, the micelles can form aggregates [6].

Figure 2-11 shows a schematic illustration of asphaltenes aggregation where (a) represents an asphaltene monomer, (b) describes an asphaltene aggregate with size ca. 3 – 4 nm, molecular weight ca. 20 – 25 kDa, and apparent “fractal” dimension between 1 – 2 and (c) shows a schematic illustration of an asphaltene aggregate with size ca. 12 – 15 nm, molecular weight ca. 200 – 400 kDa, and apparent “fractal” dimension between 2 – 2.5 [27]. The fractal structure is quantified by the fractal dimension (d_f), which is defined as $M_w \alpha R_g^{d_f}$, where M_w is the mass of the aggregates and R_g is the radius of gyration of the aggregates [28].

In the study by Gawrys (Figure 2-13), Small Angles Neutrons Scattering (SANS) was used to deduce sizes and morphologies of colloidal aggregates in solution. Proper analysis of SANS scattering intensity curves provides values of radius of gyration (R_g), molar mass, and apparent “fractal” dimension for aggregates. According to this study, an apparent “fractal” dimensions of

~ 2 suggested that asphaltenes form highly porous aggregates, which is consistent with the so-called “archipelago” model of asphaltenes [27].

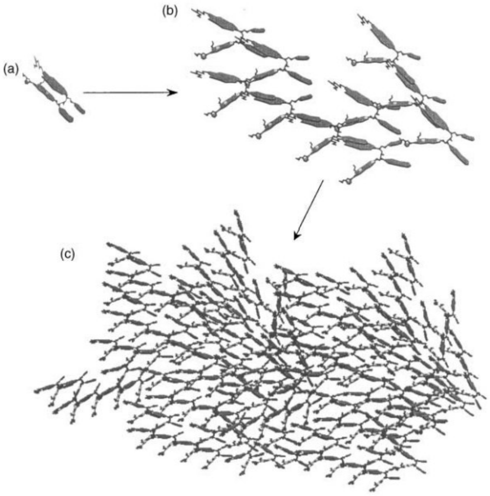


Figure 2-11: Schematic illustration of asphaltenes aggregation [24].

Figure 2-12 presents a simple schematic description of the colloidal structure of bitumen where the asphaltenes micelles are represented as spherical to exemplify the theories of solvation layer (resin shell) and effective volume. The maltenes are the oily dispersion medium [6].

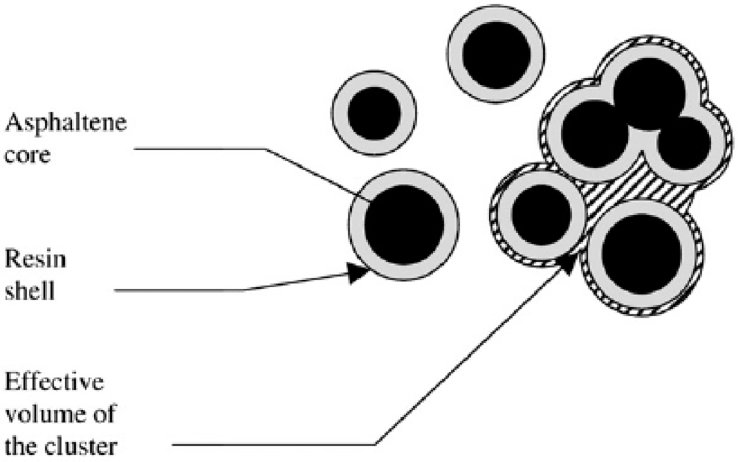


Figure 2-12: Modern colloidal structure of bitumen [6].

Another model describes the dispersion of the heteroatomic functions in the bitumen in terms of their interactions on a molecular level. It characterizes bitumen as a mixture of neutral and amphoteric molecules, where adjacent acidic and basic functional groups interact to form a viscoelastic network within the neutral fraction [29]. The description of this model is relevant in our research because acid base interactions in the bitumen structure could be affected by the influence of acid and base treatment.

2.3 Chemical treatments

2.3.1 Polyphosphoric acid treatment

The use of polyphosphoric acid (PPA) to modify bitumen is of much interest for applications in pavement construction and roofing. It allows the user to considerably harden bitumen in an easily controllable manner. Currently, PPA is the most studied acid whose reaction with bitumen is still poorly understood, so the precise mechanism can only be inferred. There are various studies of the reaction mechanism proposed for the PPA and bitumen [6, 29, 30].

PPA is an oligomer of phosphoric acid (H_3PO_4). This chemical compound can be produced by two process: dehydration of H_3PO_4 at high temperatures or by heating phosphorus pentoxide (P_2O_5) dispersed in H_3PO_4. Figure 2-13 shows the equilibria of these chemical reactions that generate diverse chain lengths and distributions. The dehydration process has the tendency to produce short chains. While the dispersion process generally produces chains with more than 10 repeat units [29].

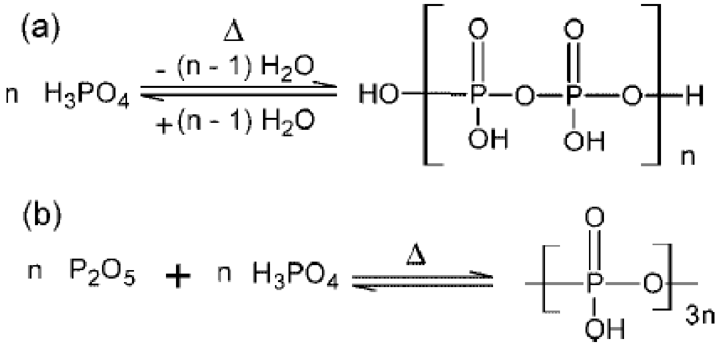


Figure 2-13: Chemical reactions for the production of PPA, (a) dehydration and (b) dispersion processes, n is an integral numeral [29].

The properties of PPA and bitumen were reviewed by Masson to better understand of their reaction [29]. He explained that the dissociation of PPA into its charged fractions (PPA$^-$ and H$^+$) is not effective because PPA has a high dielectric constant, while that of bitumen is small ($\varepsilon = 3$). So, PPA is a very weak acid in bitumen. It was postulated that "PPA can only dissociate and react with bitumen in enclaves of high dielectric constants formed from the aggregation of amphoteric heteroatomic groups into nanodomains" [29].

It was proposed that PPA neutralizes polar interactions between the stacked asphaltenes molecules, for the following reactions: protonation of basic sites or by esterification. The consequence is to increase the solvation of the asphaltenes, increasing in turn the solid fraction and thus, the viscosity [30].

Baumgardner *et al*. [31] suggested the mechanism of PPA action is dependent of the nature of the asphalt. Several mechanisms were proposed to explain the stiffening from the PPA modification of asphalt binders: formation of PPA adducts; alkylation of aromatics; cross-linking of neighboring asphalt segments; the formation of ionic clusters; and the cyclization of alkyl aromatics.

Yan *et al*. [30] found that the influence of PPA on chemical composition, physical properties and morphology of bitumens depends on the base bitumen. Some results for PPA modified bitumen B1 are shown as follow: the viscosty increases progressively when the PPA content is no more than 1 wt%. However, when the PPA concentration exceeds 1 wt%, the viscosity increases linearly (Figure 2-14).

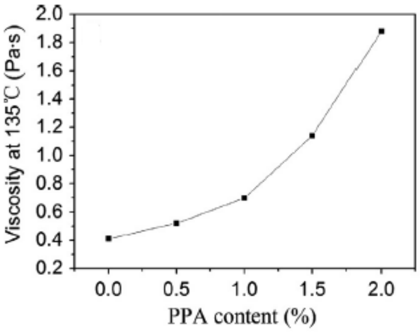


Figure 2-14: Effect of PPA on viscosity of bitumen B1 [30].

The effects of PPA on the chemical composition of bitumen B1 were the following: the increasing of PPA content produces a linear increase of the asphaltenes content from 11.64 wt% to 16.38 wt%, whereas the resins content decreased from 20.43 wt% to 15.16 wt%. It is notable that the decrease in the amount of resins is comparable to that of the increase of asphaltenes. Hence, it suggests an apparent conversion of resins into asphaltenes with the introduction of PPA. Yan et al. [30] explained after adding PPA, the cross-linking of reactive segments may occur to produce a matrix of covalently linked matter between the resins and asphaltenes; for example, resins-PPA-asphaltenes, which will favor to the addition products to behave as asphaltenes. Furthermore, the breaking of alkyl aromatics in resins into alkyl and stiff aromatics fragments may exist.

The effect of PPA on morphology of bitumen was studied using Atomic Force Microcopy (AFM). This evidenced that a great association of the dispersed phases in bitumen proceeds during modification. It indicated that the stiffness of the bitumen B1 is highest after PPA modification which is caused by an increase in the asphaltenes content. Therefore, the changes of morphology are correlated with that of physical properties and chemical composition [30].

2.3.2 Acid treatment (excluding PPA)

Herrington *et al*. [32] investigated the rheological properties of roading bitumens, modified with maleic anhydride (MAH), succinic anhydride (SAH) and various straight chain dicarboxylic acids at 150˚C and 6 h of reaction time. MAH, SAH and dicarboxylic acids at low levels of concentration (< 0.1 M) are able to change the viscoelastic properties of bitumen. The magnitudes of the complex modulus (G*), storage modulus (G') and loss modulus (G'') are increased and as the bitumen becomes more elastic in character, tan δ is decreased. They interpreted the results as the formation (or enhancement of existing) transient networks of bitumen species, attached by hydrogen bonding and dipole–dipole interactions with the dicarboxylic acids (two acid groups are needed). The networks formed by the longer chain acids were either more easily disrupted at elevated temperatures, or less rigid and more easily deformed than those involving shorter linkages.

Chaverot *et al*. [24] studied the influence of endogenous surfactants in the bitumen in the presence of an aqueous solution of hydrochloric acid (pH 2). They investigated seven bitumens of diverses origins and compositions. It was observed that all bitumens have significant amounts of endogenous surfactants. These surfactants migrated from the bulk bitumen to the water interface, so the interfacial tension of aqueous-based emulsion droplets is notably lower.

Asphaltenes are recognized to have significant amounts of basic groups that ensure good interfacial activity at acidic pH values. The results suggest that the surface-active compounds at pH 2 are asphaltene fractions of basic character which are probably in an aggregated form. The basic compounds correspond to a very small fraction no more than 0.015% of the total asphaltenes content present in bitumen [24].

Another possible influence of acids on bitumen can be inferred from work on coal. Van Bodegom *et al*. [33] investigated the pretreatment of Morwell coal with 0.1N HCl at room temperature and with 1N HCl under relflux. In brown coals, some carboxyl groups are linked with alkali or alkaline-earth ions. These ions can be easily leached out when are washed by treating the coal with low concentration aqueous solution of HCl. With the analysis of washing aqueous solution was found that Ca^{2+} was the highest cation exchangeable in the samples. Researchers concluded that this pretreatment leads to enhanced solubility of brown coals.

2.3.3 Base Treatment

Heavy oils and bitumen have on average more acidic components than conventional crude oils. When such crude oils are contacted with an aqueous alkaline solutions, water-soluble surfactants are produced in situ at the interface [34]. Specifically, the carboxylic acids present in the bitumen when contacted by an alkaline aqueous solution, form surface-active soaps because of the reaction between carboxylic acids and the alkaline species [25]. These surfactants decrease the oil/water interfacial tension to ultra-low values [34]. For example, it was found at 0.05% NaOH concentration resulted in minimum interfacial tension values in the ultra-low region ($< 10^{-2}$ mN/m) [34]. This result was based in the study by Babu *et al*. [34], who studied the effects of time and temperature on the interfacial tension behavior between two Canadian heavy oils

(Lloydminster and Cold Lake) and alkaline solutions. These native tensoactive compounds have been the topic of many studies due to their significance in several of the processes performed in the oil industry, such as, crude oil production, treatment, and transportation [25].

In enhanced oil recovery it is important to have very low values of interfacial tensions, which can be obtained by alkaline flooding. If the interfacial tension between the oil and the aqueous phase can be reduced to values close 1 mN/m or lower, the capillary forces may be overcome to the degree that the residual oil is displaced and consequently recovered [25, 35]. As has been mentioned, upon adsorption of native surfactants at the crude oil/water interface, the interfacial tension may drop to ultralow values. Nevertheless, it is worthwhile pointing out that the interfacial tension originating from the crude oil/caustic interactions is significantly affected by the type of the crude oil, caustic concentration, the type of base, the presence of electrolytes, the temperature, among others [25].

McCaffery [36] published that the minimum initial interfacial tension between heavy oils studied and caustic solution takes place with approximately 0.25 wt% NaOH in injection water. The interfacial tension was found to increase with the age of the interface. This result indicates that various of the sodium soap products, which are produced when acidic compounds in the crude oil react at the interface with sodium ions in the aqueous phase, consequently leave of the oil/water interface [36].

Model experiments have been performed to study the prospects for recovering bitumen from Nigerian tar sands using alkaline hot water. It consisted of injection of 0.04 wt % caustic solution into linear bitumen-bearing sandpacks at temperature in the range 25 to 80˚C. The results showed a bitumen recovery of up to 15% at 50˚C, which represent an increase of about 5% over the recovery at 27˚C. Nevertheless, a decline in the cumulative bitumen production was obtained at higher temperatures >50˚C [37].

Under suitable conditions, natural surfactants activated with alkaline solutions can also be used as emulsifying agents in the formation of bitumen in water emulsions. Acevedo et al. [25] studied bitumen in water emulsions stabilized with natural surfactants activated by adding different concentrations of sodium carbonate to the aqueous phase of emulsions. These surfactants were responsible for very low values of interfacial tensions achieved in the range of concentrations between 800 and 2000 ppm and for the stabilization of the bitumen-in-water emulsions formed.

Vassilev *et al.* studied alkaline solutions-bitumen interactions [38]. They found experimentally the points of the kinetic curves describing the transformation of maltenes into asphaltenes under the influence of different alkaline solutions (KOH, NaOH and $Ca(OH)_2$). They proposed general kinetics for the interaction with the following two successive steps [38]:

1. Transport of hydroxide ions (OH^-) to the bitumen surface. This step is thought to be fast because the diffusion is carried out in a liquid phase. In the alkaline solution that was obtained, the hydroxide ion concentration remained almost constant and independent of time, so the amount of OH^- entering the bitumen is negligible [38].
2. Adsorption / absorption of hydroxide ions on the bitumen surface followed by chemical reaction and diffusion into the bulk. This reaction is not reversible and very possibly progressive, because several hydroxide ions are implicated in the conversion of one molecule of maltenes to a few molecules of asphaltenes [38].

Another application of base treatment is the dilute aqueous alkaline extraction of the oil sands or any of its components to prepare concentrates of hydrocarbons, carboxylic acids, alcohols and another oxygen and sulfur compounds, which are distinguished as biological marker molecules for analytical studies. The general methodology is the following: 300 g of oil sands is treated with 600 mL of an aqueous sodium hydroxide solution (0.01N) in the range of temperature between 80˚C and reflux temperature of the aqueous slurry with a reaction time from 10 min to 48 hours. The next stage is the separation of the floating bitumen and bottom-settled sand from the aqueous phase. The latter is then acidified and extracted with methylene chloride. Finally, the organic solution is dried over sodium sulfate [3].

It is not evident if the organic solutes form a real solution in the water, or whether these are colloidally dispersed, by the action of surfactant soaps produced by the reaction between carboxylic acids and NaOH. The hydrocarbons present (>C_{15}) have vanishingly little solubilities; so, it is not probable that they would form a real solution in water [3].

Base treatment has also been investigated for coal and some parallels may be drawn with bitumen. Van Bodegom *et al.* [33] investigated the dissolution behavior of brown coals in pyridine, primary amines and aqueous solution of KOH. The results showed that the dissolution in amines and aqueous KOH is strongly dependent on temperature, while that the dissolution in pyridine is approximately independent of temperature. The solubility of brown coals in amines and aqueous solution of KOH is highest with increasing carboxylic acid group concentration in the coal. Amines are not all equally efficient for the dissolution of coal. When different amines are compared at the same temperature, EDA and MEA are best, whereas the solubility of Morwell brown coal in *n*-alkylamines at 180˚C increases with growing length of the alkyl chain.

They concluded strong bases are good solvents for brown coals for the following reasons: firstly, ester bonds have to be broken and secondly, the acidic coal fragments have to be solubilized. These are called reactive solvents due to their ability to break ester bonds by hydrolysis and saponification [33].

2.4 Viscosity of Bitumen

Rheology is the science that studies the flow and deformation of matter [11]. The viscosity is the main physical property in any process that involves the movement of fluids. The viscosity of a fluid is a measure of the frictional resistance offered by the moving fluid to an applied shearing force [3]. According to Newton's law of viscous flow, viscosity is defined as the frictional force (f) that restrict the relative movement of two adjacent layers of a fluid. This force is directly proportional to the area of the interface and the velocity gradient between them which is described in the following Equation [3]:

$$f = \eta S(dV/dR) \qquad \ldots(2\text{-}1)$$

Where η = the coefficient of viscosity (N.s/m^2), S = the interfacial area (m^2) and dV/dR = the rate of change of the velocity V (m/s) with respect to the distance R (m) from the fixed surface [39].

The fluid has Newtonian behavior when the frictional resistance is independent of the shearing force applied. Bitumen is mildly non- Newtonian because with increasing shear force, its frictional resistance reduces slightly [3]. In addition, the bitumen has a behavior of viscoelastic liquid at room temperature [6]. Viscoelasticity is the property of certain materials to exhibit both viscous behavior when they are subjected to shear flow and elastic properties when they are deformed [40].

There are various approaches to reduce the viscosity of bitumen, which are the following [3, 41]:

1. The viscosity of bitumen is greatly temperature dependent. Viscosity decreases dramatically with increasing the temperature [3]. Thus, bitumen cannot be transported in its natural recovered state, unless the temperature is increased by making use of heated pipelines or railcars over limited distances [41]. Figure 2-15 shows viscosity-temperature trend for different Alberta bitumens [42].

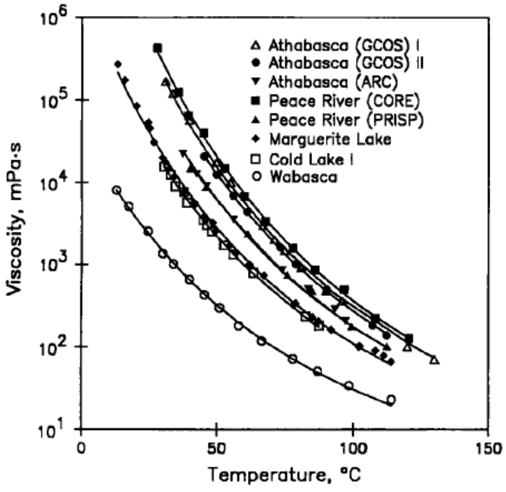


Figure 2-15: Viscosity-temperature trend for different Alberta bitumens [42].

2. Dilution with a solvent reduces the bitumen viscosity. The diluents used are petroleum-derived naphtha and natural gas condensates. A mixture of 25:75 diluent and bitumen can be transported

by pipeline which is denominated ‘dilbit’, or diluted bitumen [41]. Figure 2-16 shows change in viscosity as a function of the amount of added toluene solvent for five different samples of bitumen and heavy oil (A, B, C, D and E) [43].

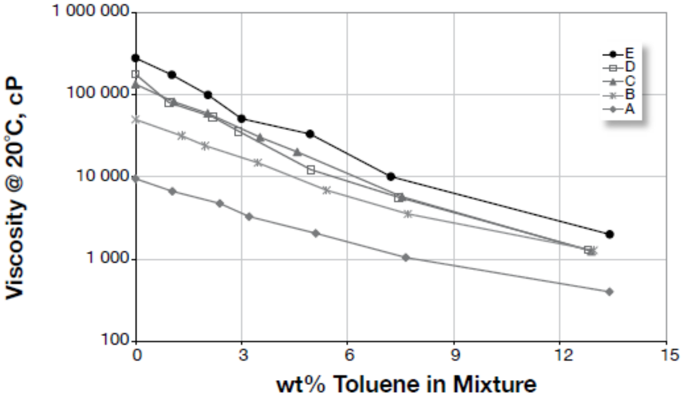


Figure 2-16: Viscosity as a function of the amount of added toluene solvent for five different samples of bitumen and heavy oil (A, B, C, D and E) [43].

3. By colloidal dispersion in a low viscosity immiscible medium [3]. In this approach the immiscible medium becomes the continuous phase that determines viscosity. The colloidal dispersion of bitumen is essentially 'particulates' in slurry transport.

4. Upgrading technologies for viscosity reduction, such as visbreaking, which is a mild thermal cracking process [41]. By reducing the molecular complexity through conversion, the viscosity is decreased.

Recently, the low temperature visbreaking behavior of oilsands bitumen was investigated as means to reduce bitumen viscosity. The results showed that viscosity reduction of bitumen does not follow a regular and monotonic decrease with an increase in bitumen conversion. These changes indicated that not only C-C bond breaking, but other interactions are also affected. So, the viscosity change over time at constant temperature was complex, with at least one local minimum and maximum being observed. This feature of the behavior could not be completely explained [44, 45, 46].

2.4.1 Factors that affect bitumen viscosity

An article written by Lesueur [6] reviews the actual understanding of bitumen structure and its influence on the rheological properties. Three parameters that affect bitumen viscosity are the following [44]:

1. Maltenes viscosity. As was explained in the section 2.2.8, the structure of bitumen can be well described as a colloidal solution. The viscosity of the maltenes corresponds to the viscosity of the continuous phase without any colloids or particulates. So, the viscosity of the bitumen would be just controlled by the maltenes viscosity, when in the absence of colloids, molecular assemblies, or separated phases of liquid and/or solid. Solely molecular mass influences the viscosity of maltenes [44].

2. Asphaltenes or aggregate content. The asphaltenes are present as aggregates as was illustrated in Figure 2-11. However, not all aggregates are asphaltenes and vice versa. It is better to focus on the aggregate content because it is hydrodynamically equivalent to a small particulate, whereas individual asphaltenes are molecules that are indistinguishable from the bulk liquid phase [44]. Just a broad general tendency is that the asphaltenes content is higher in the oil products presenting higher density and viscosity. However, heavy and viscous vacuum residues can have less asphaltenes than light ones [47]. Brauch *et al*. [47] found that feed viscosity was 1045 cSt with an asphaltenes content of 6.63%, while the visbreakate product has a less viscosity (138 cSt) with a higher asphaltenes content (10.49%). It was suggested that the aggregate content should not necessarily be correlated with the asphaltenes content. So, in this context, aggregates are defined as associated molecules that range from a small number of molecules a few nanometers in size to a very large number of molecules that form aggregates visible by light microscopy [44].

The aggregates present the highest packing density in the bitumen. Therefore, the aggregates occupy the lowest volume fraction at their maximum packing density, which is defined as Φ_m. With the solvation of the aggregates, the molecules at the boundary layer form hydrodynamically part of the aggregates and these are not part of the continuous phase. Furthermore, the volume of the aggregates can increase because these may capture molecules inside the aggregate structure [44].

Hence, the effective volume fraction of the aggregates in the bitumen (Φ_{eff}), is higher than the volume of the aggregates at the maximal packing density ($\Phi_{eff} > \Phi_m$) [44]. The viscosity of the bitumen (μ) is related to the zero-shear viscosity of the maltene phase ($\mu_{0,malt}$) and Φ_{eff}, according to Roscoe's law (Equation 2-2) [44, 6, 48]:

$$\frac{\mu}{\mu_{0,\mathrm{malt}}} = (1 - \Phi_{\mathrm{eff}})^{-2.5} \qquad \ldots(2\text{-}2)$$

However, the Equation 2-2 is not a good approximation for concentrated dispersions, due to the viscosity of these dispersions diverges as a function of volume fraction, which occurs for Φ_{eff} of about 0.6. The viscosity according to this equation does not deviate until that is achieved a volume fraction of one. Polydispersity to greater volume fractions might change the point of divergence [48].

If x_a is the mass fraction of aggregates in the bitumen, the correlation between the effective volume fraction of the aggregates in the bitumen (Φ_{eff}) is described by its solvation parameter (κ), which is shown in the Equation 2-3 [6, 44, 48].

$$\Phi_{\mathrm{eff}} = \kappa x_a \qquad \ldots(2\text{-}3)$$

3. Solvation parameter

The solvation parameter (κ) describes the increase in volume fraction of the aggregates in the bitumen because of the adsorbed molecules. The solvation constant is the ratio between the solvation parameter (κ) and minimum volume fraction at maximum packing of the aggregates (Φ_m) written as κ/Φ_m. The solvation constant at 60˚C of bitumens with an asphaltenes content of 7-25 wt% by n-heptane precipitation, is generally in the range of 3-8, with a typical value of 5.5. Nevertheless, the solvation constant increases significantly for lower asphaltene contents [6, 44].

It is hypothesized that if the aggregate content were used, instead of asphaltenes content, that a more narrow range of values for the solvation parameter can be found. However, to determine a value for the asphaltenes content is experimentally more easy [44].

According to Wang and co-workers [44] a reasonable explanation for the rapid viscosity reduction during low-temperature visbreaking, was a decrease in the effective volume fraction (Φ_{eff}) occupied by the colloidal aggregate fraction in the bitumen. A reduction in Φ_{eff} could be due to "disaggregation of clustered asphaltenes and other aggregating species, the release of trapped material and/or a potential decrease in the boundary layer volume around the aggregates" [44]. These are physical mechanisms, or mechanisms that include weak chemical interactions. Therefore, it is reasonable that such physical and weak chemical interactions could be disrupted at low temperature and low contact time conversion [44]. Of importance to this study is that low temperature acid/base treatment may be able to achieve a similar outcome.

2.4.2 Effect of emulsions on viscosity

The treatment of very viscous hydrocarbons through their emulsification in water has been studied by several authors [25, 49, 50]. Heavy and extra-heavy crude oils and bitumen can be transported when emulsified in water (O/W emulsions). These emulsions present viscosity values with several order of magnitude lower than the viscosity of the hydrocarbon itself [25]. These emulsions must have very good stability and suitable rheological properties before such emulsions can be considered for long-distance pipeline, tanker transportation and in-plant storage [50].

Orimulsion® was a technology developed by the Research and Technological Support Center of the Venezuelan National Oil Company (PDVSA Intevep). Heavy oil was transported and sold as fuel in the form of an oil in water (O/W) emulsion: a mixture of 70% heavy oil (dispersed or internal phase) and 30% water (continuous or external phase) with added phenolic or alcohol-based surfactant [51]. In general, very concentrated oil in water emulsions (70% or more of the dispersed phase) comprise of an agglomeration of polyhedral droplets separated by thin liquid films of the continuous phase (Figure 2-17) [25].

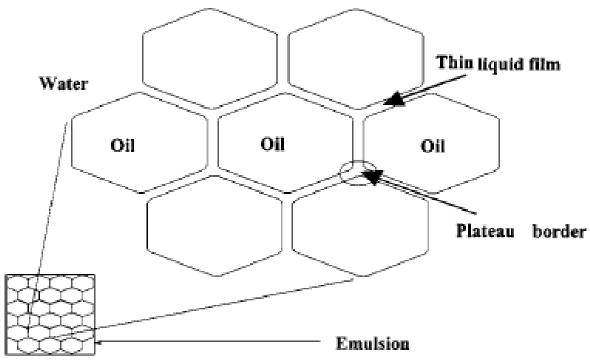


Figure 2-17: Representation of polyhedral structure of a concentrated oil in water emulsion [25].

Acevedo *et al*. [25] determined the viscosities of bitumen in water (O/W) emulsions stabilized with natural surfactants activated by adding different concentrations of sodium carbonate. Emulsions viscosity at 30˚C and 20 s^{-1}, increased slowly when the Na_2CO_3 concentration in the continuous phase was increased from 2000 to 6000 ppm. The increase in viscosity was attributed to a decrease in the mean droplet diameter, which produces an increase of the interfacial area, so the number of interactions between droplets becomes greater.

The formation of bitumen in water emulsions stabilized by natural surfactants is explained by chemical reactions that occur in the aqueous solution and at the interface. So, the sodium carbonate is ionized when it is dissolved in water (Equation 2-4). Then, carbonate ions are hydrolyzed forming a buffer solution, which maintains a constant pH in the aqueous phase (Equation 2-5) [25].

$$Na_2CO_3 \Longrightarrow 2Na^+ + CO_3^{-2} \qquad \ldots(2\text{-}4)$$

$$CO_3^{-2} + H_2O \Longleftrightarrow CO_3H^- + OH^- \qquad \ldots(2\text{-}5)$$

Then, the formation of the carboxylate ions and its adsorption at the interface take place [23]:

$$HA_w + OH^- \Longleftrightarrow A_w^- + H_2O \qquad \ldots(2\text{-}6)$$

$$A_w^- \Longleftrightarrow A_S^- \qquad \ldots(2\text{-}7)$$

If the concentration of Na_2CO_3 is increased, keeping constant pH, additional carboxylate ions are produced in the aqueous phase (Eqs. 2-5 and 2-6) and more carboxylate ions can adsorb at the interface of the bitumen/water (Eq. 2-7). If the bitumen fraction is kept constant and the concentration of surfactant is increased in the aqueous phase, it forms a larger interfacial area that is saturated by the surfactant. Therefore, the mean droplet diameter of the formed emulsions should diminish [25].

Nuñez and co-workers [50] studied the rheological behavior of concentrated bitumen in water emulsions. Results showed that the emulsion viscosity is rigorously influenced by the type of drop size distribution. The viscosity of a bimodal emulsion (Figure 2-18) is a number of times lower than the viscosity of a comparable emulsion that present a unimodal distribution. It is consequence to the fact that the large droplets control almost all the viscosity, because of their size and the fraction of small droplets contribute little to the overall friction when compared to the large droplets.

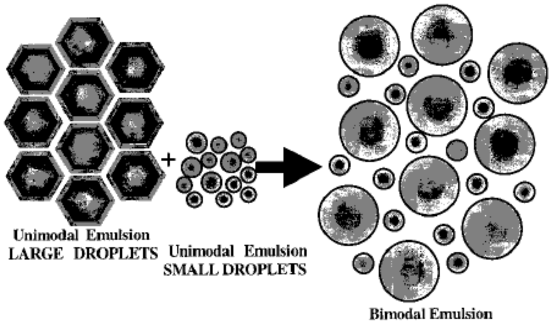


Figure 2-18: Ilustration of the formation of a bimodal bitumen in water (O/W) emulsion [50].

Figure 2-19 presents the influence of bitumen concentration on the apparent viscosity of unimodal bitumen in water emulsions analyzed at 30 °C and with a shear rate of 20 s^{-1}. As can be observed the apparent viscosity increases faster for bitumen fractions higher than 0.60. It is due to the concentration of bitumen that increases. Hence, the distance that separate the droplets is smaller, which causes the hydrodynamic interactions between droplets to increase [50].

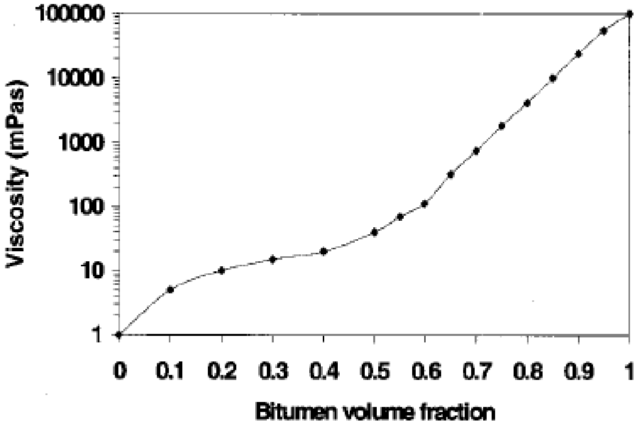


Figure 2-19: Effect of bitumen concentration on the apparent viscosity of unimodal (O/W) emulsions (mean droplet diameters of 20 μm) analyzed at 30 °C and 20 s^{-1} of shear rate [50].

Another kind of emulsions is the water-in-oil (W/O). In these emulsions, the water is the dispersed or internal phase and the oil is the continuous or external phase (Figure 2-20). If the water concentration increases, the viscosity of water-in-oil (W/O) emulsions is higher. The increase in viscosity with increase in water concentration continues until the so-called emulsion inversion point is reached, when the continuous phase changes to water. Thus, the water-in-oil (W/O) emulsion switches to an oil-in-water (O/W) emulsion. The viscosity decreases with an increase in water content for the oil-in-water (O/W) emulsions. Hence, in the emulsion inversion point the maximum apparent viscosity of the emulsion is found [52].

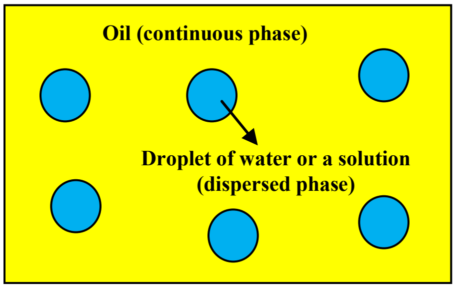


Figure 2-20: Representation of water in oil (W/O) emulsion.

A common kind of emulsion found in the oil fields is brine phase dispersed in a continuous crude oil phase, this emulsion is of type (W/O) [54]. This stable water-in-oil (W/O) emulsion may form during the production of crude oil, since co-produced water is mixed with the oil from reservoir that is transported to separation facilities. Asphaltenes and resins native to the oil are recognized as the main components with respect to stabilization of the interface. Fine solids may as well contribute to the stabilization, just as naphthenic acids [16].

Singh and co-workers [53] studied the viscosities of brine-in-heavy oil emulsions from Alaska. They found that the viscosity of these stable emulsions can increase 2-3 orders of magnitude compared to the dry oil viscosity. The stability of the emulsion can be gauged from the fact that external phase of emulsion (oil) exits even up to 90% brine fraction. This emulsion has the consistency of the peanut butter, with a viscosity > 2×10^4 cP at room temperature (Figure 2-21).

Figure 2-21: After centrifuging, the centrifuge tubes included, dry oil, brine and a middle layer of ~ 90% emulsion [53].

Furthermore, the viscosity of the Alaskan heavy oil emulsion significantly increases with the brine content. Figure 2-22 presents the measured viscosity multiplier as function of the brine fraction with ranges of temperature from 10˚C to 60˚C and a shear rate of 30 sec^{-1} [53].

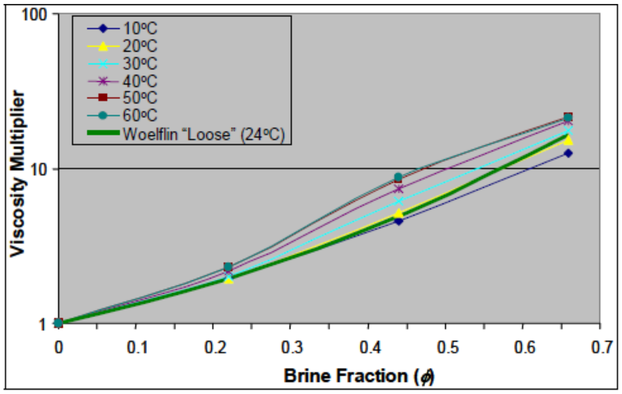


Figure 2-22: Effect of brine content on (W/O) emulsion viscosity [53].

Woelflin's "loose" emulsion data measured at 24°C refers to Woelflin's study who presented viscosity data of natural brine in crude emulsions. The natural emulsions were qualitatively categorized in three kinds namely “tight”, “medium”, and “loose”. The “tight” emulsions were categorized as ones of very small droplet size. These emulsions usually form when a wet well is subjected to high conditions of agitation. The “loose” emulsions were defined as ones that generally occur in the production from a pumping well. A “medium” emulsion was defined between a “tight” and “loose” emulsion [53].

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CHAPTER 3 – INFLUENCE OF ACID CHEMISTRY ON BITUMEN VISCOSITY

Abstract

Canadian oil sands bitumen has high density and viscosity. One of the potential causes of the high viscosity of the oil sands bitumen is acid-base interactions. The influence of acid treatment on the viscosity of bitumen was investigated. The study was performed by mixing an organic solution of Cold Lake bitumen with aqueous solutions of hydrochloric acid (0.3 M, 0.03 M, 0.01 M, 0.003 M, 0.0003 M and blank) at room temperature, with a reaction time of 2 hours. Three variables in the experimental protocol were identified that could influence the viscosity and asphaltenes content of the treated bitumen: heating, oxidation and acid concentration. The impact of oxidation as a result of heating was the major contributor to the increase in viscosity. On heating the acid treated product (0.03 M HCl) the viscosity increased from 9.9 ± 0.1 to 29.5 ± 0.8 Pa.s measured at 60 °C. However, when the product was not subjected to heating during product work-up, the viscosity of the bitumen decreased. The viscosity response was not monotonous with acid concentration. The lowest viscosity was found after treatment with an acid concentration of 0.003 M, namely, 1.8 ± 0.3 Pa.s measured at 60 °C. It was found that acid treatment disrupted chemical interactions in the bitumen by ion exchange and neutralization reactions. The most abundant exchangeable cation found in the acidic aqueous solution (0.003 M HCl) after treatment, was Ca^{2+}, with a concentration of 18 mg/L of bitumen. The morphology of bitumen was characterized by atomic force microscopy (AFM). The results showed the change of morphology after acid treatment without heating and showed the disaggregation of clustered asphalthenes.

Keywords: Oil sands bitumen, viscosity, acid, chemical treatment, chemisty of bitumen, asphaltenes.

3.1 Introduction

Alberta's oil sands are one of the major unconventional oil reserves in the world. These oil sands are complex multiphase systems constituted mainly of bitumen, sand, and water. Bitumen is the heaviest kind of petroleum that have a high density (low API gravity), high viscosity, high asphaltenes content, and poor fluidity [1]. When viewed as a hydrocarbon, it contains carbon (80-88 wt%) and hydrogen (8-12 wt%) with an hydrogen to carbon molar ratio (H/C) around 1.5 [2]. Bitumen chemistry is very complex and a typical oil sands derived bitumen contains 5 wt% sulfur, as well as lower concentrations of other heteroatoms.

In order to be suitable for pipeline transport, the fluidity of the bitumen must be improved so that it can be pumped easily. Two approaches are mainly employed. Firstly, to dilute the bitumen with 25-35% naphtha range material. Secondly, upgrading technologies for viscosity reduction of bitumen, such as visbreaking, coking and hydroconversion [3].

Recently research was carried out to investigate the low temperature visbreaking behavior of oil sands bitumen [4, 5]. The results showed that viscosity reduction of bitumen does not follow a regular and monotonic decrease with an increase in bitumen conversion. So, these changes indicated that not only C-C bond breaking, but other interactions are also affected; otherwise it would be difficult to explain the observed decrease in viscosity at mild conditions.

One of the potential interactions that could affect bitumen viscosity is intermolecular acid-base interactions. The main objective of this research was to evaluate the response of bitumen viscosity to changes in weak acid-base interactions or interactions, or bonds that may be affected by acid chemistry.

3.2 Experimental

3.2.1 Materials

Canadian Cold Lake bitumen was used for the acid treatment. It was provided through the sample bank of the Center for Oil Sands Innovation (COSI) at the University of Alberta. The characterization of Cold Lake bitumen is shown in Table 3-1.

Methylene chloride (CH_2Cl_2) 99.9%, HPLC grade supplied by Fisher Scientific.

Hydrochloric acid (HCl), 50% (v/v) Aqueous Solution (1 + 1) supplied by Ricca Chemical Company.

Milli-Q water to prepare diluted aqueous solutions of hydrochloric acid 0.3 M, 0.03 M, 0.01 M, 0.003 M and 0.0003 M.

Table 3-1: Properties of Cold Lake Bitumen.

Property	Cold Lake Bitumen
Viscosity (Pa.s)	
at 20 °C	2135 ± 11
at 60 °C	9.6 ± 0.1
Density (Kg/m^3)	
at 40 °C	1012 ± 1.1
at 60 °C	1000 ± 1.2
Asphaltenes content (wt %) [a]	16.8 ± 1.3
Elemental composition (wt %)	
H	10.0 ± 0.1
C	83.0 ± 0.2
N	0.6 ± 0.01
S	4.6 ± 0.2
O	0.7 ± 0.01
Mineral matter (wt %)	1.1 ± 0.5
Microcarbon residue (wt %)	15.8 ± 0.8
Refractive index	
at 40 °C	1.5767 ± 0.0001
at 60 °C	1.5692 ± 0.0001

[a] Asphaltenes precipitated with *n* pentane

3.2.2 Equipment and procedure

The acid treatment was performed using the following methodology: 20 g of Cold Lake bitumen was dissolved in 131.5 g of methylene chloride. The diluted aqueous solution of hydrochloric acid (100 g) was added to the organic solution. The height of liquid in the reactor was 3.7 cm. These solutions were mixed using an octagonal magnetic stir bar (Dia. x L: 1 x 5 cm) with a set speed of 400 rpm for 2 h at room temperature. Then, the product was separated using a separating funnel. The more dense (bottom) phase was the organic solution consisting of bitumen and methylene chloride. The less dense (top) phase was the aqueous solution of HCl. Emulsion formation was observed in the interface as shown in Figure 3-1. During this stage, the emulsion phase was incorporated to the organic phase. After that, methylene chloride was removed from the bitumen in a rotary evaporator at 45 °C under vacuum at 55 kPa absolute. Next, the treated bitumen was dried under two conditions: first, heating in an oven at 50 °C overnight plus 96 h at 100 °C in air atmosphere and second, without heating, overnight at ambient conditions in a fume hood. Finally, the product and the separated aqueous solution were weighed and the material balance was calculated.

It is important to point out that a blank was carried out using only water (no acid) following the same methodology. However, for the blank containing only water and an aqueous solution 0.0003 M HCl, the bitumen, methylene chloride and water formed a stable emulsion (Figure 3-2). After evaporation of CH_2Cl_2, free water was observed and it was separated by decantation.

Due to the effect of heating on the product, two additional experiments were performed. Raw bitumen was heated in the oven with the same conditions in a normal air atmosphere and in a nitrogen atmosphere. All experiments and analyses were carried out at least in triplicate to measure the repeatability and reproducibility.

Experimental decisions.

The experimental decisions were based in a previous studied of action of solvents on coal at low temperatures [12]. Reaction time of 2 h was chosen to optimize this variable, for the coal the reaction time was 24 h. The amount of feed material was 20 g to have enough sample for all analysis required. The amount of solvent chose was approximately 131.5 g, which occupied a volume of 100 mL, it is the same volume of aqueous solution of hydrochloric acid. In the study of coal was used 100 mL of solvent.

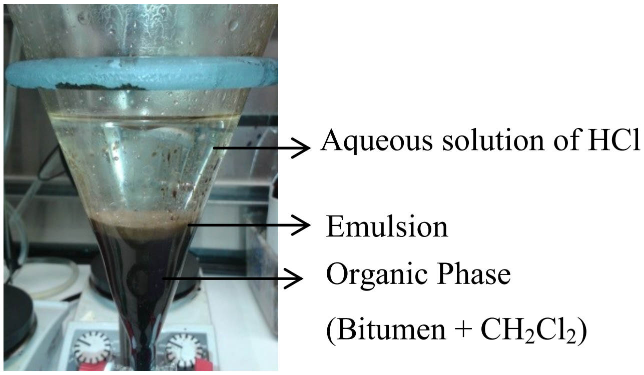

Figure 3-1: Separation of phases after acid treatment.

Figure 3-2: Blank Emulsified water phase.

3.2.3 Analyses

The hydrochloric acid was titrated with a standard solution of NaOH 0.997 M using a Mettler Toledo T50 titrator with a glass electrode employing a sensor chip DGi116-solvent. The concentration of HCl was determined to be 5.93 M.

Viscosity analyses were carried out using an Anton Paar RheolabQC rotational rheometer. The measuring cup was C-CC17/QC-LTD and the rotational spindle was CC27, diameter of 26.661 mm and length of 39.954 mm. The amount of sample required for the analysis was approximately 16 g and the analyses conditions were a constant shear rate of 10 s^{-1} and constant temperature of 60 °C.

The asphaltenes content of the bitumen was determined by the following procedure: 1 g of sample was weighed and then mixed with 40 mL of n-pentane at a 1:40 ratio. The mixture was stirred for 1 h by magnetic stirring, followed by a period of 24 h without stirring. After that, the mixture was vacuum filtered using a 0.22 µm filter paper at room temperature. The resulting filter cake was rinsed with n-pentane until the eluent became colorless. The rinsed asphaltenes samples were left in a fume hood for 3 days to ensure complete evaporation of solvent. Finally, asphaltenes were weighed.

Fourier transform infrared (FT-IR) spectroscopic analysis was performed using an ABB MB3000 Fourier equipped with a MIRacleTM Reflection Attenuated Total Reflectance (ATR) diamond crystal plate and pressure clamp. The spectra were collected with the following parameters: resolution of 4 cm^{-1}, 120 scans, detector gain of 81 and spectral region 4000 - 400 cm^{-1}.

For the mass balance all weighing was performed on a Mettler Toledo ML 3002E/03 with 3200 g capacity and 0.01 g of readability.

The pH of aqueous solutions of hydrochloric acid were measured using an Oakton pH 700 Benchtop Meter which was calibrated using a pH 4 buffer solution supplied by Fisher Scientific. The inductively coupled plasma optical emission spectrometry (ICP-OES) was carried out to quantify the metals content of the aqueous solutions before and after acid treatment. A Thermo Scientific iCAP 6000 Series ICP-OES spectrometer of Thermo Fisher Corporation, Cambridge, UK was used for this purpose. This instrument employs a high-resolution Echelle spectrometer with a charge injection device (CID) detector. The nebulizer argon flow rate was 0.6 L/min at 0.22 MPa. The metals analyzed and their corresponding wavelengths were: Ca at 393.3 nm, Fe at 259.9 nm, K at 766.4 nm, Mg at 279.5 nm, Na 589.5 nm , Ni at 221.6 nm and V at 309.3 nm.

Mineral matter content was determined using thermogravimetric analyser (TGA). For a typical analysis 4-5 mg of bitumen was weighed and put inside alumina crucible. All the analyses were performed using TGA/DSC1 with a microbalance model MX5 of measuring range 5 g and resolution 1 μg and Star^{e} software from Mettler Toledo. TGA was heated under air atmosphere to 900 °C with a heating rate of 10 °C/min. The sample was kept isothermally at 900 °C for 30 minutes. The final weight was considered to be ash (oxidized mineral matter), i.e. all material that did not form gaseous combustion products.

Micro carbon residue is indicative of the coke-forming propensity of the feedstock (ASTM D4530).[6] Micro carbon residue analysis was also conducted by thermogravimetric analysis. Analysis was performed under nitrogen atmosphere with a flow of 50 mL per minute. The equipment was heated with a heating rate of 10 °C/min to 600 °C and it was isothermally controlled at this temperature for one hour.

Simultaneous determination of CHNS using the Thermo Flash 2000 CHNS-O Combustion Analyzer.

"The autosampler, which is continuously swept with helium carrier gas, drops the sample contained within a tin (Sn) cup into a vertical quartz tube called the combustion reactor that is maintained at 1000°C. The upper portion of the combustion reactor is filled with an oxidation catalyst (tungstic oxide (WO_3) on alumina), and the lower portion is filled with pure reduced copper wires. Once the sample enters the combustion reactor, a small, fixed volume of pure oxygen is added to the helium carrier gas. The added oxygen creates a highly oxidizing atmosphere, which completely burns the sample and tin cup container. The carbon, hydrogen, nitrogen, and sulfur present in the samples are quantitatively converted to CO_2, H_2O, NO_x, and SO_2, respectively. Excess oxygen is removed in the copper reduction portion of the combustion chamber and NO_x is reduced to N_2. The carrier gas sweeps the combustion products onto the chromatographic column (Porapak QS, 4 mm ID, 2 m long), where the gases are separated. The detection of the individual gases is achieved with a thermal-conductivity detector. The Eager Xperience software program converts the output signal from the thermal conductivity detector into a chromatogram that displays the nitrogen, carbon dioxide, water and sulfur dioxide peaks. The software generates the area count data used to calculate the percentage of nitrogen, carbon, hydrogen and sulfur present in the sample. The analytical run lasts for 11 minutes" [7].

Calibrating the Thermo Flash 2000 CHNS-O.

"The instrument is calibrated using at least three samples of an organic analytical standard (OAS) at the start of each analysis day. The standard is accurately weighed directly into tin cups using a MettlerXP2U microgram balance, which is readable to 0.1 microgram. The standards span the range from ~0.5 to ~3 mg. Once the standard runs are finished, linear regression analysis is performed on the peak areas for each of the elements (C, H, N S) versus the milligrams of each element contained in the standards. The amount of each element is calculated by multiplying the known proportion of each element in the standards by the amount of sample. The equation of the regression line that fits these points is used to calculate the amount of C, H, N, and S in the samples. An acceptable regression line for each element has an R^2 value of at least 0.999. For R^2 values less than these, another set of standards are run and a new calibration curve is obtained. To monitor the accuracy of the instrument, a sample of the OAS is used as a calibration check every 4 test samples. The calibration check is treated as an unknown. The check samples are weighed, such that they are within the calibration range of the standards used. The measured values for these standards should produce results that are within ± 0.3% of the theoretical values. If they do not agree within ± 0.3%, the system is inspected for possible malfunction and, if necessary, repairs are performed on the instrument and the samples are re-analyzed" [7].

The determination of oxygen is conducted with the following procedure:

"The technique used is based on the Unterzaucher modified method. The sample is weighed in a silver foil container and dropped into the reactor furnace maintained at 1060 ºC where the sample is pyrolized. Quantitative conversion of oxygen to carbon monoxide (CO) is achieved by a layer of nickel coated carbon. The pyrolized gas mixture flows into the chromatographic column (molecular sieve 5Å) heated at 65 ºC for separation of the CO from N_2. The CO is measured using a thermal conductivity detector which produces an electrical signal proportional to the concentration. The same procedures for calibration and data reduction that apply to CHNS apply to oxygen determination" [7].

Atomic Force Microscopy Analysis.

Atomic Force Microscopy (AFM) analysis was conducted for raw bitumen (Cold Lake) and bitumen after acid treatment (0.03 M HCl) without heating to investigate the effect of acid treatment on the morphology of bitumen. The samples preparation was performed with the following procedure: First of all, raw bitumen and treated bitumen samples were dissolved in methylene chloride (CH_2Cl_2) 99.9%, HPLC grade to make 0.1 wt%, 0.01 wt% and 0.001 wt% bitumen solutions. Then, 1 cm^2 size of cleaved SiO_2 wafer (supplied by Nanofab, University of

Alberta) was cleaned with Milli-Q water and ethanol, and dried with N_2 gas to remove any contaminants and impurities from the surface. A drop (10 μL) of bitumen solution was deposited on the cleaned SiO_2 wafer. The drop was allowed to dry at room temperature conditions until all the methylene chloride was evaporated. So, the SiO_2 wafer contained only bitumen adhering to the substrate [8].

The substrate with bitumen was mounted under an atomic force microcopy probe. The topografic imaging was conducted in peak force atomic force microscopy (PF-AFM) mode using a Bruker Icon AFM (Santa Barbara, CA) with a scan rate of about 0.7 Hz in ambient conditions of temperature and humidity. Figure 3-3 shows a scheme of sample preparation procedure [8]. The AFM analysis was performed by Ph.D. Ravi Gaikwad (Postdoctoral fellow, Ingenuity Labs, University of Alberta). We conducted the sample preparation with the assistance of Dr. Ravi.

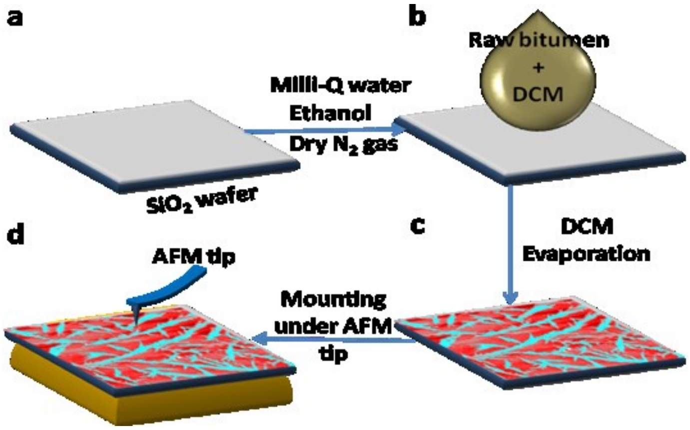

Figure 3-3: Scheme of sample preparation procedure [8].

3.3 Results and Discussion

In the study of acid treatment on bitumen, three variables were identified that could influence the viscosity and asphaltenes content of the treated bitumen.

(a) Heating. Bitumen inherently has a high stable free radical content [9], which may participate in chemistry on heating. The Cold Lake bitumen also contains many S, N and O containing functional groups (Table 3-1), which may also participate in chemistry on heating. In fact, some reactions of oilsands derived asphaltenes have been reported at temperatures near 150 °C [10]. It was therefore anticipated that prolonged heating could affect the product.

(b) Oxidation. Oxidative weathering of bitumen is known, but with heating this process is accelerated. Bitumen oxidation has been a topic of study and it was found that even at temperatures <150 °C, oxidative hardening can readily take place [11]. Thus, exposure to air during product work-up may also affect the product.

(c) Acid concentration. The acid concentration was the primary manipulated variable in the study. It should be emphasised that the objective was only to look at the impact of acid treatment, but the possible contributions of heating and oxidation, which could obscure the effect of acid concentration, necessitated the manipulation of those variable too.

3.3.1 Effect of heating without acid treatment

Blank experiments were performed with deionized water at neutral pH to determine whether heating during product work-up has an impact on its own (Figure 3-4). The viscosity and asphaltenes content of Cold Lake bitumen (Table 3-1) that was not subjected to any treatment is shown for reference.

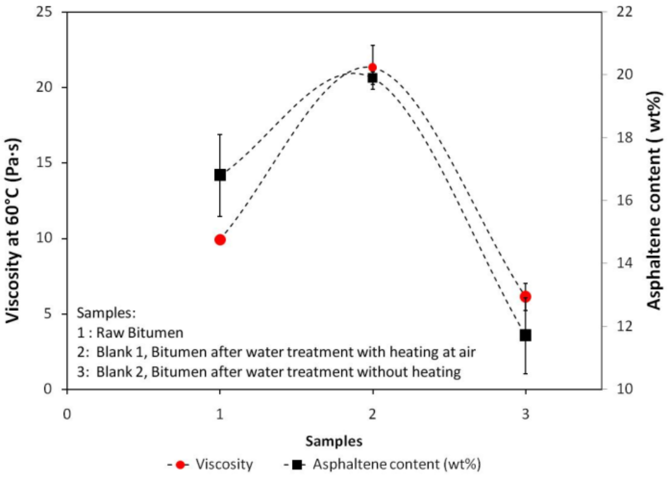

Figure 3-4: Bitumen viscosity and asphaltenes content after water treatment (blank) with and without heating during work-up.

Heating affected the viscosity and asphaltenes content, but surprisingly so did water washing. The blank experiments indicated that acid-base interactions were relevant even at neutral pH. It also confirmed our suspicions that heating may affect the chemistry and product properties.

3.3.2 Effect of heating on acid treatment

The change in viscosity and asphaltenes content of bitumen after acid treatment with an aqueous solution HCl (0.03 M) was determined with and without heating during product work-up (Figure 3-5). The viscosity and asphaltenes content of Cold Lake bitumen (Table 3-1) is shown for reference.

Heating the product during work-up had a profound impact on the viscosity and asphaltenes content. On heating the acid treated product the viscosity increased from 9.9 ± 0.1 to 29.5 ± 0.8 Pa.s. The asphaltenes content also increased from 16.8 ± 1.3 to 22.8 ± 0.5 wt%.

If the potential effect of heating had not been evaluated, it would erroneously be concluded that acid treatment with 0.03 M HCl was on the whole detrimental. However, when the product was not subjected to heating during product work-up, the viscosity of the bitumen decreased to 3.6 ± 0.3 Pa.s and the asphaltenes content decreased to 14.8 ± 0.8 wt%.

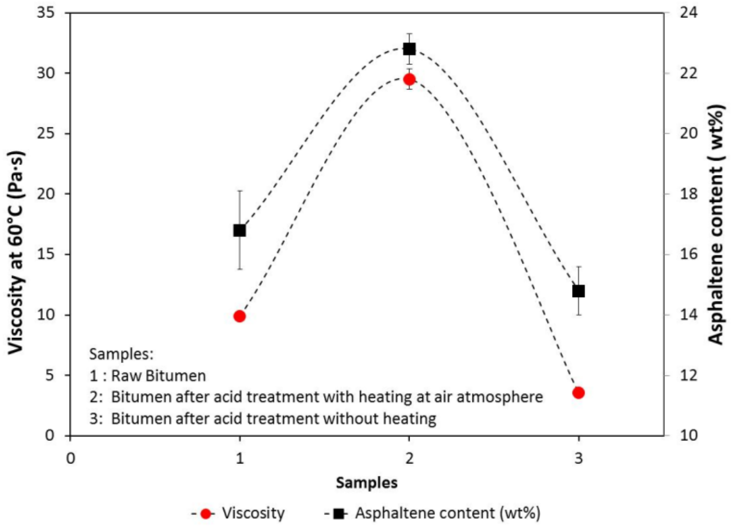

Figure 3-5: Bitumen viscosity and asphaltenes content after acid treatment (0.03 M HCl), with and without heating during work-up.

According to the mass balance, there is aqueous phase remaining in the product after treatment due to emulsion formation. The yield of aqueous solution of HCl (0.03 M) is 94 ± 2.6 wt% and 92 ± 1.2 wt% after acid treatments. The yield of bitumen increases from 100 ± 0.03 to 126 ± 5.7 wt% after of acid treatment with heating in air atmosphere, and without heating, respectively. This difference is due to that some aqueous solution and some solvent methylene chloride remain in the treated bitumen without heating. For the product after acid treatment with heating the aqueous solution and volatiles (methylene chloride) are evaporated.

The results for the acid treated bitumen that involved work-up without heating (Figure 3-5) cannot be compared directly with the other results. The interpretation of the viscosity data and asphaltenes content become complicated, because the fluid contains emulsified water. Without further work it was not clear whether the observed viscosity that was lower than that of bitumen was due to the water and methylene chloride, or a reduction in the actual bitumen viscosity.

Figure 3-6 shows FTIR spectra of raw bitumen and products after acid treatment. The strong and broad band of OH between 3600-3200 cm^{-1}, which is indicative of free water, was not observed for the bitumen after acid treatment with heating, but it can be seen in the spectrum of the acid treated product that was not heated. Considering the amount of water that should have been present in this sample, the absorption in the 3600-3200 cm^{-1} is remarkably weak. In addition, it was observed one adsorption that is related to methylene chloride at 1265 cm^{-1}, is not present in the raw bitumen and for the product with heating.

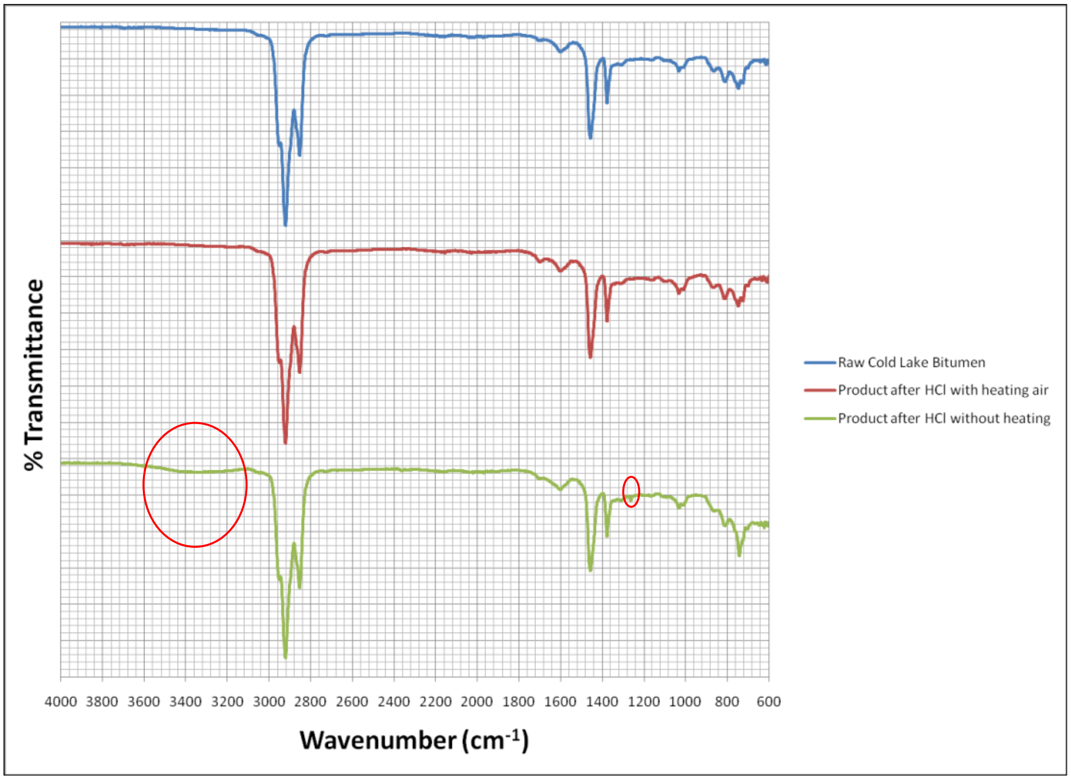

Figure 3-6: FTIR spectra of raw bitumen and products after acid treatment.

3.3.3 Effect of oxidation

The impact of oxidation as a result of heating during work-up, was anticipated to be the major contributor to the increase in viscosity that was observed (Figures 3-4 and 3-5). In order to reduce the potential variables, the raw bitumen (no mesitylene added) was subjected to the work-up procedure involving heating, without any water or dilute acid treatment. The work-up was performed under normal atmosphere (air) and under N_2 atmosphere to eliminate autoxidation (Figure 3-7).

As shown in Figure 3-7, the viscosity of Cold Lake bitumen is meaningfully higher after heating in air atmosphere with a value of 30.5 ± 1.1 Pa.s. When heating in N_2 atmosphere, the viscosity was 14.0 ± 0.3 Pa.s. This difference is due to the oxidation of bitumen in air atmosphere, which leads to an increase in the viscosity. For both atmospheres, loss of volatiles were 2 wt%.

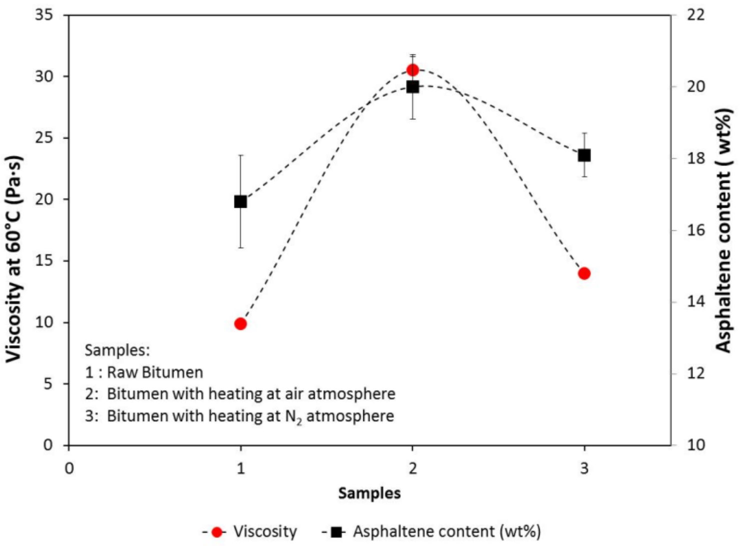

Figure 3-7: Bitumen viscosity and asphaltenes content after work-up of raw bitumen by heating in air and N_2 atmosphere.

The impact of heating, irrespective of atmosphere, was less pronounced on the asphaltenes content. The highest asphaltenes content is for bitumen with heating in air atmosphere and it was meaningfully higher than that of the raw bitumen (better than 95 % statistical confidence). The asphaltenes content of the raw bitumen and bitumen heated under N_2 were not meaningfully different.

Heating affected the bitumen properties negatively, but most of the observed increase in viscosity was due to oxidation. The increase in viscosity on heating the raw bitumen under air (Figure 3-7) and the same for the acid treated mixture (Figure 3-5), are quantitatively quite similar, but quantitatively different from that of the water treated mixture (Figure 3-4). It suggested that water on its own suppressed oxidation, but acidifying the water counteracted this effect. This aspect was not investigated further.

Another observation that could be made is that the asphaltenes content and the viscosity did not respond in the same way. Oxidation affected viscosity, but had only a minor influence on the asphaltenes content.

3.3.4 Effect of acid concentration

Due to the effect of heating and oxidation, subsequent study of acid treatment was carried out without heating. The influence of acid concentration on viscosity was determined (Figure 3-8).

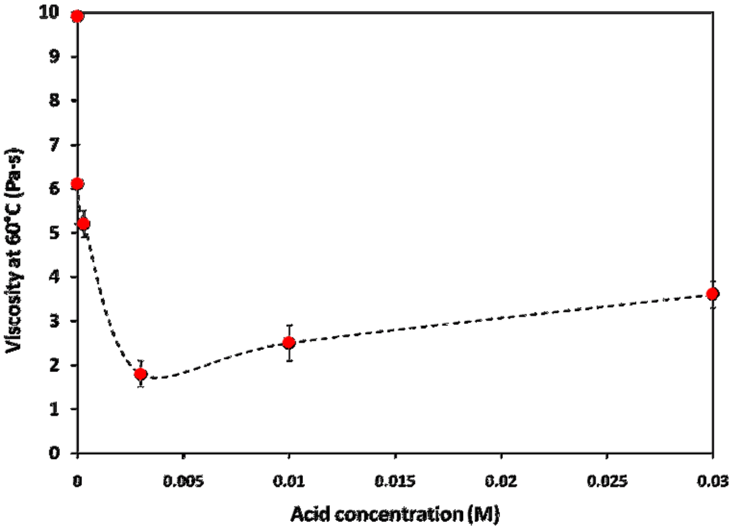

Figure 3-8: Effect of acid concentration on the viscosity of acid treated bitumen without heating during product work-up.

The raw bitumen has a viscosity of 9.9 ± 0.1 Pa.s, with the blank (water treatment) the viscosity decreases until 6.1 ± 0.9 Pa.s, then with an acid concentration of 0.0003 M the viscosity slightly reduces until 5.2 ± 0.3 Pa.s. The lowest viscosity is for an acid concentration of 0.003 M with a value of 1.8 ± 0.3 Pa.s. Then, the viscosity slightly increases until 2.5 ± 0.4 Pa.s after acid treatment with 0.01 M HCl. Finally, the viscosity achieves a near constant value with acid concentrations of 0.03 M and 0.3 M whose values are 3.6 ± 0.3 Pa.s and 3.5 ± 0.4 Pa.s, respectively.

However, the retention of water and the solvent methylene chloride by some of the samples complicates interpretation. Based on the results the impact of the asphaltenes content on viscosity cannot be discounted. The results suggest that there are at least two changes taking place. There is a possible increase in viscosity due to the increase in the asphaltenes content after acid treatment with heating. On the other hand there are chemical and/or physical changes caused by the acid treatment without heating that decreased the viscosity. Overall that latter effect dominated the viscosity response, but the contribution of water, as well as remaining methylene chloride, must still be resolved.

It was of interest to understand the reason for the change in viscosity and whether the hypothesis outlined in the introduction could be confirmed.

Table 3-2 shows the pH of different acid concentrations before and after treatment. As can be observed, the pH after acid treatment increases; for example, with 0.0003 M HCl the pH meaningfully achieved a value of 7.70, which indicated that all the acid was consumed during the reaction. At least part of the observed benefit can be attributed ion exchange and neutralization reactions.

Table 3-2: pH of Different Aqueous Solutions of HCl

Aqueous solution HCl (M)	pH initial		pH after treatment	
	x	s	x	s
Blank	8.01	0.18	8.05	0.49
0.0003	3.73	0.02	7.70	0.32
0.003	2.68	0.01	3.17	0.02
0.01	2.26	0.04	2.48	0.01
0.03	1.77	0.01	1.86	0.02
0.3	0.89	0.03	0.91	0.01

Average (x) and sample standard deviation (s) of experiments in triplicate.

Table 3-3 shows the metals content of aqueous solutions before and after of acid treatment with a concentration 0.003 M HCl. As can be observed metals content Ca, Fe, K, Mg, Na and Ni increased after acid treatment. Metal ions, such as alkali or alkaline-earth metal ions, which were associated with carboxylate groups (mainly from naphthenic acids) could be easily removed by acid treating [11]. The most abundant exchangeable cation in the samples was Ca^{2+}, with a concentration of 3.61 ± 0.29 mg/L in the water, which is equivalent to Ca removal of 18 mg/L bitumen. Bodegom et al. [12] reported that for coals washed with 0.1 N HCl at room temperature removes virtually all Ca^{2+}. It was not confirmed whether all of the Ca was removed from the bitumen. It should further be noted that some of the metal ions might have been present in connate water associated with the bitumen.

It is noteworthy that vanadium and nickel, likely associated with basic porphyrins, were virtually unaffected by the aqueous solution of HCl. The detection limits of these elements on the ICP-OES were 0.002 mg/L for V and 0.004 mg/L for Ni. The results indicate that less than 0.1 mg/L of Ni and V were leached from the bitumen.

Table 3-3: Metals Content of Aqueous Solutions Before and After Acid Treatment with a 5:1 ratio of 0.003 M HCl to Bitumen.

Metal	Concentration in aqueous phase (mg/L)	
	Initial [a]	After acid treatment
Ca	0.0560 ± 0.0059	3.61 ± 0.29
Fe	- [b]	1.45 ± 0.10
K	- [b]	0.19 ± 0.14
Mg	0.0022 ± 0.0024	0.69 ± 0.06
Na	0.4025 ± 0.0338	2.12 ± 0.33
Ni	- [b]	0.014 ± 0.003
V	- [b]	- [b]

[a] Metals introduced by the commercially obtained HCl.

[b] Below detection limit.

3.3.5 Atomic Force Microscopy Analysis

It was of importance to understand the effect of acid on the raw bitumen morphology. Hence, we monitored the change in the morphology of raw bitumen before and after acid treatment using Atomic Force Microcopy (AFM). The topography images of raw bitumen and bitumen after of acid treatment (0.03 M HCl) without heating, which were prepared with a solution 0.001 wt% of methylene chloride are illustrated in Figures 3-9 (a) and 3-9 (b), respectively. Figure 3-9 (c) and 3-9 (d) are the corresponding cross section images of the topographies.

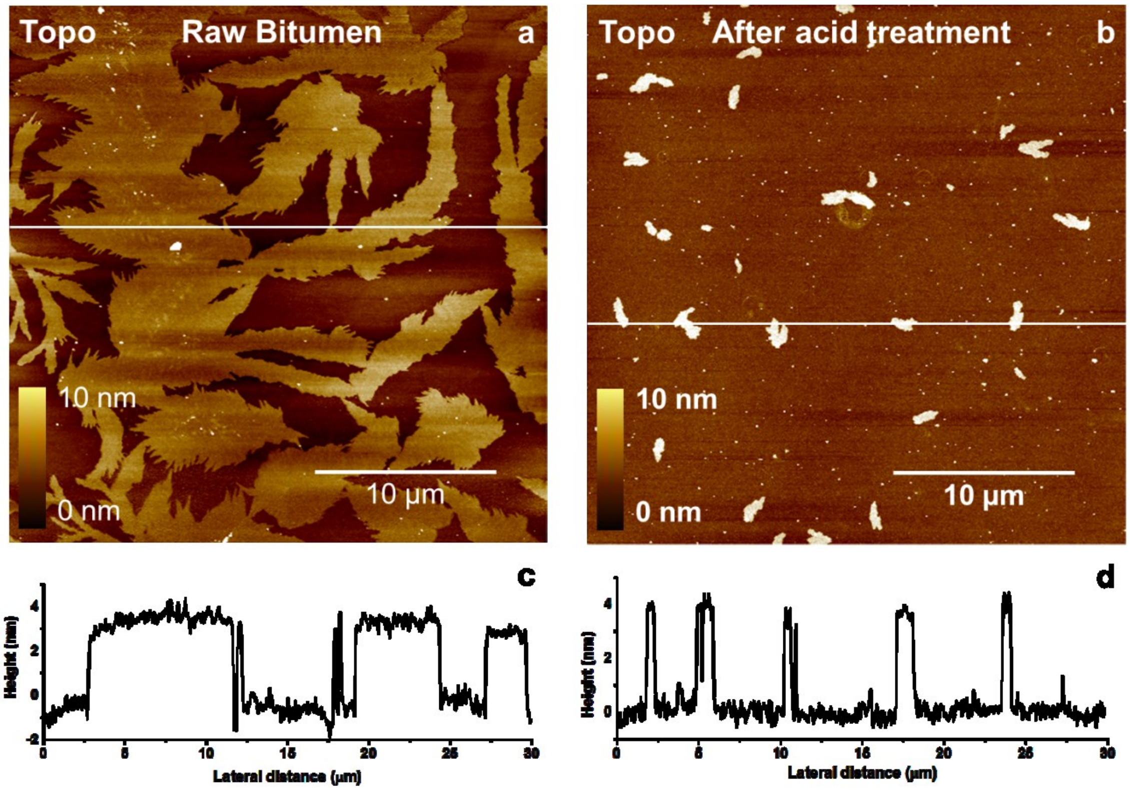

Figure 3-9: AFM topography images. (a) Raw bitumen,(b) Bitumen after of acid treatment (0.03 M HCl) while (c) and (d) are the respective cross-section images of the topographies.

As can be observed, there are clearly two phases in raw bitumen, specifically the dispersed phase and the matrix phase. This dispersed phase could be associated with asphaltene aggregates and/or other aggregating species. This is confirmed in a previous research related to the morphologies of asphaltene aggregates, which formed self-assembled fractal structures [8]. The cross section (Figure 3-9 c) of the raw bitumen shows larger domains of the order of few microns while that for acid treated bitumen (Figure 3-9 d) shows smaller domains in the order of couple of microns. The height of these domains still remains the same indicating the two dimensional disaggregation of components in the raw bitumen.

For the treated bitumen (0.03 M HCl), the areas of the dispersed phase are clearly decreased. This proves that dispersed phases in bitumen are disaggregated during acid treatment. This change of morphology is correlated with that of physical property (viscosity) [13]. According to

Wang and co-workers [4] a reasonable explanation for the rapid viscosity reduction during low-temperature visbreaking, was a decrease in the effective volume fraction (Φ_{eff}) occupied by the colloidal aggregate fraction in the bitumen. A reduction in Φ_{eff} could be due to "disaggregation of clustered asphaltenes and other aggregating species, the release of trapped material and/or a potential decrease in the boundary layer volume around the aggregates". "These are physical processes, or processes involving weak chemical interactions. Hence, it is conceivable that low temperature and low contact time conversion could disrupt such physical and weak chemical interactions" [4].

The same explanation can be applied for acid treatment as was demonstrated in this study with the change of morphology of bitumen and the viscosity reduction. The disaggregation of clustered asphalthenes and other aggregating species can be by acid treatment. The release of trapped material and the removal of salts and solids that might have been present in connate water associated with the bitumen are also accomplished by acid treatment.

3.4 Conclusions

a) The treatment with low acid concentrations in the range of 0.0003-0.3 M HCl may disrupt some chemical interactions in the bitumen to affect physical properties such as the viscosity.

b) Acid treatment resulted in a complex viscosity response with respect to the involved variables as heating, acid concentration, the solvent methylene chloride and the formation of an emulsion on the viscosity changes.

c) Asphaltenes are not the only 'bad actors' in the description of bitumen viscosity.

d) The drastic change in viscosity after heating in air atmosphere can be attributed to the oxidation of bitumen, which leads to an increase in the viscosity.

e) The change of bitumen morphology observed by Atomic Force Microscopy (AFM) analysis after acid treatment without heating showed the disaggregation of clustered asphaltenes and other aggregating species, which correlated with the viscosity reduction.

Part of the work presented in this chapter was also published as a preprint paper [14].

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CHAPTER 4 – IMPACT OF SOLVENT METHYLENE CHLORIDE AND EMULSION FORMATION DURING THE ACID TREATMENT

Abstract

The effect of solvent (methylene chloride) and emulsion formation during the work-up procedure of acid treatment (0.003M HCl) was investigated. The results showed that some solvent (CH_2Cl_2) remained trapped in the bitumen structure according to the mass balance, FTIR analysis and ^{1}H-NMR analysis. The impact of remaining methylene chloride (2.3 wt% by FTIR) for the blank experiment was to reduce the viscosity from 97.5 Pa.s (raw bitumen) to 32 Pa.s (blank) at 40˚C. For some samples, even under constant conditions, the rate of evaporation of solvent was not reproducible, the solvent content had to be quantified analytically. It was determined that the asphaltenes content of the emulsion was 52 wt% based on the oil present in the emulsion. Not only did the asphalthenes stabilize the emulsion, but it also stabilized by inorganic solids particles (such as clay minerals). The mineral matter content of emulsion was 4.3 ± 1.6 wt %. The effect of the emulsion was to increase the viscosity due to the presence of emulsified water droplets in the bitumen. The lowest viscosity, after correcting for the residual methylene chloride, was obtained for the bitumen after acid treatment that was separate from the emulsion with a value of 12.6 Pa.s at 40˚C. The water treatment indicated only to wash the bitumen with water affected the viscosity, which decreased significantly from 97.5 Pa.s (raw bitumen) until 19 Pa.s at 40˚C (corrected for the residual methylene chloride). Finally, other physical properties of treated bitumen were improved, such as the density.

4.1 Introduction

The response of bitumen viscosity to changes in acid-base interactions, or bonds that may be affected by acid chemistry, was investigated in Chapter 3. The observations highlighted two aspects of the work-up procedure that likely affected the observed viscosity values: residual solvent methylene chloride and emulsion formation. Since it was not always feasible to prevent the formation of emulsions and some samples strongly retained the solvent, the approach that was taken was to rather quantify these effects, so that measurements could be corrected.

Dilution with a solvent reduces the bitumen viscosity, which in its native state has a viscosity greater than 10^4 mPa·s [1]. The diluents industrially used are petroleum-derived naphtha and natural gas condensates that are added to meet Canadian pipeline specifications: 0.33 Pa.s at 7.5 °C [2]. A mixture of 25:75 diluent and bitumen can be transported by pipeline which is denominated 'dilbit', or diluted bitumen [3]. Hence, it was likely that methylene chloride would have a similar effect on viscosity.

Another approach employed for bitumen transport is by colloidal dispersion in a low viscosity immiscible medium [1]. In this approach the immiscible medium becomes the continuous phase that determines viscosity. The colloidal dispersion of bitumen is essentially 'particulates' in slurry transport. The treatment of very viscous hydrocarbons through their emulsification in water has been studied by several authors [4, 5, 6]. Heavy and extra-heavy crude oils and bitumen can be transported when oil is emulsified in water (O/W emulsions). These emulsions present viscosity values with several orders of magnitude lower than the viscosity of the hydrocarbon itself [4]. However, the emulsions that were formed during the acid treatment investigation was not of this type, the oil remained in the continuous phase.

A common kind of emulsion found in the oil fields is brine dispersed in a continuous crude oil phase; this emulsion is of the water-in-oil type [7]. Refinery desalter emulsions are usually considered to be of the water-in-oil (W/O) type too. Bitumen contains endogenous surface active material that provides stability to the emulsion [8]. Asphaltenes and resins native to the oil are recognized as the main components with respect to stabilization of the interface between oil and water. Naphthenic acids may as well contribute to the stabilization, just as fine solids [9]. These types of emulsions have higher viscosity than the oil, because the emulsified water acts like solids suspended in the oil. Hence, it was likely that emulsions would increase viscosity.

According to the previously reported work [10], the contribution of emulsified water and remaining methylene chloride had to be resolved to quantitatively determine the viscosity response of bitumen to acid treatment. The main objective of this research was to study the impact of solvent, methylene chloride, and emulsions formed by the treated bitumen on viscosity.

4.2 Experimental procedure

4.2.1 Materials

Materials used were as the same that in Chapter 3.

4.2.2 Equipment and procedure

4.2.2.1 Effect of methylene chloride during work-up procedure of acid treatment

Raw bitumen (approximately 20 g) was mixed with CH_2Cl_2 (approximately 131.6 g). The CH_2Cl_2 was subsequently removed by evaporation in a rotary evaporator at 45°C under vacuum at 55 kPa absolute. This is the same work-up procedure used for acid treated bitumen in Chapter 3. The extent of solvent removal was determined at different evaporation times, namely, 1 h, 2 h: 36 min, 10 h: 40 min, 16 h: 53 min and 33 h: 46 min. Then, samples were left overnight at ambient conditions in a fume hood to allow evaporation of any residual methylene chloride that may have remained. The sample with 1 h was further dried in an oven under N_2 atmosphere at 50 °C for 64 h and 129 h: 27 min of heating. In all steps, the masses of bitumen and round flask were noted for material balance.

Finally, it was decided to standardize on 17 hours in the rotavap for work-up procedure of acid treatment in order to try to evaporate the higher amount of CH_2Cl_2 without leaving the sample overnight at ambient conditions in a fume hood. Due to the effect of solvent on the viscosity, methylene chloride was added in the same amount to all samples (approximately 170.9 g) for the blank and treated bitumen.

All experiments were carried out at least in triplicate in order to measure the repeatability and reproducibility.

4.2.2.2 Effect separation of emulsion interface in the acid treatment

The impact of emulsion formation was studied at one constant concentration of acid washing. The acid treatment was performed using the following methodology: 20 g of Cold Lake bitumen was dissolved in approximately 131.6 g of methylene chloride. A diluted aqueous solution of hydrochloric acid 0.003 M (100 g) was added to the organic solution. The height of liquid in the reactor was 3.7 cm. These solutions were mixed using an octagonal magnetic stir bar (Dia. x L: 1 x 5 cm) with a set speed of 400 rpm for 2 h at room temperature. Then, the reactor was washed with approximately 39.3 g of methylene chloride to transfer all the product to a separating funnel. Therefore, the total amount of solvent used was approximately 170.9 g. Next, the product was separated using a separating funnel. The material was left overnight to get a good phase separation. The more dense (bottom) phase was the organic solution consisting of bitumen and methylene chloride. The less dense (top) phase was the aqueous solution of HCl. Emulsion formation was observed in the interface, which was separated from the product (Figure 4-1). This emulsion remained sticky and it stuck to the walls of the separating funnel (Figure 4-2). So, this emulsion was washed with methylene chloride (74.4 g) to recover the major amount from the funnel.

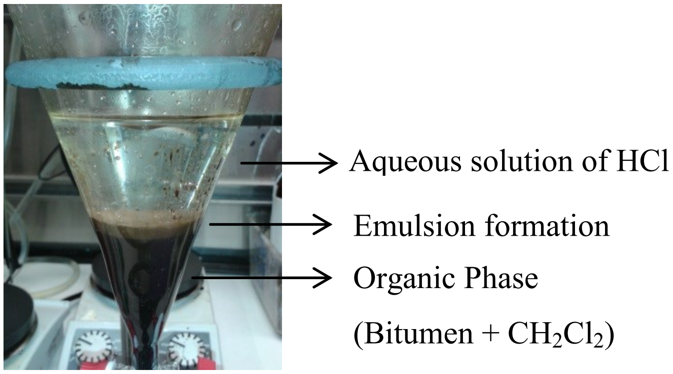

Figure 4-1: Separation of phases after acid treatment.

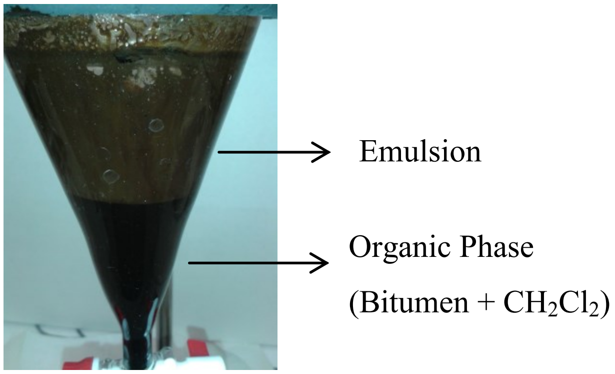

Figure 4-2: Emulsion stuck to the walls of the separating funnel and organic phase.

After that, methylene chloride was removed from the organic phase product and the emulsion respectively in a rotary evaporator at 45 °C and under vacuum at 55 kPa absolute over a period of 17 h. Finally, the product, emulsion and the separated aqueous solution were weighed and the material balance was calculated. It is important to point out that a blank was carried out using only water (no acid) following the same methodology. In the blank experiment the aqueous phase formed a stable emulsion with the bitumen and methylene chloride and water. Nevertheless, the organic phase (bitumen plus methylene chloride) after water treatment could be separated of the emulsion because the emulsified phase was in the top (Figure 4-3).

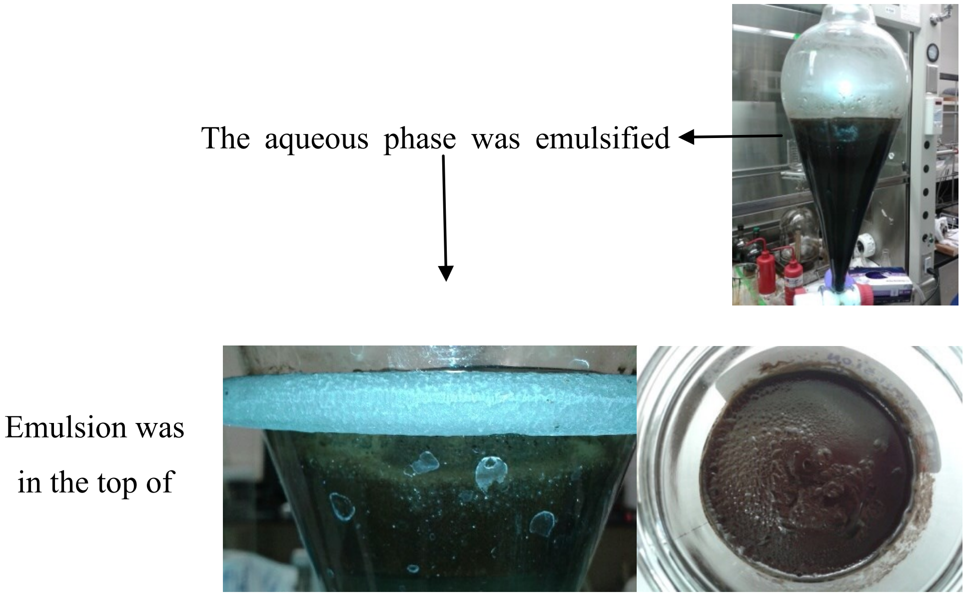

Figure 4-3: Emulsion formation in the water treatment.

The methodology of treated bitumen that had incorporated of emulsified phase after acid treatment was described in Chapter 3, refer to section 3.2.2. The organic phase and emulsion were separated together and after of rotavap the solvent (CH_2Cl_2), the product was left overnight at ambient conditions in a fume hood. The samples of treated bitumen with emulsion were kept for 5 months to study the emulsion stability and viscosity of the products. These samples were stored clear glass vials with screw-top closures within of a closed box at room temperature and kept the samples in the dark. After 5 months, viscosity analyses were performed on the samples.

All experiments were carried out at least in triplicate in order to measure the repeatability and reproducibility.

4.2.2.3 Identification of samples

Table 4-1 summarizes the identification of all the different samples that were prepared by this experimental procedure (sections 4.2.2.1 and 4.2.2.2) and some samples of Chapter 3 that were used in this study. These samples were assigned with an identifier, which will be used in the following sections to avoid any confusion and ambiguity.

Table 4-1: Identification of samples.

Samples	Description	Identifier
Raw Bitumen	Reference, without any treatment	Ref
Blank: raw bitumen after washing with CH_2Cl_2 and drying	* Total time in the rotavap: 1 h * Overnight at ambient conditions in a fume hood	Blank-RB-1
	Total time in the rotavap: 2 h: 36 min * Overnight at ambient conditions in a fume hood	Blank-RB-2
	(1st Rotavap) Total time in the rotavap: 10 h: 40 min * Overnight at ambient conditions in a fume hood	Blank-RB-10
	(2nd Rotavap) * For this experiment was used the same sample from 1st Rotavap. * Total time in the rotavap: 10 h: 40 min + 6 h: 13min: **16 h: 53 min** * Overnight at ambient conditions in a fume hood	Blank-RB-16
	(3rd Rotavap) * For this experiment was used the same samples from 1st Rotavap and 2nd Rotavap, * Total time in the rotavap: 10 h: 40 min + 6h: 13min + 16 h: 50 min: **33 h: 46 min** * For the 3rd rotavap the sample was not left overnight in the fume hood.	Blank-RB-33
	* Total time in the rotavap: 17 h * The sample was not left overnight in the fume hood.	Blank-RB-17
	The sample with 1 h in the rotavap was further dried in an oven under N_2 atmosphere at 50 °C for 64 h and 129 h: 27 min of heating.	Blank-RB-1-O
Blank: bitumen after water treatment without emulsion	Oil phase that was separated from a mixture that had an emulsion. Total time in the rotavap: 17 h	Blank-WT-WE
Blank: bitumen after water treatment with emulsion	Oil phase plus emulsified phase Fresh sample was obtained in the procedure of Chapter 3	Blank-WT-E
Treated bitumen (0.003 M HCl) without emulsion	Oil phase that was separated from a mixture that had an emulsion. Total time in the rotavap: 17 h	B-HCl-WE
Separate emulsion after acid treatment	Emulsion formed during acid treatment Total time in the rotavap: 17 h	E
Treated bitumen (0.003 M HCl) with emulsion	Oil phase plus emulsified phase Fresh sample was obtained in the procedure of Chapter 3	B-HCl-E-00
Treated bitumen (0.003 M HCl) with emulsion	Oil phase plus emulsified phase Stored for 5 months	B-HCl-E-51
Treated bitumen (0.000 3 M HCl) with emulsion	Oil phase plus emulsified phase Stored for 5 months	B-HCl-E-52

4.2.3 Analyses

Viscosity analyses were carried out using an Anton Paar RheolabQC rotational rheometer as described in Chapter 3. The measurements were conducted differently though. For a typical analysis 4 g of sample was employed and the viscosity was determined at constant shear rate of 2.50 s^{-1} and different temperatures 20 °C, 30 °C, 40 °C and 60 °C.

The asphaltenes content of the bitumen was determined by the same procedure as described in Chapter 3.

Fourier transform infrared (FT-IR) spectroscopic analysis was performed by the same procedure as described in Chapter 3.

Refractive Index (RI) measurements were conducted using an Anton Paar Refractometer Abbemat 200. These measurements were determined relative to air at different temperatures 40 °C and 60 °C. Resolution of refractive index measurement is 0.0001. This automatic refractometer uses reflected rather than transmitted light to measure the refractive index. The measuring principle is the following: the sample on top of the measuring prism is irradiated from different angles by a light-emitting diode (LED), using light of a single wavelength (monochromatic light), specifically the sodium D spectral line at 589.3 nm. At the interface between sample and prism the incident beam is either refracted into the sample or reflected back into the prism. A sensor array is used to detect the reflected beam. From this sensor, the critical angle for total reflection (α_{crit}) is calculated and used to determine the refractive index (RI) of the sample [11].

The ^1H Nuclear Magnetic Resonance (NMR) analyses were performed using a NMReady^{TM} 60 spectrometer of Nanalysis Corporation. First of all, a quick autoshimming was conducted in the equipment with deuterated chloroform. For the sample preparation 0.2 g of bitumen was dissolved in 800 µL of chloroform-d Aldrich 99.96 atom % D, this solution was transferred to a NMR tube Norell® U.S. Patent No. 7,673,780 and placed in the sample bath to keep warm at 30 ± 1 °C in a time of at least 5 min. The analysis was conducted with the following parameters:

spectral width: 14 ppm, number of scans: 32, points: 4000, scan delay: 20 sec. All spectra obtained were analyzed using MestReNova software version 9.0.0-12821 © 2013 Mestrelab Research S.L. Peak integration was carried out on the baseline corrected spectrum using 4 - 0.4 ppm as aliphatic hydrogen range, 9 - 6.5 ppm as aromatic hydrogen range and 5.6 – 5.0 ppm as hydrogen resonance of methylene chloride remaining.

Density analyses were determined with an Anton Paar Model DMA 4500 M density meter at 40 °C and 60 °C using the crude oil (API) method. First, samples were heated at 60 °C and then, for manual injection, a small amount of sample (2 mL) is injected into the clean and dry U-tube using an appropriate syringe; it is important to avoid the formation of bubbles. The density meter was checked with a density standard "Ultra Pure Water" Anton Paar. The certificate value at 20 °C is 0.99820 ± 0.00002 g/cm^3 and the experimental value was 0.99820 g/cm^3.

Microscopy analysis was conducted using a Carl Zeiss Discovery.V20 stereomicroscope. This microscope has a zoom range of 20:1, high end magnification of up to 345x (with eyepiece 10x), with objective PlanApo S 1.0x FWD 60 mm. The camera is an AxioCam ERc5s and the software AxioVision Rel. 4.8. The samples were put at microscope slides precleaned from Fisher Scientific, size 25 × 75 × 1 mm.

Mineral matter content was determined using thermogravimetric analyser (TGA) as explained in Chapter 3.

For the mass balance all weighing was performed as described in Chapter 3. However, for this analysis a Mettler Toledo Model XP1203S with 1210 g capacity and 1 mg of readability was used.

The pH of aqueous solutions of hydrochloric acid were measured as described in Chapter 3.

All analyses were conducted at least in triplicate to measure the repeatability and reproducibility.

4.2.4 Calculations

4.2.4.1 The residual methylene chloride

The residual methylene chloride in the bitumen was calculated by the mass balance of the bitumen after of rotavap for the samples Blank-RB-1, Blank-RB-2, Blank-RB-10, Blank-RB-16, Blank-RB-33 and Blank-RB-17 according to Equations 4-1 and 4-2.

g residual CH_2Cl_2 = g bitumen after rotavap – g initial bitumen …(4-1)

Residual CH_2Cl_2 (wt%) = (g residual CH_2Cl_2 / g bitumen after rotavap) x 100 …(4-2)

Examples of sample calculations are shown in Appendix 4.

In addition, the residual methylene chloride in the bitumen was calculated by FTIR analysis and ^{1}H-NMR analysis. Examples of sample calculations are shown in Appendices 5 and 6, respectively.

4.2.4.2 Asphaltenes content

Asphaltenes content (wt%) = (g asphaltenes in emulsion / g O/W emulsion) x 100 …(4-3)
based on total emulsion

g asphaltenes in emulsion = g emulsion total · $x_{\text{asphaltenes in emulsion}}$ …(4-4)
$x_{\text{asphaltenes in emulsion}}$ = mass fraction of asphaltenes in emulsion

An example of sample calculation is shown in Appendix 7.

Asphaltenes content (wt%) = (g asphaltenes in emulsion / g oil emulsion) x 100 …(4-5)
based oil in the emulsion

Asphaltenes content (wt%) = ((g precipitated asphaltenes) / (g initial bitumen) (1-$x_{CH_2Cl_2}$)) * 100
only treated bitumen basis …(4-6)
$x_{CH_2Cl_2}$ is the mass fraction of methylene chloride

Asphaltenes content (wt%) = (g total asphaltenes after treatment / g feed bitumen) x 100
in bitumen after treatment
based in feed material ...(4-7)

Examples of sample calculations are shown in Appendix 8.

4.2.4.3 Viscosity

For defined liquid mixtures the following mixing rules are recommended in the API-TDB and DIPPR manuals [12]:

$$\mu_m = \left(\sum_{i=1}^{N} x_i \mu_i^{1/3} \right)^3$$

for liquid hydrocarbons ...(4-8)

Where:

μ_m = mixture viscosity, cP

x_i = mole fraction of component i

μ_i = viscosity of component i, cP

Examples of sample calculation are shown in Appendices 9 and 10.

Another correlation for the mixtures of bitumen and solvent is the following [13]:

$$\log(\mu_m + 0.8) = \sum_{i=1}^{n} x_i [Mi/Ma]^{0.5} \log(\mu_i + 0.8)$$

...(4-9)

Where:

μ_m = liquid-mixture viscosity, mPa.s

x_i = mole fraction of component i

Mi = molar mass of component i, g/mol

Ma = average molar mass, $\sum xiMi$, g/mol

μ_i = viscosity of component i, mPa.s

An example of sample calculation is shown in Appendix 10.

4.2.4.4 Density

$$\delta_{mix} = x_{CH_2Cl_2} \cdot \delta_{CH_2Cl_2} + (1 - x_{CH_2Cl_2})\ \delta_{bitumen} \qquad \ldots(4\text{-}10)$$

Where:

δ_{mix} = density of blending

$\delta_{bitumen}$ = density of bitumen

$\delta_{CH_2Cl_2}$ = density of methylene chloride

$x_{CH_2Cl_2}$ = volume fraction of methylene chloride

The measurements of densities were performed at 40 ˚C and 60 ˚C.

These density values of methylene chloride were calculated using NIST/TRC Web Thermo Tables (WTT) [14].

$\delta_{CH_2Cl_2}$ at 40 ˚C = 1288.40 kg/m^3, uncertainty of 0.45 kg/m^3

$\delta_{CH_2Cl_2}$ at 60 ˚C = 1249.74 kg/m^3, uncertainty of 0.65 kg/m^3

Examples of sample calculations are shown in Appendix 11.

4.2.4.5 Yield

$$\text{yield (wt\%)} = \frac{\text{grams obtained}}{\text{initial grams of feed}} \text{ x } 100 \qquad \ldots(4\text{-}11)$$

An example of sample calculation is shown in Appendix 12.

4.2.4.6 Student's t-test

Two tailed test. A probability of p = 0.05 (95% confidence level) [15].

degrees of freedom = $n_1 + n_2 - 2 = 4$ …(4-12)

Where:

n_1 = the number of replicates for sample 1 = 3

n_2 = the number of replicates for sample 2 = 3

The critical **t** value looked in the t-Table is 2.776

Calculated $t = (x_1 - x_2)/s_d$ …(4-13)

Where:

x_1 = mean of sample 1

x_2 = mean of sample 2

s_d = the standard deviation of the difference between the means

If calculated t > critical t. A difference between two means is significant

4.3 Results

4.3.1 Effect of methylene chloride during work-up procedure of acid treatment

The effect of residual methylene chloride that could not be removed during the work-up procedure was investigated for the acid treatment of bitumen. For this, a blank of raw bitumen washing with CH_2Cl_2 was carried out with drying in the rotary evaporator to remove the solvent over different times (1 h, 2 h: 36 min, 10 h: 40 min, 16 h: 53 min and 33 h: 46 min). Table 4-2 shows mass balance of bitumen after washing with CH_2Cl_2 and drying for which the remaining methylene chloride in the bitumen was determined. The residual methylene chloride content was determined by mass balance of bitumen before and after rotary evaporation of the solvent. It is described in Appendix 4.

Table 4-2: Mass balance bitumen after washing with CH_2Cl_2 and drying.

Sample	Identifier	Total time in the rotavap	Weight initial bitumen, g	Weight bitumen after rotavap, g	Remaining methylene chloride, wt %
Raw bitumen after washing with CH_2Cl_2 and drying	Blank-RB-1*	1 h	20.008	23.793	15.9
	Blank-RB-2	2 h: 36 min	20.116 ±0.021	22.496 ± 0.528	10.6 ± 2.5
	Blank-RB-10	10 h: 40 min (1st Rotavap)	20.092 ±0.008	21.217 ± 0.100	5.3 ± 0.5
	Blank-RB-16	16 h: 53 min (2nd Rotavap)	20.092 ± 0.008	20.580 ± 0.018	2.4 ± 0.1
	Blank-RB-33	33 h: 46 min (3rd Rotavap)	20.092 ± 0.008	20.363 ± 0.051	1.3 ± 0.2
	Blank-RB-17	17 h	20.082 ± 0.009	20.589 ± 0.090	2.5 ± 0.5

*For the sample Blank-RB-1 the standard deviation was not specified because the analysis was performed only with one sample.

After evaporation, the sample (Blank-RB-1) with remaining methylene chloride of 15.9 wt% was dried in an oven under N_2 atmosphere at 50 °C, first for 64 h and then, 129 h: 27 min of heating. The samples (Blank-RB-1 and Blank-RB-1-O) were analysed by FTIR to measure the adsorption peaks of solvent. The mass balance of the sample (Blank-RB-1-O) is not reported because sample was taken and used for this analysis.

Figure 4-4 shows the FTIR spectra of different samples in the region between 1230-1700 cm^{-1}. Methylene chloride, which is shown as reference, raw bitumen washed with methylene chloride after rotary evaporation of the solvent and left overnight in a fumehood (Blank-RB-1) and raw bitumen washed with methylene chloride after rotavap and with dried in the oven at 50˚C under N_2 atmosphere over a period of time 64 h and 129 h : 29 min (Blank-RB-1-O).

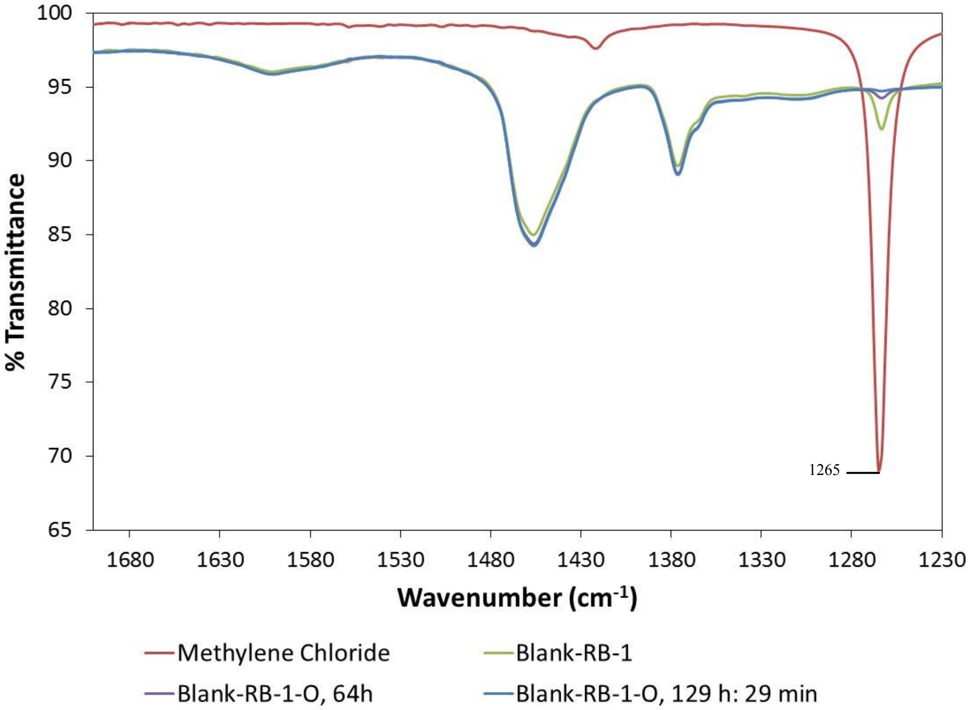

Figure 4-4: Absorptions related to methylene chloride for FTIR spectra of methylene chloride and raw bitumen washing with methylene chloride after rotavap and dried (Blank-RB-1 and Blank-RB-1-O).

It was decided to standardize on 17 hours of rotary evaporation after bitumen washing with CH_2Cl_2 for subsequent experiments. This work-up procedure resulted in 2.5 ± 0.5 wt% CH_2Cl_2 remaining in the bitumen, as was explained previously; the residual methylene chloride content was determined by mass balance of bitumen before and after rotary evaporation of the solvent. In addition, the residual methylene chloride was calculated by FTIR using an internal standard calibration curve based on the strong absorption at 1265 cm^{-1} (Figure 4-4), which is described in the Appendix 5. Table 4-3 shows the calculated residual methylene chloride using FTIR analysis for the blanks corresponding to raw bitumen after washing with methylene chloride. These results were compared with the mass balance, as can be observed the calculated methylene chloride has similar values using FTIR and mass balance analyses.

Table 4-3: Calculated CH_2Cl_2 in Blanks by FTIR and mass balance analyses.

Samples	CH_2Cl_2 (wt %)	
	by FTIR	by Mass Balance
Blank-RB-17	2.3	2.5
Blank-RB-1	15.5	15.9
Blank-RB-1-O, 64 h	3.2	Not measured

Figure 4-5 shows a comparison of FTIR spectrums in the region 600 to 1400 cm^{-1} of bitumen after acid treatment that was separated without emulsion (B-HCl-WE), blank of raw bitumen after washing with CH_2Cl_2 and drying (Blank-RB-17). Infrared spectra of bitumen after water treatment (Blank-WT-WE) and solvent methylene is shown for reference. As can be observed treated bitumen (B-HCl-WE) with respect to Blank-RB-17 presents differences in the intensity of bands corresponding the remaining methylene chloride at 1265 cm^{-1} and 731 cm^{-1}, which are slightly more intense for treated bitumen.

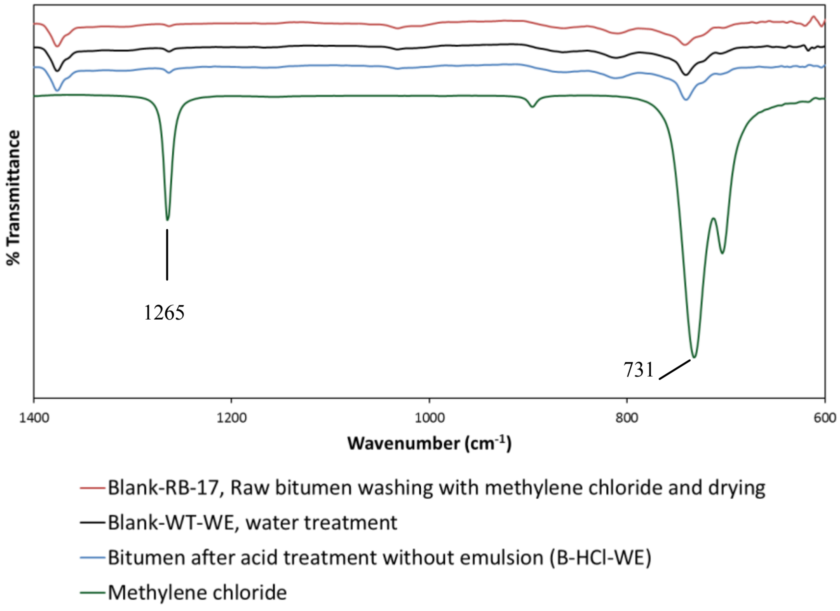

Figure 4-5: Comparison of FTIR spectrums, bitumen after acid treatment that was separated without emulsion (B-HCl-WE), blanks and methylene chloride.

For ^{1}H-NMR analysis, the total aliphatic hydrogen percentage was integrated in the range 0.4 - 4.0 ppm and the total aromatic hydrogen percentage was integrated in the range 6.5 - 9.0 ppm. The results for the ^{1}H NMR analyses of the bitumen after of the water treatment (Blank-WT-WE) and acid treatment (B-HCl-WE) that were separated without emulsion are presented in Table 4-4. A signal between 5.6 – 5.0 ppm was indicative hydrogen resonance of methylene chloride remaining. As can be observed, the total aliphatic hydrogen content, the total aromatic hydrogen content and the total methylene chloride hydrogen content of the blank (Blank-WT-WE) and treated bitumen (B-HCl-WE) were not statistically meaningfully different to the 95 % statistical confidence.

Table 4-4: The aliphatic hydrogen percentage, aromatic hydrogen percentage and methylene chloride hydrogen percentage in the bitumen after water treatment (Blank-WT-WE) and acid treatment without emulsion (B-HCl-WE).

Samples	Aliphatic Hydrogen, %	Aromatic Hydrogen, %	Methylene chloride Hydrogen, %
Blank, water treatment without emulsion (Blank-WT-WE)	91.1 ± 0.8	8.2 ± 0.7	0.7 ± 0.1
Bitumen after acid treatment without emulsion (B-HCl-WE)	91.1 ± 0.7	7.8 ± 0.4	1.1 ± 0.3

Table 4-5 shows the calculated residual methylene chloride in products (Blank-WT-WE) and (B-HCl-WE) using FTIR and 1H-NMR analyses. At the Appendixes 5 and 6 are shown examples of calculation for these analyses, respectively. The values determined by FTIR is considered more accurate, because they are directly determined from a calibration curve. The values from ^{1}H-NMR analysis also depend on the elemental analysis of the material and the calculation is more error prone.

Table 4-5: Calculated CH_2Cl_2 in products by FTIR and ^1H-NMR analyses.

Samples	CH_2Cl_2 (wt %)	
	by ^1H-NMR	by FTIR
Blank, water treatment without emulsion (Blank-WT-WE)	3.0 %	4.5 %
Bitumen after acid treatment without emulsion (B-HCl-WE)	5.0 %	5.8 %
Treated bitumen with emulsion after 5 months (B-HCl-E-51)	Not measured	3.9 %

The impact of this amount of CH_2Cl_2 on the viscosity of the bitumen was determined. Figure 4-6 presents viscosity of raw bitumen (Ref) and bitumen after washing with solvent and 17 hours of rotary evaporation (Blank-RB-17) as function of temperature in natural logarithm scale. In addition, Figure 4-7 shows viscosity as function of temperature in nominal scale to quantify the impact of solvent on the viscosity.

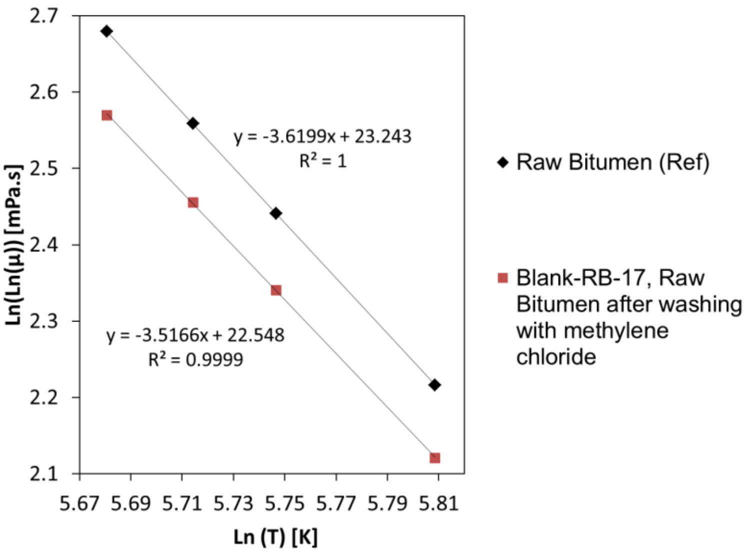

Figure 4-6: Viscosity of raw bitumen (Ref) and Blank -RB-17, bitumen after washing with solvent evaporation over a period of 17 h as function of temperature in natural logarithm scale.

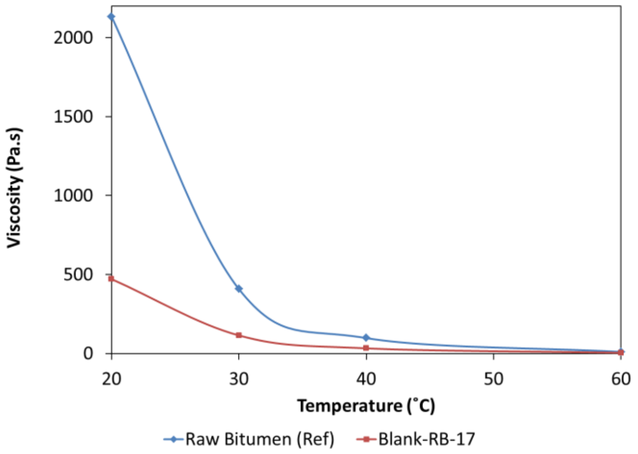

Figure 4-7: Viscosity of raw bitumen (Ref) and Blank -RB-17, bitumen after washing with solvent evaporation over a period of 17 h as function of temperature in nominal scale.

The literature provides correlations developed for the preparation of 'dilbit' to calculate the viscosity of the bitumen for a specified extent of dilution [13, 16]. The viscosity for the diluted bitumen (2.3 wt% CH_2Cl_2 by FTIR) was calculated with the correlations 4-8 [12] and 4-9 [13]. The calculated results were compared with the measured results (Table 4-6).

Table 4-6: Viscosity of 'Dilbit' Blank-RB-17.

Temperature (°C)	μ, Pa.s Experimental	μ, Pa.s Calculated Eq. (4-8)*	Percent Error (%)	μ, Pa.s Calculated Eq. (4-9)*	Percent Error (%)
60	4.2	6	48	4.5	7
40	32	63	97	38	19
30	114	261	129	139	22
20	471	1362	189	638	35

* An average molecular mass of 577 g/mol was employed for the bitumen in Eq. (4-8) and Eq. (4-9) [17].

4.3.2 Effect separation of emulsion interface in the acid treatment

The results of the emulsion interface (E) that was physically separated from oil phase (Figure 4-2) are shown in this section. During the process of separation of the emulsion interface, it stuck to the walls of the funnel. For this reason, the emulsion was washed with 74.448 ± 0.011 g of methylene chloride in order to recover a higher amount of emulsified phase from the funnel. Then, the emulsified phase was dried in the rotary evaporator for 17h to obtain the bitumen that was trapped in the emulsion after acid treatment. Figure 4-8 shows the product separated from the emulsion.

Product 0.003M HCl after acid treatment without emulsion (B-HCl-WE)

Separation of emulsion after acid treatment (E)

Figure 4-8: Treated bitumen (B-HCl-WE) separated of emulsion (E).

The masses of bitumen (B-HCl-WE), aqueous solution of HCl (0.003 M) and emulsion (E) were determined after acid treatment; as well as, the yield of treated bitumen (B-HCl-WE) and aqueous solution (Table 4-7). The bitumen yield was corrected for the residual methylene chloride that remained in the bitumen after the treatment, using the value obtained by FTIR analysis (5.8 wt% CH_2Cl_2). An example of sample calculation is shown in Appendix 13.

Table 4-7: Mass balance during acid treatment and yields of treated bitumen (B-HCl-WE) and aqueous solution of HCl (0.003 M).

Samples	Initial weight, g feed material	Weight after treatment, g	Yield, wt%
Bitumen (B-HCl-WE)	20.056 ± 0.021	20.336 ± 0.746	96 ± 3.6
Aqueous solution of HCl	100.050 ± 0.002	86.106 ± 2.101	86 ± 2.1
Emulsion	-	11.510 ± 1.046	-
Methylene chloride	170.924 ± 0.008	Not measured	-

4.3.2.1 Characteristics of emulsion

Figure 4-9 presents microscopy analysis of the emulsion (E) separated after acid treatment with 0.003 M HCl. For this emulsion (Table 4-8), it was determined experimentally that the asphaltenes content was 4.1 wt% based on the total W/O emulsion; the measured asphaltenes amount in emulsion was 0.4719 g (Appendix 7). It was calculated that the remaining methylene chloride in bitumen after treatment was 5.8 wt% based on the analysis by FTIR (Table 4-5), so the bitumen in emulsion was 0.8995 g. Therefore, the calculated asphaltenes content based on just the oil present in the emulsion was 52 wt%. All calculations are described in Appendixes 7 and 8.

Table 4-8: Asphaltenes content and oil content in the emulsion.

Samples	Asphaltenes content based on total emulsion (wt%)	Mass of asphaltenes in the emulsion (g)	Mass of oil in the emulsion (g)	Asphaltenes content based oil in the emulsion (wt%)
Separate emulsion after acid treatment (E)	4.1	0.4719	0.8995	52

Emulsion Asphalthenes precipitated from the emulsion

Figure 4-9: Microscopy images of emulsion (E) and asphaltenes in emulsion after acid treatment.

Figure 4-10 shows FTIR spectra of the emulsion (E) and asphaltenes precipitated from the emulsion after acid treatment where characteristics bands of asphaltenes spectrum are observed in the emulsion as high intensity bands in the region of 916-1101 cm^{-1}.

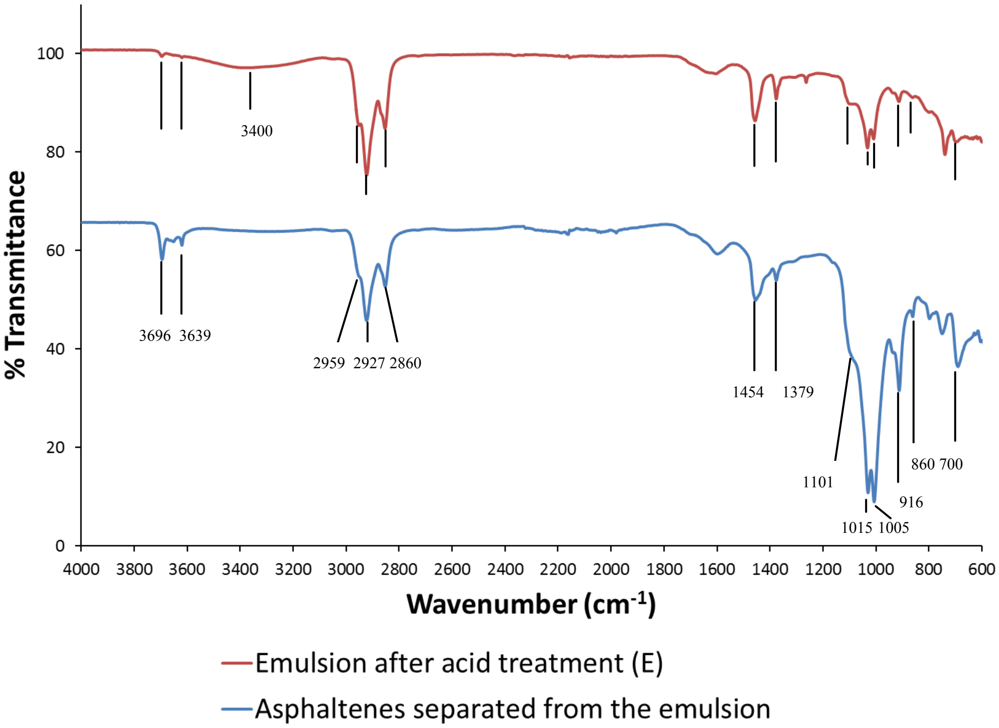

Figure 4-10: FTIR spectrums of emulsion (E) and asphaltenes precipitated from the emulsion after acid treatment.

Table 4-9 shows the mineral matter content of raw bitumen (Ref), emulsion and asphaltenes precipitated from the emulsion. As can be observed the mineral matter increases with respect to raw bitumen. It is due to mineral matter is more concentrated in emulsion and significantly more concentrated in the asphaltenes fraction.

Table 4-9: Mineral matter content.

Samples	Mineral matter content (wt %)
Raw bitumen	1.1 ± 0.5
Emulsion	4.3 ± 1.6
Asphaltenes precipitated from emulsion	27.3 ± 0.3

4.3.2.2 Properties of product after acid treatment without emulsion and with emulsion

Figure 4-11 shows viscosities of raw bitumen (Ref), blank of feed material after washing with CH_2Cl_2 and drying (Blank-RB-17), another blank of bitumen after water treatment that was separated from a mixture that had an emulsion (Blank-WT-WE) and bitumen after acid treatment that was separated from emulsion (B-HCl-WE) as function of temperature in natural logarithm scale.

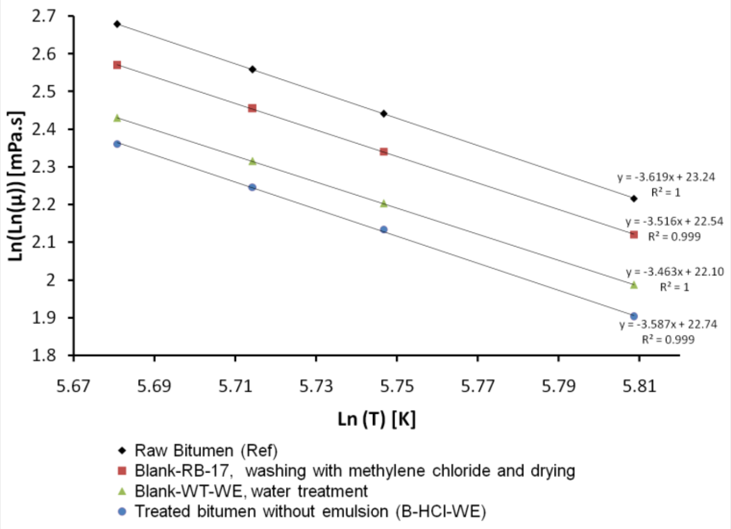

Figure 4-11: Viscosity of raw bitumen (Ref), blanks and bitumen after acid treatment (B-HCl-WE) as function of temperature in natural logarithm scale.

The effect of emulsion on the viscosity was investigated (Table 4-10) for the blank of bitumen after water treatment and for the treated bitumen (0.003 M HCl). Both cases, with emulsion and without emulsion, for the products with emulsion the results are shown with fresh treated bitumen previously reported in the Chapter 3, refer to Figure 3-8. In addition, the sample (B-HCl-E-51) of bitumen after acid treatment that was separated together with emulsion, and that was stored at glass vials with screw-top closures within of a box at room temperature for 5 months; to study the stability of product. The results show the experimentally determined values for viscosity and the calculated viscosities of products after correction for methylene chloride (Appendix 9). For this calculation Equation 4-8 was used and the values of solvent remaining were those determined by FTIR analysis (Table 4-5).

Table 4-10: Effect of emulsion on the viscosity.

Samples	Experimental Viscosity (Pa.s)		Calculated viscosity corrected for residual CH_2Cl_2 (Pa.s) Eq. (4-8)	
	40˚C	60˚C	40˚C	60˚C
Raw bitumen (Ref)	97.5 ± 0.5	9.6 ± 0.1	-	-
Blank, water treatment without emulsion (Blank-WT-WE)	8.6 ± 2.1	1.5 ± 0.2	19.0	3.2
Blank water treatment with emulsion (Blank-WT-E)	Not measured	6.1 ± 0.9	-	Not calculated*
Bitumen after acid treatment without emulsion (B-HCl-WE)	4.7 ± 0.7	0.8 ± 0.001	12.6	2.1
Treated bitumen with emulsion (B-HCl-E-00)	Not measured	1.8 ± 0.3	-	3.7
Treated bitumen with emulsion after 5 months (B-HCl-E-51)	57.5 ± 22	8.1 ± 2.2	119.8	16.7

* The solvent content of the sample (Blank-WT-E) was not quantified analytically

In addition, the influence of emulsion on the viscosity measured at different temperatures was investigated. Figure 4-12 presents viscosities of fresh product after acid treatment 0.003 M HCl that was separated without emulsion (B-HCl-WE) and the samples of treated bitumen that were separated together with emulsion and stored for 5 months (B-HCl-E-51) and (B-HCl-E-52) as function of temperature in natural logarithm scale.

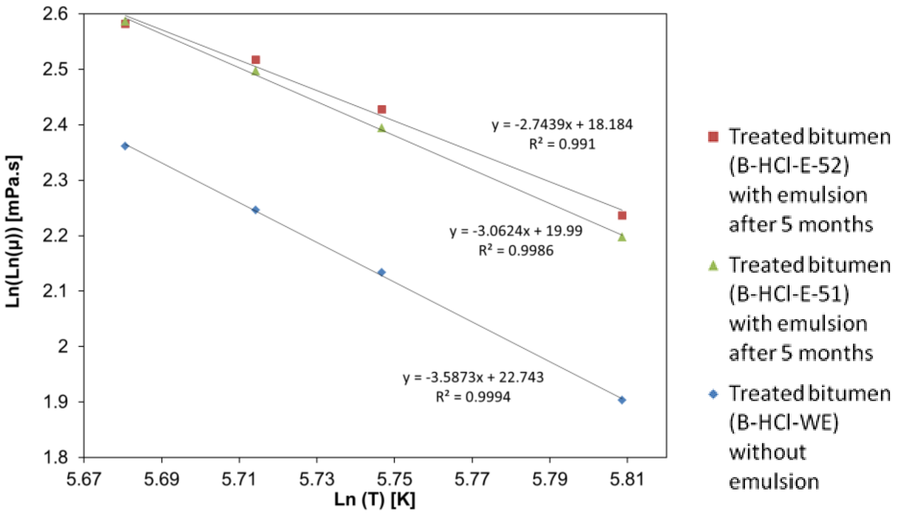

Figure 4-12: Viscosity of bitumen after acid treatment without emulsion (B-HCl-WE) and with emulsion after 5 months, samples (B-HCl-E-51) and (B-HCl-E-52) as function of temperature in natural logarithm scale.

Figure 4-13 presents the region of 1900-1500 cm^{-1} for the samples (Ref) and bitumen after acid treatment separated together with emulsion and stored for 5 months (B-HCl-E-52) to show carbonyl region of the spectrum in order to study the possible oxidation treated bitumen. In addition, Table 4-11 shows the height of absorptions around 1700 cm^{-1} corresponding to carbonyl group and 1600 cm^{-1} of skeletal vibrations, involving carbon to carbon stretching within the aromatic ring.

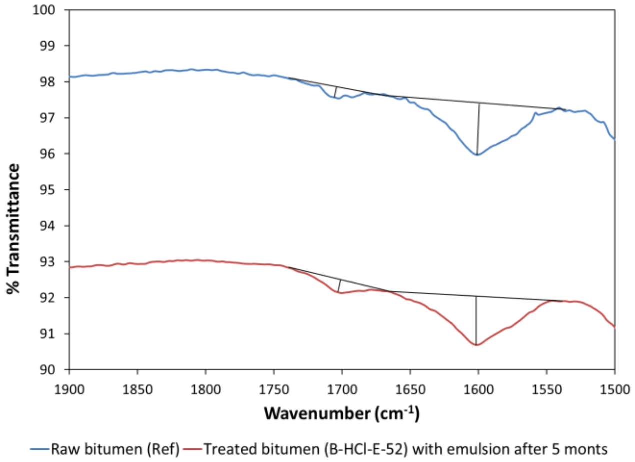

Figure 4-13: Region of 1900-1500 cm^{-1} for FTIR spectrums of raw bitumen (Ref) and bitumen after acid treatment that was separated together with emulsion and stored for 5 months (B-HCl-E-52).

Table 4-11: Height of absorptions for FTIR spectrums of raw bitumen (Ref) and (B-HCl-E-52).

Samples	Height of C=O absorption (%)	Height of C$\overset{\cdots}{-}$C absorption (%)	C=O/ C$\overset{\cdots}{-}$C Ratio
Raw bitumen	0.295	1.420	0.21
B-HCl-E-52	0.336	1.346	0.25

Figure 4-14 presents the region of 4000-2000 cm^{-1} for the samples (Ref) and bitumen after acid treatment separated together with emulsion and stored for 5 months (B-HCl-E-51) to show the broad band of OH between 3600-3200 cm^{-1}, for the bitumen with emulsion. Considering the amount of water that should have been present in this sample, the absorption in the 3600-3200 cm^{-1} is remarkably weak.

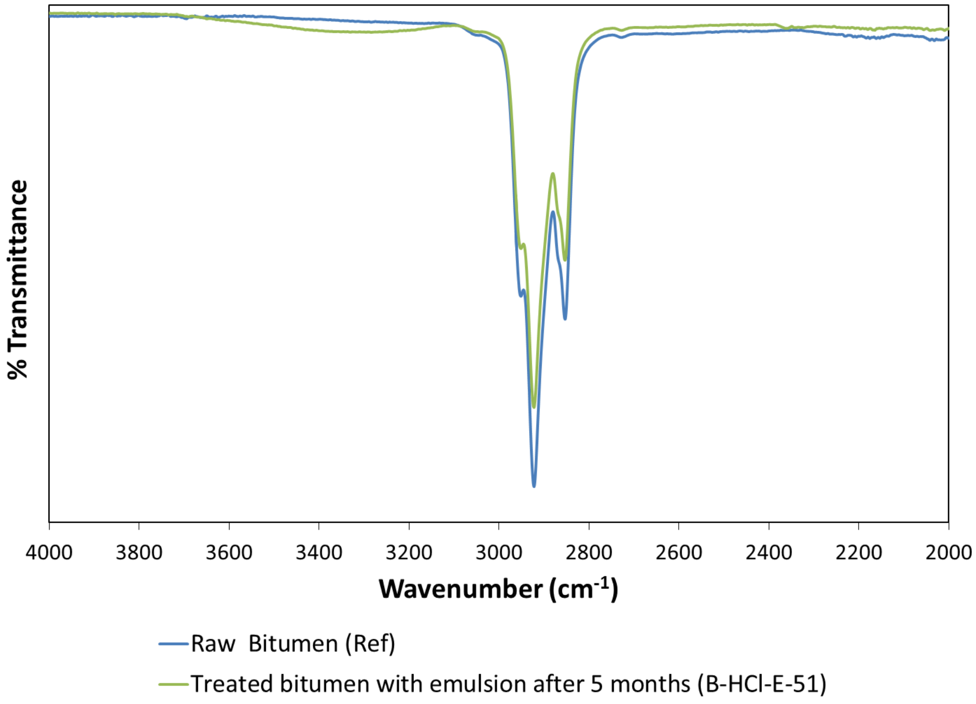

Figure 4-14: Region of 4000-2000 cm^{-1} for FTIR spectrums of raw bitumen (Ref) and bitumen after acid treatment that was separated together with emulsion and stored for 5 months (B-HCl-E-51).

Total asphaltenes content in bitumen feed basis was calculated for the bitumen after acid treatment (B-HCl-WE), which was compared with the raw bitumen (Ref) (Table 4-12). For this calculation (Appendix 8), treated bitumen was corrected by subtracting the 5.8 wt % methylene chloride based on the analysis by FTIR (Table 4-5). As can be observed, the asphaltenes content after acid treatment was not significantly different from that of the raw bitumen (better than 95 % statistical confidence).

Table 4-12: Asphaltenes content calculated for the raw bitumen and for the product (B-HCl-WE) on bitumen feed basis.

Samples	Asphaltenes content (wt %)
Raw Bitumen (Ref)	16.8 ± 1.3
Treated Bitumen with 0.003M HCl (B-HCl-WE)	19.4 ± 0.2

Density was analyzed for raw bitumen (Ref), blank of feed material after washing with CH_2Cl_2 and drying (Blank-RB-17). Another blank of bitumen after water treatment that was separated from a mixture that had an emulsion (Blank-WT-WE) and bitumen after acid treatment that was separated from emulsion (B-HCl-WE). The densities of these samples were analyzed as function of temperature at 40˚C and 60˚C (Table 4-13). The direct measurement of density for the blanks and treated bitumen involves bitumen plus remaining methylene chloride, 2.3 wt% CH_2Cl_2 for the Blank-RB-17 (Table 4-3), 4.5 wt% CH_2Cl_2 for the Blank-WT-WE and 5.8 wt% for the product B-HCl-WE (Table 4-5). These values of remaining solvent were determined by FTIR analysis. In addition, these experimental densities were corrected for residual solvent methylene chloride using Equation 4-10 (Appendix 11).

Table 4-13: Direct measurement of density and densities calculated for products.

	Experimental Density		Calculated Density corrected for residual CH_2Cl_2 Eq.(4-10)	
Samples	at 40˚C (kg/m^3)	at 60˚C (kg/m^3)	at 40˚C (kg/m^3)	at 60˚C (kg/m^3)
Raw bitumen (Ref)	1012 ± 0.01	1000 ± 0.01	-	-
Blank -RB-17	1014 ± 0.02	1002 ± 0.02	1009	997
Blank-WT-WE	1017 ± 3.8	1004 ± 1.7	1007	995
Treated bitumen (B-HCl-WE)	1018 ± 1.5	1004 ± 1.1	1005	992

Table 4-14 shows the values of refractive index for raw bitumen (Ref), blank of feed material after washing with CH_2Cl_2 and drying (Blank-RB-17), blank of bitumen after water treatment that was separated from a mixture that had an emulsion (Blank-WT-WE) and bitumen after acid treatment that was separated from emulsion (B-HCl-WE) as function of temperature at 40˚C and 60˚C. These values are the results obtained directly by measurement. For blanks and treated bitumen the measurements include the remaining methylene chloride. The refractive index of the methylene chloride experimentally determined is 1.4117 at 40°C and 1.4038 at 60°C.

Table 4-14: Refractive indexes of raw bitumen (Ref), blanks, and bitumen after acid treatment that was separated without emulsion (B-HCl-WE) at 40˚C and 60˚C.

Samples	nD at 40˚C	nD at 60˚C
Raw bitumen (Ref)	1.5767 ± 0.0001	1.5692 ± 0.0001
Methylene Chloride	1.4117 ± 0.0001	1.4038 ± 0.0001
Blank -RB-17	1.5761 ± 0.0001	1.5686 ± 0.0002
Blank-WT-WE	1.5754 ± 0.0005	1.5682 ± 0.0004
Bitumen after acid treatment without emulsion (B-HCl-WE)	1.5719 ± 0.0001	1.5666 ± 0.0006

Table 4-15 shows the pH of deionized water and aqueous solution of HCl before and after treatment.

Table 4-15: pH of deionized water and aqueous solution 0.003 M HCl.

Samples	pH initial		pH after treatment	
	x	s	X	S
Milli-Q water	6.70	0.27	-*	-*
Aqueous solution 0.003 M HCl	3.06	0.02	3.68	0.02

*Not measured due to emulsion formation

4.4 Discussion

4.4.1 Retention of methylene chloride by bitumen

According to the mass balance of raw bitumen washing with methylene chloride (Table 4-2), some solvent remained trapped in the bitumen structure in spite of prolonged evaporation under vacuum at 45˚C. The methylene chloride remaining in the bitumen decreases with a longer evaporation time, from 15.9 wt% for 1 h until 1.3 wt% for a total time of 33 h: 46 min. The boiling point of methylene chloride is 39.84˚C [18] at atmospheric pressure (101.325 kPa). Using Clausius-Clapeyron equation, it was calculated that the boiling point of methylene chloride at 55 kPa is 24 ˚C.

A study of Wen et al. [19] about the estimation of diffusion coefficients in bitumen solvent mixtures showed the range of the diffusivity of solvents (heptane, hexane, pentane, naphtha, toluene and kerosene) into bitumen is around 10^{-8} m^2/s. They concluded the diffusivity decreases as the viscosity of bitumen increases. As well as, light molecular weight solvents diffuse faster than heavy molecular weight solvents.

In our study, even with a maximum time of 33 h: 46 min, not all methylene chloride could be evaporated, despite this solvent is very volatile (24 ˚C at 55 kPa). The bitumen could act as a "spiderweb", in which some methylene chloride remains trapped in the bitumen structure (Figure 4-15). Solvent entrapment in the bitumen is common in the industrial processes; for example, during flotation stage from bitumen extraction of oil sands, approximately 3% of micro emulsified water still remains [8]. In this example, water is a separate phase; however, methylene chloride dissolves into the bitumen.

Figure 4-15: Representation of bitumen as a "spiderweb" that traps solvent.

Trapping of compounds by asphaltene aggregates has been a topic of research. As asphaltenes are components of bitumen structure, it is an issue that is relevant to mention. A study of Derakhshesh [20] showed that two polyaromatic hydrocarbons (PAHs) (pyrene and phenanthrene), which are otherwise soluble, were significantly occluded within asphaltene nanoaggregates. It was suggested possibly that there is a formation of host−guest complexes. Where the structure-forming components are “hosts” and the occluded components are “guests”. In this sense, occlusion represents physical entrapment by whatever mechanism within the noncovalent matrix of asphaltene nanoaggregates. A hypothesis is that the remaining methylene chloride could form this kind of host−guest complexes with bitumen.

In Figure 4-4 it can be observed that there is one strong absorption at 1265 cm^{-1} related to CH_2Cl_2 wagging in the methylene chloride FTIR spectrum, which is shown as reference. This absorption is lower in intensity for raw bitumen washing with methylene chloride after evaporation and left overnight in a fumehood (Blank-RB-1) compared to the methylene chloride FTIR spectrum, which shows that some solvent remains in the bitumen structure. This absorption is remarkably weak when bitumen washing with methylene chloride after rotavap is dried in the oven under N_2 atmosphere at 64 h (Blank-RB-1-O). It is not observed when bitumen is dried for 129 h : 29 min, which suggests that the majority of solvent is evaporated during this longer time.

Furthermore, it was determined (quantitatively) what the amount of residual methylene chloride in bitumen is by FTIR using an internal standard calibration curve (Appendix 5), with values of 15.5 wt% CH_2Cl_2 for the Blank-RB-1, 3.2 wt% CH_2Cl_2 (Blank-RB-1-O, 64 h) and 2.3 wt% CH_2Cl_2 for the Blank-RB-17 (Table 4-3). These results were compared with the values obtained by mass balance, as can be seen the calculated methylene chloride had similar values using FTIR and mass balance analyses (Table 4-3).

A study of heavy oil or oil sands bitumen [20] that has been extracted with toluene showed results of toluene residual in mixture after rotary evaporation at 1 kPa and different times. For example, for the sample AG9 after rotary evaporation at 40˚C and 1 kPa during 2 hours, the calculated toluene residual in mixture was 15.20 % based on the measurement of gas chromatograph-mass spectrometer (GC-MS). The results indicated that the rate of evaporation of the solvent is highly variable because of differences in the properties of the bitumen. In spite of constant conditions, the evaporation is not reproducible for a given sample. In addition, residual toluene is still normally present in samples that have lost significant amounts of volatile compounds.

For the methylene chloride similar behavior was observed for the rate of evaporation of solvent. Even under constant conditions, the evaporation was not reproducible for 17 hours of rotary evaporation. As can be seen in FTIR spectrums (Figure 4-13), the treated bitumen (B-HCl-WE) with respect to Blank-RB-17 presents differences in the intensity of bands corresponding to the remaining methylene chloride at 1265 cm^{-1} and 731 cm^{-1}, which are slightly more intense for treated bitumen. According to the quantitative analysis (Table 4-5) by FTIR, the residual methylene chloride was 5.8 wt% for the treated bitumen (B-HCl-WE), 4.5 wt% for the Blank-WT-WE and as discussed previously 2.3 wt% for the Blank-RB-17 (Table 4-3). This result corroborates the methylene chloride residual was higher for the treated bitumen (B-HCl-WE) than blanks, in spite of the same conditions of evaporation. In addition, the remaining solvent was calculated by ^1H NMR analysis (Table 4-5) whose values were 5.0 wt% for the product (B-HCl-WE) and 3.0 wt% for the Blank-WT-WE.

4.4.2 Impact of residual methylene chloride on viscosity

There are many equations used to determine the viscosity of crude oil as function of temperature. The standard approach for viscosity estimation is to take two measurements at two different temperatures. Once this data is obtained the ASTM method is to fit the following equation to the data given [22]:

$$\ln[\ln(\mu)] = a1 + a2 \ln(T) \qquad \text{...(4-14)}$$

Where T is the absolute temperature (K) and μ is the viscosity (mPa.s) [23].

The manner in which the viscosity data was described in Figure 4-5, should result in a linear viscosity-temperature relationship for oils according to Equation 4-12, where $\ln[\ln(\mu)] \alpha \ln(T)$.

As can be observed in Figure 4-6, the natural logarithm of viscosity exhibits a linear relationship with temperature for raw bitumen feed material (Ref) and for Blank-RB-17, with correlation coefficient for linear regression (R^2) equal to 1 and 0.999, respectively. It was evidenced that the viscosity decreases by effect of remaining solvent, which was 2.3 wt% by FTIR analysis. In spite of this low concentration, the reduction of viscosity is significantly as shown in Figure 4-3. The viscosity decreases from 2135 Pa.s (Ref) until 471Pa.s (Blank-RB-17) at 20˚C. Then, the viscosity reduces of 408 Pa.s (Ref) to 114 Pa.s (Blank-RB-17) at 30˚C. For the temperature of 40˚C, the viscosity decreases from 98 Pa.s (Ref) until 32 Pa.s (Blank-RB-17). The lowest viscosity is at 60˚C, the viscosity reduces of 9.6 Pa.s (Ref) to 4.2 Pa.s (Blank-RB-17). Therefore, the effect of remaining solvent during work-up procedure of acid treatment is to reduce the viscosity. It is logical because an approach to reduce the viscosity of bitumen is dilution with a solvent. Furthermore, the viscosity of bitumen is significantly temperature dependent and tends to drop quickly with increasing temperature.

As presented in Table 4-6, the viscosities calculated of 'dilbit' (Blank-RB-17) with the correlation (Eq. 4-9) resulted in a better approximation to the viscosities measured than correlation (Eq. 4-8). As evidenced by the lower percent error in the 7 - 35 % range. An important assumption in the use of this equation is that of the average molecular mass of the bitumen, which was taken as 577 g/mol based on literature [17]. A study by Mehrotra [13] found although the viscosities calculated from Equation (4-9) were within an order of magnitude of the data, these were not completely satisfactory. It is concluded the blend viscosity predictions are enhanced substantially by use of a temperature-dependent viscous interaction parameter. Yarranton et al. [16] found predicted viscosities of the mixtures of bitumen and toluene using mixing rules correlations, presented an average absolute percent relative deviation (AAPRD) of 17%, and a maximum absolute percent relative deviation (MAPRD) of 47%.

A study of Jiang and co-workers [21] concluded that it is not feasible to determine reliable viscosity measurements for a heavy oil or oil sands bitumen sample that has been extracted with toluene through solvent addition and evaporation experiments. Viscosity values determined on residual bitumen after solvent removal were found to be too low due to residual toluene remains in the sample. For instance, for a calculated toluene residual in mixture of 2.57% by GC-MS analysis, the viscosity decreased from 9502 cP (original viscosity) to 6373 cP at 20 ˚C. This result is consistent with our study that a small amount of residual solvent in bitumen has a significant impact on the viscosity reduction of the sample.

4.4.3 Characteristics of emulsion interface in the acid treatment

Emulsion formation was an important issue to investigate in the acid treatment of bitumen. Emulsions can form when considerable mixing of oil and water is conducted [8]. A recent review by Kilpatrick [24] has outlined three main contributors to emulsion stabilization: asphaltenes, carboxylic acids, fine inorganic particles, and combinations of these three kinds of components. In this study the emulsion was separated from the product to separately evaluate the emulsion (E) and the treated bitumen (B-HCl-WE). According to the mass balance (Table 4-7), the amount of emulsion formed was 11.510 ± 1.046 g. This emulsion showed the presence of free water, which indicated that not all water was emulsified (Figure 4-9). It was determined that the asphaltenes content in the emulsified bitumen phase was 4.1 wt% based on the total (O/W) emulsion and 52 wt% based on the oil present in the emulsion (Table 4-8). This result indicates that the oil phase presents in the emulsion is rich in asphaltenes. The total asphaltenes amount of the bitumen after acid treatment (B-HCl-WE) was 3.882 g, of which 0.4719 g migrated to the oil and water interface to stabilize the emulsion (Appendix 8).

Adams et al. [8] studied the role of asphaltenes in oil and water emulsions. They found that no emulsions were formed using the reconstituted maltenes (including volatiles). However, when reconstituting the oils with as little as 5 wt% of the original asphaltenes content, an emulsion was formed. This result is consistent with our study that asphaltenes contribute to emulsion formation. Therefore, the role of asphaltenes to the interfacial activity was corroborated. As was cited in the literature review, the pH of the aqueous phase is important in bitumen-water interfaces [25], so an acidic pH could promote the basic surface active groups of asphaltenes [26].

In the FTIR spectrum of asphaltenes precipitated from the emulsion (Figure 4-10) it is notable that the absorption bands in the range 916-1101 cm^{-1} and 3639-3696 cm^{-1} range, can possibly be due to clay minerals [1]. The last of the bands at 3696 cm^{-1} could be attributed to outer SiO-H vibrations, characteristic of kaolin [1]. The majority of these characteristics bands are observed in the spectrum of the emulsion (Figure 4-10). This result coincides with Fourier transform infrared spectroscopy (FTIR) studies of asphaltenes by Strausz [1], where it was found that significant quantity of clay minerals concentrated in the asphaltenes fraction of the bitumen.

As seen in FTIR spectrum of the emulsion (Figure 4-10), the broad band of OH in the region of 3400 cm^{-1} can be observed clearly, which is indicative of free water. Furthermore, both spectrums shows the following absorptions: aromatic C-H out-of-plane bend and $(CH_2)_n$ rock (ρ) at the region of 700-860 cm^{-1}, the symmetrical bending vibration (δ_s CH_3) at 1379 cm^{-1}; CH_2 scissor (δ_s) and CH_3 asymmetrical bending (δ_{as}) at 1464 cm^{-1}; CH_2 and CH_3 symmetrical stretching (ν_s) at 2860 cm^{-1}; CH_2 asymmetrical stretching (ν_{as}) at 2927 cm^{-1} and CH_3 asymmetrical stretching (ν_{as}) at 2959 cm^{-1} [26].

The information on the nature of the functional groups of the emulsion suggests that not only asphaltenes stabilized the emulsion. It also was stabilized by inorganic solids particles (such as clay minerals). These inorganic solids accompany bitumen during its recovery from a reservoir.

The mineral matter content of raw bitumen was 1.1 ± 0.5 wt%, it was 4.3 ± 1.6 wt% for the emulsion and 27.3 ± 0.3 for the asphaltenes precipitated from emulsion (Table 4-9). The review of Kilpatrick [24] indicated that inorganic solid fines, namely clays, silicas, and iron oxides, can play most important roles in enhancing water-in-crude oil emulsion stability, particularly when modified through the adsorption of resins and asphaltenes to make them strongly interfacially active. Inorganic particle size and wettability are key factors with respect to the effectiveness of inorganic solids in enhancing this stability. The particles that are most effective for stabilizing emulsions are in the range of a few hundred nanometers in size. Figure 4-16 [28] shows an example of emulsion stabilization by resin/asphaltene films and Figure 4-17 illustrates how inorganic particles at the interface can stabilize water-in-oil emulsions when an enough asphaltene aggregates adsorb [28].

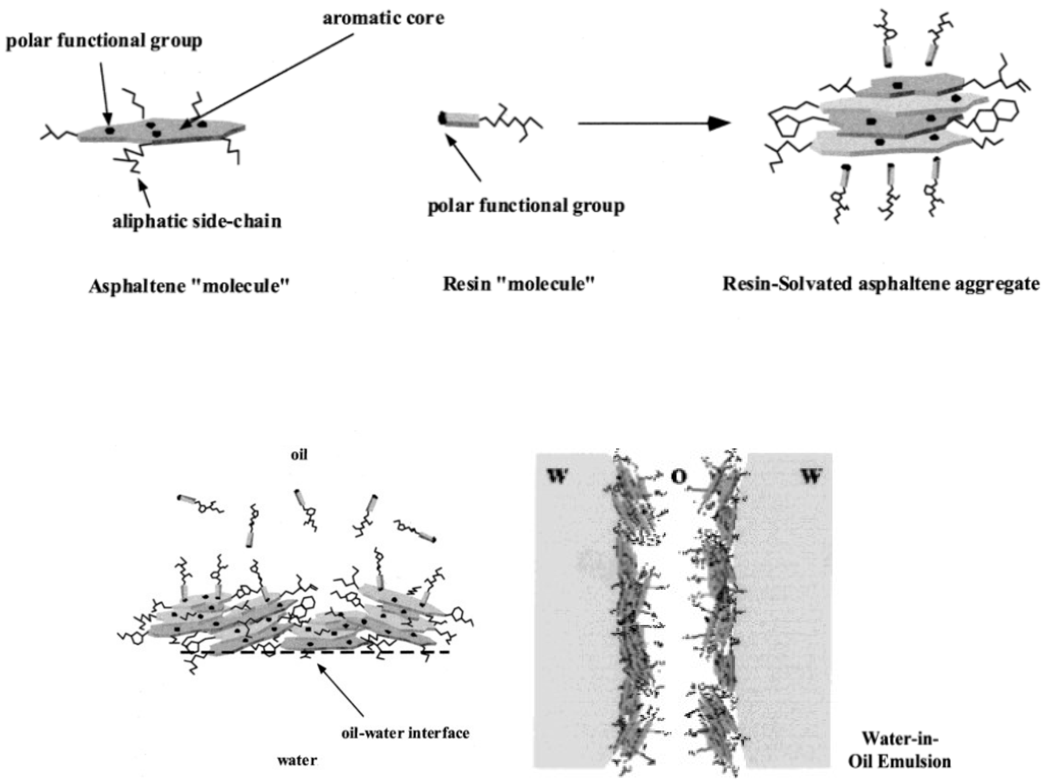

Figure 4-16: Emulsion stabilization by resin/asphaltene films [28].

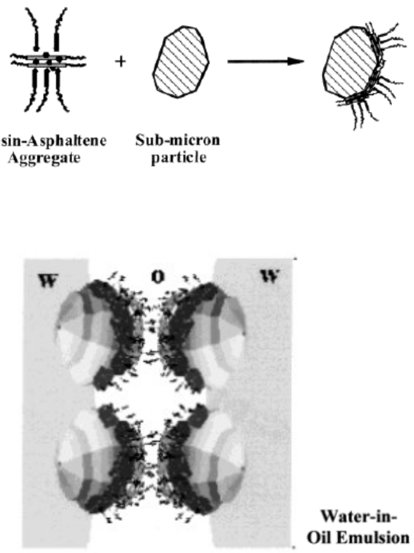

Figure 4-17: Particle-stabilized emulsions with the adsorption of asphaltenes and resins [28].

4.4.4 Effect of emulsion on the viscosity of treated bitumen

As was explained previously, the viscosity of raw bitumen after washing with methylene chloride (Blank-RB-17) decreased due to the effect of remaining solvent. As shown in Figure 4-11, a linear relationship of the natural logarithm of viscosity with temperature was obtained for the bitumen after of water treatment separated of emulsion (Blank-WT-WE) with correlation coefficient for linear regression (R^2) equal to 1. This linear relationship was lower than Blank-RB-17 ($R^2 = 0.999$). From literature we know that oil-bearing formations are generally saline; for that reason, when small amounts of water are emulsified in the oil they have dissolve chlorides and other salts. Fine solid particles (circa 1 μm diameter or less) can accumulate at the oil/water interface [22], as discussed previously in the Section 4.4.3, the mineral matter content of emulsion was 4.3 ± 1.6 wt%. Surprisingly, when the bitumen was washed with water, it affected the viscosity. This may be due to water washing that removes the salt, water, and fine solids from the bitumen, similar to the desalting operation in a refinery [22]. In addition, it could be speculated that acid-base interactions may be relevant even at neutral pH. Kilpatrick [24] has outlined interactions of asphaltenes and naphthenic acids indicating that naphthenic acids can modestly enhance asphaltene emulsion stability at neutral pH.

The effect of emulsion formation on the viscosity can be seen from the data presented in Table 4-10. As can be observed, the bitumen after water treatment (Blank-WT-WE) that was separated from the emulsion has an experimental viscosity at 60˚C of 1.5 Pa.s; however, the viscosity increases for the Blank-WT-E that has an emulsion with a value of 6.1 Pa.s. The same behavior is seen for bitumen after acid treatment. The lowest experimental viscosity (0.8 Pa.s) is for treated bitumen that was separated from the emulsion (B-HCl-WE), then viscosity increases until 1.8 Pa.s for treated bitumen that has emulsified water (B-HCl-E-00). The highest experimental viscosity is for treated bitumen with emulsion after 5 months (B-HCl-E-51) with a value of 8.1 Pa.s. The higher viscosity of the aged sample is not just caused by the emulsion, but likely due to other effects.

Once these values are corrected for the residual methylene chloride (Equation 4-8) [12], Table 4-10 shows that the emulsified treated bitumen (B-HCl-E-00) had a calculated viscosity of 3.7 Pa.s at 60 ˚C and the oil recovered from the emulsified bitumen (B-HCl-WE) had a calculated viscosity of 2.1 Pa.s at 60 ˚C. The emulsified oil had an increase of 43 % on the viscosity. From literature we know that W/O emulsions can cause a problem for processing of crude oil due to the increased viscosity of resulting fluid [8]. It was anticipated that the increased viscosity was at least in part due to emulsified water present in the bitumen. The treated bitumen with emulsion after 5 months (B-HCl-E-51) exhibited poor storage stability because the viscosity increased significantly. The calculated viscosity of the aged sample was 16.7 Pa.s at 60 ˚C (Table 4-12). According to FTIR spectrum (Figure 4-14), the broad band of OH between 3600 - 3200 cm^{-1} is observed for the bitumen with emulsion (B-HCl-E-51), which is not present for the Reference (Raw bitumen). It was observed that some of the water coalesced as a separated aqueous phase (clean layer of water) after 5 months storage. So, it is speculated that the emulsion is not stable. In addition, the sample (B-HCl-E-51) presented a high standard deviation during the measurement of viscosity at the different temperatures (Table 4-10).

As can be seen in Figure 4-12, a linear relationship was obtained of the natural logarithm of viscosity as function of temperature for treated bitumen that was separated of emulsion (B-HCl-WE) with correlation coefficient for linear regression (R^2) equal 0.9994. For product after acid treatment with emulsion after 5 months (B-HCl-E-51) of R^2 was 0.9986. The observed deviation from linear behavior was not due to random scatter, but the data had an observable curvature. A deviation was also observed for treated bitumen (B-HCl-E-52) that has emulsion after 5 months storage. The linear regression coefficient R^2 was 0.991 and as with the B-HCl-E-51 sample, the deviation was due to a curvature in the data and not due to random scatter. Deviations from the indicated linear relationship are normally observed when there is a second phase present; such as, liquid phase or precipitation of a solid [29]. In this case, there are 2 phases in the emulsion, aqueous phase and oil phase. In addition, it is clear that the viscosities increased due to emulsified water and ageing of products.

Figure 4-13 shows a very slight increase in the intensity in the carbonyl band around 1700 cm^{-1} for the product (B-HCl-E-52) after 5 months when it is compared to the raw bitumen (Ref). The calculated peak ratio of the carbonyl to skeletal vibrations, involving carbon to carbon stretching within the aromatic ring for the product B-HCl-E-52 (Table 4-11), indicates this ratio is not significantly higher with respect to the raw bitumen. However, it could be speculated that it is due to oxidative (or other free radical related) ageing of treated bitumen with emulsion. The increased viscosity could be correlated to the formation of carbonyl (C=O) even though the oxidation was at room temperature, it suggests that bitumen is very reactive. A study by Siddiquee [30] indicated that the oxidation of bitumen conducted at low temperatures is responsible by an increase in the viscosity and density. In our previous study [10], the oxidation of bitumen took place at 100˚C during the heating of treated bitumen. Another reason for the increase in viscosity after storage can possibly be due to the separation distance between water droplets in the emulsion that decreased. Larger droplets generates more friction, which clearly promotes an increase in viscosity [6].

The change in viscosity could not be attributed to the asphaltenes content. As observed in Table 4-12, the calculated asphaltenes content on bitumen feed basis after acid treatment (B-HCl-WE) was 19.4 ± 0.2 wt% and the raw bitumen had a value of 16.8 ± 1.3 wt%. In spite of asphaltenes content that was not significantly different (better than 95 % statistical confidence), the viscosity of the treated bitumen was meaningfully lower. It is possibly due to disaggregation of clustered asphalthenes that occurred as was shown in Chapter 3 by the Atomic Force Microscopy analysis (AFM) and by asphaltenes that were found to migrate to the oil and water interface.

4.4.5 Effect of acid treatment on physical properties of bitumen

The lower viscosity as function of temperature (Figure 4-11) for bitumen after acid treatment separated of emulsion (B-HCL-WE) suggests that acid treatment could disrupt acid-base, donor-acceptor interactions and remove metal ions linked with carboxyl groups that may be affected in the bitumen at acidic pH. As can be observed in Table 4-15, the pH after acid treatment increases from 3.06 until 3.68, which can be attributed to ion exchange and neutralization reactions. On the other hand, from Chapter 3 we know by Atomic Force Microscopy Analysis (AFM) that disaggregation of clustered asphaltenes and other aggregating species is produced after acid treatment, which is correlated with the viscosity reduction.

Nevertheless, residual solvent contributed to the viscosity reduction for the Blank-WT-WE and treated bitumen (B-HCL-WE). Once these values were corrected for the residual methylene chloride (Equation 4-8) [12], Table 4-10 shows that the Blank-WT-WE had a calculated viscosity of 19.0 Pa.s at 40˚C and the bitumen after acid treatment (B-HCl-WE) had a calculated viscosity of 12.6 Pa.s at 40˚C. The experimental viscosity of raw bitumen was 97.5 Pa.s at 40 ˚C. Therefore, it was determined that the viscosity reduction was caused by water treatment and acid treatment, respectively.

The density of a crude oil is a function of its molecular composition [22]. The calculated densities corrected (Table 4-13) for residual solvent methylene chloride (Equation 4-10), at 40˚C were similar for the bitumen after water treatment (Blank-WT-WE) and acid treatment (B-HCl-WE) that were separated of emulsion with values of 1007 kg/m^3 and 1005 kg/m^3, respectively and with values of 995 kg/m^3 and 992 kg/m^3 at 60˚C, respectively. The density and composition relationship is related with hydrogen content, to a first approximation the density will decrease as hydrogen content increases [22]. According to the results of ^{1}H-NMR analysis, the aliphatic hydrogen percentage and aromatic hydrogen percentage in the bitumen after water treatment (Blank-WT-WE) and acid treatment (B-HCl-WE) without emulsion, were not statistically meaningfully different to the 95 % statistical confidence. So, both densities were comparable due to similar aliphatic and aromatic hydrogen content. On the other hand, the calculated density of the product (B-HCl-WE) was significantly lower when are compared to Raw bitumen (Ref). The effect of acid treatment was to reduce the density of bitumen, so this physical property of bitumen was improved. However, this change did not seem to originate from an increase in aliphatic hydrogen content. It suggests that acid treatment could disrupt chemical interactions in the bitumen that produces a reduction of density.

Refractive index (RI), is defined as the ratio of the velocity of light (of specified wavelength) in air, to its velocity in the substance under analysis [31]. This property contains information about the composition of the substance, for hydrocarbons of the same carbon number it varies in relation to their chemical structures. The value of RI follows the order: RI paraffins < RI naphthenes < RI aromatics and it increases with molecular weight [32]. Therefore, within the same boiling fraction a lower refractive index is indicative of the presence of a higher content of paraffinic compounds and high values, of a higher content of aromatic compounds [1].

The refractive indexes (RI) of treated bitumen with aqueous solution of HCl (B-HCl-WE) (Table 4-14) was meaningfully lower than that of raw bitumen after washing with CH_2Cl_2 and drying (Blank-RB-17) (better than 95 % statistical confidence) from 1.5761 ± 0.0001 to 1.5719 ± 0.0001 at 40˚C and from 1.5686 ± 0.0002 to 1.5666 ± 0.0006 at 60˚C. These changes could not be ascribed to changes in density. One reason that may contribute to this change is the molecular weight. A study by Abdul-Halim [33] indicated the refractive index of high molecular weight hydrocarbon is higher than that for low molecular weight fractions. In previous work it was pointed out that alkali or alkaline-earth metal ions, which were associated with carboxylate groups (mainly from naphthenic acids) could be easily removed by acid treating [10, 34]. Figure 4-18 shows a representation of Ca^{2+} linked with carboxylate groups. One hypothesis is when exchangeable cations are removed with aqueous solution of HCl, that this chemical interaction is disrupted, so smaller molecules are formed. It is important to point out that solvent remaining in the samples have some influence in the measurement; nevertheless, the values of RI for both blanks are not significantly different to 95 % statistical confidence.

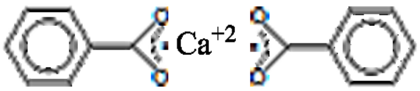

Figure 4-18: Representation of Ca linked with carboxylate groups.

4.5 Conclusions

The impact of solvent (methylene chloride) and emulsion formation in the acid treatment of Cold Lake bitumen and subsequent interpretation of the results revealed the following:

a) Some solvent (CH_2Cl_2) remained trapped in the bitumen structure. The remaining solvent for the product after acid treatment was 5.8 wt% by FTIR analysis in spite of 17 h in the rotavap under vacuum at 45˚C. For some samples, even under constant conditions, the rate of evaporation of solvent was not reproducible. So, a small amount of residual solvent had a significant impact on the viscosity reduction of the bitumen.

b) The emulsion formation was an important issue to investigate in the acid treatment. It was determined that the asphaltenes content of the emulsion was 52 wt % based on the oil present in the emulsion. The information on the nature of the functional groups of the emulsion suggested that not only asphaltenes stabilized the emulsion. The emulsion was also stabilized by inorganic solids particles (such as clay minerals). The mineral matter content of the emulsion was 4.3 ± 1.6 wt % and 27.3 ± 0.3 wt% for the asphaltenes precipitated from the emulsion.

c) The effect of the emulsion on viscosity was an increase in viscosity due to the presence of emulsified water droplets in the bitumen. The lowest viscosity corrected for the residual methylene chloride at 60˚C was 2.1 Pa.s, which was obtained for the treated bitumen separate of emulsion. The treated bitumen with emulsion after 5 months did not exhibit good storage stability, because the viscosity increased significantly with respect to the fresh product with a calculated value of 16.7 Pa.s at 60 ˚C (acid washed with 0.003 M HCl).

d) The viscosity versus measurement temperature relationship deviated slightly due to a curvature in the data and not due to random scatter from the typical linear $\ln[\ln(\mu)]$ versus $\ln(T)$ response for treated bitumen (0.003 M HCl and 0.0003 M HCl) with emulsion after

5 months. Such deviation is normally observed when there is a second phase present, such as the aqueous phase.

e) The blank experiments (water treatment) indicated that only to wash the bitumen with water affected the viscosity, which decreased significantly (19.0 Pa.s at 40˚C) when compared to the viscosity of raw bitumen (97.5 Pa.s at 40˚C). It may be due to water acting as an "extractant" that removed the salt, water, and solids from the bitumen, similar to the desalting operation in a refinery. In addition, acid-base interactions may be relevant even at neutral pH. However, the lowest viscosity found was for bitumen after acid treatment that was separated of emulsion (12.6 Pa.s at 40˚C). These values were corrected for the residual methylene chloride.

f) The change in viscosity could not be attributed to the asphaltenes content. In spite of an increase in the asphaltenes content after acid treatment, it was not significantly different from that of the raw bitumen (better than 95 % statistical confidence), but its viscosity was lower.

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CHAPTER 5 – IMPACT OF BASE TREATMENT ON BITUMEN VISCOSITY

Abstract

Evidence was provided that the physical properties and chemical composition of bitumen was affected by acid treatment. The influence of base treatment on bitumen properties, such as viscosity, was investigated and compared to its effect with the acid treatment. The study was conducted by mixing an organic solution of Cold Lake bitumen with aqueous solutions (0.003 N) of lithium hydroxide (LiOH) and ethanolamine ($HOCH_2CH_2NH_2$) individually at room temperature. The results showed that the propensity for emulsion formation was higher after base treatment compared to acid treatment due to the formation of surface-active soaps. The influence of base treatment on viscosity of bitumen depends on the base strength. The viscosity reduction at 40 °C when compared to viscosity of raw bitumen (97.5 Pa.s), was higher for bitumen treated with LiOH than for bitumen treated with ethanolamine, with calculated values corrected for the residual methylene chloride of 15.0 Pa.s and 26.4 Pa.s, respectively. The extent of viscosity reduction was influenced in a similar way when a strong base (LiOH) was used compared to a strong acid (HCl).

Keywords: Oilsands bitumen, viscosity, base, ethanolamine, lithium hydroxide.

5.1 Introduction

One of the potential interactions that could affect bitumen viscosity is intermolecular acid-base interactions. A study was conducted to investigate the impact of acid treatment on bitumen viscosity [1], and was presented in Chapter 3. The results showed that the treatment with low acid concentrations (0.0003-0.3 M HCl) may break some chemical interactions in the bitumen that also may affect physical properties such as the viscosity. If these interactions were acid-base interactions, it should in principle be possible to achieve the same effect by base treatment as acid treatment.

Heavy oils and bitumen have on average more acidic components than conventional crude oils [2]. Therefore, the main objective of this research was to evaluate the response of bitumen viscosity to the influence of base treatment. If acid groups are primarily responsible for hydrogen bonding to cause aggregation and high viscosity, rather than acid-base interactions, then base treatment should improve viscosity more than acid treatment.

Two different bases were selected for the study. The stronger base, LiOH, could disrupt stronger acid-base interactions and the extent of Li^+ incorporation in the product would be indicative of the extent of acid-base interaction. Ethanolamine is a weaker base and would disrupt only weaker acid-base interactions.

5.2 Experimental

5.2.1 Materials

Toluene ≥ 99.5 %, certified ACS supplied by Fisher Scientific.

Ethanolamine ($HOCH_2CH_2NH_2$) > 95% supplied by Fisher Scientific.

Lithium hydroxide anhydrous (LiOH) > 96% supplied by Fisher Scientific.

Hydrochloric acid, 1N standard solution, Acros Organics. This standard solution was used for the titration of concentrated solutions of bases.

The rest of the materials and bitumen are as referred to in Chapter 3.

5.2.1.1 Standardization

First of all, stock solutions 1N of lithium hydroxide and 1N of ethanolamine were prepared. Then, the titration was performed on a sample (10 mL) taken from the solutions to confirm the base concentration. A standard solution 1N of HCl (Acros Organics) was used as titrant with phenolphthalein as indicator. The equivalence point was determined by color change when the indicator changed from pink to colorless. Table 5-1 shows the results of titration of samples taken from the stock solutions of lithium hydroxide (LiOH) and ethanolamine. After the concentration was verified for each base, then diluted solutions were prepared by individually diluting the stock bases to produce solutions of 0.003N LiOH and 0.003N ethanolamine.

Table 5-1: Titration of aqueous solutions of LiOH and ethanolamine.

Samples	Number	HCl volume, mL	Concentration, N	Average concentration, N
Aqueous solution lithium hydroxide	1	10.6	1.06	1.05 ± 0.01
	2	10.5	1.05	
	3	10.5	1.05	
Aqueous solution ethanolamine	1	10.3	1.03	1.03 ± 0.01
	2	10.4	1.04	
	3	10.3	1.03	

Table 5-2 presents the pH of diluted aqueous solutions 0.003N of LiOH and 0.003N of ethanolamine which are compared with the pH of Milli-Q water.

Table 5-2: pH of Milli-Q water and diluted aqueous solutions of base treatment.

Samples	pH
Milli-Q water	6.70 ± 0.27
Initial aqueous solution 0.003N LiOH	11.63 ± 0.01
Initial aqueous solution 0.003N ethanolamine	10.80 ± 0.01

5.2.2 Equipment and procedure

The base treatment with lithium hydroxide or ethanolamine was performed using the same procedure as for the acid treatment. In a typical experiment 20 g of Cold Lake bitumen was dissolved in approximately 131.5 g of methylene chloride. The diluted aqueous solution of base 0.003 N (100 g) was added to the organic solution. The height of liquid in the reactor was 3.7

cm. These solutions were mixed using an octagonal magnetic stir bar (Dia. x L: 1 x 5 cm) with a set speed of 400 rpm for 2 h at room temperature. Then, the reactor was washed with approximately 39.3 g of methylene chloride to transfer the entire product to a separating funnel. Next, the product was separated using a separating funnel. It was left overnight in the separating funnel to get a good phase separation. However, it was observed that the water phase was completely emulsified (Figure 5-1). The more dense phase (bottom phase) was the organic solution consisting of bitumen and methylene chloride. The less dense phase (top phase) was the emulsion. So, the organic product could be separated from the emulsified phase. After that, methylene chloride was removed from the product in a rotary evaporator at 45 °C under vacuum at 55 kPa absolute over a period of 17h. Finally, the product and emulsion were weighed and the material balance was calculated.

Two additional experiments were carried out for the bitumen after base treatment with LiOH. The purpose of these experiments was to determine if it was possible to reduce emulsion formation. In the first experiment toluene was employed as organic solvent (Figure 5-2). In the second experiment a concentration of 1.05 N LiOH was employed with methylene chloride as organic solvent. In both cases it was found that the water phase was totally emulsified. Therefore, these lines of experimentation were abandoned after finding the emulsion.

Two blank experiments were also conducted. The first blank experiment (Blank-RB-17), was performed as part of the investigation reported in Chapter 4. Blank-RB-17 consisted of washing raw bitumen with CH_2Cl_2 and then removing the solvent by rotary evaporation at 45°C under vacuum at 55 kPa absolute over a period of 17 h. The second blank experiment (Blank-WT-WE) also was conducted as part of the investigation reported previously in Chapter 4. It comprised of water treatment of the bitumen using the same methodology as for acid and base treatments.

All experiments were carried out at least in triplicate to measure the repeatability and reproducibility.

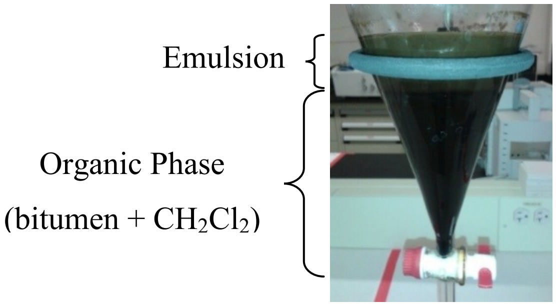


Figure 5-1: Base treatment with LiOH using methylene chloride as organic solvent.

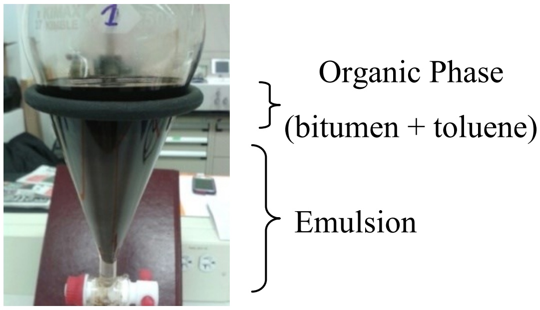


Figure 5-2: Base treatment with LiOH using toluene as organic solvent.

5.2.3 Analyses

Viscosity analyses were carried out using an Anton Paar RheolabQC rotational rheometer following the procedure as described in Chapter 4. However, in this procedure, the viscosity was measured only at a temperature of 40 °C.

The asphaltenes content of the bitumen was determined by the same procedure as described in Chapter 4.

Fourier transform infrared (FT-IR) spectroscopic analysis was performed using the procedure described in Chapter 4.

Refractive Index (RI) measurements were conducted by the same procedure as described in Chapter 4.

The ^{1}H Nuclear Magnetic Resonance (NMR) analyses were performed using the procedure described in Chapter 4.

Density analyses were determined by the same procedure as described in Chapter 4.

For the mass balance all weighing was performed as described in Chapter 4.

The pH of aqueous solutions of lithium hydroxide and ethanolamine were measured as described in Chapter 4. A pH 11 buffer solution supplied by Fisher Scientific was used for this analysis.

5.2.4 Identification of samples

Table 5-3 summarizes the identification of all the different samples that were prepared for this study, as well as the three samples from Chapter 4 that were used in this study in order to compare results. These samples were assigned with an identifier, which will be used in the following sections to avoid any confusion and ambiguity.

Table 5-3: Identification of samples.

Samples	Description	Identifier
Raw Bitumen	Reference, without any treatment	Ref
Blank: raw bitumen after washing with CH_2Cl_2 and drying	This blank experiment was performed as part of the investigation reported in Chapter 4.	Blank-RB-17
Blank: bitumen after water treatment without emulsion	This blank experiment was performed as part of the investigation reported in Chapter 4.	Blank-WT-WE
Treated bitumen (0.003 N LiOH) without emulsion	Oil phase that was separated from a mixture that had an emulsion. Total time in the rotavap: 17 h	B-LiOH-WE
Treated bitumen (0.003 N Ethanolamine) without emulsion	Oil phase that was separated from a mixture that had an emulsion. Total time in the rotavap: 17 h	B-ETHA-WE
Treated bitumen (0.003 M HCl) without emulsion	This experiment of bitumen after acid treatment was performed as part of the investigation reported in Chapter 4.	B-HCl-WE

5.2.5 Calculations

5.2.5.1 Standardization

$N_{base} = (N_{acid} \times V_{acid})/V_{base}$ … (5-1)

Where:

N_{base} = Normality of aqueous solution of base, N
N_{acid} = Normality of standard solution of HCl, N
V_{acid} = Volume of HCl solution in the titration, mL
V_{base} = Volume of base, mL

An example of sample calculation is shown in Appendix 13.

5.2.5.2 The residual methylene chloride

As explained in Chapter 4, the residual methylene chloride in the bitumen was calculated by FTIR analysis and ^{1}H-NMR analysis. Examples of sample calculations are shown in Appendices 5 and 6, respectively.

5.2.5.3 Bitumen in emulsion

An example of sample calculation is shown in Appendix 14.

5.2.5.4 Asphaltenes content

Equation 4-6 described in Chapter 4 was used for this calculation. Another equation used was the following:

Asphaltenes content (wt%) = (g asphaltenes in treated bitumen / g feed bitumen) x 100
in treated bitumen
based in feed material …(5-2)

An example of sample calculation for the base treatment is shown in Appendix 15.

5.2.5.5 Viscosity corrected for the residual methylene chloride

Equation 4-8 presented in Chapter 4 was used to correct for the effect of the residual methylene chloride on the viscosity of products.

An example of sample calculation is shown in Appendix 9.

5.2.5.6 Density corrected for the residual methylene chloride

Equation 4-10 presented in Chapter 4 was used to correct for the effect of the residual methylene chloride on the density of products.

An example of sample calculation is shown in Appendix 11.

5.2.5.7 Yield

Equation 4-11 described in Chapter 4 was used at this calculation. In addition, the yield of emulsion was calculated with the following equation:

$$\text{yield of emulsion (wt\%)} = \frac{\text{grams obtained emulsion}}{\text{initial grams of basic aqueous solution}} \text{ x } 100 \qquad \ldots(5\text{-}3)$$

An example of sample calculation for the base treatment is shown in Appendix 16.

5.2.5.8 Student's t-test

It is described in Chapter 4.

5.3 Results

5.3.1 Residual methylene chloride after base treatment

Figure 5-3 shows a comparison of FTIR spectrums in the region 600 to 1400 cm^{-1} of raw bitumen after washing with CH_2Cl_2 and drying (Blank-RB-17), treated bitumen with LiOH and ethanolamine, and methylene chloride that was employed as solvent, which is shown as reference. As can be observed treated bitumen (B-LiOH-WE) and (B-ETHA-WE) with respect to Blank-RB-17 presents differences in the intensity of bands corresponding the remaining methylene chloride at 1265 cm^{-1} and 731 cm^{-1}, which are most intense for treated bitumen.

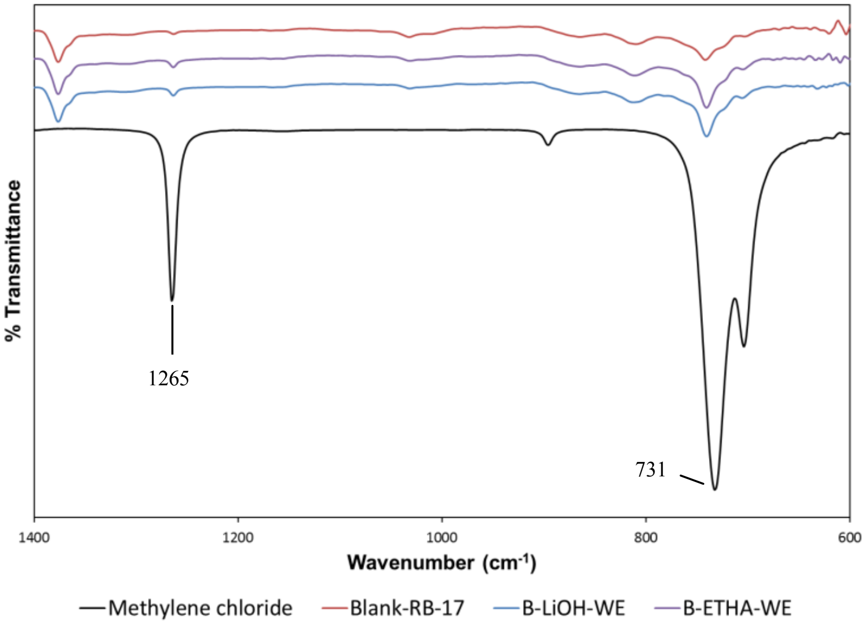


Figure 5-3: Comparison of FTIR spectrums bitumen in the region 600 to 1400 cm^{-1} after base treatment with LiOH and ethanolamine, Blank-RB-17 and methylene chloride.

It was determined analytically the amount of residual methylene chloride by FTIR using an internal standard calibration curve (Appendix 5). The height of absorptions around 1600 cm^{-1} of skeletal vibrations, involving carbon to carbon stretching within the aromatic ring and around 1265 cm^{-1} related to CH_2Cl_2 wagging in the methylene chloride, were determined for each sample. Figure 5-4 shows these absorptions for the B-LiOH-WE and B-ETHA-WE and Table 5-

4 shows the height of both absorptions for the samples after base treatment. With the values of C=O/ C⎓C ratio were determined the amount of residual methylene chloride by using the calibration curve (Figure A5-1). The residual methylene chloride was 2.3 wt% for the Blank-RB-17, refer to Table 4-3 (Chapter 4) and 6.4 wt% for the products after of the base treatment (Table 5-6).

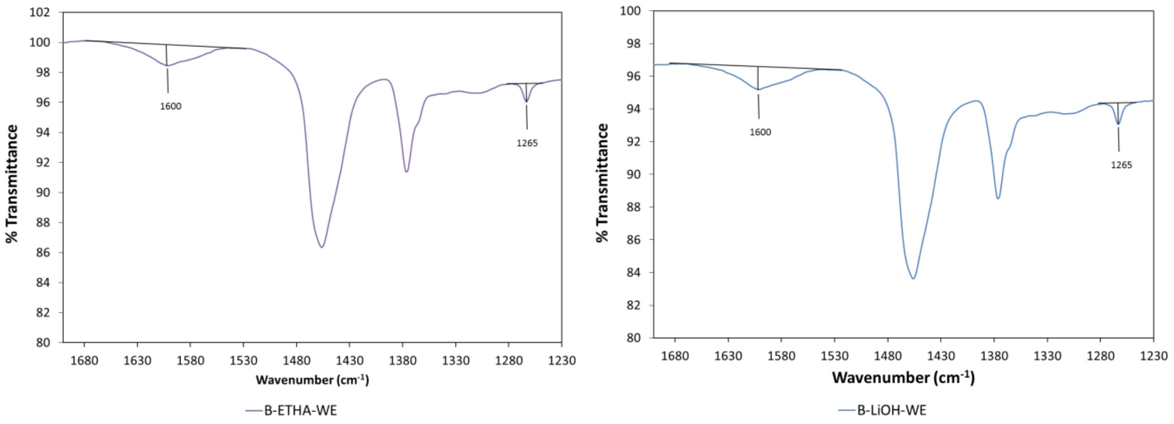


Figure 5-4: Region of 1700-1230 cm^{-1} for FTIR spectrums of B-LiOH-WE and B-ETHA-WE.

Table 5-4: Height of absorptions for FTIR spectrums of B-LiOH-WE and B-ETHA-WE .

Samples	Height of C-Cl absorption (%)	Height of C⎓C absorption (%)	C-Cl/ C⎓C Ratio
B-LiOH-WE	1.244	1.385	0.9
Blank-ETHA-WE	1.202	1.390	0.9

For ^{1}H-NMR analysis, the total aliphatic hydrogen percentage was integrated in the range 0.4 - 4.0 ppm and the total aromatic hydrogen percentage were integrated in the range 6.5 - 9.0 ppm. The results for the ^{1}H NMR analyses of the bitumen after base treatment with lithium hydroxide and ethanolamine are presented in Table 5-5. A signal between 5.6 – 5.0 ppm was indicative hydrogen resonance of methylene chloride remaining in the samples. As can be seen, the total methylene chloride hydrogen content of the treated bitumen with LiOH and ethanolamine were not statistically meaningfully different to the 95 % statistical confidence. On the other hand, the treated bitumen with ethanolamine presented a slight increase of aliphatic hydrogen content and a lower aromatic hydrogen content with respect treated bitumen with LiOH.

It is important to point out that the raw bitumen was analyzed by ^{1}H NMR analyses. However, unsatisfactory results were obtained due to a lot of noisy of spectrums at different parameters and bitumen concentrations in the chloroform-d Aldrich 99.96 atom % D, using a NMReady^{TM} 60 spectrometer of Nanalysis Corporation. For ease of reference, the values obtained of ^{1}H NMR by a study of Cold Lake Bitumen were included in Table 5-5 [3].

Table 5-5: The aliphatic hydrogen percentage, aromatic hydrogen percentage and methylene chloride hydrogen percentage in the bitumen after base treatment with LiOH and ethanolamine.

Samples	Aliphatic Hydrogen, %	Aromatic Hydrogen, %	Methylene chloride Hydrogen, %
Raw bitumen (Ref)	91.0 ± 1.0*	9**	-
B-LiOH-WE	91.0 ± 1.0	8.3 ± 0.9	0.7 ± 0.1
B-ETHA-WE	93.5 ± 0.7	5.4 ± 0.9	1.1 ± 0.3

*Experimental value by ^{1}HNMR analysis of Cold Lake Bitumen [3]

**Calculated value = 100% - 91% = 9%

Table 5-6 shows the calculated residual methylene chloride in products (B-LiOH-WE) and (B-ETHA-WE) using FTIR and ^{1}H-NMR analyses. At the Appendixes 5 and 6 are shown examples of calculation for these analyses, respectively. The results obtained by FTIR analysis were selected for the processing of experimental data to correct the remaining solvent in the products.

Table 5-6: Calculated CH_2Cl_2 in products after base treatment by FTIR and ^{1}H-NMR analyses.

Samples	CH_2Cl_2 (wt %)	
	by ^{1}H-NMR	by FTIR
Treated bitumen (B-LiOH-WE)	3.0	6.4
Treated bitumen (B-ETHA-WE)	5.0	6.4

5.3.2 Incorporated ethanolamine

Figure 5-5 shows a comparison of spectrums FTIR of raw bitumen (Ref) and the product after base treatment (B-ETHA-WE) in the region 3500 to 2800 cm^{-1}. For the product new absorptions were not detected in this region due to primary amine salts when bitumen was treated with ethanolamine. It is important to point out that the concentration of base is very low with a value of 0.003 N (aqueous solution of ethanolamine). On the other hand, the H of alcohol and amine groups in ethanolamine could not be identified by ^{1}H-NMR analysis.

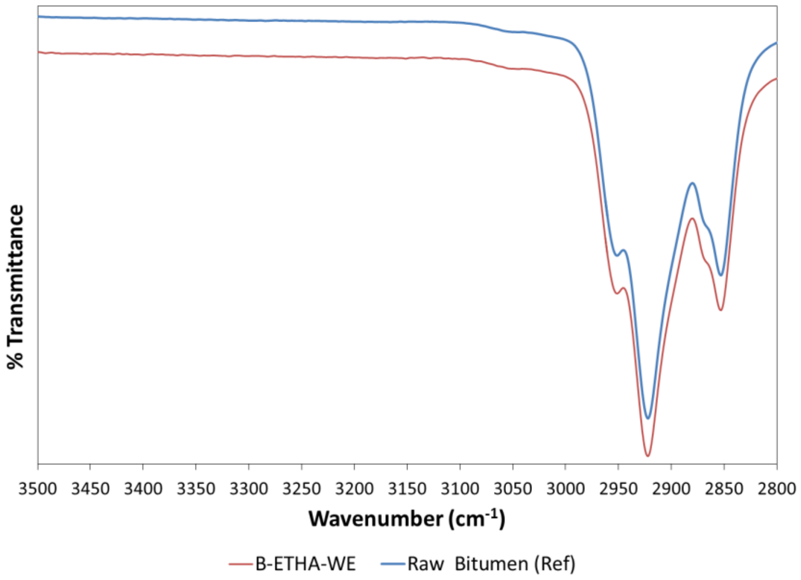


Figure 5-5: Comparison of FTIR spectrums bitumen in the region 3500-2800 cm^{-1} of Raw bitumen (Ref) and the product B-ETHA-WE.

5.3.3 Material balances

Tables 5-7, 5-8 and 5-9 show the results of mass balance for bitumen after water treatment (Blank-WT-WE) and base treatment with LiOH and ethanolamine, respectively, as well as, the yield of treated bitumen and emulsion formed for water and base treatments. The yields of bitumen were corrected for the residual methylene chloride that remained in the bitumen, determined by FTIR analysis; a sample calculation is shown in Appendix 16. As can be seen in these Tables, the yield of bitumen corrected for the remaining solvent were 90 wt%, 91 wt% and 86 wt% for the water treatment and base treatment with LiOH and ethanolamine, respectively. The remainder of the bitumen was trapped in the emulsion phase.

Table 5-7: Mass balance during water treatment and yields of products.

Samples	Initial weight, g feed material	Weight after treatment, g	Yield, wt%
Bitumen (B-WT-WE)	20.032 ± 0.028	18.937 ± 0.966	90 ± 4.8
Deionized water	100.071 ± 0.002	The aqueous solution was emulsified	-
Emulsion	-	111.208 ± 0.499	111 ± 0.5
Methylene chloride	170.886 ± 0.001	Not measured	-

Table 5-8: Mass balance during base treatment with LiOH and yields of products.

Samples	Initial weight, g feed material	Weight after treatment, g	Yield, wt%
Bitumen (B-LiOH-WE)	20.043 ± 0.033	19.573 ± 0.287	91 ± 1.4
Aqueous solution of LiOH	100.064 ± 0.019	The aqueous solution was emulsified	-
Emulsion	-	115.292 ± 1.271	115 ± 1.3
Methylene chloride	170.888 ± 0.011	Not measured	-

Table 5-9: Mass balance during base treatment with ethanolamine, and yields of products.

Samples	Initial weight, g feed material	Weight after treatment, g	Yield, wt%
Bitumen (B-ETHA-WE)	20.080 ± 0.014	18.526 ± 0.430	86 ± 2.1
Aqueous solution of Ethanolamine	100.065 ± 0.004	The aqueous solution was emulsified	-
Emulsion	-	117.641 ± 0.506	118 ± 0.5
Methylene chloride	170.886 ± 0.003	Not measured	-

The aqueous phase formed a stable emulsion with the bitumen and methylene chloride. Table 5-10 shows the mass balance of emulsions components. The amount of bitumen in the emulsion was 1.95 g for the water treatment, 1.72 g for the base treatment with LiOH and 2.74 g for the base treatment with ethanolamine. The yields of emulsion formed in the aqueous layer were 111 wt%, 115 wt% and 118 wt% for the water treatment and base treatment with LiOH and ethanolamine, respectively. Therefore, the yields were above of 100 wt% due to the presence of bitumen and organic solvent in the emulsified aqueous layer.

Table 5-10: Mass balance of emulsion components.

Samples	Water, g	Calculated Bitumen in Emulsion, g	Calculated Methylene chloride in the emulsion , g
Emulsified phase of Bitumen (B-WT-WE)	100.071 ± 0.002	1.95	9.19
Emulsified phase of Bitumen (B-LiOH-WE)	100.064 ± 0.019	1.72	13.51
Emulsified phase of Bitumen (B-ETHA-WE)	100.065 ± 0.004	2.74	14.84

5.3.4 Viscosity and Asphaltenes content

Table 5-11 shows direct viscosity measurements at 40 ℃ of bitumen feed (Ref), treated bitumen with water (Blank-WT-WE), bitumen after base treatment with 0.003N LiOH (B-LiOH-WE) and ethanolamine (B-ETHA-WE), and treated bitumen with the aqueous solution of 0.003 M HCl (B-HCl-WE). These experimental viscosities were corrected for residual solvent methylene chloride, refer to Equation 4-8, Chapter 4, where an example of sample calculation is shown in Appendix 9. The values of remaining solvent were those determined by FTIR analysis (Table 4-5, Chapter 4 and Table 5-6, Chapter 5).

Table 5-11: Direct measurement of viscosity and calculated viscosity of products at 40°C

Samples	Experimental Viscosity at 40˚C (Pa.s)	Calculated Viscosity corrected for the residual CH_2Cl_2 (Pa.s), Eq.(4-8)
Raw bitumen (Ref)	97.5 ± 0.5	-
Blank-WT-WE	8.6 ± 2.1	19.0
B-LiOH-WE	4.9 ± 1.3	15.0
B-ETHA-WE	8.6 ± 1.4	26.4
B-HCl-WE	4.7 ± 0.7	12.6

Asphaltenes content on a bitumen feed basis was calculated for the bitumen after water treatment (Blank-WT-WE) and base treatment (B-LiOH-WE) and (B-ETHA-WE), which were compared with the raw bitumen (Ref) (Table 5-12). For this calculation, the bitumen content was adjusted to correct the methylene chloride present in the treated product as determined by FTIR analysis (Table 4-5, Chapter 4 and Table 5-6, Chapter 5). The calculation is given by Appendix 15. It is important to point out, the content of asphaltenes in emulsion was not determined, so the calculation does not include these asphaltenes that migrate to oil and water interface, which was explained in a previous study (Chapter 4). The asphaltenes content of the emulsion phase was not measured the focus was on the bitumen after the base treatment and not the emulsion phase. As can be observed, the asphaltenes content of Blank-WT-WE and treated bitumen were not statistically meaningfully different with respect to raw bitumen (Ref) (better than 95 % statistical confidence).

Table 5-12: Asphaltenes content on a bitumen feed basis.

Samples	Asphaltenes Content (wt %)
Raw Bitumen	16.8 ± 1.3
Blank-WT-WE	16.0 ± 0.2
B-LiOH-WE	15.9 ± 0.5
B-ETHA-WE	15.1 ± 0.9

5.3.5 Density and Refractive index analysis

Density was analyzed for raw bitumen (Ref), blank of the bitumen after water treatment (Blank-WT-WE) and bitumen after base treatment with LiOH and ethanolamine as function of temperature at 40˚C and 60˚C. The values presented in Table 5-13 for blank and treated bitumen are direct measurements of density and calculated densities subtracting the solvent methylene chloride, 4.5 wt% for the Blank-WT-WE and 6.4 wt% for the treated bitumen (B-LiOH-WE) and (B-ETHA-WE) according to Equation 4-10, refer to Chapter 4.

Table 5-13: Direct measurement of density and densities calculated for products.

	Experimental Density		Calculated Density corrected for residual CH_2Cl_2 Eq.(4-10)	
Samples	at 40˚C (kg/m^3)	at 60˚C (kg/m^3)	at 40˚C (kg/m^3)	at 60˚C (kg/m^3)
Raw bitumen (Ref)	1012 ± 0.01	1000 ± 0.01	-	-
Blank-WT-WE	1017 ± 3.8	1004 ± 1.7	1007	995
B-LiOH-WE	1021 ± 0.4	1008 ± 0.5	1007	995
B-ETHA-WE	1012 ± 0.1	999 ± 0.1	997	986

Table 5-14 shows the values of refractive index for raw bitumen (Ref), methylene chloride, Blank-WT-WE and bitumen after base treatment (B-LiOH-WE) and (B-ETHA-WE) as function of temperature at 40˚C and 60˚C. These values are the results obtained directly by measurement. The blank and treated bitumen values include the contribution of methylene chloride. The refractive index of the methylene chloride experimentally determined is 1.4117 at 40°C and 1.4038 at 60°C.

Table 5-14: Refractive indexes of raw bitumen (Ref), methylene chloride, blank, and bitumen after base treatment with LiOH and ethanolamine at 40˚C and 60˚C.

Samples	nD at 40˚C	nD at 60˚C
Raw bitumen (Ref)	1.5767 ± 0.0001	1.5692 ± 0.0001
Methylene Chloride	1.4117 ± 0.0001	1.4038 ± 0.0001
Blank-WT-WE	1.5754 ± 0.0005	1.5682 ± 0.0004
B-LiOH-WE	1.5749 ± 0.0007	1.5673 ± 0.0013
B-ETHA-WE	1.5728 ± 0.0009	1.5660 ± 0.0001

5.4 Discussion

5.4.1 Emulsion formation in the base treatment

From the literature review (Chapter 2) we know that several chemical compound classes are present in the bitumen. Among them, bitumen contains a mixture of carboxylic acids, with different molecular structures and molecular weights. These carboxylic acids when they are neutralized by an alkaline aqueous solution, can form surface-active soaps. These potentially water-soluble surfactants can be produced and are more concentrated at the interface [4]. It was speculated that emulsion formation in the aqueous layer was due to the presence of these surface-active soaps that were formed by the base treatment of Cold Lake bitumen with aqueous solution of lithium hydroxide (0.003 N) and ethanolamine (0.003 N) (Figure 5-1). This low concentration is enough to produce neutralization of the carboxylic acids (AH) present at the bitumen/water interface, forming the carboxylate ions (A^-), whose interfacial activity properties were described in literature [4]. Acevedo et al. [4] studied bitumen in water emulsions stabilized with natural surfactants activated by adding different concentrations of sodium carbonate (Na_2CO_3) to the aqueous phase of the emulsions. They found that at a Na_2CO_3 concentration of as low as 500 ppm in the aqueous phase carboxylate ions were produced.

Rivas [5] proposed a mechanism to produce neutralization of the carboxylic acids with ethanolamine (MEA) present at the oil/water interface (Figure 5-6). When the oleic phase that contains the carboxylic acid was put in contact with aqueous phase, the carboxylic acid due to its affinity by both phases, it can diffuse toward the aqueous phase or the region close to the oil water interface for partitioning between both phases according to its coefficient of partition (equilibrium 1). The amount of carboxylic acid at the aqueous phase is ionized in protons and carboxylate ions (AO^-) according to ionization constant (equilibrium 2).

On the other hand, MEA contained in the aqueous phase is ionized in hydroxyl ions and protonated amine (equilibrium 6). The hydroxyl ions react with protons according to equilibrium 5 of hydrolysis of water. The reaction between the protons and hydroxyl ions alters the equilibrium 2 which is displaced toward the right producing a high concentration of carboxylate ions. These ions react with protonated amine to form amine carboxylate salt (equilibrium 3), which with its affinity double was diffused according to its coefficient of partition between both phases (equilibrium 4). So, amine carboxylate salt is adsorbed at the oil/water interface [5].

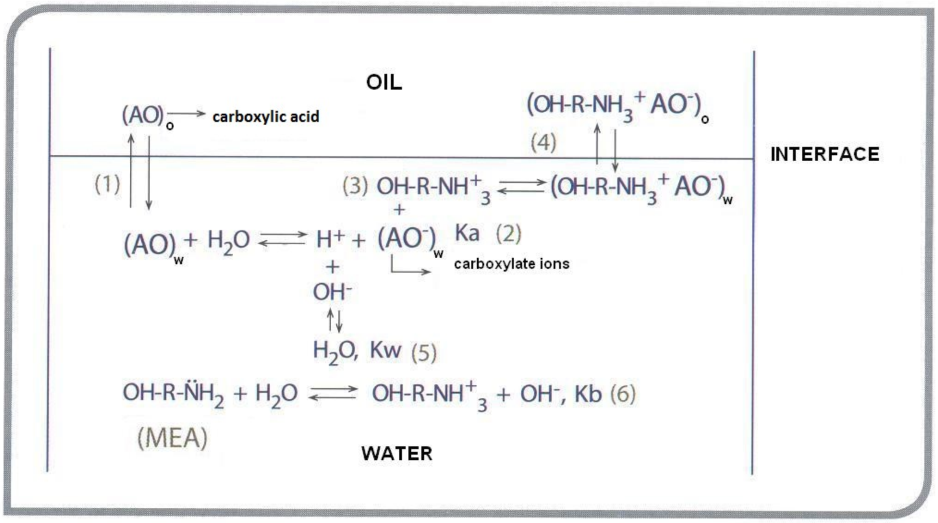
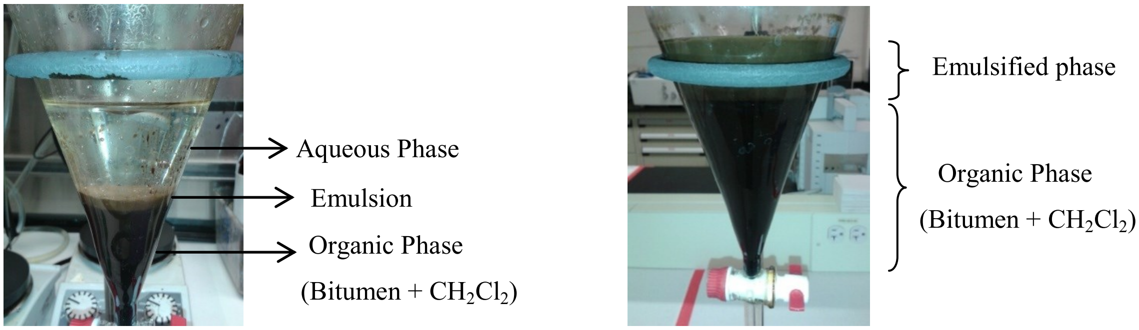


Figure 5-6. Proposed mechanism of neutralization at the oil/water interface using ethanolamine (MEA) [5].

On the other hand, as was explained in the Chapter 4, asphaltenes and fine inorganic particles also act to stabilize and form oil and water emulsions. Adams et al. [6] studied the role of asphaltenes in oil and water emulsions. They observed extensive emulsion formation for high pH 12 (basic) water solutions suggesting the significance of acidic surface active molecules. The results of Adams et al. showed that for high pH emulsions, the aqueous layer changed a tan or brown color for oils with total acid number (TAN) values > 0.4 mg KOH/g oil indicating water soluble charged acids. Figure 5-4 b illustrates the observed color of the aqueous solution after base treatment with lithium hydroxide, which was brown.

The pH of diluted aqueous solutions 0.003N of LiOH and ethanolamine were 11.63 ± 0.01 and 10.80 ± 0.01, respectively (Table 5-2). As was explained previously, alkaline aqueous solution can form surface-active soaps in the bitumen. Therefore, basic pH suggesting higher interfacial activity in the bitumen, inclusive to neutral pH, because for Blank-WT-WE (pH deionized water: 6.70 ± 0.27), the aqueous phase was emulsified. Acid treatment of bitumen has shown that for acidic pH the emulsion formation propensity is lower [1]. It can be observed in Figure 5-7 where the separation of phases after acid treatment and base treatment are compared. In the acid treatment, there is clearly three phases: aqueous phase, emulsion and organic phase. It is not produced in the base treatment where the aqueous layer is completely emulsified.



(a) (b)

Figure 5-7: Separation of phases after (a) acid treatment (0.003 M HCl) and (b) base treatment (0.003 N LiOH).

For the base treatment with LiOH, the organic solvents used to dissolve the bitumen were methylene chloride and toluene. For both solvents it was found that the emulsion formed was stable (Figures 5-1 and 5-2). From the studies of Adams et al. [6], it was demonstrated that a fraction of the least soluble asphaltenes (toluene-soluble and methylene chloride soluble) were acting as the primary emulsion stabilizing components [4].

5.4.2 Effect of base treatment on bitumen viscosity

The viscosity of Cold Lake bitumen measured at 40 ˚C (Table 5-11) that was not subjected to any treatment is shown for reference and it has a value of 97.5 Pa.s. The viscosity measured decreased to 8.6 Pa.s. for the Blank-WT-WE. In the Chapter 4 it was observed that water washing of the bitumen affected the viscosity. The lowest experimental viscosity (4.9 Pa.s) after base treatment was found for the bitumen treated with 0.003 N LiOH, which suggests that it was useful to also to disrupt stronger acid-base interactions in the bitumen in order to decrease the viscosity. On the other hand, for the bitumen after base treatment with 0.003 N ethanolamine the viscosity measured decreased to 8.6 Pa.s, the same value obtained for the water treatment. This difference between both bases is because lithium hydroxide is a strong base with a pK_b at 25˚C of -0.53 [7] and the ethanolamine is a weak base with a pK_b of 4.50 that corresponds a dissociation constant (K_b) 3.18×10^{-5} [8].

However, this viscosity reduction presented for the Blank-WT-WE and treated bitumen with LiOH and ethanolamine included the contribution for the remaining solvent. The residual methylene chloride of these samples were 4.5 wt% for the blank and 6.4 wt% for the products after base treatment determined by FTIR analysis. Once these values were corrected for the residual methylene chloride refer to Equation 4-8 (Chapter 4), the Blank-WT-WE had a calculated viscosity of 19.0 Pa.s at 40˚C and the bitumen after base treatment (B-LiOH-WE) and (B-ETHA-WE) had a calculated viscosity of 15.0 Pa.s at 40˚C and 26.4 Pa.s at 40˚C, respectively. The experimental viscosity of raw bitumen was 97.5 Pa.s at 40 ˚C. Therefore, it confirmed the viscosity reduction by only water treatment and base treatment. It is noteworthy that viscosity of treated bitumen with LiOH is comparable statistically (95 % statistical confidence) to viscosity of bitumen after acid treatment (B-HCl-WE) whose calculated value was 12.6 Pa.s at 40°C.

Hydrochloric acid is a strong acid with a pK_a at 25˚C of -6.1 [6]. It suggests acid-base interactions in the bitumen are affected similarly irrespective of whether a strong base (LiOH) or strong acid (HCl) is used, albeit reverse chemistry took place and that there were no other interactions that were disrupted beyond pure acid-base interactions. In addition, it was demonstrated that the viscosity reduction is higher for the strong base than a weak base. Hence, it suggests that ethanolamine affects only weak acid-base interactions in the bitumen. Ethanolamine may react in water according to Equation 5-4, to produce hydroxyl ions and the protonated amine, which has a very low dissociation constant (3.18×10^{-5}) [8]. The ionic product constant of water (K_w) at 25˚C is 1.01×10^{-14} according to Equation 5-5.

$$\text{OH-R-NH}_2 + \text{H}_2\text{O} \rightleftarrows \text{OH-R-NH}_3^+ + \text{OH}^- \qquad ...(5\text{-}4)$$

$$\text{H}_2\text{O} \rightleftarrows \text{H}^+ + \text{OH}^- \qquad ...(5\text{-}5)$$

In the literature review (Chaper 2) was referred the base treatment for coal and some parallels may be drawn with bitumen. A study by Van Bodegom [9] indicated that the class of good solvents for brown coals is restricted to strong bases because of their capacity to break ester bonds. Our study showed that the strong base (LiOH) was more efficient for the viscosity reduction in the bitumen more than weak base.

In Chapter 3, it was shown that dispersed phases in bitumen are disaggregated after acid treatment, which was postulated as one of the reasons for the observed viscosity reduction. So, the base treatment and water treatment (Blank) can possibly lead to similar disaggregation. Furthermore, the release of trapped material, the removal of salts and solids that might have been present in connate water associated with the bitumen and/or a potential reduction in the boundary layer volume around the aggregates, could all potentially explain the decrease in viscosity after base treatment. These are physical processes, or mechanisms comprising weak chemical interactions [10].

Table 5-12 showed that the asphaltenes content on a bitumen feed basis of Blank-WT-WE and treated bitumen with LiOH and ethanolamine were not statistically meaningfully different with respect to raw bitumen (Ref) (better than 95 % statistical confidence). Nevertheless, the viscosities were meaningfully lower for the products after treatment than that of raw bitumen (Table 5-11). Therefore, bitumen viscosities cannot be estimated from their asphaltenes contents alone [11]. A study by Bukka [11] presented a comparative analysis of Athabasca (Alberta, Canada) and Asphalt Ridge bitumens, mainly in terms of their viscosities and asphaltene contents. Asphalt Ridge bitumen, although containing only 7% asphaltenes, had a viscosity value of 80 Pa.s at 50 °C while Athabasca bitumen, with 17% asphaltenes, had a viscosity of only 5 Pa.s at 50 °C. These results indicated that in addition to asphaltenes there are other compositional properties of the bitumen which affect its viscosity.

Hence, Bukka *et al.* [11] studied what compositional properties other than asphaltene content may influence bitumen viscosity. They found the presence of larger amounts of compounds containing carboxylic groups in the Sunnyside (SS) bitumen, which has the higher viscosity. Analysis indicated that these carboxylic acid compounds were found to reach a maximum level in the resin fraction. They suggested that these compounds seem to lead to more hydrogen-bonding interaction between aromatics and resins with the suspended asphaltenes in the composite bitumen. With respect to Nellensteyn's model these interactions result in higher viscosity for the bitumen with higher carboxylic acid content. Nellensteyn's model proposes bitumen to be a colloidal system in which the asphaltenes are suspended in viscous oils where the suspension is considered to be stabilized by polar molecules that belong to the aromatics and resins group [11]. Other research [12] about the influence of carboxylic acid content on bitumen viscosity observed that the stabilization of the asphaltenes suspension can also be carried out by other functional groups, such as aldehydes, ketones, amines, amides and sulfoxides.

One hypothesis of our study was if acid groups are primarily responsible for hydrogen bonding to cause aggregation and high viscosity, rather than acid-base interactions, then base treatment should improve viscosity more than acid treatment. However, according to the results obtained the viscosities were comparable using the strong base (LiOH) and the hydrochloric acid. Furthermore, the viscosity was higher for the weak base (ethanolamine) than that of strong acid (HCl). It is speculated that to disrupt acid-base interactions is more important than hydrogen-bonding interaction in the viscosity reduction of bitumen. Therefore, intermolecular acid-base interactions are one of the main interactions that affect bitumen viscosity

As referred in Chapter 2, a model describes the dispersion of the heteroatomic functions in the bitumen in terms of their interactions on a molecular level. It characterizes bitumen as a homogenous mixture of neutral and amphoteric molecules, where adjacent acidic and basic functional groups interact to form a viscoelastic network within the neutral fraction [13]. The description of this model is relevant in our research because acid-base interactions in the bitumen structure were affected by the influence of acid and base treatment.

A study of molecular interactions involving coal-derived aphaltenes [14] that employed IR spectroscopy with amine mixtures indicated that hydrogen bonding involving phenolic-OH and nitrogen bases **(O-H- - - N)** produce to proton-transfer complexes **(O^{-}---$^{+}$H-N)** , which partially accounted for the high viscosity of the coal liquids. Our study for the treated bitumen with ethanolamine, new absorptions corresponding to amine functional groups were not detected in the region 3500-2800 cm^{-1}. It is important to point out that the concentration of base was very low with a value of 0.003 N (aqueous solution of ethanolamine).

A study by Gray, et al. [15] postulated the existence of a supramolecular assembly of molecules in a asphaltene aggregate where acid-base interactions and hydrogen bonding are ilustrated in blue color (Figure 5-8). This study indicated that acid-base interactions is an important aspect of this description.

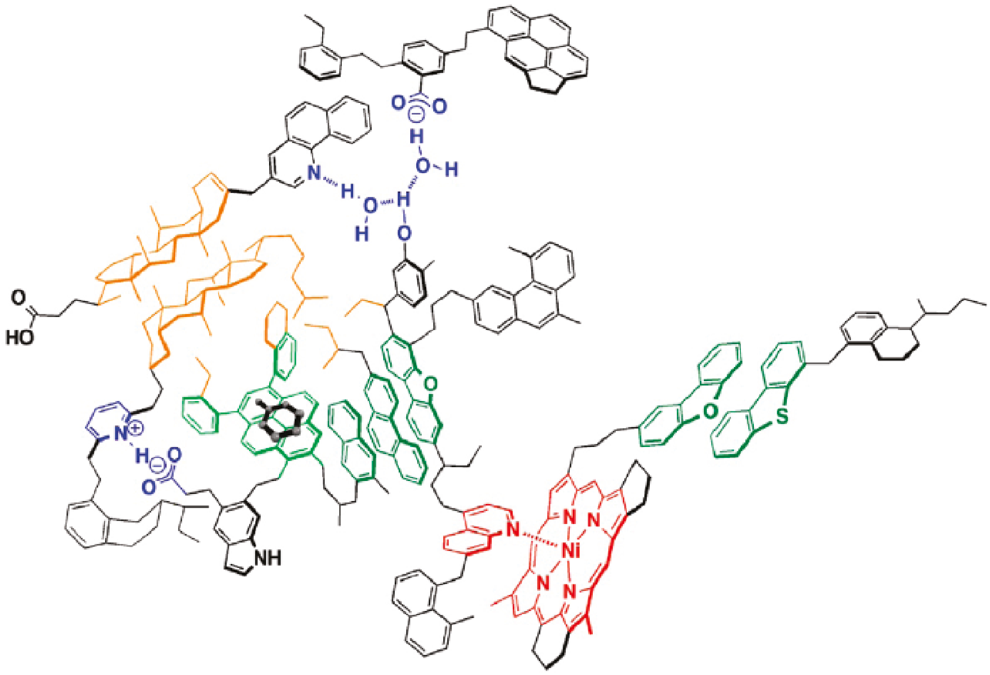


Figure 5-8: Acid-base interactions and hydrogen bonding ilustrated in blue color of a supramolecular assembly of molecules in a asphaltene aggregate [15].

5.4.3 Effect of base treatment on physical properties of bitumen

The impact of base treatment with LiOH and ethanolamine, and water treatment was to reduce the density of feed material (Reference), so this physical property of bitumen was improved as was viscosity (Table 5-13). The treated bitumen with ethanolamine has a lower calculated density at 40˚C and 60˚C with values of 997 kg/m^3 and 986 kg/m^3, respectively than bitumen after base treatment with LiOH with calculated densities of 1007 Kg/m^3 at 40˚C and 995 Kg/m^3 at 60˚C. According to the results of ^{1}H-NMR analysis, the aliphatic hydrogen percentage of treated bitumen with ethanolamine is slightly higher than after treatment with the strong base, with values of 93.5% and 91.0%, respectively, so it is reasonable that the density of weak base is lower due to hydrogen content increases [16]. Nevetheless, treated bitumen with LiOH did not show a meaningful change in the aliphatic/aromatic hydrogen content of the bitumen due to treatment when is compared to raw bitumen (Table 5-5). It suggests that the density change does not seem to originate from an increase in aliphatic hydrogen content. It suggests that base treatment could disrupt chemical and physical interactions in the bitumen that produces a reduction of density.

As can be observed in Table 5-14, the bitumen after base treatment with ethanolamine presented the lowest RI at the temperatures of 40˚C and 60˚C (1.5728 and 1.5660, respectively). The lower refractive index could be related to an increased aliphatic content, as is suggested by the higher aliphatic hydrogen content (Table 5-5). On the other hand, the RI of treated bitumen with LiOH was slightly higher than that of the weak base. It suggests a more aromatic character, which is related to the results ^{1}H-NMR analysis, where the aromatic hydrogen content was 8.3% after strong base treatment and 5.4% after ethanolamine treatment. However, the decrease of refractive index is influenced by the residual methylene chloride in the products, where the refractive index of the solvent is 1.4117 at 40°C and 1.4038 at 60°C, which is lower than that of the bitumen.

5.5 Conclusions

The most important conclusions of base treatment with lithium hydroxide and ethanolamine were the following:

a) The emulsion formation propensity was higher after the base treatment than acid treatment because of the reaction between carboxylic acids and the alkaline species that produces surface-active soaps. The yields of treated bitumen products were 91 wt% after base treatment with LiOH and 86 wt% for the treated bitumen with ethanolamine. The remainder of the treated bitumen was trapped in the emulsion phase.

b) The residual methylene chloride in the products is an issue during the work up procedure of base treatment. It was determined that the remaining solvent was 6.4 wt% by FTIR for the treated bitumen irrespective of the base used.

c) The viscosity reduction was higher for the bitumen treated with LiOH than using ethanolamine. Weak and strong acid-base interactions contributed to bitumen viscosity.

d) The extent of viscosity reduction as measured at 40 ˚C after treatment with a strong base (LiOH) was comparable to that after treatment with a strong acid (HCl) with the same concentration (0.003 N). Calculated viscosity values corrected for the residual methylene chloride of 12.6 Pa.s and 15.0 Pa.s, were found for acid and base treatment respectively.

e) Base treatment was complimentary to acid treatment. Stronger acid-base interactions in the bitumen could be affected similarly, irrespective of whether LiOH or HCl. However, base treatment was more prone to emulsion formation than acid treatment.

f) Disrupting acid-base interactions was found to be more important than disrupting hydrogen-bonding interactions in the viscosity reduction of bitumen.

g) The effect of base treatment was to reduce the density of bitumen, so also this physical property of bitumen was improved.

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CHAPTER 6 – CONCLUSIONS AND RECOMMENDATIONS

6.1 Introduction

One of the important interactions that could affect bitumen viscosity is intermolecular acid-base interactions, where several chemical compound classes with acidic and basic functional groups are present in the bitumen. There are different models that describe the structure of bitumen as a colloidal system [1]. These models describe the dispersion as result of the heteroatomic functions in the bitumen and their interactions on a molecular level. These models further characterize bitumen as a homogenous mixture of neutral and amphoteric molecules, where adjacent acidic and basic functional groups interact to form a viscoelastic network within the neutral fraction [2].

The project was focused to specifically investigate the response of bitumen viscosity to the influence of acid and base treatment at near ambient conditions. In this chapter the main conclusions that have been obtained in the development of this project are presented, as well as the recommendations that arose as a consequence of the work.

Treatment resulted in a complex viscosity response with respect to variables such as heating, concentration, the solvent methylene chloride and the formation of an emulsion. A commonly employed work-up procedure in bitumen research that involved solvent washing and removal of the solvent by evaporation, interfered with the results from acid-base treatment. These aspects had to be explicitly addressed.

6.2 Major conclusions

a) It was postulated that the treatment of bitumen with low acid concentrations in the range of 0.0003-0.3 M HCl and low base concentrations (0.003 N LiOH and 0.003 N ethanoalmine) may disrupt some chemical interactions in the bitumen to affect physical properties such as the viscosity and the density. The work demonstrated that this was indeed the case. Both acid and base treatment was capable of decreasing viscosity, but only a minor decrease in density was observed.

b) For the acid treatment, the drastic change in viscosity after heating in air atmosphere in order to remove residual solvent can be attributed to the oxidation of bitumen, which leads to an increase in the viscosity and an increase in the asphaltenes content. Due to the effect of heating and oxidation, subsequent sample workup after acid treatment and base treatment was carried out without heating in contact with air.

c) Residual solvent (methylene chloride, with a normal boiling point temperature of 40°C) was found in bitumen samples after acid and base treatment in spite of 17 h evaporation time in a rotary evaporator under vacuum (55 kPa absolute) at 45˚C. It was determined analytically by FTIR analysis that the remaining solvent in the bitumen was between 2.3 and 6.4 wt%. For some samples, even under constant conditions, the rate of evaporation of solvent was not reproducible. So, a small amount of residual solvent always remained trapped and had a significant impact on the viscosity reduction of the bitumen. The measured viscosity values had to be corrected for the amount of residual solvent in each sample.

d) The blank experiments (water treatment) indicated that only to wash the bitumen with water affected the viscosity. Viscosity decreased significantly (19.0 Pa.s at 40˚C corrected for the residual methylene chloride) when compared to the viscosity of raw bitumen (97.5 Pa.s at 40˚C). It may be due to water acting as an "extractant" that removed the salt, water, and solids from the bitumen, similar to the desalting operation in a refinery. In addition, acid-base interactions may be relevant even at neutral pH.

e) The extent of viscosity reduction as measured at 40 ˚C after treatment with a strong base (LiOH) was comparable to that after treatment with a strong acid (HCl) with the same concentration (0.003 N). Calculated viscosity values corrected for the residual methylene chloride of 12.6 Pa.s and 15.0 Pa.s, were found for acid and base treatment respectively.

f) Base treatment was complimentary to acid treatment. Stronger acid-base interactions in the bitumen could be affected similarly, irrespective of whether LiOH or HCl was employed. However, base treatment was more prone to emulsion formation than acid treatment.

g) Disrupting acid-base interactions was found to be more important than disrupting hydrogen-bonding interactions in the viscosity reduction of bitumen. This inference is based on the near equal decrease in viscosity after acid or base treatment, whereas only the base treatment decreased acidic hydrogen that could have been involved in hydrogen bonding.

h) Although weak and strong acid-base interactions contributed to bitumen viscosity, the extent of viscosity reduction was higher for bitumen treated with LiOH (strong base) than using ethanolamine (weak base).

i) The change in viscosity could not be attributed to the asphaltenes content. In spite of an increase in the asphaltenes content after acid treatment without heating, it was not significantly different from that of the raw bitumen (better than 95 % statistical confidence). Also, the asphaltenes content on a bitumen feed basis of blank samples (water treatment only) and treated bitumen with LiOH and ethanolamine were not statistically meaningfully different. Nevertheless, the viscosities were meaningfully lower for the products after treatment when compared to that of raw bitumen.

j) The change of bitumen morphology observed by Atomic Force Microscopy (AFM) analysis after acid treatment without heating showed the disaggregation of clustered asphaltenes and other aggregating species, which correlated with the viscosity reduction.

k) Emulsion formation was an important issue to investigate. It was determined that the asphaltenes content of the emulsion was 52 wt % based on the oil present in the emulsion after treatment with 0.003 M HCl. The information on the nature of the functional groups of the emulsion suggested that asphaltenes were not the only material that stabilized the emulsion. The emulsion was also stabilized by inorganic solids particles (such as clay minerals). The mineral matter content of the emulsion was 4.3 ± 1.6 wt % and 27.3 ± 0.3 wt% for the asphaltenes precipitated from the emulsion.

l) The effect of the emulsion was to increase viscosity due to the presence of emulsified water droplets in the treated bitumen. The lowest viscosity corrected for the residual methylene chloride at 40˚C was 12.6 Pa.s, which was obtained for the treated bitumen (acid washed with 0.003 M HCl) that was separated from the emulsion.

m) The longer term stability of the emulsion was evaluated by keeping two emulsified samples for 5 months (0.003 M HCl and 0.0003 M HCl) before being re-analyzed. Both samples of treated bitumen with emulsion after 5 months did not exhibit good storage stability, because the viscosity increased significantly with respect to the fresh product; for example, treated bitumen (acid washed with 0.003 M HCl) had a calculated value of 119.8 Pa.s at 40 ˚C after 5 months.

n) The viscosity versus measurement temperature relationship deviated slightly due to a curvature in the data and not due to random scatter from the typical linear ln[ln(μ)] versus ln(T) response for treated bitumen (0.003 M HCl and 0.0003 M HCl) with emulsion after 5 months. Such deviation is normally observed when there is a second phase present, such as the aqueous phase.

o) The emulsion formation propensity was higher after the base treatment than acid treatment because of the reaction between carboxylic acids and the alkaline species that produces surface-active soaps. The yields of treated bitumen products separated from the emulsion were 96 wt% after acid treatment with HCl, 91 wt% after base treatment with LiOH and 86 wt% for the treated bitumen with ethanolamine. The remainder of the treated bitumen was trapped in the emulsion phase.

6.3 Recommendations

- Perform the Atomic Force Microscopy Analysis (AFM) for the products after water treatment and base treatment to confirm the disaggregation of clustered of asphaltenes.

- Conduct the separation of bitumen into strong and weak acids and bases, and neutral components through ion exchange chromatography (IEC).

- Establish a comparison between low temperature thermal conversion and chemical treatments (acid and base) in the response of bitumen viscosity.

- Develop a workup procedure for the acid and base treatment that does not include organic solvent washing and removal of the solvent to avoid trapped of solvent in the bitumen.

6.4 Presentations and Publications

The list of presentations and publications are the followings:

- Gonzalez, V.; De Klerk, A.; Yang, S.; Prasad, V. *Co-Feeding Propane/Butane during Low Temperature Thermal Conversion of Cold Lake Bitumen*. Poster session presented at: 3rd Science Forum Helmholtz – Alberta Initiative. University of Alberta, Edmonton, Canada, September 19, 2013.

- Gonzalez, V.; De Klerk, A.; Zachariah, A.; Yang, S. *Influence of the acid treatment on Cold Lake bitumen viscosity*. Poster session presented at: Oil Sands Conference. University of Alberta, Edmonton, Canada, 28-30 April, 2014.

- Gonzalez, V.; De Klerk, A.; Yang, S.; Prasad, V. Influence of acid chemistry on bitumen viscosity. *Prepr. Pap.-Am. Chem. Soc., Div. Energy Fuels* **2015**, *60* (1), 9-12.

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2) Masson, J.F. Brief Review of the Chemistry of Polyphosphoric Acid (PPA) and Bitumen. *Energy Fuels*. **2008**, *22*, 2637–2640.

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- ASTM D4124 – 09: Standard Test Method for Separation of Asphalt into Four Fractions; ASTM International: West Conshohocken, United States, 2009.
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APPENDICES

Appendix 1: Standard Test Method for Separation of Asphalt into Four Fractions (ASTM D4124-09)

The summary of method ASTM D4124-09 is the following: the bitumen is first separated into alkane-insoluble asphaltenes and alkane-soluble maltenes. This is done by blending 2 g of bitumen in 200 mL of iso-octane (2,2,4-trimethylpentane). The ratio is equivalent to 100 mL of solvent per 1 g of sample. The mixture is refluxed with stirring near the boiling point of iso-octane for a period of 2 to 3 h. The asphalthenes are separated from the maltene solution by suction filtration and then the iso-octane is distilled off of the maltene fraction using a rotary evaporator [1].

As second stage, the maltenes in solution; typically 1 g in 10 mL of *n*-heptane, are then adsorbed onto calcined CG-20 alumina packed in a glass chromatographic column. By pumping an eluotropic series of elution solvents upwards through the chromatographic column, the maltenes are additional fractionated into saturate, naphthene aromatic, and resin fractions. Saturates are first eluted using 150 mL of *n*-heptane and 33 mL of toluene. Then, the entire introduction of toluene (100 mL), followed by the elution of 75 mL of a blend 50:50 toluene:methanol, are used to separate the naphthene aromatics fraction. After that, trichloroethylene (150 mL) is used to separate the resins. Finally, eluted fractions are recovered by solvent removal prior to final weighing [1].

References

1) ASTM D4124 – 09: Standard Test Method for Separation of Asphalt into Four Fractions;
2) ASTM International: West Conshohocken, United States, 2009.

Appendix 2: Procedure of separation of bitumen into strong and weak acids and bases, and neutral components through ion exchange chromatography (IEC)

This procedure is the following: the bitumen (16 g) is dissolved in 64 g of a blend of benzene, tetrahydrofuran and ethanol 45/45/10 vol% respectively. This solution is passed through an anionic ion-exchange resin (AG MP-1). This resin has quaternary ammonium functional groups linked to a styrene divinylbenzene copolymer lattice. The second ion-exchange resin is a cationic (AG MP-50) which is attached in series with the first one. The cationic resin is composed of sulfonic acid functional groups connected to a styrene divinylbenzene copolymer lattice. The elution for the acids is performed with a blend of benzene and formic acid, whereas the bases are eluated with a blend of benzene and 1-propyl amine. (Figure A2-1) [1].

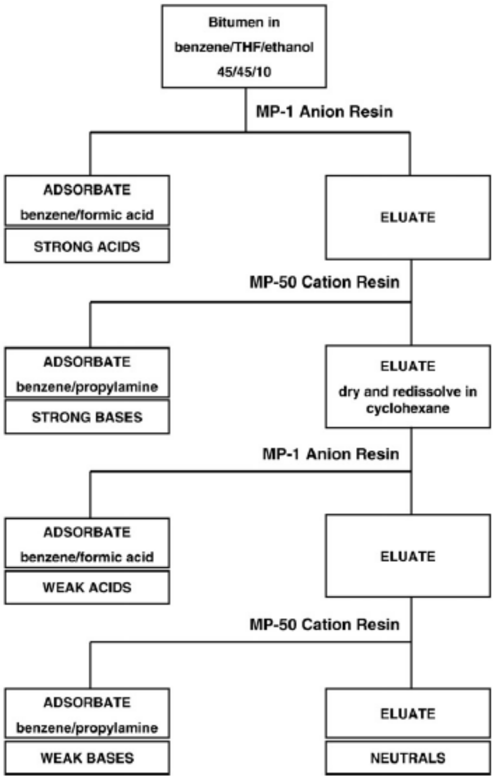

Figure A2-1: IEC fractions corresponding to strong and weak acids and bases and neutrals [1].

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1) Lesueur, D. The colloidal structure of bitumen: Consequences on the rheology and on the mechanisms of bitumen modification. *Adv. Colloid Interface Sci.* **2009**, *145*, 42-82.

Appendix 3: Procedure of separation of bitumen into acids, bases, neutral and amphoterics components through ion exchange chromatography (IEC)

In this methodology, the bitumen is dissolved in cyclohexane where amphotherics and bases are adsorbed in the cation resin. After that, they are separated in the anion resin (Figure A3-1) [1].

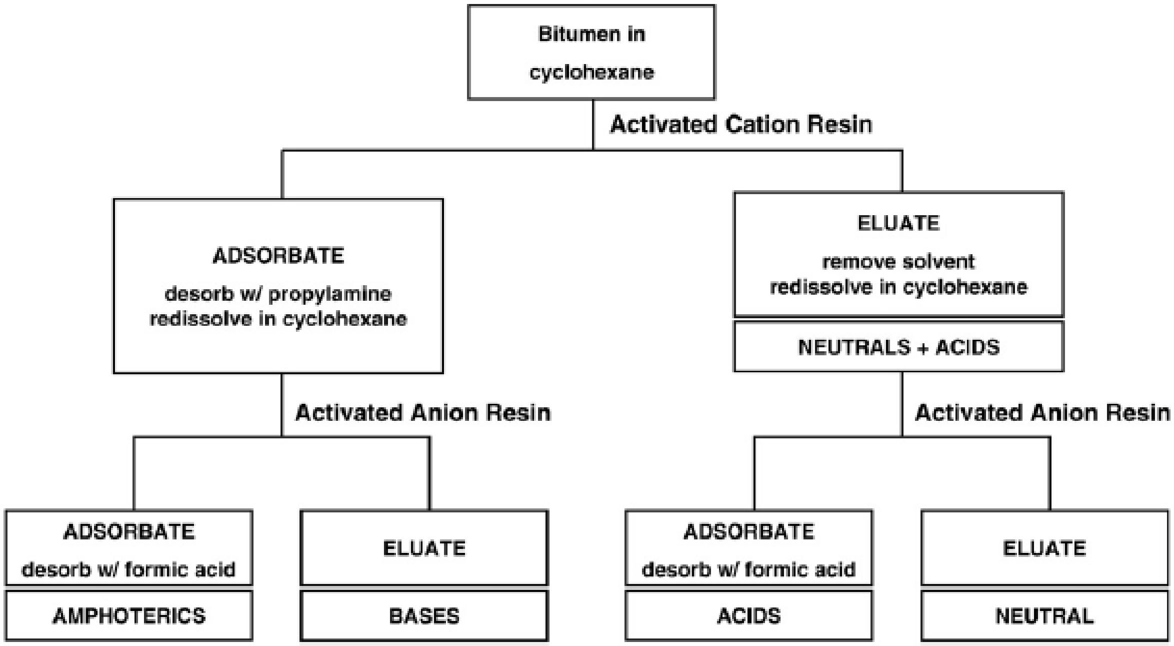

Figure A3-1: IEC fractions corresponding acids, bases, amphoterics and neutrals [1].

References

1) Lesueur, D. The colloidal structure of bitumen: Consequences on the rheology and on the mechanisms of bitumen modification. *Adv. Colloid Interface Sci.* **2009**, *145*, 42-82.

Appendix 4: The residual methylene chloride in the bitumen by mass balance

For example, for the Blank-RB-1 (Table 4-3):
g residual CH_2Cl_2 = g bitumen after rotavap – g initial bitumen
g residual CH_2Cl_2 = 23.793 g - 20.008 g = 3.785 g
Residual CH_2Cl_2 (wt%) = (g residual CH_2Cl_2 / g bitumen after rotavap) x 100
Residual CH_2Cl_2 (wt%) = (3.785 g / 23.793 g) x 100
Residual CH_2Cl_2 (wt%) = 15.9 %

For example, for the Blank-RB-2 (Table 4-3):
g residual CH_2Cl_2 = 22.496 g - 20.116 g = 2.380 g
Residual CH_2Cl_2 (wt%) = (2.380 g / 22.496 g) x 100
Residual CH_2Cl_2 (wt%) = 10.6 %

For example, for the Blank-RB-10 (Table 4-3):
g residual CH_2Cl_2 = 21.217 g - 20.092 g = 1.125 g
Residual CH_2Cl_2 (wt%) = (1.125 g / 21.217 g) x 100
Residual CH_2Cl_2 (wt%) = 5.3 %

For example, for the Blank-RB-16 (Table 4-3):
g residual CH_2Cl_2 = 20.580 g - 20.092 g = 0.488 g
Residual CH_2Cl_2 (wt%) = (0.488 g/ 20.580 g) x 100
Residual CH_2Cl_2 (wt%) = 2.4 %

For example, for the Blank-RB-17 (Table 4-3):
g residual CH_2Cl_2 = 20.589 g - 20.082 g = 0.507 g
Residual CH_2Cl_2 (wt%) = (0.507 g / 20.589 g) x 100
Residual CH_2Cl_2 (wt%) = 2.5 %

Appendix 5: Calculated methylene chloride by FTIR

It was determined (quantitatively) the amount of residual methylene chloride by FTIR using an internal standard calibration curve (Figure A5-1).

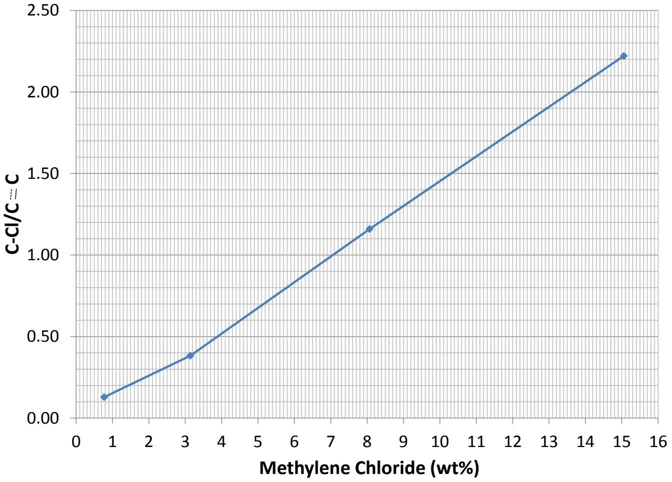

Figure A5-1: Internal standard calibration curve.

The height of absorptions around 1600 cm^{-1} of skeletal vibrations, involving carbon to carbon stretching within the aromatic ring and around 1265 cm^{-1} related to CH_2Cl_2 wagging in the methylene chloride, were determined for each sample. For example, Figure A5-2 shows these absorptions for the Blank-RB-17.

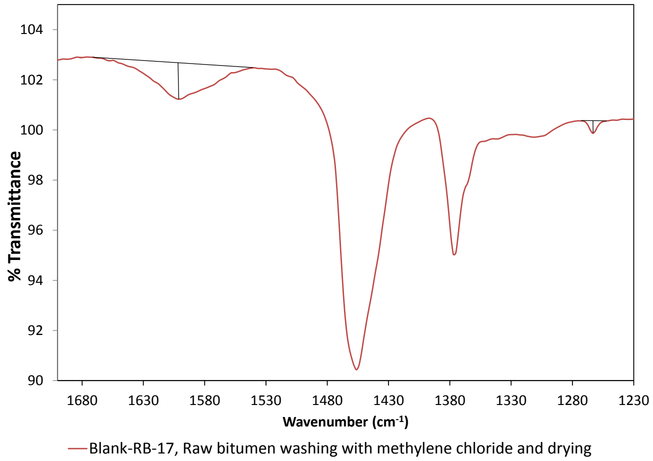

Figure A5-2: Region of 1700-1230 cm^{-1} for FTIR spectrum of Blank-RB-17.

Table A5-1 shows the height of both absorptions for all samples studied

Table A5-1: Height of absorptions for FTIR spectrums.

Samples	Height of C-Cl absorption (%)	Height of C$\overset{\cdots}{-}$C absorption (%)	C-Cl/ C$\overset{\cdots}{-}$C Ratio
B-HCl-WE	1.046	1.371	0.8
Blank-WT-WE	0.793	1.349	0.6
Blank-RB-17	0.396	1.436	0.3
B-HCl-E-51	0.545	1.077	0.5
Blank-RB-1	2.714	1.190	2.3
Blank-RB-1-O, 64 h	0.571	1.327	0.4

With values of C=O/ C$\overset{\cdots}{-}$C ratio were determined the amount of residual methylene chloride by using the internal standard calibration curve (Figure A5-1).

Tables 4-3 and 4-4 (Chapter 4) show the calculated residual methylene chloride using FTIR analysis.

Appendix 6: Calculated methylene chloride by ^{1}H-NMR

The mass of bitumen per mass of H in bitumen from the elemental analysis of bitumen is the following:

100 g bitumen ——— 10 g H

The mass of methylene chloride per mass of H in methylene chloride based on its molecular formula is the following:

84.9 g CH_2Cl_2 ——— 2 g H

$$\frac{\dfrac{H_{\text{bitumen}}}{W_{\text{bitumen}}} = \dfrac{10}{100}}{\dfrac{H_{CH_2Cl_2}}{W_{CH_2Cl_2}} = \dfrac{2}{84.9}}$$

$(H_{\text{bitumen}} \text{ x } W_{CH_2Cl_2})/(H_{CH_2Cl_2} \text{ x } W_{\text{bitumen}}) = (10 \text{ x } 84.9)/(2 \text{ x } 100)$

$H_{\text{bitumen}} / H_{CH_2Cl_2} = 849 W_{\text{bitumen}} / 200 W_{CH_2Cl_2}$

Since NMR gave the H mass ratio. It can be calculated the bitumen to methylene chloride mass ratio. Example with the sample Blank-WT-WE:

The results of ^{1}H-NMR (Table 4-4, Chapter 4) for this sample are as follows:

$H_{\text{bitumen}} = 91.1 + 8.2 = 99.3$

$H_{CH_2Cl_2} = 0.7$

Therefore;

$99.3/0.7 = 4.245 \text{ x } (W_{\text{bitumen}} / W_{CH_2Cl_2})$

Rearranging;

$W_{CH_2Cl_2} / W_{\text{bitumen}} = 4.245/141.86$

$W_{CH_2Cl_2} / W_{\text{bitumen}} = 0.0299$

So, we have two equations:

$$\begin{cases} W_{CH_2Cl_2} = 0.0299\, W_{\text{bitumen}} \\ W_{CH_2Cl_2} + W_{\text{bitumen}} = 1 \end{cases}$$

$0.0299\ W_{bitumen} + W_{bitumen} = 1$

$1.0299\ W_{bitumen} = 1$

$W_{bitumen} = 0.97$

$W_{CH_2Cl_2} = 1\text{-}0.97 = 0.03$

$\%\ CH_2Cl_2 = (W_{CH2Cl2} / (W_{bitumen} + W_{CH_2Cl_2}))\ x\ 100$

$\%\ CH_2Cl_2 = (0.03/(0.97 + 0.03))\ x\ 100$

$\%\ CH_2Cl_2 = 3$ wt%

Appendix 7: Calculation of asphaltenes and bitumen in emulsion for the acid treatment

a) Asphaltenes in emulsion

Asphaltenes content (wt%) = (g asphaltenes in emulsion / g O/W emulsion) x 100
based on total emulsion

Asphaltenes content (wt%) = (0.04250g/ 1.031g) x 100
based on total emulsion

Asphaltenes content (wt%) = 4.1 %
based on total emulsion

g asphaltenes in emulsion = g emulsion total · $x_{\text{asphaltenes in emulsion}}$

g asphaltenes in emulsion = 11.51g x 0.041

g asphaltenes in emulsion = 0.4719 g

b) Bitumen in emulsion.

Initial weight of bitumen = 20.056 g

Weight of bitumen after acid treatment (B-HCl-WE) = 20.336 g

5.8 wt% CH_2Cl_2 in bitumen weight after treatment

g bitumen in emulsion = 20.056g – (1-0.058) 20.336g

g bitumen in emulsion = 0.8995 g

Appendix 8: Calculation of asphaltenes content for the acid treatment

Asphaltenes content (wt%) = (g asphaltenes in emulsion / g oil emulsion) x 100
based oil in the emulsion

Asphaltenes content (wt%) = (0.4719 g / 0.8995 g) x 100 = 52 wt%
based oil in the emulsion

5.8 wt% CH_2Cl_2 in bitumen weight after treatment

Asphaltenes content (wt%) = ((g precipitated asphaltenes) / (g initial bitumen) (1-0.058)) x 100
only treated bitumen basis

Asphaltenes content (wt%) = ((0.176) / (1.052)(1-0.058)) x 100
only treated bitumen basis

Asphaltenes content (wt%) = 17.8 %
only treated bitumen basis

Initial weight of bitumen = 20.056 g

Weight of bitumen after acid treatment (B-HCl-WE) = 20.336 g

Asphaltenes content only treated bitumen basis = 17.8 wt%

g asphaltenes in treated bitumen = 20.336 g x (1-0.058) x 0.178

g asphaltenes in treated bitumen = 3.41 g

But there was 0.4719 g asphaltenes in emulsion

Total asphaltenes = 3.41 g + 0.4719 g

Total asphaltenes = 3.882 g

Asphaltenes content (wt%) = (g total asphaltenes after treatment / g feed bitumen) x 100
in bitumen after treatment
based in feed material

Asphaltenes content (wt%) = (3.882 g/ 20.056 g) x 100
in bitumen after treatment
based in feed material

Asphaltenes content in bitumen after treatment based in feed material (wt%) = 19.4 %

Appendix 9: Calculation of viscosity corrected for the residual methylene chloride

1. First of all, the viscosity of methylene chloride was calculated at 40 ˚C and 60 ˚C.

Low-temperature viscosity correlations usually adopt that $\ln_{\mu}$ is a linear function of reciprocal absolute temperature. Above a reduced temperature of approximately 0.7, this relation is no longer valid [1].

Therefore, reduced temperature (Tr) of methylene chloride was determined:

40 ˚C = 313.15 K

60 ˚C = 333.15 K

Tr = T/Tc

The critical temperature (Tc) of methylene chloride is 510 K [1].

Tr = 333.15/510 = 0.65

Tr = 313.15/510 = 0.61

As reduced temperature is below of 0.7, it is valid assumes low-temperature viscosity correlations. The correlation used was the following [1].

$\ln_{\mu} = A + B/T$

μ = liquid viscosity at T, cP

T = absolute temperature (K)

A of CH_2Cl_2 = -8.061 [1]

B of CH_2Cl_2 = $1.185\text{x}10^3$ [1].

μ of CH_2Cl_2 at 37.51°C (310.66K) = 0.3707 cP

$\ln_{\mu 60°C} / \ln_{\mu 37.51°C} = (A + B/333.15) / (A + B/310.66)$

$\ln_{\mu 60°C} / \ln 0.3707 = (-8.061 + 1.185\text{x}10^3/333.15) / (-8.061 + 1.185\text{x}10^3/310.66)$

$\ln_{\mu 60°C} / -0.992 = -4.504/-4.247$

$\ln_{\mu 60°C} = -1.052$

μ at 60°C = 0.3492 cP

To calculate the viscosity at 40°C was used the same procedure whose value was the following:

μ at 40°C = 0.3682 cP

2. Calculation of viscosity corrected for the residual methylene chloride.

Example for the sample Blank-WT-WE according to the Equation 4-9 (Chapter 4).

1cP = 1 mPa.s

μ_m at 40˚C = 8563.3 cP

Molar mass of CH_2Cl_2 = 84.93 g/mol

Molar mass of Cold Bitumen = 577 g/mol [2]

4.5 wt% CH_2Cl_2 in bitumen weight after treatment

$$\text{moles}_{CH_2Cl_2} = \frac{4.5\ g}{84.93 \frac{g}{mol}} = 5.30x10^{-2}\ \text{moles}$$

$$\text{moles}_{\text{bitumen}} = \frac{95.5\ g}{577 \frac{g}{mol}} = 0.1655\ \text{moles}$$

$$\text{mole fraction}_{CH_2Cl_2} = \frac{5.30x10^{-2}\text{moles}}{0.1655\ \text{moles}\ +5.30x10^{-2}\ \text{moles}} = 0.24$$

According to the Equation 4-9 (Chapter 4)

$$\mu_m = (x_{CH_2Cl_2} \cdot \mu^{1/3}_{CH_2Cl_2} + (1- x_{CH_2Cl_2})\ \mu_b^{1/3})^3$$

$$8563.3 = (0.24(0.3682)^{1/3} + (1-0.24)\ \mu_b^{1/3})^3$$

$$\sqrt[3]{8563.3} = 0.1720 + 0.76\mu_b{}^{1/3}$$

$$\mu_b{}^{1/3} = \frac{-0.1720 + \sqrt[3]{8563.3}}{0.76}$$

$$\mu_b = \left(\frac{-0.1720 + \sqrt[3]{8563.3}}{0.76}\right)^3$$

μ_b = 19019.6 cP = 19.0 Pa.s at 40°C

References

1) Reid, R.C.; Prausnitz, J.M.; Poiling, B.E. The Properties of Gases and Liquids; Fourth Edition; McGraw-Hill Book Company: New York, 1987; pp 471, 439, 442.
2) Mehrotra, A. K.; Eastick, R.R.; Svrcek, W.Y. Viscosity of Cold Lake Bitumen and Its Fractions. *Can. J. Chem. Eng.* **1989**, *67*, 1004-1009.

Appendix 10: Viscosity calculation of 'DilBit'

1. Correlation Eq.4-8 (Chapter 4)

$\mu_m = (x_{CH_2Cl_2} \cdot \mu^{1/3}_{CH_2Cl_2} + (1- x_{CH_2Cl_2})\ \mu_b^{1/3})^3$

Example:

Sample Blank-RB-17

Molar mass of CH_2Cl_2 = 84.93 g/mol

Molar mass of Cold Bitumen = 582 g/mol [1]

2.3 wt% CH_2Cl_2 in bitumen weight after treatment

$\text{moles}_{CH_2Cl_2} = \frac{2.3\ g}{84.93 \frac{g}{mol}} = 2.71 x 10^{-2}\ \text{moles}$

$\text{moles}_{\text{bitumen}} = \frac{97.7\ g}{582 \frac{g}{mol}} = 0.1679\ \text{moles}$

$\text{mole fraction}_{CH_2Cl_2} = \frac{2.71 x 10^{-2} \text{moles}}{2.71 x 10^{-2}\ \text{moles}\ + 0.1679\ \text{moles}} = 0.14$

Viscosity of CH_2Cl_2 ($\mu_{CH_2Cl_2}$) at 60 °C = 0.3492 cP

Viscosity of bitumen (μ_b) at 60 °C = 9600 cP

Viscosity 'DilBit' (μ_m) at 60 °C = ?

$\mu_m = (x_{CH_2Cl_2} \cdot \mu^{1/3}_{CH_2Cl_2} + (1- x_{CH_2Cl_2})\ \mu_b^{1/3})^3$

$\mu_m = (0.14\ (0.3492)^{1/3} + (1- 0.14)\ (9600)^{1/3})^3$

$\mu_m = (9.86 x 10^{-2} + 18.28)^3$

μ_m = 6205.49 cP = 6.2 Pa.s at 60 °C

$$\text{Percent error} = \left(\frac{|\mu\text{experimental} - \mu\text{calculated}|}{\mu\text{experimental}}\right) x100$$

$$\text{Percent error} = \left(\frac{|4.2 - 6.2|}{4.2}\right) x100 = 48\%$$

2. Correlation Eq.4-9 (Chapter 4)

$$\log(\mu_m + 0.8) = \sum_{i=1}^{n} x_i [Mi/Ma]^{0.5} \log(\mu_i + 0.8)$$

Example:

Sample Blank-RB-17

Viscosity 'DilBit' (μ_m) at 60 °C = ?

$\text{mole fraction}_{\text{bitumen}} = \frac{0.1679 \text{ moles}}{2.71 \text{x} 10^{-2} \text{ moles } + 0.1679 \text{ moles}} = 0.86$

Ma = average molar mass, $\sum xiMi$, g/mol

Ma = 0.14 x 84.93 + 0.86 x 582 = 512 g/mol

$\log(\mu_m + 0.8) = 0.14(84.93/512)^{0.5}\log(0.3492 + 0.8) + 0.86(582/512)^{0.5}\log(9600+0.8)$

$\log(\mu_m + 0.8) = 0.14(84.93/512)^{0.5}\log(0.3492 + 0.8) + 0.86(582/512)^{0.5}\log(9600+0.8)$

$\log(\mu_m + 0.8) = 3.44\text{x}10^{-3} + 3.65$

$\log(\mu_m + 0.8) = 3.65344$

$\mu_m + 0.8 = 4502.36$

$\mu_m = 4501.56$ mPa.s = 4.5 Pa.s

$$\text{Percent error} = \left(\frac{|\mu\text{experimental} - \mu\text{calculated}|}{\mu\text{experimental}}\right)\text{x}100$$

$$\text{Percent error} = \left(\frac{|4.2 - 4.5|}{4.2}\right)\text{x}100 = 7\%$$

References

1) Mehrotra, A.K. Development of Mixing Rules for Predicting the Viscosity of Bitumen and Its Fractions Blended with Toluene. *Can. J. Chem. Eng*. **1990**, *68*, 839–848.

Appendix 11: Calculation of density corrected for the residual methylene chloride

Example: Sample B-HCl-WE

5.8 wt% CH_2Cl_2

$V_{CH_2Cl_2}$ = 5.8 g / 1.2884 g/mL = 4.50 mL

$V_{bitumen}$ = 94.2 g / 1.012 g/mL = 93.08 mL

Volume fraction CH_2Cl_2 = 4.50/(4.50+93.08) = 0.046

$\delta_{bitumen}$ corrected for the residual methylene chloride at 40°C = ?

$\delta_{mix} = x_{CH_2Cl_2} \cdot \delta_{CH_2Cl_2} + (1 - x_{CH_2Cl_2})\, \delta_{bitumen}$

$1018 = 0.046 \cdot 1288.40 + (1-0.046)\, \delta_{bitumen(Blank\text{-}RB\text{-}17)}$

$1018 = 59.2664 + 0.954\, \delta_{bitumen(Blank\text{-}RB\text{-}17)}$

$\delta_{bitumen(Blank\text{-}RB\text{-}17)}$ at 40 ˚C = 1005 kg/m^3

$\delta_{bitumen}$ corrected for the residual methylene chloride at 60°C = ?

$1004 = 0.046 \cdot 1249.74 + (1-0.046)\, \delta_{bitumen(Blank\text{-}RB\text{-}17)}$

$1004 = 57.4880 + 0.954\, \delta_{bitumen(Blank\text{-}RB\text{-}17)}$

$\delta_{bitumen(Blank\text{-}RB\text{-}17)}$ at 60 ˚C = 992 kg/m^3

Appendix 12: Yield of acid treatment

$$\text{yield (wt\%)} = \frac{\text{grams obtained}}{\text{initial grams of feed}} \text{ x } 100$$

g bitumen after treatment corrected for the residual solvent = 20.336 (1-0.058) = 19.157 g

$$\text{yield treated bitumen (wt\%)} = \frac{19.157 \text{ g}}{20.056 \text{ g}} \text{ x } 100$$

yield treated bitumen = 96 wt%

Appendix 13: Standardization

$N_{base} = (N_{acid} \times V_{acid})/V_{base}$

$N_{ethanolamine} = (1N \times 10.3\ mL)/10\ mL = 1.03\ N$

Appendix 14: Bitumen in emulsion after base treatment

Initial weight of bitumen = 20.080 g

Weight of bitumen after base treatment (B-ETHA-WE) = 18.526 g

6.4 wt% CH_2Cl_2 in bitumen (B-ETHA-WE) weight after treatment

g bitumen in emulsion = 20.080g – (1-0.064) 18.526g

g bitumen in emulsion = 2.74 g

Appendix 15: Asphaltenes content for the base treatment

Asphaltenes content (wt%) = ((g precipitated asphaltenes) / (g initial bitumen) (1-X_{CH2Cl2})) x 100

only treated bitumen basis

Asphaltenes content (wt%) = ((0.176) / (1.073)(1-0.064)) x 100

only treated bitumen basis

Asphaltenes content (wt%) = 17.5 %

only treated bitumen basis

Initial weight of bitumen = 20.080 g

Weight of bitumen after base treatment (B-ETHA-WE) = 18.526 g

Asphaltenes content only treated bitumen basis = 17.5 wt%

g asphaltenes in treated bitumen = 18.526 g x (1-0.064) x 0.175

g asphaltenes in treated bitumen = 3.035 g

Asphaltenes content (wt%) = (g asphaltenes in treated bitumen / g feed bitumen) x 100

in treated bitumen

based in feed material

Asphaltenes content (wt%) = (3.035 g/ 20.080 g) x 100

in treated bitumen

based in feed material

Asphaltenes content in treated bitumen based in feed material (wt%) = 15.1 %

Appendix 16: Yield of base treatment

The yield of treated bitumen was calculated as follows:

$$\text{yield of treated bitumen (wt\%)} = \frac{\text{grams obtained treated bitumen}}{\text{initial grams of feed}} \text{ x } 100$$

g bitumen after treatment corrected for the residual solvent = 19.573 (1-0.064) = 18.320 g

$$\text{yield treated bitumen (B} - \text{LiOH} - \text{WE) (wt\%)} = \frac{18.320 \text{ g}}{20.043 \text{ g}} \text{ x } 100$$

yield treated bitumen = 91 wt%

The yield of emulsion was calculated with the following equation:

$$\text{yield of emulsion (wt\%)} = \frac{\text{grams obtained emulsion}}{\text{initial grams of basic aqueous solution}} \text{ x } 100$$

$$\text{yield emulsion (B} - \text{LiOH} - \text{WE) (wt\%)} = \frac{115.292 \text{ g}}{100.064 \text{ g}} \text{ x } 100$$

yield of emulsion (B-LiOH-WE) = 115 wt%