Low Temperature Pyrolysis and its Application in Bitumen Processing

by

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Abstract

Observations in literature date back to 1926 to suggest that bitumen should not be treated like a residuum but more like a young crude oil. This is because of its high reactivity at low temperatures. Taking these observations into consideration, lower temperatures (400 °C and lower) were used to improve pyrolysis product quality (particularly liquid viscosity). A major problem in visbreaking is the formation of coke. The effect of specific solvent properties on coke suppression during mild pyrolysis was investigated. It was noticed that coke suppression was based on the overall availability of transferable hydrogen and methyl-groups present in the system, not just donor hydrogen by solvents. In light of these results it was suggested to co-feed light hydrocarbons to help in coke suppression and improve liquid yields. As an extension of the coke suppression studies, the influence of reaction time was investigated. Various regimes were seen when neat bitumen was pyrolysed that affected product quality. A complex relationship was observed between bitumen viscosity and the asphaltene fraction with at least one local maxima and one local minimum being observed. Two orders of magnitude decrease in viscosity was seen when bitumen was heated for 30 minutes at 400 °C. This was not accompanied by a change in the asphaltenes content. Based on this, it was argued that asphaltenes fraction could donate its hydrogen and methyl groups, and, in a solvent deasphalting-visbreaking sequence, the most meaningful difference in the product quality is observed when the reaction time given was equal to the induction period of coke formation of the feed.

Keywords: Thermal cracking, H-donor, coke suppression, viscosity.

Preface

(Mandatory due to collaborative work)

Chapter-3 in this thesis has been published as "Zachariah, A.; Wang, L.; Yang, S.; Prasad, V.; De Klerk, A. Suppression of coke formation during bitumen pyrolysis. *Energy Fuels* **2013,** *27,* 3061-3070." A colleague of our research group Lin Wang was responsible for collecting semi-batch reactor data **Figure 3-5** and **Table 3-5** specifically. I was responsible for all other data collection and manuscript composition. Dr. Arno de Klerk was the supervisory author and was involved with concept formulation and manuscript composition.

Acknowledgements

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Chapter - 1 Introduction

1.1 Background

Oil sands are a natural mixture of sand, clay, water and heavy oil known as bitumen. The term bitumen is used because of its similar appearance and odor to tar. Natural deposits of bitumen have been reported in several countries but Canada in particular has significant reserves of oil sands bitumen. Alberta specifically has an estimated resource of 2.5 trillion barrels of bitumen.[1] Because of the large quantity it is a major energy resource and long term research has been initiated to extract this heavy oil.

There are several challenges when one deals with bitumen because of its high viscosity, molecular weight and its tendency to coke. A major issue is low fluidity causing difficulty in transportation. By primary upgrading, bitumen fluidity is improved. But be it mining, extraction, upgrading or transportation, the challenge in bitumen chemistry is in understanding the properties of bitumen (both chemical and physical) and its reactivity.[2] Thermal conversion, probably the oldest of all refining processes, plays an important role in the oil sands industry. Whatever the upgrading strategy, it is impossible to make significant advances without thermal conversion.

Industry today operates on the basis of increasing rate to reduce cost of production. This of course is under the assumption that the value of carbon is low and rejection of carbon would be the best economic option. When carbon rejection takes place by delayed coking for example, the heteroatoms and heaviest molecules are rejected as coke thereby resulting in a much lighter sweeter product. There are options of hydrogen addition that reduces carbon rejection but this is expensive. As carbon becomes more valuable and as environmental awareness increases, retention of carbon is desired. Having said this one needs to keep in mind the economics involved as well. This work discusses how low

temperature pyrolysis can be used to suppress carbon formation while improving the fluidity of bitumen.

There have been observations where short duration of subjection to low temperatures made bitumen a much lighter and more fluid crude with A.P.I gravities of about 16 to 22 (958 to 920 kg·m^{-3}) without significant carbon (coke) formation. Additionally there was no reported degradation of the asphaltenes.[3] Asphaltenes are the "highest molecular weight, most aromatic fraction"[4] present in the bitumen matrix and are believed to be coke precursors. If there was a significant viscosity reduction without much carbon formation and without degradation to the heaviest molecules in the matrix, mild temperatures might have played a role in controlling selectivity during pyrolysis. Literature attributes this to differences in apparent activation energy for the production of lighter and heavier molecules.[5] An observation reported by Ball[3] included no co-gas production. Light gases have high hydrogen: carbon (H: C) ratios and consequently the need to produce coke to balance the H: C ratio for the feed and products will be more if more gases are produced.

Because of 1) the possibility of increased liquid selectivity thus higher liquid yields, 2) reduced coke make, 3) reduced co-gas production and 4) the fact that there is still a knowledge gap about oil sands bitumen pyrolysis in this temperature regime, we decided to choose low temperatures (400 °C and lower) as the temperature regime in our pyrolysis studies.

One of the key anticipated advantages of low temperature pyrolysis is the suppression of coking. The typical minimum industrial operating temperatures are around 430-460 °C. Having said this, even at low temperatures prolonged pyrolysis leads to coking.[6] This is because of hydrogen disproportionation and radical addition reactions. Explained by an atom balance the lighter material gets more hydrogen rich during pyrolysis and the heavier molecules get more and more hydrogen deficient and ultimately form coke. In order to compensate for the lack of hydrogen, hydrogen must be added to the system in some form. This was not overlooked by researchers and in both petroleum upgrading and direct coal

liquefaction solvents were used as reaction moderators. [6] Visbreaking was combined with donor solvents as a method of hydrogen generation to enable increased suppression of coke.[7][8]

This work kept in mind that carbon is valuable and that liquid yields with good quality is desirable. The goal of this work was not just to increase the production of lighter liquids but also to increase the value of products.

1.2 Objective

The primary objective was to understand the pyrolysis behavior of Cold Lake bitumen at 400 °C. This work specifically looked at coke and liquid yields and the quality of pyrolysis liquids were examined. Additionally the effect of specific solvent properties on coke yield, liquid yield and gas make was investigated.

1.3 Scope of work

Before any experimental investigations a literature review was conducted (Chapter-2). The literature review helped in understanding the characteristics of the feed and the mechanism by which thermal cracking takes place. A review on current process technologies used in industry (specifically visbreaking) was done. The temperature regime investigated in our studies (400 °C) was lower than the typical visbreaking temperatures (430 °C to 460 °C) but has direct application to visbreaking.

As part of the experimental investigations, three major questions were addressed:

A) The first study (Chapter-3) of this thesis investigated the effect of solvents on coke make at 60 mins and 400 °C using a batch reactor system. Coke was defined as the fraction of solids that remained on a 0.22 μm filter paper when extracted with methylene chloride. This was done to compare liquid and coke yields at this temperature versus yields obtained from literature. Also, since literature[6][7][8] described solvents act as reaction moderators, the:

a) Solvent concentration on coke suppression was investigated. b) Individual contribution of different solvent properties on coke suppression was investigated.

As part of the study, comparison of yields from batch and semi batch reactors was performed. Results obtained showed that the notion of over cracking of lighter liquids to gas usually held were more complicated. The semi batch reactor studies were performed by a colleague of our research group. Based on these results a new hypothesis was formulated, namely that hydrogen rich gases like methane to butane can potentially act as methyl radical donors, participate in the reaction mechanism and cause coke suppression.

B) In Chapter-4 the sequence of solvent deasphalting (SDA) and visbreaking was investigated. This was investigated because of the following reasons. a) Wang et al.[9] found that the inverse relationship between temperature and time for viscosity reduction by visbreaking did not hold true at lower temperature pyrolysis of bitumen and b) Not only did the presence of a solvent, suppress coking but also, the overall availability of transferable hydrogen and methyl-groups, suppressed coking also. It was hence argued that if the asphaltenes fraction from bitumen possesses hydrogen and methyl groups that can be donated; there might be benefit in harvesting this hydrogen-rich material before rejecting the asphaltenes by solvent deasphalting (SDA).

We did not see a significant difference in product quality when the sequence was varied. It was argued that this was due to insufficient time to cause a meaningful change by hydrogen transfer. This led to questioning the role of reaction time in bitumen pyrolysis both in Chapter-3 and Chapter-4. Wiehe[4] described an induction period to coke formation. Was the observed coke suppression just an extension of the induction period? Were we just delaying the inevitable or was there actual coke suppression?

C) In Chapter-5, a detailed study of batch reactor bitumen pyrolysis with time was done to understand the effect of reaction time on bitumen properties. Different

regimes were observed in bitumen pyrolysis that changed properties like viscosity, asphaltene content and the micro carbon residue (MCR). The viscosity trend with the asphaltene content was complex. Surprisingly, after a constant decrease in the viscosity with pyrolysis time there was an increase. This was also observed by Wang et al.[9] during analysis of viscosity after thermal treatment at different temperatures. Conversion was defined in terms of the viscosity change when Cold Lake bitumen was subjected to a specific time and temperature. After this study it was clear that in the SDA-Visbreaking study (Chapter-4) sufficient time was indeed the reason as to why there was no difference in liquid quality. The effect of *n*-butane addition on the induction period and product quality was also investigated.

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Chapter - 2 Literature Review

2.1 Introduction

As the world moves towards increasing dependence on heavier crude, nonconventional feedstocks such as heavy oil and bitumen are being used meet current demands. The world heavy oil and bitumen resources which are about 7 trillion barrels of oil exceeds the resources of conventional oils and is expected to become the principal source of crude oils in the early decades of the 21st century. Alberta, occupies a prominent position in the world bitumen resources and because of this, there are lots of current studies on how to upgrade bitumen.[1]

Heavy crudes are often based on their API gravity which are in the range of less than 10 while those of conventional oils have API gravities higher than 20 (933 kg·m^{-3}).[2] Heavy crudes also contain significant quantities of sulphur, nitrogen and metals that makes processing difficult. Oil sands derived bitumen comprises of tens of thousands of different molecules with broad ranges of molar masses.[3] It would therefore be useful in the design and operation of process equipment if one knows the chemical composition of the feedstock. Characterization is not possible on a molecular basis so bitumen has been characterized by fractions to make the understanding a little easier.

2.2 Bitumen Characterization

Most methods of bitumen characterization have been developed based on solubility and adsorption. The most common method employed for separation of heavy oil into different fractions is saturates, aromatics, resins and asphaltenes (SARA) type of classification.

In this method of characterization bitumen is first separated into asphaltenes and maltenes using *n*–pentane or *n*-heptane. Maltenes are by definition the class of compounds that are soluble in *n*-pentane, *n*-heptane and toluene. Asphaltenes are by definition a class that are insoluble in *n*-pentane or *n*-heptane. Asphaltenes are precipitated following the ASTM D6560-12 standard method.[4] According to this

method, for a fixed volume of oil, 40 times the volume of n–pentane is added to it and stirred for 24 hours. The precipitated asphaltenes are filtered and dried. The maltenes can further be separated using chromatography based on the adsorption interactions with high surface area chromatographic materials. The fraction of maltenes adsorbed from a solution in n-pentane by an Attapulgus clay or silica gel is called resins and the fraction not adsorbed is called oils. Oils may be fractionated into aromatics and saturates. The fraction of oil that is adsorbed by a silica/alumina column from the n-pentane: oil solution is called aromatics and the non-adsorbed fraction is called saturates.

This method of separation of component classes is called SARA analysis and the standard method is the ASTM D4124-09.[5] Solids are defined as the fraction of material that are insoluble in any paraffinic solvents (n-pentane or n-hexane) nor toluene or methylene chloride. These fractions do not give any details about the chemistry, but combine solubility and adsorption to make classifying the feedstock easier to some degree. Having said this, it is but obvious that each fraction does not have definite distinctions between the physical and chemical properties and thus one needs to keep this in mind while comparing data. Figure 2-1 shows the schematics of SARA analysis of bitumen.
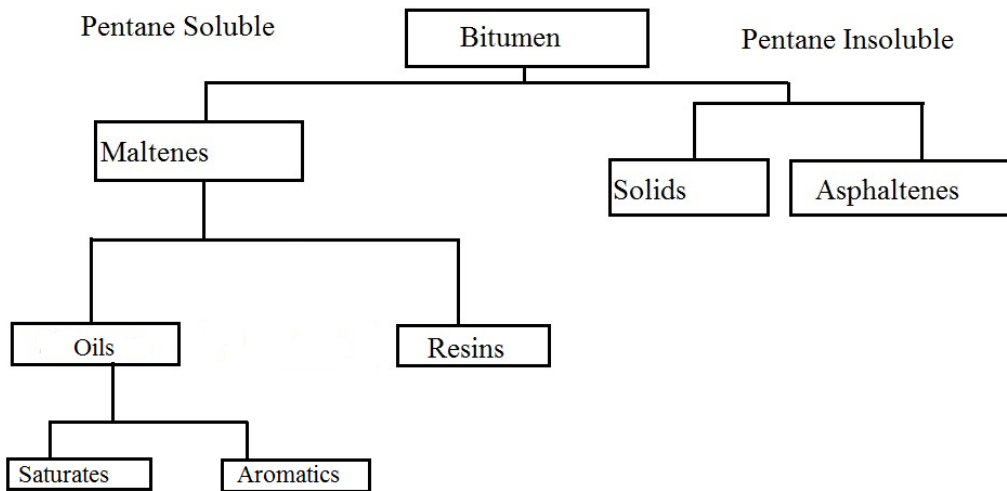
Figure 2- 1: Schematics of SARA analysis of bitumen

2.2.1 Asphaltenes

Asphaltenes are a solubility class and precipitate from heavy oil on addition of a paraffinic solvent to bitumen. They are the most polar and most aromatic fraction separated from unprocessed crude oils.[3] Because of the natural aggregation tendency of these molecules measuring the molar mass is difficult and there always will be strong arguments from various researchers about the exact molecular structure. It is however possible to find representitve structures for asphaltene molecues using analytical data.

Qian et al. [6] suggested a mean molecular weight of 1238 amu for a typical asphaltene molecule using field desorption mass spectrometry. As pointed out before, the aggregation tendency causes variation in the molecular weights and researchers have indicated the mean value be in the range of 1000 to 2000 amu. [7][8] In literature there are two different types of molecular structures that are mentioned: 1) Pericondensed and 2) Archipelago type of structure.

The pericondensed structure was suggested by Mullings and Groenzin[9] and this consisted of a larger multinuclear core with several alkyl chains attached to the core. In contrast to this structure the archipelago type of representation contain smaller groups of aromatic cores that are associated together by aliphatic bridges. Studies [10][11] have shown that the archipelago structures seem to be more abundant than the pericondensed ones. Figure 2-2 shows an imaginary average molecular structure of asphaltenes. Pyrolysis studies[12] of asphaltenes have shown the existence of bridges that link the aromatic clusters to each other.
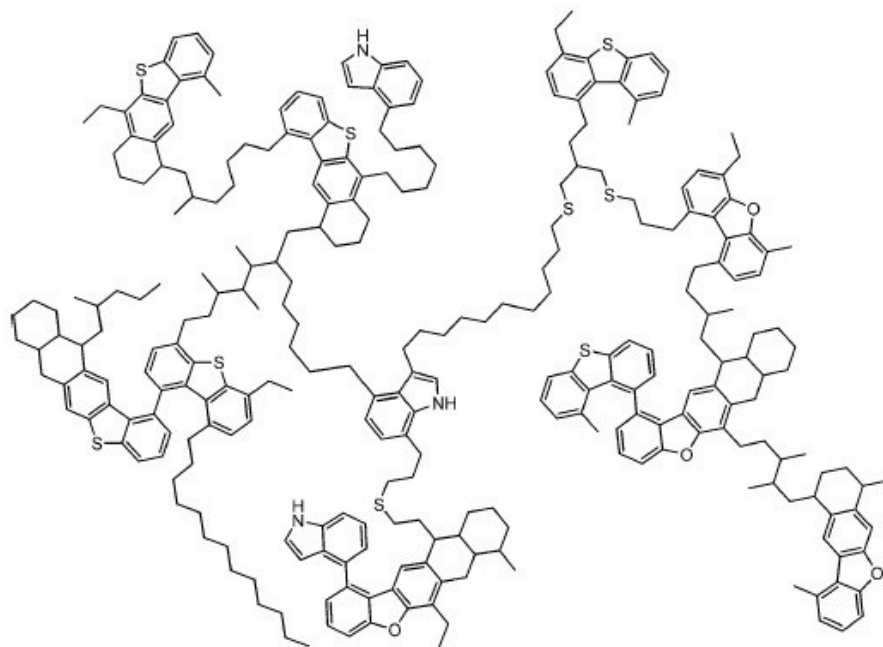
Figure 2-2: Archipelago structure representative of Asphaltenes[11]

Asphaltenes are reactive molecules and any aggregates affect the viscosity with pyrolysis time. The trend however, is complex and this observation has been reported in Chapter-5.

2.2.2 Viscosity

The resistance offered by a moving fluid to the shearing force applied, because of the internal friction between the layers, is called the viscosity. It is especially important in industries where transportation of material is important. Efficient bitumen transportation is a constant industrial challenge and viscosity reduction is vital to reduce transportation costs.

Canadian oil sands derived bitumen is characterized by a very high viscosity, typically of the order 10^4 mPa·s (cP) at 40 °C.[1] Such a high viscosity makes it impractical to extract bitumen from oil wells using conventional oil recovery technologies and difficult to transport bitumen by pipeline without any pretreatment. However, the viscosity of Alberta bitumens is strongly dependent

on temperature. The viscosity-temperature trend for different types of bitumen is seen in the Figure 2-3.[13]
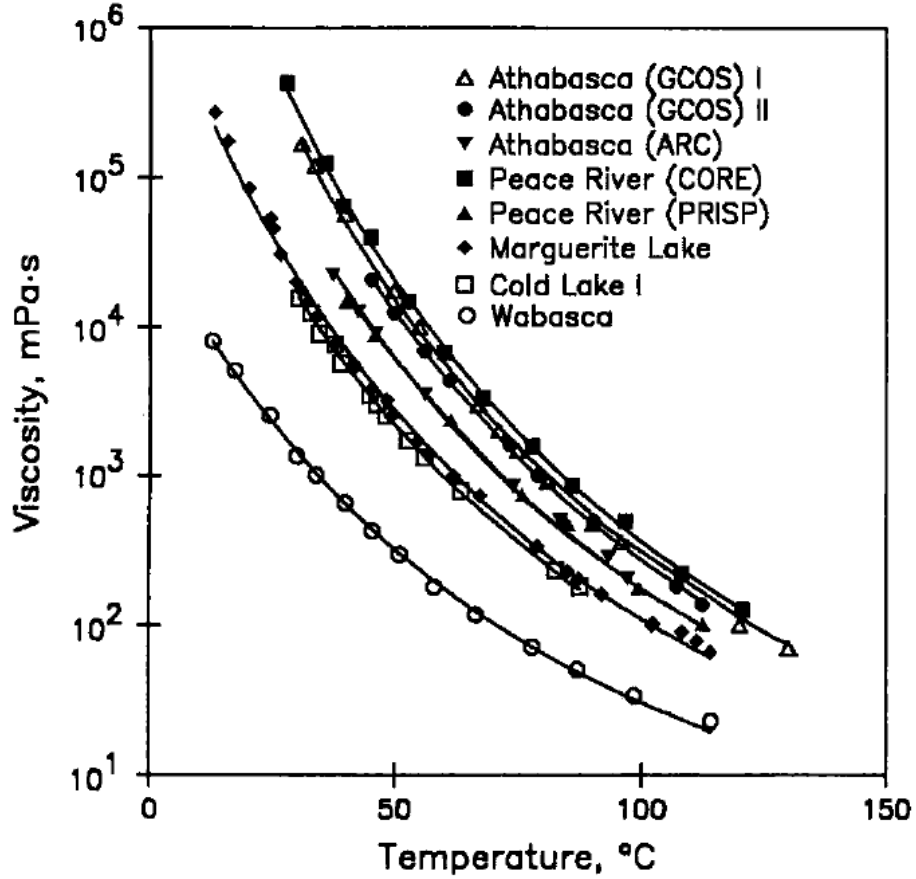
Figure 2-3: Viscosity-Temperature data for Alberta bitumens[13]

There are many correlations used to estimate the viscosity of crude oil. The standard approach for viscosity estimation is to take two measurements at two different temperatures. Once this data is collected the ASTM method is to fit the following equation to the given data:

$$\ln[ln(\mu)] = a1 + a2 \ln(T) \qquad \qquad \dots 2\text{-}1$$

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

Puttagunta et al.[14] recommended a similar equation (Equation 2-2) to calculate the viscosity of Alberta feeds in Pa.s. This method was said to be satisfactory for

the design of upgrading processes since the temperature is high enough that the residues are free flowing liquids.[15]

$$\ln \mu = 2.30259 \left[\frac{b}{\{(1+(T-\frac{30}{303.15})\}^s} \right] + B_0 P exp (dT) \qquad \ldots 2\text{-}2$$

Where C = -3.0020

S = 0.0066940b + 3.53641

B_0 = 0.004742b + 0.0081709

d = -0.0015646b + 0.0061814

$b = log_{10} (\mu_{30°C}) - C$

In this equation, T is the temperature in °C, P is the pressure in MPa, and $\mu_{30°C}$ is the measured viscosity in Pa.s at 30 °C and 101.3 kPa.

The viscosity of bitumen as measured at a specific temperature is lowered by two ways.

a) Conversion   b) Solvent addition

The addition of gaseous and liquid diluents to bitumens decreases their viscosity. The solubility of light gases in bitumens is depended on the temperature, time, pressure and the nature of the gas and bitumen.[16][17] By optimizing the temperature and/or the volume of diluent (gas or liquid), bitumen viscosity maybe reduced to meet pipeline specifications 350 cSt and 19 °API (940 kg·m⁻³) at minimum pipeline temperature (7.5 °C).[18] The viscosity reduction when upto 25 % naphthalene was added to bitumen is seen in Figure 3-6. The principle of visbreaking (thermal treatment) and types of visbreakers are explained in 2.4.1 Visbreaking.

2.2.3 Hydrogen/ Carbon (H/C) Ratio

The hydrogen/ carbon (H/C) ratio is an important property of crude oils. It gives an indication of the value of the oil. Greater the H/C ratio, the higher the value of the oil. Elemental analysis of bitumen has shown that bitumen and petroleum are

composed primarily (to the extent of about 99.4-99.9 wt%) of three classes. Hydrocarbon elements (H,C), organic heteroatoms (N, O, S) and metals (Ni, V). The specific weight percentages in literature[1] are given to be around the following percentages.

1) Carbon and Hydrogen (over 90%)
2) Nitrogen
3) Oxygen — combined wt% of up to about 9.9%
4) Sulphur
5) Metals in the organometallic form such as Vanadium and nickel (up to 0.6%).

The oxygen level in the feed is usually found by difference. There has been a significant amount of data collected by subjecting various types of bitumen to elemental analyses. From the data collected, it was observed that the elemental composition of Alberta bitumens vary between narrow limits.

Table 2-1: Range of elemental compositions of various Alberta bitumens.[1]

Element	Wt%	Standard Deviation (wt%)
Carbon	83.1	0.5
Hydrogen	10.3	0.3
Nitrogen	0.4	0.1
Oxygen	1.1	0.3
Sulphur	4.6	0.5

In conventional crudes H/C values vary considerably and may go as high as 2-2.3 in very light oils and as low as 1.4 in very heavy oils.[20] One factor for this difference is the residue fraction present in bitumen which has more aromatics causing a lower H/C.

"In the range of fuel materials, the molar ratio of hydrogen to carbon gives an indication of heating value and the combustion properties".[19]   For perspective and comparison, the H/C ratios of fuels are listed in the table below (Table 2-2).

Table 2-2: H/C ratios for different fuels.[19]

Fuel	H/C Ratio
Methane	4
Gasoline	1.9
Diesel	1.9
Light Crude	1.8
Bitumen	1.4-1.6
Coal	0.5-0.8

Based on the H/C ratio, the processing steps change to meet product specifications. In order to change the hydrogen to carbon ratio the feed may either be disproportionated to remove a carbon rich stream, or hydrogenated. Final process objectives and the economics drive disproportionation or hydrogenation or both.

2.3 Thermal Cracking

Thermal conversion is one of the oldest conversion processes in the petroleum industry. The primary objective is conversion of larger molecules to smaller ones by bond breakage. Thermodynamics governs breakage of bonds and typical bond dissociation energies required for cleavage are seen in Table 2-3. Cleavage of carbon-carbon, carbon-sulphur and carbon-hydrogen bonds govern the level of upgrading.

Table 2-3: Bond dissociation energies for primary upgrading[20]

Chemical Bond	Energy, kJ/mol
C-C (aliphatic)	355
C-H (n-alkane)	410
C-H (aromatic)	462
C-S*	322
C-N (in amine)	351
C-O (in methoxy)	343

Estimated from methyl sulfide and methyl radical formation from dimethyl sulfide with additivity data from literature.

Depending upon the targeted products, the feed undergoes different thermal and catalytic processes. In general, a residue upgrading unit aims to improve the H/C ratio, reduce the average boiling point and lower the content of heteroatoms. Thermal cracking increases in rate at higher temperatures. The steps that occur during thermal cracking are initiation, propagation and termination. The mechanism for aliphatic hydrocarbons is shown in Figure 2-4.
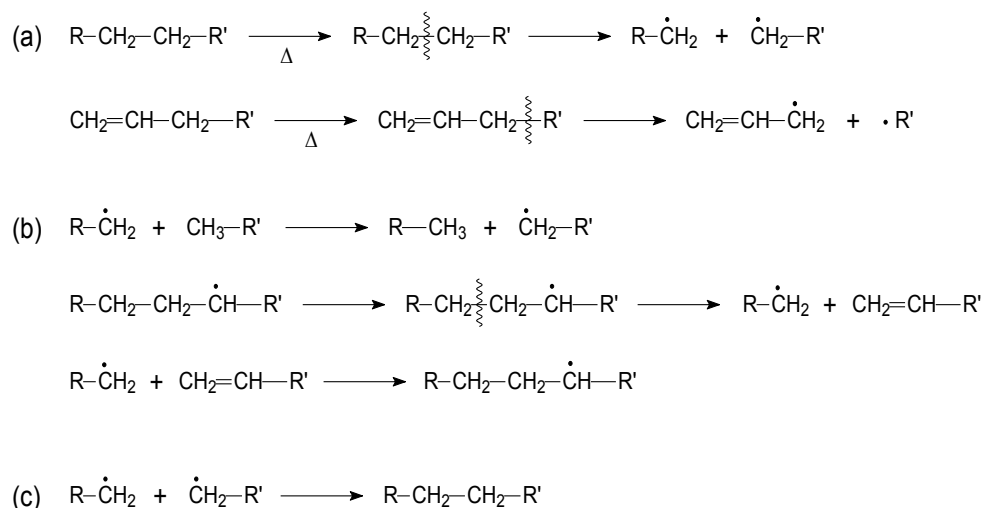
Figure 2-4: Steps involved in thermal cracking a) initiation b) propagation and c) termination reactions[21]

Thermal cracking starts with the initiation step (a), where homolytic cleavage of thermodynamically favorable bonds (more likely the carbon-sulfur or carbon-carbon) occurs and results in free radical formation. Each dissociation step produces two free radicals. The propagation step involves reaction of free

radicals. During propagation there is abstraction of a hydrogen atom from a hydrocarbon (or the bitumen matrix).[21] The probability of β-scission performed on produced radicals to form alkyl radicals and olefins is high. This mechanism has been formalized and is used to successful explain products from thermal cracking.[22] It is important to remember that even though the propagation reactions continue, the primary initiation reactions continue as well. Ultimately thermal cracking reactions terminate by addition of radicals seen in Figure 2-4(c). These addition reactions are undesirable because it results in a boiling point increase of products which defies the purpose of pyrolysis. In termination, free radicals may collide and combine releasing energy.

In order to prevent free radical addition a source of hydrogen must be present in order to cap radicals and prevent them from addition. This can be done in form of hydrogen gas addition or H-donor solvents. Solvents were used as a hydrogen addition source in our studies and the mechanism of solvent-radical interactions is discussed in *section 2.3.2 Effect of Solvents on coking*.

2.3.1 Mechanism of Coke formation

Coke formation is a problem where it is not the purpose of the process. For example coke formation is the purpose of a delayed coking process. Coking causes reduced liquid yield and catalyst deactivation. There are various mechanisms proposed by which hydrocarbon feed turns to coke. An accepted understanding is that thermal conversion leads to hydrogen disproportionation that ultimately over time leads to the formation of a carbon rich hydrogen deficient material referred to as coke. Hydrogen disproportionation starts occurring at temperatures even below 200 °C[23][24] and thus even at low temperatures coke formation can't be prevented if sufficient time is given. Having said this, there is an induction period during thermal conversion during which no coke is formed. The onset of coke formation is associated with the partitioning of the liquid phase into two, the new phase being termed as a mesophase.

This new phase is lean in hydrogen and readily forms coke as hydrogen disproportionation proceeds.[25][26] Liquid-liquid phase separation was also

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observed by Shaw et al.[27] in pyrene-tetralin-hydrogen mixtures. They worked in the temperature regime of 347-427 °C and pressures of up to 19 MPa and also suggested that coke formation can be the result of such phase separation followed by hydrogen disproportionation. Abedi et al.[28] modelled a phase diagram for a mixture of heavy oil (Athabasca vacuum bottoms, dodecane and hydrogen). The reaction conditions were 152-452 °C with pressures of 2-7 MPa. They reported an irreversible precipitation of asphaltenes for the heavy liquid phase about 377 °C. This precipitation behavior was not seen for the light liquid phase even at higher temperatures (427 °C). The experimental results point to a link between asphaltene precipitation and multiphase behavior. This links the possible relation between asphaltene fraction conversion to mesophase and ultimately coke make which was explained by Wiehe.[26]

Wiehe[26] suggested a kinetic model that successfully explains some phenomena occurring during coking of heavy oil and bitumen. According to this theory asphaltenes are the major contributing factor to coke make. Asphaltenes are composed of thermally stable polynuclear aromatic cores with groups connected to the cores by thermally less stable bonds. During thermal conversion there is cracking of these bonds, they form free radicals and the pendant groups break off from the aromatic cores. These aromatic cores are initially soluble in the maltene fraction. During this time, the dispersed asphaltenes that have radicals on the aromatic cores can abstract hydrogen from hydroaromatics in the matrix and terminate the free radicals. As thermal conversion increases, the amount of transferrable hydrogen decreases, while there is continuous increase in the formation of aromatic cores. This is when a liquid-liquid phase separation occurs, because the asphaltenes are not soluble in the remaining maltenes anymore. Hence a new phase is seen that contains primarily aromatic cores. The phase separation mechanism as described by Wiehe is shown in Figure 2-5 where A-core represents the aromatic core.

Because radicals are extremely reactive and with little to no remaining hydrogen to abstract, addition of aromatic cores take place to form toluene insoluble coke

that is carbon rich. The induction period of coke formation is the amount of time required to reach the solubility limit of aromatic cores in the maltenes.
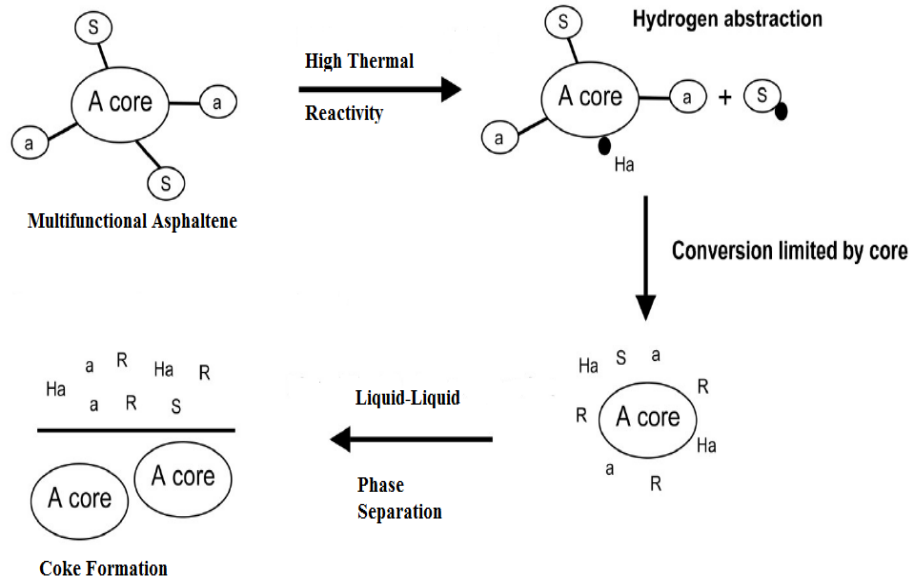
Figure 2-5: Phase separation mechanism of the formation of coke from thermolysis of resids[26]

Rahmani et al.[29] extended Wiehe's model[26] and added hydrogen transfer to asphaltenes using solvents.

2.3.2 Effect of Solvents on coking

The chemistry of thermal cracking shown in Figure 2-4 illustrates the undesirable reactions (radical addition) that may take place after free radicals are formed. Free radicals are extremely reactive and when the local concentration is high, the probability that two free radicals may recombine with each other and form a stronger bond than that which previously existed is high. There also exists a probability that a free radical may combine with an unsaturated compound (olefin). In both cases it leads to the production of heavier products which defies the purpose of pyrolysis.

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Most free radical chemistry work was initially performed with model solvents. The investigation was then extended to coal liquefaction where much work in the field of free radical chemistry was published in the field of coal. Coal liquefaction involves thermal conversion at 400 °C to 500 °C and it involves the formation of free radicals.[30] Literature suggests that sufficient stabilization of radical fragments, derived thermally from coal would lead to higher conversion. [31] Since then there have been more studies that helped in understanding the H-donor mechanism better. The work on coal can also be applied to bitumen.
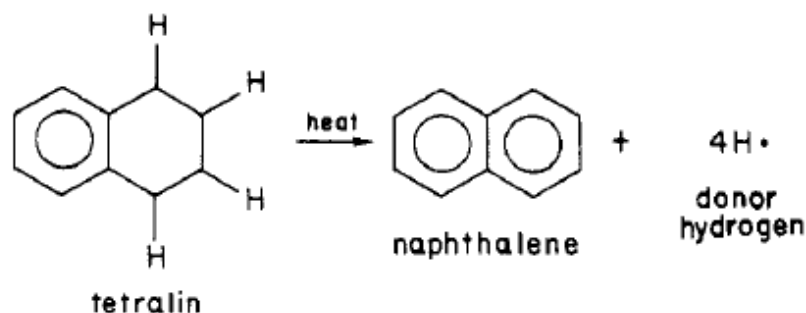
Figure 2-6: Hydrogen donor action of tetralin (1,2,3,4 tetrahydronaphthalene)[31]

Tetralin (1,2,3,4 tetrahydronaphthalene) which is the prototypical hydrogen donor solvent was one of the solvents used in our studies. The mechanism by which tetralin donates hydrogen is shown in Figure 2-6. Tetralin is capable of donating a hydrogen atom (H•) to the free radical species that is formed during pyrolysis. By transferring hydrogen to the reactive radical, the radical with the unpaired electron is terminated and results in a stable molecule with paired electrons. Termination of the free radical in this way prevents other free radical addition reactions taking place. During this process, tetralin gets dehydrogenated and finally converts into naphthalene.

Similar reactions may be performed by different solvents that are inherently hydrogen rich. Solvents can function as hydrogen donor solvents as they have the ability to dehydrogenate and donate the resulting hydrogen to hydrogen-deficient reacting species. Khorasheh, et al.[32] performed reactions with tetralin and hexadecane where they observed that the yields of olefins were highly suppressed.

Their experimental observations also showed reduced coking compared to thermal pyrolysis of hexadecane without the H-donor solvent (tetralin).

Coal liquefaction studies have shown that solvents can be used as reaction moderators to improve liquid yield by H-shuttling as well. Mesitylene was used in our studies as an H-shuttling solvent. Mesitylene has the ability to donate hydrogen but it does not attain stability like tetralin on H-donation. It hence shuttles the hydrogen and is termed a hydrogen shuttler. In addition to this the effect of pure dilution was checked by adding naphthalene as a solvent during pyrolysis reactions. The reaction chemistry involved is explained in Chapter-3 and the reaction mechanism by which these specific solvents interact with free radicals is shown in Figure 3-2.

2.4 Technologies employed in bitumen processing

There are three main classes of thermal conversion technologies commercially used today to process bitumen: a) Viscosity reduction (Visbreaking) b) Coking and 3) Residue hydroconversion.[33] Residue hydroconversion is a process where pyrolysis and hydrotreating are combined to hydrogenate cracked products mainly to increase the quality of cracked products. Visbreaking and Coking have been discussed briefly since the processes are purely thermal in nature. More attention will be paid to visbreaking since this is the process that was investigated.

2.4.1 Visbreaking

Gary et al. [34] gives a particularly useful description of visbreaking. "Visbreaking is a relatively mild thermal cracking operation mainly used to reduce pour points and viscosities of vacuum tower bottoms to meet No. 6 fuel oil specifications. It may also be used to reduce the amount of cutting stock required to dilute the resid to meet these specifications. Long paraffinic side chains attached to the aromatic cores are said to be the primary cause of high pour points and viscosities of resids".[34]

Visbreaking is a technology where optimum time and temperature is given to get rid of the side chains causing a viscosity decrease. Since its introduction in the

1920's visbreaking has been extensively used to upgrade vacuum bottoms, produce distillates and visbroken residue.

Residue that needs upgradation is preheated by heat exchangers. This heated residue is then sent into a visbreaking furnace for a set amount of time at a specified temperature to reach wanted conversion. After this, the visbroken material is passed through a soaking zone and the product is quenched. Products are sent for fractionation by distillation after this. Visbreakers are of two types:

a) Coil Visbreaking: This is high temperature operation (473 °C to 500 °C) for a usually about 1-3 minutes.[34] The process scheme of coil visbreaking is seen in Figure 2-7.

b) Soaker Visbreaking: Relatively lower temperature operation (427 °C to 433 °C) and longer reaction times.[34] The process scheme of soaker visbreaking is seen in Figure 2-8.

Having said this, the temperature and time ranges are tailored to the feed being processed. The product yields and properties from both coil visbreaking and soaker visbreaking are similar in nature but the soaker operation has the advantage of lower energy consumption and longer run times before having to shut down to remove the coke from the furnace tubes.
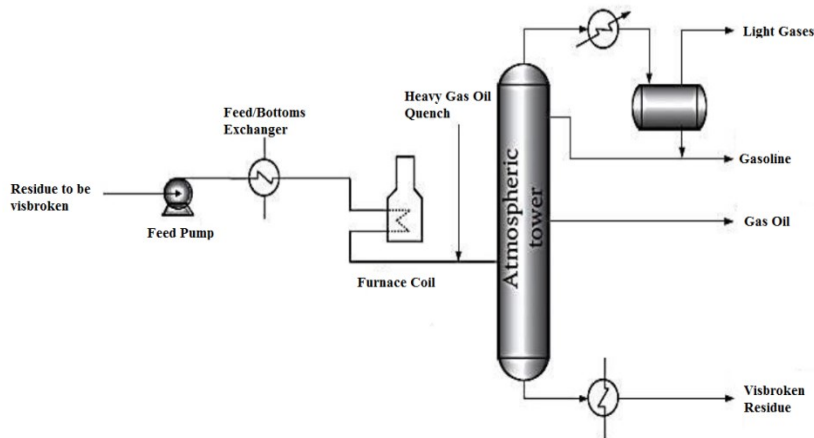
Figure 2-7: Process scheme of a coil visbreaker[35]
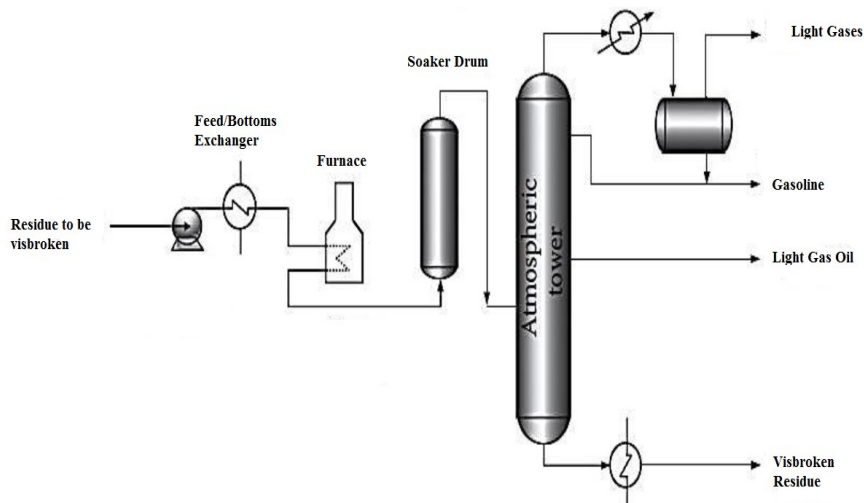
Figure 2-8: Process scheme of a soaker visbreaker[35]

Researchers have investigated different aspects of visbreaking over time. Development of thermal cracking reaction pathways and kinetics were investigated under the visbreaking conditions stated. The main variables taken into consideration were time, temperature and pressure.[36][37] Most industrial processing conditions are above 430 °C the primary reason being higher rate. In our studies we used 400 °C and below to minimize coking and increase liquid yields. There is not much literature available on thermal conversion below 400 °C and has been summarized in section *2.5 Low temperature Pyrolysis.*

2.4.2 Coking

Coking is a unit process in which there is conversion of heavy oil and vacuum residues into solid coke of different grades and lighter fractions that are further processed to be converted into higher values products like transportation fuels. From a chemical reaction viewpoint coking is a severe cracking process where in one of the end products is primarily a carbon enriched solid phase product. In order to eliminate all volatiles from petroleum coke, it must be calcined at

approximately 980-1315 °C. Refineries do not calcine coke as part of oil upgrading.

Initially coking was primarily used to pretreat vacuum residues to prepare coker gas oil streams that were suitable as feed for a catalytic cracker unit. This caused a reduction in the coke formation on the cracker catalyst and thereby allowed increased cracker throughputs.[34] In recent years the coking process has also been used to prepare hydrocracker feedstocks and also to produce a high quality needle coke. However, the high sulphur content in bitumen causes production of coke with high sulphur content since most of the sulphur is retained in the coke.[38] Because of the high sulphur content in the coke this is difficult to sell.

The main types of coking are delayed coking and fluid coking. In delayed coking two or more reactors called cokers are charged with the feedstock and they are used to hold or delay the heated feedstock while cracking takes place. Coke is deposited in the drums as a solid and is hydraulically cut using water after a cycle of operation. Fluid coking on the other hand is a process where in once the feed is continuously fed to the reactor, a part of the formed coke is transferred to a heater as a fluidized solid. This is where some of it is burned and recirculated to provide the heat necessary for the cracking process.

2.4.3 Residue Hydroconversion

Residue hydroconversion processes are processes that reduce boiling range of residue boiling range feedstocks as well as remove substantial amounts of impurities as metals, sulphur, nitrogen and high carbon forming compounds. The products however are still very aromatic and may require a severe hydrotreating operation.

Process selection has tended to favour hydroconversion processes which maximize distillate yield and minimize byproducts (especially coke). The feed conversion level that can be achieved is 25-65% in residue hydroconversion processes.[34]

2.5 Low temperature Pyrolysis

"Residues are operationally defined as the fraction of petroleum, heavy oil or bitumen that does not distill under vacuum. Bitumen's are defined as any natural mixture of solid and semisolid hydrocarbons."[19] Based on the API gravity, the viscosity and the residue content, the United Nations Institute for Training and Research (UNITAR) classified bitumen a residuum. Bitumen is processed today as a residuum because whatever the geological origin of the feed, the residue fraction is 40% and higher.[19]

A simulated distillation study on the feed used in our experimental studies (Cold Lake Bitumen) showed an initial boiling point of 242 °C. With such a high initial boiling point, almost all of the material is in the atmospheric residue range. One would therefore expect the material to be less reactive based on the conversion strategies for residues typically used with crude oils. But a more detailed review of the older literature revealed several interesting observations on the reactivity of bitumen.

In 1926, Egloff and Morrell[39] investigated the thermal conversion of Athabasca bitumen at 400 °C and 0.6 MPa. They observed that the Alberta tar does lend itself particularly to cracking at low temperatures and pressures. The main purpose of the study, however, was to induce coking and not suppress it. Henderson and Weber[40] just like Egloff and Morrell investigated low temperature upgrading of Athabasca bitumen. At 370 °C there was reported viscosity decrease by two magnitudes as well as density decrease. The amount of material in the residue boiling fraction was reduced along with insignificant co-production of gas.

Ball[41] in 1941 essentially reported the same observations. When Athabasca bitumen was subjected to 360 °C for 32 minutes a product with lower viscosity, lower density and conversion that had "no fixed carbon and virtually free gases" was obtained. From these observations bitumen seemed to be more reactive than predicted from the visbreaking of conventional heavy oil fractions. Mild thermal

treatment of Athabasca bitumen by Erdman and Dickie [42] at 350 °C for 24 hours in a batch reactor yielded a viscosity decrease from 34 to 0.2 Pa.s. Product viscosity was measured at 38 °C. There was more evidence of the reactivity of bitumen.

Speight[43] summarized literature published before 1973 where bitumen was visbroken at temperatures lower than conventional visbreaking temperatures and there was agreement on the fact that bitumen readily converted at lower temperatures. Even the asphaltene fraction, that makes up about 15-20% of the feed were considered to be heat sensitive, with decompositions taking place at temperatures >150 °C.[44]

Based on its reactivity inferred from the above observations, bitumen should not be considered a residuum but a "young or virgin oil that has not been subjected to the temperatures and pressures regular oil-fields have."[41] In light of these observations made by several researchers[39][40][41][42][43][44] it might be of greater value to use lower temperatures for visbreaking conversion purposes.

Clearly there have been observations of low temperature reactivity, but most of these observations were disregarded in the interest of higher rate and cheaper products. The subsequent experimental work looked at coke suppression, higher viscosity reduction and continuous monitoring of the overall H/C of the liquids. This gave an indication of product yields as well as product quality. In the interest to further the knowledge of low temperature pyrolysis, all experimental work was performed at 400 °C and lower.

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Chapter - 3 Suppression of coke formation during bitumen pyrolysis

Abstract

In this chapter mild pyrolysis (400 °C) of bitumen was investigated to establish ways in which coke formation can be suppressed. Bitumen was diluted to various degrees with solvents that had different hydrogen transfer properties, namely, hydrogen donation, hydrogen shuttling and a solvent with poor hydrogen transfer properties. Additionally the concentration of light products generated during bitumen pyrolysis was manipulated by pressure and batch/semi-batch operation. Coke formation was suppressed by light material, whether added as a solvent, or generated *in situ* during pyrolysis. As anticipated, hydrogen transfer was important, but coke formation was reduced by 35 % at 10 % concentration of even a poor hydrogen transfer solvent. Hydrogen availability and the H:C ratio of the reaction mixture were found to be particularly influential in determining whether coke formed. The results showed that light gases produced during pyrolysis were not irreversible reaction products, but continued to participate in the reaction network to moderate the pyrolysis process and suppress coke formation. Applied to industrial operation, evidence was provided to indicate that liquid yield can be increased and coke formation can be suppressed during visbreaking by co-feeding light gases, typically C_4 and lighter hydrocarbons.

Keywords: Thermal cracking, visbreaking, pyrolysis, bitumen, coke, hydrogen transfer

3.1 Introduction

Thermal conversion is the oldest of all refining processes. To this day thermal conversion is industrially employed for the upgrading of heavy oils and bitumens.[1] Conversion takes place through thermal cracking (pyrolysis) of the molecules and the chemistry follows a free radical mechanism (*see 2.3 Thermal Cracking*). Three main classes of thermal conversion technology are found for bitumen: visbreaking, coking and residue hydroconversion. Visbreaking is a mild pyrolysis process that was originally developed to reduce the viscosity sufficiently for fuel oil applications. Coking is a prolonged pyrolysis process that disproportionates the bitumen into a carbon-rich coke fraction and more hydrogen-rich lighter fractions. Residue hydroprocessing is a process where pyrolysis and hydrotreating are combined to hydrogenate the cracked products as they are produced to increase the quality and yield of liquid products.

The role of thermal upgrading changed over time, as society became more sensitive about the use of carbon. This is especially evident in the changing role of mild pyrolysis as is found in visbreaking, since the emphasis shifted from the production of fuel oil to the increased production of lighter liquid products that have higher value. It is the latter application, namely, the mild pyrolysis of bitumen to increase the yield of lighter liquid products, which is considered in this chapter.

In order to increase the yield of lighter liquid products, mild pyrolysis has to be operated at higher conversion. Practically, the maximum conversion is limited by coke formation in the furnace and stability of the atmospheric residue fraction, although there are other constraints too.[5][3] There is a stoichiometric limit on how much pyrolysis conversion can be performed before carbon rejection by coke has to take place in order to balance the H:C ratio of the feed and products. Coke formation can be suppressed by hydrogen addition, which increases the H:C ratio of the product and decreases the need for carbon rejection. This strategy is employed in residue hydroconversion to obtain an overall increase in H:C ratio of the products, either through direct catalytic hydrogenation with H_2, or indirect

hydrogenation by hydrogen-transfer from an appropriate hydrogen-donor solvent. The latter approach has extensively been used in direct coal liquefaction.[4] Petroleum refiners did not overlook the analogy and visbreaking combined with hydrogen-donor solvents was investigated,[5][6] as well as hydrothermal conversion,[7] and ways to generate hydrogen during visbreaking, such as Aquaconversion.[8] Another source of coke formation is free radical addition reactions. Industrially steam is employed to reduce coke formation by increasing turbulence in the flow where feed vaporization is insufficient to do so,[5] and to reduce free radical addition in the vapor phase by dilution. Hydrogen donor solvents can perform a similar function, but with the added ability to terminate free radical reactions through intermolecular hydrogen-transfer.

Bitumen pyrolysis is a well-established, mature and industrially practised conversion process, yet, there are still some opportunities for improvement.

Model solvents were chosen to differentiate different possible mechanisms of coke suppression and although real bitumen was used, this should not be considered an applied study with direct industrial application. The outcome was unexpected and it generated some new insights into the parameters that are important for suppressing coke formation during visbreaking. Our working hypotheses were:

(a) Lowering the operating temperature will decrease coke formation. There is an inverse relationship between temperature and time required for the same level of cracking conversion in visbreaking.[5] Better liquid selectivity is obtained by operating at lower temperature due to the difference in apparent activation energy for the production of lighter and heavier molecules.[5] This hypothesis was not verified by the present study, but it informed the choice of pyrolysis temperature; all experiments were conducted at 400 °C.

(b) Co-feeding a liquid solvent with bitumen will suppress coke formation. The solvent can reduce free radical addition reactions by dilution and by free radical termination in the case of hydrogen donor solvents. Hydrogen donor solvents are

preferred and literature indicates that the hydrogen donor ability of a solvent is crucial to increase liquid yield,[4] and decrease coke formation.[9] This hypothesis was investigated.

(c) Decreasing the production of light gases during bitumen pyrolysis will suppress coke formation. Light gases have higher H:C ratios than liquid products. Consequently, the need to produce coke through hydrogen disproportionation in order to balance the H:C ratio of feed and products will diminish if less light gases are produced. For example, producing pentane (C_5H_{12}) as opposed to producing methane (CH_4), reduces the stoichiometric coke requirement by 40 %. Over-cracking of lighter liquids at longer residence time was cited as one of the main reasons for increased light gas production.[10] This hypothesis was investigated.

3.2 Experimental

3.2.1 Materials

The experimental investigation was performed with Canadian Cold Lake bitumen, which was supplied through the sample bank of the Center for Oil Sands Innovation (COSI) at the University of Alberta. Two different samples of Cold Lake bitumen were used, one that was aged and one that was fresh (Table 3-1). These two samples had different coking propensities, as can be seen from the difference in micro carbon residue (MCR) values.

The solvents employed were selected based on their different hydrogen-transfer abilities. The hydrogen donor solvent, tetralin (1,2,3,4-tetrahydronaphthalene) 99 %, was supplied by Sigma Aldrich. Mesitylene (1,3,5-trimethylbenzene) 98 %, also supplied by Sigma Aldrich, was employed as solvent with hydrogen shuttling ability. Naphthalene +99 % supplied by Fischer Scientific, was employed as solvent with poor hydrogen-transfer ability. Praxair supplied nitrogen 99.999 % as compressed cylinder gas.

Table 3-1: Characterization of the Cold Lake bitumen used as feed material

Description	Aged Cold Lake bitumen	Fresh Cold Lake bitumen
Micro carbon residue (wt %) [a]	17.8 ± 0.5	15.0 ± 0.7
Asphaltene content (wt %)	17.6	13.4 ± 1.0
Viscosity at 60 °C (mPa·s)	16200	9600 ± 300
Elemental analysis (wt %)		
carbon	82.6	82.6
hydrogen	9.5	10.3
nitrogen	0.7	0.6
sulfur	4.8	4.7
oxygen (by difference)	2.4	2.6

3.2.2 Equipment and Procedure

All pyrolysis experiments were performed in a semi-batch reactor (Figure 3-1) that was operated either in batch, or semi-batch mode. The setup was constructed using Swagelok 316 stainless steel tubing and fittings. The reactor was heated by placing it in a heated fluidized sand bath. The temperature inside the reactor was monitored and indirectly controlled by adjusting the temperature of the heated fluidized sand bath. During batch mode operation the reactor was purged and pressurized with nitrogen and then the ball valves V01 and V02 were closed before the reactor was placed in the heated fluidized sand bath. During semi-batch mode operating the same procedure was followed, but ball valve V02 was left open and the pressure inside the reactor was controlled by adjusting the back pressure regulator PCV02.

For a typical experiment the reactor was filled with 5-8 g material (bitumen and solvent), purged and leak tested with nitrogen. If required, the reactor was then pressurized to the desired pressure, before being placed into the preheated fluidized sand bath heater. The heat-up time from room temperature to 400 °C was 5 minutes. The duration of each run was 1 hour, measured from the time heating started. Cooling down at the end of the experiment also took 5 minutes. The reactor was then depressurized.
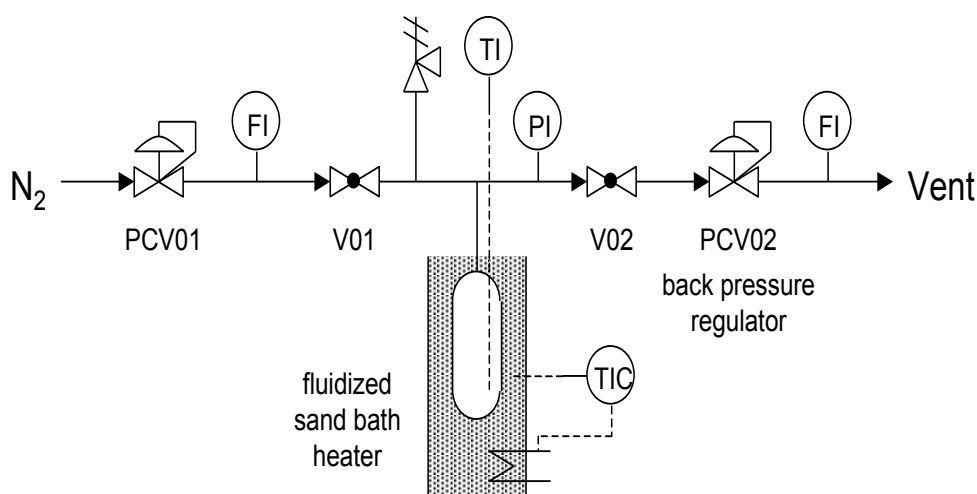
Figure 3-1: Semi-batch reactor employed for pyrolysis of bitumen.[11]

The light gases produced during the reaction and on depressurization were collected in a gas bag and afterwards analyzed. After removing and cleaning the reactor, the reactor and product were weighed to determine the weight of product. The reaction product was removed from the reactor with methylene chloride in a ratio of 1:40. The mixture was stirred for an hour and then the coke was extracted from the diluted pyrolysis product by filtration. The coke fraction was dried and weighed. Material balances for the experiments were typically in the range 97-103 %. All experiments were performed at least in triplicate.

3.2.3 Analyses

The gaseous products were analyzed using an Agilent 7890A gas chromatograph equipped with both flame ionization and thermal conductivity detectors. A Hay Sep R column, 2.44×0.003 m (8 ft × ⅛ inch) was employed. The carrier gas used for analysis was helium with a constant flow of 25 ml·min^{-1}. The injector temperature was set at 200 °C. The temperature program used started at 70 °C for 7 minutes, then ramping at 10 °C·min^{-1} to 250 °C and holding for 2 minutes, followed by ramping at 30 °C·min^{-1} to 300 °C and holding for 8 minutes.

Viscosity analyses were performed using an Anton Paar RheolabQC viscometer. The RheolabQC was calibrated with a Newtonian viscosity standard specimen whose kinematic viscosity was measured using a capillary viscosimeter of the Ubbelohde type, which was traceable to the national standard of the viscosity. The sample measuring cup used was C-CC17/QC-LTC and on average 4 g of the samples was required for analysis.

A Mettler Toledo ML 3002 balance (3200 g capacity with 0.01 g readability) was used for weighing of reactors, samples and products. Pressurized reactors were weighed before and after reaction, as well as after depressurization. In this way it was possible to also determine the gas yield gravimetrically.

3.3 Results and Discussion

3.3.1 Pyrolysis of diluted bitumen

Three different model solvents were evaluated for their ability to increase the liquid yield from bitumen pyrolysis, namely, tetralin, mesitylene and naphthalene. The solvents were selected based on the difference in their hydrogen-transfer capabilities. It was found that at 4:1 dilution (20 wt% bitumen in solvent), all of the solvents were capable of increasing liquid yield and decreasing coke yield (Table 3-2). Qualitatively the results were similar to that of a previous asphaltene pyrolysis study at 430 °C, where tetralin, methyl naphthalene and naphthalene were employed as solvents at 3:1 solvent to asphaltene ratio.[12]

As expected, the best results were obtained with tetralin, which is the prototypical hydrogen donor solvent. The liquid yield after 1 hour pyrolysis of neat bitumen at 400 °C was 79.0 ± 2.5 wt%, but for bitumen in tetralin, the liquid yield increased to 87.0 ± 1.0 wt%. The improvement in liquid yield was mainly due to the suppression of coke formation. The coke yield decreased from 7.5 ± 0.2 % for neat bitumen pyrolysis to 2.0 ± 0.8 % for bitumen diluted in tetralin. Although a slight decrease in gas yield was also observed, it was within the experimental error. Tetralin is capable of donating hydrogen (H•) to the free radical species (B•) formed during bitumen pyrolysis (Figure 3-2a). By transferring a hydrogen atom, which also has an unpaired electron, the free radical is terminated to produce a molecule with paired electrons (H:B). During this process the tetralin is dehydrogenated to 1,2-dihydronaphthalene, which is also a hydrogen donor solvent. The 1,2-dihydronaphthalene can likewise donate hydrogen to free radical species, ultimately being converted into naphthalene. By terminating free radical species, without the solvent being converted into a free radical product (except as intermediate), coking is suppressed.

Table 3-2: Product yields from pyrolysis of aged Cold Lake bitumen at 400 °C for 1 hour, without and with dilution in a 4:1 solvent to bitumen mass ratio.[a]

Feed material	Product yield (wt %)					
	liquid		coke		gas	
	x	s	x	s	x	s
bitumen	79.0	2.5	7.5	0.2	13.5	3.5
tetralin + bitumen	87.0	1.0	2.0	0.8	11.0	2.5
mesitylene + bitumen	85.0	1.5	3.0	0.3	12.0	3.0
naphthalene + bitumen	82.7	1.3	3.8	0.5	13.5	3.0

[a] Average (x) and sample standard deviation (s) of three experiments are reported.

Possibly the most dramatic demonstration of coke suppression due to an excess of hydrogen donor solvent, was provided by the study of Peng.[13] She demonstrated that the coke yield from asphaltene pyrolysis could be decreased from 38 to 2 wt % by conducting the pyrolysis in the presence of tetralin. The asphaltenes employed in her study was a C_5-precipitated asphaltene fraction from Athabasca bitumen. The pyrolysis conditions employed were 430 °C for 1 hour at a tetralin to asphaltene ratio of 3:1. Similar results were reported with the hydrogen donor solvent tetrahydroquinoline.

Although it was anticipated that dilution will play a role in preventing free radical addition reactions, it was surprising that to see that both mesitylene and naphthalene were capable of at least halving the coke yield. Neither of these solvents are hydrogen donor solvents.
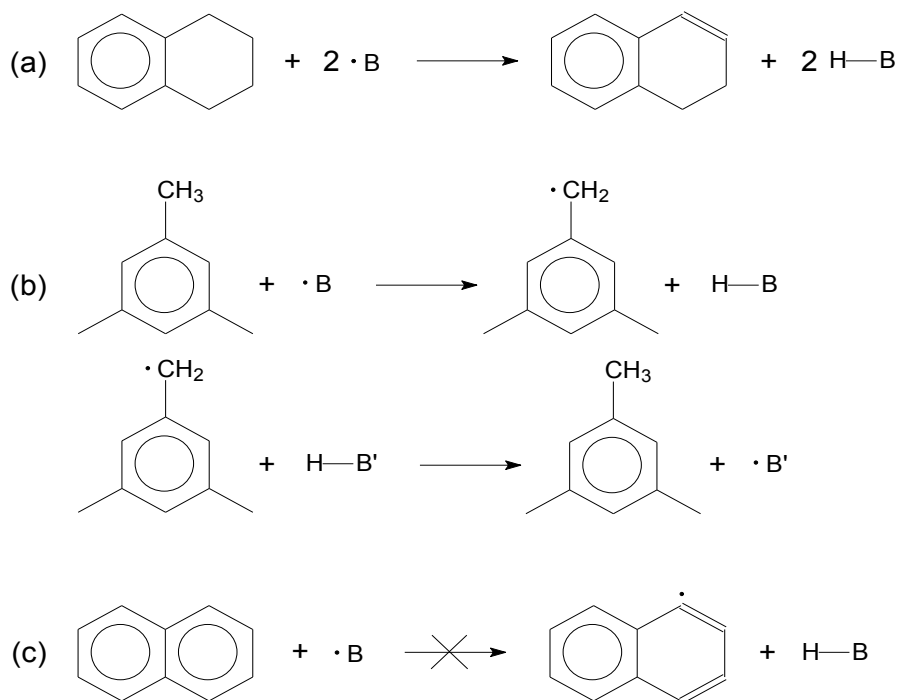
Figure 3-2: Hydrogen transfer action of solvents: (a) tetralin as hydrogen donor, (b) mesitylene as hydrogen shuttler, (c) naphthalene that is not normally active for hydrogen transfer[11]

Mesitylene is a hydrogen shuttling solvent. It is capable of transferring hydrogen to free radicals formed by bitumen pyrolysis in an analogous way to tetralin, but

by doing so, the mesitylene becomes a free radical (Figure 3-2b). This may help to terminate free radical species capable of forming coke, but the mesitylene must ultimately get the hydrogen back from the bitumen, or itself run the risk of free radical addition. Mesitylene is sterically crowded and self-termination to form mesitylene dimers is difficult and no clear evidence was found that mesitylene dimerization is a meaningful termination pathway. Nevertheless, dimerization was reported for another hydrogen shuttling solvent, methyl naphthalene, during pyrolysis of diluted bitumen at 400 °C and 13.8 MPa H_2 pressure.[14] Under such a high hydrogen pressure it is possible to hydrogenate some the naphthalene to tetralin, which is a hydrogen donor solvent. It is also possible to form dimers, because ring-addition is not sterically hindered as in the case of mesitylene. Mesitylene is only a hydrogen shuttling solvent and not a hydrogen donor solvent.

Naphthalene is a poor hydrogen transfer solvent (Figure 3-2c). The aromatic C–H bonds have high bond dissociation energies, typically of the order of 472 ± 3 kJ·mol^{-1}, compared to 375 ± 3 kJ·mol^{-1} for the C–H of a methyl group attached to an aromatic ring as is found in mesitylene.[15] However, aromatic solvents that contain no alkyl groups are not completely inert.[16][17] The potential participation of naphthalene in free radical propagation by hydrogen abstraction from an aromatic C–H bond depends both on the temperature and the naphthalene concentration. For example, it was reported that the thermal conversion of benzene relative to *n*-hexadecane was 5 times lower when the molar concentration of *n*-hexadecane in benzene was increased from 0.01 to 0.05.[17] Another mechanism that was suggested for naphthalene participation in free radical propagation involves the transfer of hydrogen to one of the carbon atoms in the naphthalene ring to create monohydronaphthalene. This is also called the ipso-mechanism. Some hydrogen exchange was reported for phenanthrene as solvent with coal, but almost no exchange took place with anthracene.[18] In addition, little support was found that the ipso-mechanism was a significant contributor in coal dissolution by 1-methylnaphthalene.[19] Yet, naphthalene was capable of reducing the coke from 7.5 ± 0.2 % for neat bitumen pyrolysis to 3.8 ± 0.5 % for bitumen diluted in naphthalene. Dilution seemed to play a more significant role

than hydrogen transfer ability, because naphthalene was effective at reducing the coke yield without being as active for hydrogen transfer as tetralin or mesitylene.

In the pyrolysis experiments (Table 3-2), the bitumen concentration was 20 %. With so much solvent, it is conceivable that the solvent interfered with free radical addition reactions and in-cage reactions were more easily disrupted. The physical separation (dilution) of free radical species by the solvent was apparently the dominant force for suppressing coke formation, so that even naphthalene, which is not an efficient hydrogen transfer solvent, was effective in reducing the coke yield during pyrolysis compared to neat bitumen.

On a solvent free basis, it was found that disproportionation of hydrogen from liquid phase to gas phase products increased with in increasing hydrogen transfer ability of the solvent.[20] The H:C ratio of gas phase products was the highest with tetralin as solvent (H:C = 3.07) and the lowest with undiluted bitumen (H:C = 2.95). Conversely, the H:C of the liquid phase products was the lowest with tetralin as solvent (H:C = 1.14) and the highest with undiluted bitumen (H:C = 1.37). The lower H:C ratio of the liquid phase product after pyrolysis of 20% bitumen in tetralin is mainly due to the retention of material in the liquid phase that was rejected as coke during bitumen pyrolysis (Table 3-2).

3.3.2 Effect of solvent dilution on coke yield

If dilution played an important role in suppressing coke, then the coke yield should be sensitive to the solvent concentration. The participation of poor hydrogen transfer solvents, such as naphthalene, in free radical transfer also decreases in relation to concentration.[16][17] It was therefore anticipated that a decrease in solvent concentration will lead to a gradual increase in coke yield, but this was not what was observed (Figure 3-3).

Even with the least amount of solvent evaluated, 10 % naphthalene, the presence of a solvent caused the coke yield during pyrolysis to be decreased from 7.5 % for neat bitumen to around 5 %. This decrease in coke yield was not due the hydrogen

transfer ability of the solvent, since naphthalene is a poor hydrogen transfer solvent. A benefit of better hydrogen transfer and hydrogen donation was seen mainly at higher solvent concentrations. At lower solvent concentration, the coke yield was within experimental error similar for all of the solvents.
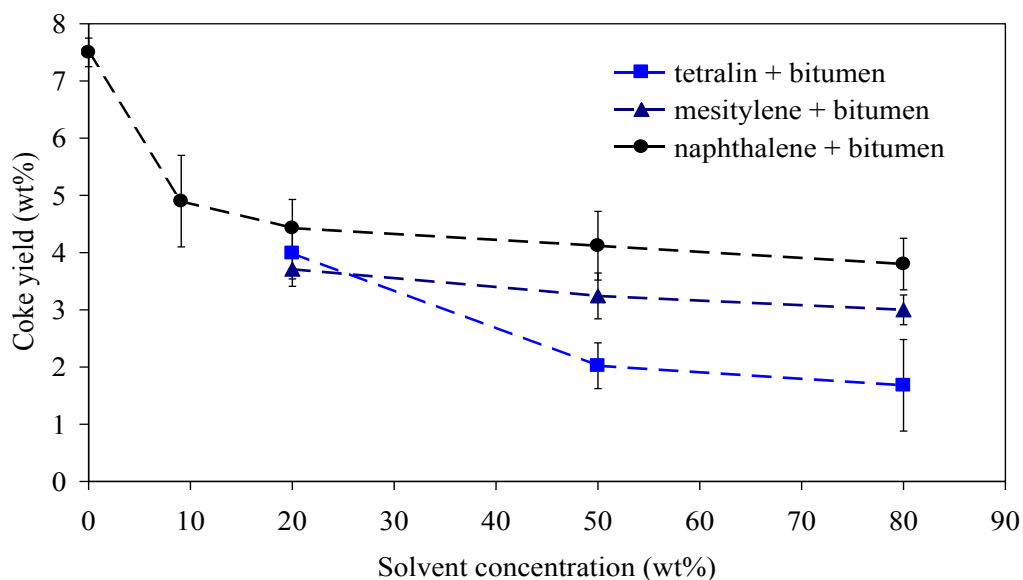
Figure 3-3: Effect of solvent concentration on the coke yield from pyrolysis of aged Cold Lake bitumen at 400 °C for 1 hour.[11]

The effect of solvent concentration of the different solvents on coke yield (Figure 3-3) indicated that at least four mechanisms were at work to suppress coke formation:

(a) Hydrogen donation was important. Tetralin is a good hydrogen donor solvent and the contribution of hydrogen donation can be seen from the difference in coke yield between tetralin and mesitylene, which is not a hydrogen donor solvent. At a solvent concentration of 50 % and higher there was a meaningful difference at 95 % confidence level based on a two-tailed Student t-test comparison of the means.

(b) Hydrogen shuttling was important. Mesitylene is a good hydrogen shuttling solvent and the contribution of hydrogen shuttling can be seen from the difference in coke yield between mesitylene and naphthalene, which is a poor hydrogen

shuttler. The difference was meaningful for a solvent concentration of 20 % and higher at 90 % confidence. Even so, the difference was not meaningful with respect to tetralin.

(c) Dilution was important. The effect of dilution can be seen from the impact of solvent concentration on the coke yield. The coke yield monotonically decreased with an increase in solvent concentration for all solvents over the whole concentration range studied. However, the contribution of dilution is surprisingly small. Even though the average values for coke yield decreased with increasing solvent concentration, the incremental differences between a 1:1 and 4:1 solvent to bitumen were not statistically significant.

(d) Despite its poor hydrogen transfer capability, naphthalene reduced coke yield significantly compared to neat bitumen. Furthermore, naphthalene was able to suppress coke formation significantly even when the solvent to bitumen ratio was 1:10. In addition to those mechanisms already mentioned, there was at least one important mechanism (or more) that was actively suppressing coke formation.

3.3.3 Effect of solvent dilution on pyrolysis

The effect of solvent dilution on pyrolysis extended beyond the impact on coke yield. The liquid yield was also affected by formation of light gases (Table 3-3).

As the solvent to liquid ratio was decreased, the contribution of free radical stabilisation through hydrogen donor and hydrogen transfer activity diminished. The decrease in liquid yield was expected from the increase in coke yield (Figure 3-3). The accompanying increase in gas yield with decrease in solvent concentration (Tables 3-2 and 3-3) was observed only for bitumen pyrolysis diluted with tetralin and mesitylene; the gas yield for bitumen pyrolysis diluted with naphthalene remained constant.

Table 3-3: Gas and liquid yields from pyrolysis of aged Cold Lake bitumen at 400 °C for 1 hour diluted with different solvent types and concentrations.[a]

Feed material	Solvent:bitumen	Product yield (wt %)			
		gas		liquid	
		x	s	x	s
bitumen [b]	0	13.5	3.5	79.0	2.5
tetralin + bitumen	0.25:1	12.2	2.7	83.8	1.5
	1:1	11.5	3.0	86.5	2.0
mesitylene + bitumen	0.25:1	13.0	2.8	83.3	2.0
	1:1	12.5	2.6	84.4	2.2
naphthalene + bitumen	0.25:1	13.5	2.5	82.0	1.7
	1:1	13.4	2.5	82.5	1.9

[a] Average (x) and sample standard deviation (s) of three experiments are reported.
[b] Repeated from Table 2 for ease of reference.

Although the increased gas yield found with tetralin and mesitylene were within the range of experimental error, the increase was monotonic with the decrease in solvent concentration. Conversely, the light gas yield of neat bitumen pyrolysis is the same as that of bitumen pyrolysis in naphthalene, irrespective of the naphthalene concentration. The change seems to be inversely related to change in production of methane (Table 3-4). The methane exhibited the same trend as the total light gas yield; the methane concentration decreased as the solvent concentration was decreased. The increase in light gas yield at lower solvent concentration was mainly due to an increase in the formation of C_2 and heavier hydrocarbons.

Table 3-4: Methane content of light gas produced during pyrolysis of aged Cold Lake bitumen at 400 °C for 1 hour diluted with different solvent types and concentrations.[a]

Feed material	Solvent:bitumen	Methane content (mol %)	
		x	s
bitumen	0	30	4
tetralin + bitumen	0.25:1	31	6
	1:1	34	1
	4:1	41	5
mesitylene + bitumen	0.25:1	34	2
	1:1	42	2
	4:1	48	8
naphthalene + bitumen	0.25:1	29	1
	1:1	32	2
	4:1	30	1

[a] Average (x) and sample standard deviation (s) of three experiments are reported.

It appeared as if at least a portion of the light gases was produced specifically to compensate for the lack of a hydrogen transfer medium. If the reaction mixture has too little material with hydrogen transfer capability, free radical propagation during pyrolysis is not sufficiently moderated. It is not suggested that the pyrolysis mechanism is altered, but rather that the propagation pathway is affected in such a way that more molecules with hydrogen transfer capability are produced until some form of pseudo-equilibrium is reached. Differently put, if the medium has insufficient hydrogen transfer capability, free radical propagation by repeated β-scission will continue uninterrupted, thereby creating more and more lighter products that will ultimately moderate the reaction (Figure 3-4). This

interpretation is supported by the change in the methane concentration of the light gas (Table 3-4). Both the light gas yield and the C_2 and heavier hydrocarbon concentration of the light gas increased as the hydrogen transfer ability of the medium decreased.
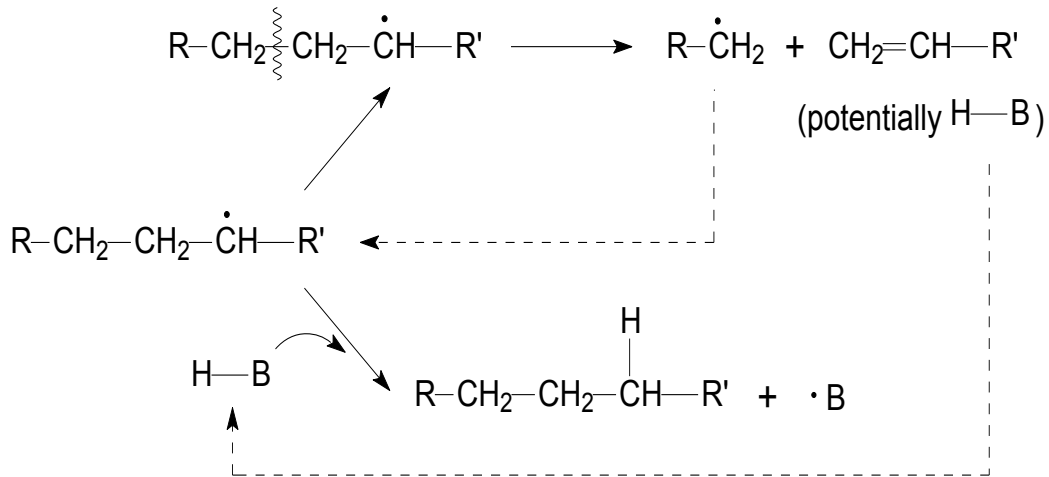
Figure 3-4: Free radical propagation leading to repeated β-scission to produce material that have hydrogen transfer capability and that is able to moderate the reaction.[11]

This observation led to the formulation of a different hypothesis about the role and need for light gases during pyrolysis that was different from that outlined in the introduction.

3.3.4 Role of light gases in bitumen pyrolysis

The working hypothesis outlined in the introduction was that any lighter products formed in a closed system will run the risk of over-cracking to produce light gas.[10] It is therefore beneficial to remove the lighter products as soon as they are formed. Based on the reported observations (Table 3-3), a new hypothesis was formulated. It was postulated that lighter products are beneficial and that removing such products from the reaction system will promote over-cracking to increase the production of light gas and through hydrogen disproportionation increase coke formation.

These two hypotheses differ with respect to what the dominant mechanism is: over-cracking of products due to longer residence time, or over-cracking of products and increased coke formation due to a lack of moderation by hydrogen transfer. The hypotheses are not mutually exclusive, but highlight different aspects of the overall pyrolysis process as being important.

The effect of increasing pressure as means to exploit vapor liquid equilibrium (VLE) to maintain a higher liquid phase concentration of lighter products was studied using a semi-batch reactor. Semi-batch reactor operation resembles a delayed coking process, apart from the fact that all the liquid feed is introduced to the reactor at the same time. The pressure in the reactor was kept constant by a back pressure regulator, which released vapor phase material in excess of what was required to maintain the pressure (Figure 3-1). For a given pressure the concentration of the lighter products in the liquid phase will remain constant, under the assumptions that the lightest products govern the vapor pressure of the mixture and that the concentration of the lighter products in the vapor phase does not vary much over time. The concentration of naphtha-range products in the gas phase product was minor.

It was found that as the pressure was increased, the coke yield decreased (Figure 3-5). It supported the previous observations (Figure 3-3), which indicated that a solvent suppressed coke formation. The light products produced by pyrolysis became the hydrogen transfer solvent. The increase in pressure from 1 to 2 MPa decreased coke yield, the difference being statistically significant at 99% confidence. A further increase in pressure had less of an effect on coke yield, even though coke yield decreased monotonically with an increase in pressure and the change was statistically significant at 90% confidence. This behaviour mimicked that of hydrogen transfer solvents; a little solvent made a big difference, but further suppression of coke formation was only weakly dependent on solvent concentration.
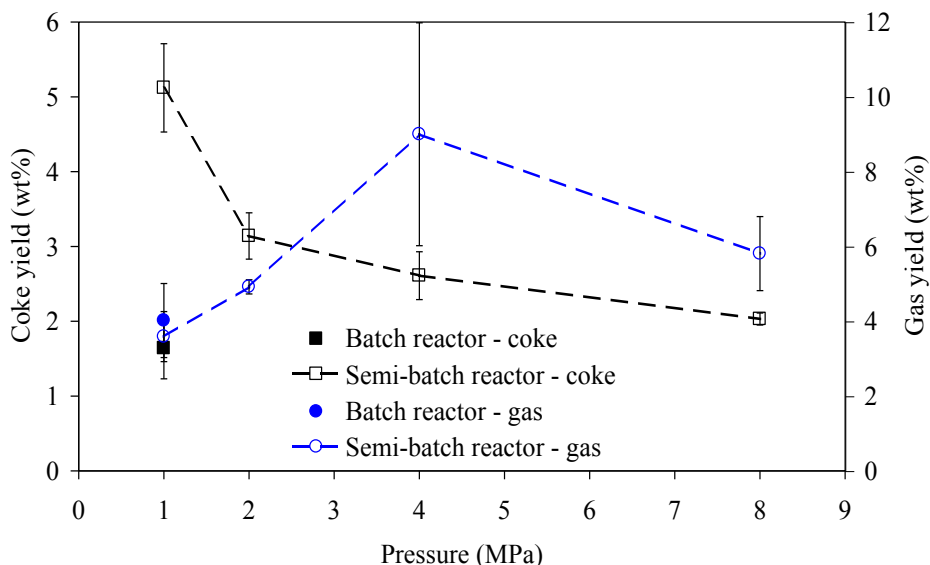
Figure 3-5: Coke yields (batch □, semi-batch ■) and gas yields (batch ○, semi-batch ●) obtained after pyrolysis of fresh Cold Lake bitumen at 400 °C for 1½ hours in batch and semi-batch reactors at different pressure conditions.[11]

Sachanen pointed out that the influence of pressure depends on the composition of the matrix, which is determined to some extent by pressure through VLE.[5] The main implication is that observed effect of pressure will be sensitive to the matrix, the nature of the VLE and how vapor material is removed from the system. This will be illustrated by examples from literature, which initially seem to be in contradiction to the present results, but are not contradictory when the experimental details are considered.

When bitumen was pyrolyzed in the range 500-530 °C and 100-650 kPa as a thin film, the effect of pressure on coke yield was inconclusive.[21] There was evidence that as the film thickness increased that pressure increased coke yield at ~500 °C, but the same effect was not observed at 530 °C. The vapor phase was diluted by N_2 sweep gas flow and light product evolution was not restricted by VLE; the main effect of pressure was on the nature and size of bubble evolution.

The effect of pressure on delayed coking of Athasbasca bitumen was investigated in a pilot plant and it was found that coke yield increased monotonically with an increase in pressure from 0.25 to 1.1 MPa.[22] During this investigation steam was

continuously fed to the coker and the hot and cold separator vessels were kept at the same pressure as the coker. The removal of light material was dominated by steam stripping. As the pressure was increased, the removal of lighter products was not decreased, because the rate of removal was determined by the rate of steam stripping. The temperature and duration of the operation were not reported and at high temperature and long residence time, the effect of pressure on coke yield may merely be a reflection of changes in stoichiometry. The increase in coke yield may be due to a different aspect of the operation, namely the increase in water content of the oil phase with increasing pressure. It was reported that coke yield from bitumen pyrolysis at 430 °C for 30 minutes increased in the order: toluene-bitumen mixture < neat bitumen < toluene-water-bitumen mixture.[23] On the other hand, very different behaviour was seen when bitumen was hydrothermally upgraded in such a way that the asphaltenes were extracted into the water-rich phase.[7]

Coke yield is only one aspect of the impact of pressure on selectivity. Another aspect to consider is the yield of light gases. The yield of light gases increased with an increase in pressure (Figure 3-5). It was not a monotonic increase and it was not clear why the highest gas yield was obtained at 4 MPa, or why the sample standard deviation for the experiments at 4 MPa was much higher than usual. The experiment at 4 MPa was repeated four times. The directional increase in gas yield with increase in pressure supports the hypothesis that an increase in vapor phase residence time leads to over-cracking. In order to confirm the specific contribution of residence time, one can vary the volumetric ratio of the liquid and gas phase, but this avenue of investigation was not pursued.

If Sachanen's[5] view on the impact of pressure on pyrolysis is correct, then it is likely that the outcome of experiments in a closed system (batch) at the same pressure as an open system (semi-batch), would be different.

One set of experiments was performed in batch mode (Figure 3-5), where the pressure was allowed to develop autogenously. The autogenous pressure reached 2.2 MPa. In a closed system all the light products formed during pyrolysis remain

in the reactor and the liquid phase concentration of light products is governed by VLE. As anticipated, the lighter products produced during pyrolysis performed the role of hydrogen transfer solvents and coke formation was lower in the batch reaction than in any of the semi-batch reactions (Figure 3-5). Surprisingly, the gas yield was not much different from that found during pyrolysis in semi-batch mode at 1 and 2 MPa, even though batch mode represented the longest residence time. The results indicated that the light gas yield was not primarily determined by over-cracking of light products due to a longer residence time at pyrolysis conditions.

The results indicated that even though operating pressure and VLE may play a role, that there is another aspect that influences the yield distribution. The liquid yield obtained from pyrolysis in a closed system was meaningfully higher than the highest liquid yield obtained by semi-batch pyrolysis, which was obtained at 8 MPa (Table 3-5). The difference was statistically significant at 95 % confidence.

Table 3-5: Liquid yields obtained after pyrolysis of fresh Cold Lake bitumen at 400 °C for 1½ hours in batch and semi-batch reactors at different pressure conditions.[a]

Description of experiment	Liquid yield (wt %)		
	x	s	n
Semi-batch, 1 MPa	91.29	0.82	3
Semi-batch, 2 MPa	91.94	0.50	3
Semi-batch, 4 MPa	88.39	3.17	4
Semi-batch, 8 MPa	92.15	1.05	3
Batch, autogenous	94.34	0.78	4

3.3.5 Relationship of viscosity to coke yield

Viscosity is a measure of the resistance of flow. Viscosity may therefore be an indicator of material to be restricted to the local environment, making it more susceptible for in-cage reactions and coke formation. Since the viscosity of bitumen is sensitive to solvent dilution,[24] and coke formation was suppressed even at low solvent dilution (Figure 3-3), it was speculated that this might be related to the decrease in viscosity.
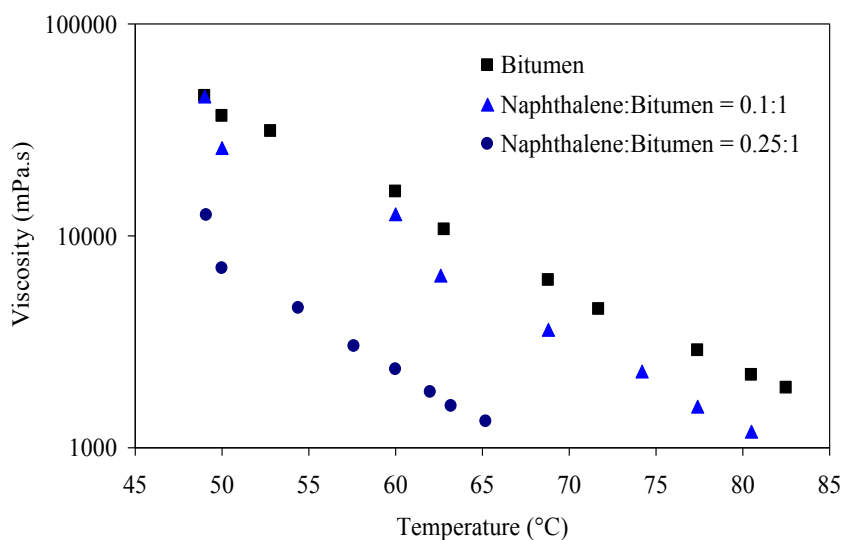
Figure 3-6: Viscosity of neat bitumen (■), and mixtures with 0.1:1 (▲) and 0.25:1 (●) ratios of naphthalene to bitumen.[11]

The viscosity of neat bitumen and bitumen mixed with naphthalene was measured (Figure 3-6). Although there was a significant difference in the viscosity at low temperature, the difference did not correlate with the change in coke yield. Even when the data was expressed as function of temperature to estimate the viscosity at reaction temperature (not that we suggest such an extrapolation is prudent or accurate), no correlation was found. If the change in viscosity was partly responsible for the change in coke yield, it was not apparent from the viscosity data collected at temperatures below the pyrolysis conditions.

3.3.6 Explaining coke suppression in terms of the Wiehe-model

Wiehe[25] proposed a model that describes coke formation during pyrolysis. It so happened that the model was developed based on the pyrolysis of the vacuum residue fraction of Cold Lake bitumen at 400 °C, which is the heavy fraction of the feed employed in this study. Key elements of the model are:

(a) There is an induction period in pyrolysis during which no coke is formed. The length of the induction period before coke begins to form is related to the solubility of the asphaltenes in the matrix. As long as the asphaltene fraction is solubilized and does not form a separate liquid domain, coke formation is suppressed.

(b) The asphaltene concentration reaches a maximum value at the end of the induction period. The asphaltene concentration starts to decrease once coke starts to form, suggesting a causal relationship between the decrease in the asphaltene content and increase in coke content of the reacting mixture.

(c) Asphaltenes are more reactive than the maltenes and as pyrolysis progresses, the asphaltenes are converted into more carbon rich compounds, also referred to as asphaltene cores. Once these compounds reach the "solubility" limit, separate ordered liquid phase domains (mesophase) are formed, which are dispersed in the continuous liquid phase. The mesophase is deficient in hydrogen. Without sufficient hydrogen to stabilize free radicals conversion continues to produce toluene insoluble material until coke is finally formed.

(d) Not all asphaltenes are equally aggregated in the liquid phase. The asphaltene molecules that are more aggregated tend to form a mesophase more easily. Ultimately all aggregated asphaltenes end up in a mesophase and with prolonged pyrolysis the aggregation number of the asphaltenes remaining in the liquid phase approaches unity. That is, the asphaltenes in the pyrolyzed liquid that did not form coke are unassociated. The asphaltenes also approach a constant H:C ratio and the liquid phase reaches a constant ratio of asphaltenes to non-volatile maltenes.

The size of the mesophase can be manipulated to inhibit coke formation. The asphaltenes can be partly extracted into the water-rich phase during hydrothermal conversion, which effectively prevents an oil-based mesophase from forming.[7] Fine solids can be added to act as adsorption and nucleation sites for asphaltenes to form smaller mesophase domains.[26][27] Even though fine solids reduced the rate of coke formation, with prolonged pyrolysis the coke yield was not altered,[26] except in the case of native clay that already contained 6 % carbonaceous material.[28] The size of the mesophase domains can also be manipulated by solvent dilution. Smaller mesophase domains (and coke particles) are produced by pyrolysis of more diluted bitumen in solvent mixtures,[27] as well as dilution with solvents having a lower molecular mass.[26] As the concentration of the bitumen in the solvent increases or the molecular mass of the solvent increases, coalescence of mesophase domains increase to produce larger domains (and coke particles). The rate of coke formation is accelerated by the formation of larger mesophase domains, because the area to volume ratio decreases. The smaller transfer area per unit volume effectively restricts the availability of hydrogen that is supplied from the continuous phase to prevent free radical addition reactions. Differently put, the probability of in-cage reactions is increased and thereby the probability of coke formation in the more hydrogen deficient mesophase is increased.

The Wiehe-model for open systems,[25] and the modification of the Wiehe-model for closed systems,[12] employ a maximum solubility limit to describe when asphaltene molecules will form a mesophase.

In order to apply the Wiehe-model to the present results, it should be recognized that there are two opposing forces at work. On the one hand there is the solubility limit of the asphaltenes that can be increased or decreased to suppress or promote coke formation. On the other hand coke formation can be suppressed or promoted by the presence or absence of transferable hydrogen to stabilize the pyrolysis products.

Let us first consider the impact of the solubility limit. Light material and asphaltenes compete for solvency in the bitumen.[29] It was found that coke formation was suppressed with an increase in pressure (Figure 3-5) and even more so in a closed system, despite the increase in light material. This was contrary to the expectation that the solubility limit would be decreased to promote coke formation. Further verification was obtained by performing the pyrolysis of bitumen in a paraffinic solvent, n-decane (Table 3-6). The coke yield was 3.3 ± 0.9 %, which is not significantly different from 3.7 ± 0.3 % that obtained with mesitylene (Figure 3-3). The paraffinic nature of the solvent, which should have decreased asphaltene solubility, did not cause an increase in coke yield. The higher light gas yield that was observed was as a result of thermal cracking of the n-decane.

Table 3-6: Effect of a paraffinic solvent on the product yields from pyrolysis of aged Cold Lake bitumen at 400 °C for 1 hour at a 0.25:1 solvent to bitumen mass ratio.[a]

Feed material	Product yield (wt %)					
	liquid		coke		gas	
	x	s	x	s	x	s
n-decane + bitumen	82.4	1.0	3.3	0.9	14.3	0.3

[a] Average (x) and sample standard deviation (s) of three experiments are reported.

One experiment was also performed at conditions that could potentially increase the solubility limit. When aged bitumen was pyrolyzed for 1 h at 400 °C in a mixture with a 90 % mesitylene concentration, the coke yield was 3.3 %. There was no indication of increased suppression of coke formation. It should be noted that a higher mesitylene concentration could potentially also result in an increase in asphaltene aggregation size (increased correlation length),[30] but this does not change the conclusion. Coke yield was not meaningfully affected.

At 20 % solvent concentration, there was little difference in the coke yield obtained with tetralin, mesitylene, naphthalene and n-decane as solvents (Figure

3-3 and Table 3-6). Coke yield was also a weak function of solvent concentration. It is therefore unlikely that the induction period, which is related to the asphaltene solubility limit, can be used to explain observed the coke yields.

The results in this study pointed to hydrogen availability as the dominating factor in controlling coke yield. In the context of the Wiehe-model, it indicated that both physical and chemical factors played a role in coke suppression. Both the size of the mesophase domains (physical factor), as well as the availability of transferable hydrogen (chemical factor) mattered.

3.3.7 Phase behaviour

Phase behaviour is an important aspect to consider in the description of coke suppression. Phase behaviour was not experimentally investigated and the relative contribution of phase behaviour compared to chemical suppression of coke formation was not determined. Some indication of the phase behaviour at the experimental conditions can nevertheless be obtained from other studies.

The phase behaviour of an Athabasca vacuum residue and *n*-decane mixture up to 350 °C and 3 MPa was reported by Saber and Shaw.[31] At 350 °C there was a concentration region from around 5-45 % bitumen where two liquid phases (L1L2) co-existed at pressures above 1.8-2.2 MPa. The pressure above which an L1L2 region was found increased with temperature. A three liquid phase (L1L2L3) region was found in mixtures of Athabasca vacuum residue and *n*-pentane at around 45 % bitumen at less severe conditions.[32] The additional liquid phases were not identified as mesophases.

Based on the aforementioned literature,[31][32] it seems likely that the experiments that were conducted at high solvent concentration and high pressure were in a region where more than one liquid phase was present. Based on the results (Figure 3-3) coking was not promoted by conditions where the probability of multiple liquid phases was highest. It seems that multiple liquid phases affect coking only if one of the phases is a mesophase. The prediction of mesophase formation is more challenging and was not attempted. Mesophase formation

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depends not only on the composition and operating conditions, but also on the mechanical and thermal history of the bitumen.[33]

3.3.8 Hydrogen availability and implications for industrial operation

Coke formation is the result of hydrogen disproportionation. Hydrogen disproportionation is in turn regulated by local hydrogen availability. The importance of hydrogen donation during pyrolysis to suppress coke formation is undisputed. Hydrogen shuttling and dilution also contributed in their own ways. Yet, the observed coke suppression could not be fully explained just in terms of these three solvent-based effects even in the context of the Wiehe-model. Light material, whether added as a solvent, or generated *in situ* during pyrolysis, affected coke formation in other ways too. Observations from this study and literature are:

(a) The coke yield after prolonged pyrolysis is affected only by the H:C ratio of the feed mixture, since stoichiometry determines the hydrogen disproportionation between different phases. Coke cannot be avoided if there is too little hydrogen. The rate also has an effect. For example, during pyrolysis in the temperature range 430-550 °C the gas phase products are more olefinic (lower H:C ratio) at higher temperature and when the gas phase products are removed, the remaining H:C ratio of the remaining product is indirectly increased, which resulted in coke suppression.[34] For semi-batch systems it indicates that for prolonged operation it is best to operate at higher temperatures and lower pressures, so that the pyrolysis gases can be as olefinic as possible. Increased pressure during coking is detrimental.[22] The beneficial effect of pressure that was observed (Figure 3-5) is due to the change in the H:C ratio for incomplete pyrolysis. More generally put, an increase in pressure to keep the H:C ratio of the liquid phase as high as possible is beneficial for visbreaking-type of operation, because hydrogen disproportionation is not complete. Pressure is not beneficial for delayed coking-type of operation, because hydrogen disproportionation is driven to completion.

(b) Co-feeding a solvent, or retaining light pyrolysis materials that act as solvents, suppresses coke formation. The solvent modifies the physical properties of the

mixture and is effective at concentrations as low as 10 % (Figure 3-3), the lowest concentration tested in the work. The solvent suppresses coke formation, even when the solvent itself does not have good hydrogen transfer properties. The solvent does not have to be hydrogen-rich to do so. For example, in this study the main solvents employed had lower H:C ratios than bitumen: bitumen (1.4) > mesitylene (1.3) > tetralin (1.2) > naphthalene (0.8).

(c) At high solvent to bitumen ratio, the nature of the solvent determines whether hydrogen donation becomes the dominant mechanism for coke suppression or not. Hydrogen donor solvents can reduce coke formation significantly, by increasing the H:C ratio of the bitumen and decreasing the H:C ratio of the solvent. In order to re-use the solvent in a continuous process, the solvent must be regenerated by hydrogen addition. This is typical of the design of direct liquefaction processes.[4] The beneficial effect of hydrogen donor solvents is well-known.

(d) The most significant finding of the present study was to highlight the role of dissolved light pyrolysis gases as coke suppressants. At the standard pyrolysis conditions evaluated, 400 °C and 1 h, the lowest coke yield and highest liquid yield was obtained by pyrolysis in a closed system (Table 3-5 and Figure 3-5). Dissolved light gases contribute to the stabilization of free radicals. This led us to question the commonly held assumption that the production of light gases during pyrolysis is irreversible.

A reaction network that illustrates the action of light materials in coke suppression is shown in Figure 3-7, which includes the bond dissociation energy (BDE) of the reactions involved.[15] In the reaction network the light material is represented by methane (CH_4) and ethane (C_2H_6), and a phenyl radical ($\bullet C_5H_6$) represents the aromatic free radicals that are produced by pyrolysis of the bitumen. The reasoning can be explained in the following way. The pyrolysis study by Khorasheh and Gray[17] demonstrated that hydrogen can be transferred from benzene to hexadecane cracking products, despite the higher BDE of aromatic C–H bonds than that of aliphatic C–H bonds. The benzene in their study was present at 95-99 % concentration. It highlighted the importance of reaction probability

(concentration), not just probability of reaction (rate constant). Thus, as the concentration of light material is increased, the probability is increased that the light material can be involved in reactions to stabilize free radicals that were formed by pyrolysis. Even though the probability of abstracting hydrogen (•H) or methyl (•CH$_3$) radicals from neutral compounds decreases with increasing BDE, the probability of such an event increases with increasing concentration of the species. Of particular interest is that it is energetically equally demanding to perform hydrogen transfer from toluene as methyl transfer from ethane (Figure 3-7).
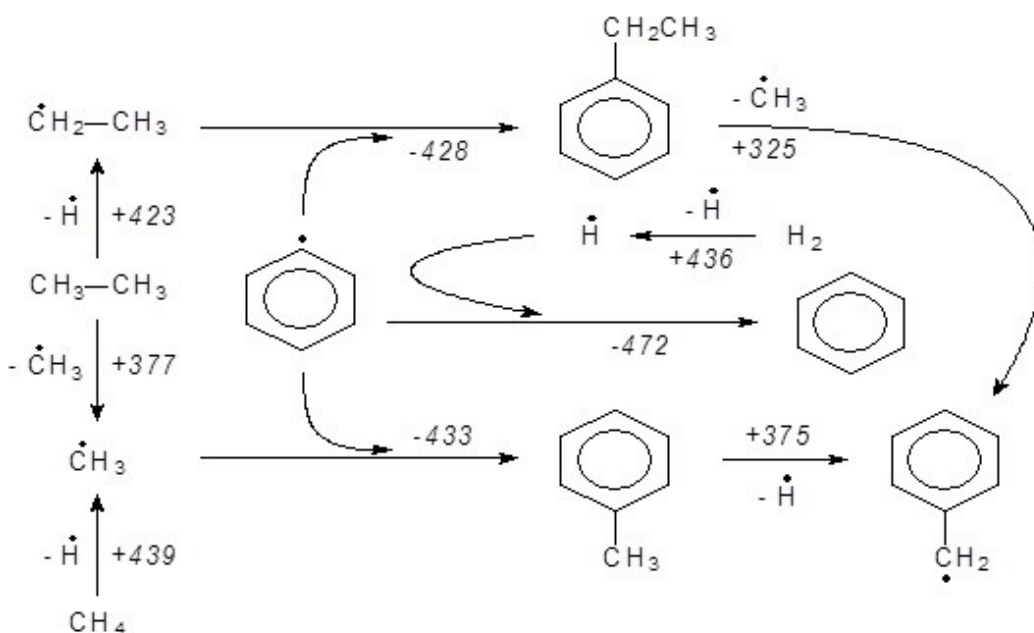
Figure 3-7: Reaction network to illustrate the potential contribution of light gas to suppress coke formation during pyrolysis. The light gases are represented by methane and ethane. Pyrolysed aromatic products are represented by the phenyl radical. Homolytic bond dissociation energies (kJ·mol^{-1}) at 25 °C are provided to give an indication of bond strength. Although reactions are represented as mono-directional, all reactions are reversible.[11]

The present work has some practical implications for industrial operation of visbreaking processes. First, it has shown that it is possible to suppress coking during visbreaking by co-feeding light hydrocarbons. The light hydrocarbons can be in the C$_4$ and lighter range. Second, it indicated that there is benefit to conduct visbreaking at higher pressure, because it will increase the concentration of lighter

pyrolysis products in the liquid phase to serve the same purpose as an added solvent. Third, it can be inferred from the present work that it is best to operate with the least vapor volume fraction practical. Only light material dissolved in the liquid phase will help to suppress coke formation. The concentrations of light material in the vapor and liquid phases are determined by VLE, which is not directly affected by the volumetric ratio of the phases, but the amount of material in the vapor phase determines how much material is subject to potential over-cracking, with no benefit to the process.

3.4. Conclusions

Coke suppression during mild pyrolysis of oil sands bitumen was studied experimentally. Two approaches were followed. The first was to dilute the bitumen to various degrees with solvents that had different hydrogen transfer properties, namely, hydrogen donation (tetralin), hydrogen shuttling (mesitylene) and a solvent with poor hydrogen transfer properties (naphthalene). The second was to employ pressure and the method of operation (batch versus semi-batch) to manipulate the light product concentration in the undiluted bitumen. Based on the results, the following observations were made:

(a) Hydrogen donation was important, but the contribution of hydrogen donation to suppress coke formation compared to the other solvent effects became meaningful only at a solvent concentration of 50 % and higher.

(b) Hydrogen shuttling was important and the coke yield from the pyrolysis of bitumen in a solvent active for hydrogen shuttling was consistently lower than for a solvent with poor hydrogen transfer ability.

(c) The presence of a solvent was important, with the coke yield being halved at 20 % solvent concentration, irrespective of the hydrogen transfer capabilities of the solvent. In fact, even at 1:10 solvent to bitumen ratio was coke suppression significant. This is likely a physical effect, with transport in the mixture being improved, but the explanation of the effect was not confirmed.

(d) The contribution of increasing dilution to coke suppression was minor, even though coke yield decreased with increase in solvent concentration for all solvents studied.

(e) Lighter products produced during bitumen pyrolysis also served as a solvent and the coke yield could be manipulated through pressure in a semi-batch pyrolysis. Increasing pressure caused more of the lighter products to remain in the liquid phase, which decreased the formation of coke.

(f) The benefits of operating at increased pressure described in (e) is limited to mild and incomplete pyrolysis, as is found in visbreaking processes. An increase in operating pressure is not likely to benefit processes that involve more extensive pyrolysis, as is applied during delayed coking.

(g) The light gas yield was not primarily determined by over-cracking of the light products exposed to pyrolysis conditions for longer. In an open system, where light products could leave the system, the liquid yield remained fairly constant due to a trade-off between coke suppression and over-cracking to increase the light gases. In a closed system this was not the case and the liquid yield increased. It was postulated that this is related to the H:C ratio of the total reacting mixture.

(h) The production of light gases could partly be explained by the need to produce material that is capable of hydrogen transfer to moderate free radical propagation. In the absence of such material, intramolecular free radical propagation by β-scission can continue uninterrupted, since there are insufficient molecules to transfer hydrogen to terminate or transfer the propagation process.

(i) The use of a paraffinic solvent and the increased production of light paraffinic products did not result in increased coke formation. This suggested that the solubility limit in the Wiehe-model, which determines when a separate liquid domain is formed and leads to coke formation, was not an important factor in this study. The results pointed to hydrogen availability as the dominating factor in controlling coke yield. Interpreted in terms of the Wiehe-model, it indicated that

the size of the liquid domains and the availability of transferable hydrogen mainly determined the coke yield.

(j) The results indicated that light gas formation during pyrolysis should not be considered as an irreversible reaction product. The light gases continue to participate in the reaction network, likely as hydrogen and methyl transfer agents, to moderate the pyrolysis process and suppress coke formation.

(k) Ways to suppress coke and improve liquid yield during visbreaking were suggested. First, by co-feeding light hydrocarbons (e.g. C_4 and lighter) coke formation can be suppressed. Second, it is beneficial to operate mild pyrolysis at higher pressure to increase the concentration of light products in the liquid phase. Third, it is preferable to limit the volume fraction of vapor-space.

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Chapter - 4 Solvent Deasphalting and Visbreaking Sequence

Abstract

Solvent deasphalting (SDA) followed by visbreaking enables higher visbreaking conversion before the onset of coking. This processing sequence is industrially practiced. It was proposed that at milder visbreaking conditions there might be benefit to reverse the process steps, so that transferable hydrogen and methyl groups in the asphaltenes fraction can be incorporated into the liquid product before SDA. At a visbreaking temperature of 380 °C no meaningful benefit could be demonstrated for visbreaking followed by SDA compared to SDA followed by visbreaking. Yet, some observations suggested that the premise of transferring hydrogen from the asphaltenes to enrich the aliphatic hydrogen content of the liquid product should not be rejected. The refractive index, micro carbon residue yield and fraction of aliphatic hydrogen all indicated that a slightly higher aliphatic content was obtained when low temperature visbreaking was followed by SDA.

Key Words: Solvent Deasphalting, Visbreaking, asphaltenes.

4.1 Introduction

One of biggest challenges in the production of bitumen from the Canadian oilsands is the lack of bitumen fluidity (*See Chapter-2, section 2.2.2 Viscosity*). Depending on the origin of the oilsands derived bitumen, its viscosity is in the range of 10^2-10^4 Pa·s at 20 °C and its density is in the range 6-12 °API (990-1030 kg·m^{-3}). Once the bitumen is recovered, the poor fluidity remains a problem. In order to transport the bitumen by pipeline to market, the viscosity and density must be reduced to 350 cSt and 940 kg·m^{-3} (19 °API) at minimum pipeline temperature (7.5 °C).[1]

Industrially there are several ways in which bitumen viscosity and density are decreased. The process of interest in this study is the use of solvent deasphalting (SDA) in combination with visbreaking, because it also has potential for application on smaller scale in field upgrader units.

The sequence of process steps that is industrially practiced is SDA followed by visbreaking (Figure 4-1). This is a logical sequence, because conversion in the visbreaker is limited by coke formation.[2] The induction period before the onset of coke formation depends on the asphaltene content.[3] Removal of the asphaltenes by SDA before visbreaking enables higher conversion of the deasphalted oil (DAO) during visbreaking and can therefore improve viscosity reduction.
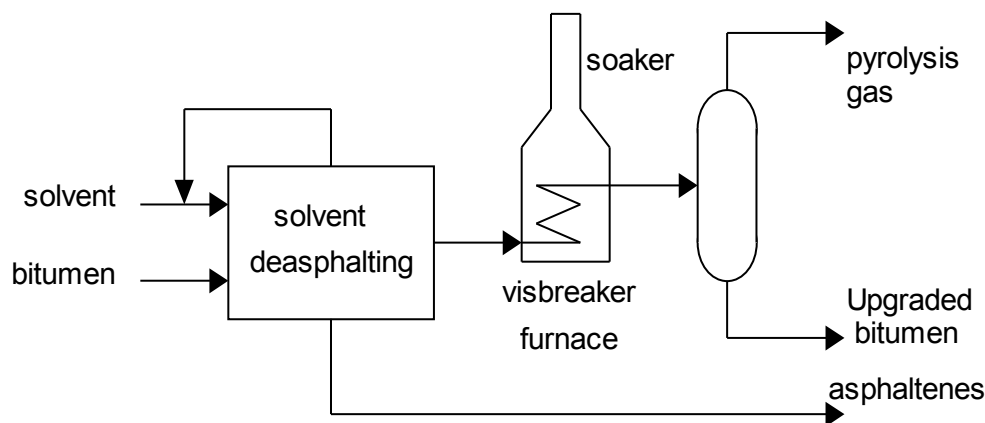
Figure 4-1: Industrially practised processing sequence for upgrading.[4]

So, why is this sequence the topic of investigation? First, it was found that the inverse relationship between temperature and time for viscosity reduction by visbreaking did not hold true at lower temperature visbreaking of oilsands derived bitumen.[5] Second, it was found that coke formation was influenced by both physical and chemical effects (*See Chapter -3, 3.3.2 Effect of solvent dilution on coke yield*). The presence of an aromatic solvent, irrespective of its hydrogen transfer properties, suppressed coking (physical effect).[6] The overall availability of transferable hydrogen and methyl-groups, and not just donor-hydrogen, also suppressed coking (chemical effect) even though coking was suppressed more when the hydrogen and/or methyl groups could be donated permanently.

It was argued that if the asphaltenes fraction from bitumen possesses hydrogen and methyl groups that can be donated; there might be benefit in harvesting this hydrogen-rich material before rejecting the asphaltenes by SDA. Furthermore, if the visbreaking conditions were less severe, it may well be possible to significantly decrease the viscosity of the total bitumen before coke formation limits conversion.

The most advantageous sequence of SDA and visbreaking was not clear for visbreaking of oilsands derived bitumen at temperatures below 400 °C. The objective of this study was to evaluate the impact of this sequence experimentally.

4.2 Experimental

4.2.1 Materials

The experimental investigation was performed with Canadian oilsands derived bitumen from the Cold Lake region, which was supplied through the sample bank of the Institute for Oil Sands Innovation (IOSI) at the University of Alberta. The feed was characterized (Table 4-1).

Table 4-1: Properties of Cold Lake Bitumen

Property	Cold Lake Bitumen
Density at 30 °C ($kg \cdot m^{-3}$)	1013.2 ± 1.0
Refractive index at 30 °C	1.5788 ± 0.0032
Viscosity at 60 °C (Pa·s)	9.55 ± 0.15
Asphaltene content (wt %)	18.6 ± 1.2
Micro carbon residue (wt %)	17.8 ± 0.5
Elemental analysis (wt %)	
C	82.9 ± 0.1
H	10.1 ± 0.01
N	0.6 ± 0.002
S	4.9 ± 0.03
O (by difference)	1.5

4.2.2 Equipment and procedure

There were two steps in the experimental procedure. Comparative analysis of Cold Lake bitumen was done when it was subjected to solvent deashphalting followed by visbreaking and vice versa. All experiments were performed in a batch reactor placed in a fluized sand bath. The entire setup was constructed using Swagelok SS 316 tubing and fittings. A thermocouple was fitted inside the micro batch reactor to accurately measure the temperature of the reactants. The detailed experimental apparatus was the same as described in Chapter-3. A typical experiment used 8-10 g of bitumen. Reactors were purged three times with nitrogen before pressurizing it to 4 MPa. This was repeated three times, material balance calculations made and standard deviations reported. The heat up time was 5 minutes and the cool down period was 4 minutes.

The products after quenching were extracted with methylene chloride and filtered through a 0.22 μm pre-weighted filter paper. 98% of the methylene chloride was stripped out by rotary evaporation at 45 °C and 850 mbar for 20 minutes. The products were dried overnight at 50 °C to constant mass. Material balances ensured complete removal of methylene chloride. This was followed by a solvent deasphalting of the thermally treated oil. The asphaltene content was used was found using the ASTM recommended procedure (ASTM D6560-12).[7] A ratio of 40:1 of *n*-pentane to feed was used, the mixture subjected to magnetic stirring for 24 hours and vacuum filtered through a pre-weighted 0.22 μm filter paper. Pentane was rotary evaporated and the now deasphalted oil was dried for 24 hours to constant mass. Mass balances ensured complete pentane removal from deasphalted oil. The reverse was done by deasphalting Cold Lake bitumen first followed by thermal treatment before both sets of products were analysed and compared.

4.2.3 Analyses

The following analytical instruments were employed to characterize the products:

(a) **Density:** Measurements were made using an Anton Paar DMA 4500M. The instrument was calibrated with distilled water and could be temperature controlled to an accuracy of 0.01°C. Density measurements were measured to 0.00001 g/cm3.

(b) **Refractive index**: Mesurements were made using an Anton Paar Abbemat 200 and determined relative to air using the sodium D-line (589 nm). The refractometer was factory calibrated with official standards from the national metrology institute of Germany and the refractive index results are accurate to ±0.0001 nD. The temperature was controlled at to an accuracy of ± 0.05 °C and all measurements were made at 30°C.

(c) **Viscosity:** Anton Paar RheolabQC with C-CC17/QC-LTC measuring cup. The RheolabQC was calibrated with a Newtonian viscosity standard specimen (blended hydrocarbons) whose kinematic viscosity was measured using a capillary viscosimeter of the Ubbelohde type, which was traceable to the national standard of the viscosity.

(d) **Micro carbon residue (MCR):** The micro carbon residual percentage was calculated from analysis using a Mettler Toledo thermogravimetric analyzer (TGA/DSC). This instrument was equipped with the ultra-micro balance cell and DTA sensor. The instrument was capable of measuring simultaneous heat flow and weight change of samples. The micro carbon residual percentage analysis was carried out with nitrogen as carrier gas. All micro carbon residue measurements were determined in accordance with the standard test method ASTM D4530.[8]

(e) **Elemental analysis:** CHNOS analysis was performed on a thermo Scientific Flash 2000 CHNS-O Organic Elemental analyzer.

 (f) **Proton nuclear magnetic resonance (^{1}H NMR):** The [1]H Nuclear Magnetic Resonance (NMR) spectra were obtained using a Nanalysis 60 MHz NMReady-60 spectrometer. The instrument was pre calibrated with D-chloroform. 0.2g of oil was dissolved in 1 ml of D-chloroform, placed in 5 mm NMR tubes and analysed using the following parameters: spectral width 14 ppm; digital resolution: 0.03 H; number of scans per sample: 16; active scan time: 4.7 seconds. The average scan time was 14.7 seconds and 4000 points were recorded per scan.

4.3 Results and Discussion

4.3.1 Material balance.

Visbreaking and SDA were performed in the same way, but in different sequence for the two sets of experiments. The material balances are reported (Table 4-2). The yields are quite similar, with SDA-Visbreaking resulting in a slightly higher liquid yield than Visbreaking-SDA. The coke found during Visbreaking-SDA is mineral matter with associated bitumen and not polyaromatic coke.[5] When SDA is performed first the mineral matter is removed with the asphaltenes. Based on the material balance, there is no benefit to perform visbreaking on the total bitumen. In fact, visbreaking of the DAO resulted in a marginally higher liquid yield, 80.1 ± 0.3 versus 79.2 ± 0.4, compared to visbreaking of the bitumen.

Table 4-2: Material Balances for Different Process Sequences with Visbreaking Conducted at 380 °C for 0 minutes

Products	Product yield (wt %)	
	SDA-Visbreaking	**Visbreaking-SDA**
Gases	0.7 ± 0.3	1.1 ± 0.5
Liquids	80.1 ± 0.3	79.2 ± 0.4
Solids		
asphaltenes before	18.6 ± 1.2	0
asphaltenes after	0.6 ± 0.03 [a]	18.3 ± 1.2
coke	0	1.4 ± 0.04

[a] *SDA was repeated on the visbroken product from the SDA-Visbreaking sequence to determine whether additional asphaltenes were formed during visbreaking.*

4.3.2 Liquid product characterization

The liquid products from SDA followed by visbreaking and visbreaking followed by SDA were characterized in terms of density, refractive index, viscosity, micro carbon residue and elemental composition (Table 4-3). As with the material balance, the processing sequence did not seem to affect the product properties in a meaningful way.

In the introduction it was postulated that it might be beneficial to retain the asphaltenes for visbreaking (VB), because the asphaltenes can also be a source of transferable hydrogen and methyl-groups. The following observations were made:

(a) It was found that the refractive index of the liquid product from visbreaking followed by SDA was slightly lower than that of the liquid from SDA followed by visbreaking. When the refractive index was measured at temperatures in the range 20-40 °C (Figure 4-2), this difference was consistently observed. A lower refractive index is indicative of a product with more aliphatic character, i.e. both paraffinic and naphthenic character.[9]

(b) The MCR value was consistent with the refractive index, with the liquid product from SDA followed by visbreaking being more prone to form coke. Furthermore, when the MCR content of the deasphalted oil before visbreaking was measured, it was 21.8 ± 4.1 wt%. It suggested that SDA did not reduce the coking tendency of the liquid, because the MCR of the bitumen was 17.8 ± 0.5 wt %.

Table 4-3: Characterization of Liquid Products Obtained by the Different Process Sequences

Property	SDA-Visbreaking	Visbreaking-SDA
Density at 30 °C (kg·m^{-3})	984.1 ± 1.3	984.0 ± 1.9
Refractive index at 30 °C	1.5439 ± 0.0003	1.5429 ± 0.0006
Viscosity at 60 °C (Pa·s)	0.75 ± 0.13	0.89 ± 0.10
MCR (wt %)	10 [a]	6 [a]
Elemental analysis (wt %)		
C	84.3 ± 0.05	84.2 ± 0.08
H	10.7 ± 0.01	10.7 ± 0.01
N	0.4 ± 0.06	0.4 ± 0.08
S	4.0 ± 0.02	4.1 ± 0.008
O (by difference)	0.6	0.6

[a] *Based on a single analysis only.*
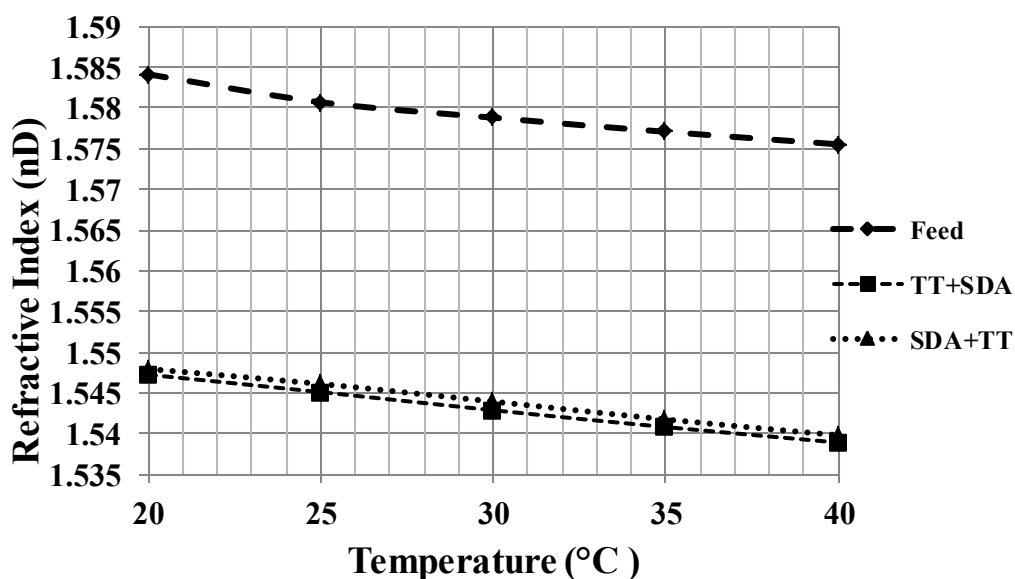
Figure 4-2: Refractive index variation from 20-40°C for a)--◊-- bitumen feed b) (--■--) Thermal Treatment+ SDA and c) (…▲…) SDA + Thermal Treatment

Based just on the results presented here, there was a risk of over-interpreting the data. It was necessary to look at a more direct measurement of the nature of the hydrogen in order to verify the inferences.

4.3.3 Hydrogen disproportionation

The bitumen feed and the liquid products obtained by the two different process sequences of SDA and visbreaking, were analyzed by ^{1}H NMR (Table 4-4). The cut-off between aliphatic and aromatic hydrogen was taken as $\delta = 6.3$ ppm, with lower shift-values being aliphatic and higher shift values being aromatic. Olefinic hydrogen overlaps the cutoff, as does hydrogen attached to some heteroatom functional groups.[10] It should be pointed out that the aliphatic versus aromatic hydrogen distribution is a poor predictor of the amount of aliphatic versus aromatic carbon. However, it is a direct measure of the nature of the hydrogen distribution, which was of interest to our study.

The observed changes in the aliphatic hydrogen content between the bitumen feed and upgraded products were minor. In isolation the changes were not statistically meaningful, but it supported the observation that the liquid product from visbreaking-SDA contained more potentially transferable (aliphatic) hydrogen than the liquid product from SDA-visbreaking.

Table 4-4: ^{1}H NMR Characterization of Liquids

Liquid sample	Aliphatic H-content (wt %)
Cold Lake bitumen feed	94.5 ± 0.6
SDA-Visbreaking liquid	92.8 ± 0.9
Visbreaking-SDA liquid	93.9 ± 0.6

4.4 Conclusions

The present study investigated the potential advantage of retaining asphaltenes in the liquid feed to low temperature visbreaking, in order make use of the transferable hydrogen in the asphaltenes. At the selected visbreaking temperature, 380 °C, no meaningful benefit could be demonstrated for visbreaking followed by SDA over SDA followed by visbreaking.

Although the results cannot be claimed to represent statistically meaningful differences, some observations suggested that the initial premise of transferring hydrogen from the asphaltenes to enrich the aliphatic hydrogen content of the liquid product, should not be rejected:

(a)   The refractive index of liquids from visbreaking-SDA indicated that it was more aliphatic in character.

(b)   The MCR of liquids from visbreaking-SDA indicated that it was less prone to form coke, i.e. more aliphatic.

(c)   The liquids from visbreaking-SDA had a higher percentage aliphatic hydrogen than that of SDA-visbreaking based on ^{1}H NMR.

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Chapter - 5 Coke, Viscosity and Asphaltene Regimes during bitumen pyrolysis

Abstract

The influence of pyrolysis time on bitumen properties was investigated in this chapter. Literature describes an induction period before coking. The reason for this investigation was to answer the question: Was the observed coke suppression in the previous chapters an extension of the induction period? Were we just delaying the inevitable or were we causing a meaningful suppression? From our previous studies involving coke suppression, it seemed like both the size of the mesophase domains as well as the availability of transferable hydrogen played a role in coking. The initial intention was to understand if there was an extension in the induction period. When time was varied a series of regimes were observed during neat bitumen pyrolysis that made us probe neat bitumen pyrolysis further. The effect of time on resultant physical properties and asphaltene content of the pyrolysis liquids was looked at closely. The study can be applied to not just visbreaking but delayed coking as well.

Keywords: Bitumen pyrolysis, coke, induction period, viscosity, asphatlene content, mesophase.

5.1 Introduction

The Alberta oil sands have always been associated with the terms high viscosity, low hydrogen/carbon ratio, low fluidity. As part of a study, the volume of condensate required to dilute bitumen to make it more fluid is expected to more than double to 750,000 barrels per day by 2020.[1] Opportunity to improve this current way of processing by reducing the volume of condensate being used today is evident. Apart from dilution, thermal treatment has been used to reduce viscosity.

Visbreaking is a process technology that combines time, pressure and temperature to reduce viscosity. These units, more common in smaller refineries in Europe than North America have the prime goal of having a short enough residence time at a specified temperature where there is no significant coke production. Depending on the type and severity of operation, conversion is typically the order of 6-12% and temperatures and pressures are around 430 °C to 460 °C and around 1 MPa. [2][3][4]

Thermal conversion at these temperatures point to free radical chemistry running reaction mechanisms.[5] Once free radicals are formed, the probability of free radical addition exists, because of the high reactivity of these species. This causes addition products with higher molecular weight structures to be formed. This defies the purpose of the operation. In order to operate at maximum efficiency one needs to minimize coking so that liquid yields are improved.[6]

Literature describes an induction period before coke formation starts taking place.[7] This has been described in detail in Chapter-2, (*2.3.1 Mechanism of Coke formation*). The key elements of the model are as follows:

a) The length of this induction period is related to the solubility of the asphaltenes in the bitumen matrix. As long as they remain soluble and do not form a separate liquid domain, coke formation is suppressed.

b) At the end of the induction period, the asphaltene concentration reaches a maximum value. At this point, the asphaltene concentration starts to decrease

once coke starts to form. This suggests some relationship between the asphaltenes and coke make.

c) Asphaltenes are a reactive and are converted into more carbon rich compounds also called asphaltene cores. Once these cores reach the solubility limit, separate ordered liquid phase domains called mesophase is formed.

d) With local hydrogen availability being scarce, free radical conversion continues to produce higher carbon rich material until coke is formed.

In chapter-3 the investigation probed how solvents can moderate pyrolysis reactions by hydrogen transfer and cause suppression of coke by capping free radicals. The previous investigation however employed one specific reaction time. This did not take into account the induction period of the feed. This directionally pointed to ask the question: a) Were we operating within the induction period? b) Was the observed coke suppression just an extension of the induction period or was it a true suppression because of hydrogen donation, shuttling and transfer? In order to investigate this, we decided to vary the reaction time when bitumen was pyrolysed in batch reactors.

During the course of the study it was observed that there were a series of regimes during neat bitumen pyrolysis that needed to be understood first before analyzing data with solvent addition. It was desired to understand coke suppression but also the effect of time on product quality as determined by viscosity, hydrogen/carbon (H/C) ratio, asphaltene content and Micro carbon residue (MCR).

Interesting observations were made about the effect of conversion time on liquid viscosity at low temperatures. The influence of time on viscosity was studied by Wang et al.[8] Reactions were performed in a semi batch reactor at lower temperatures (340 °C to 400 °C). Whatever the temperature investigated, there seemed to be an initial drop in viscosity of bitumen followed by an increase. Our experiments were performed in batch mode to a) repeat the time- viscosity experiments and b) understand what properties were actually causing this change.

5.2Experimental

5.2.1 Materials

The experimental investigation was performed with Canadian Cold Lake bitumen and the feed was characterized (Table 4-1). Even though this study dwelled more on neat bitumen pyrolysis as a function of reaction time, liquefied *n*-butane was used to further understand the solvent effect on induction time. Liquefied butane (99.0%) was provided by Praxair for light gas studies and nitrogen (99.999%) used for purging reactors was also supplied by Praxair.

5.2.2 Equipment and Procedure

All neat bitumen pyrolysis experiments were performed in micro batch reactors. The reactors were placed in a fluidized sand bath. The experimental setup and procedure was exactly the same as in Chapter-3 (*see 3.2.2 Equipment and Procedure (Figure 3-1))*.

The experimental procedure where bitumen was diluted with *n*-butane before pyrolysis was slightly different even though the reactor setup was the same. Similar stainless steel batch reactors were used. In a typical experiment about 8 grams of bitumen was used. The entire setup was constructed using Swagelok SS 316 tubing and fittings. The reactor threads were coated with vacuum grease (Vac Goop provided by Swagelok), after the reactor was charged with Cold Lake bitumen. The reactor was then purged three times with nitrogen to remove any air present. It was desired to add *n*-butane in the liquid phase based on results from Chapter-3 (*3.3.8 Hydrogen availability and implications for industrial operation)*. Since butane boils at -1 °C the temperature to which the reactor needed to be cooled was below this. In our case -17 °C to give a sufficient temperature differential so as to a) have enough time to charge the reactor and b) to allow butane to continue to remain in the liquid phase. The reactor was connected to the butane cylinder. The valve of the butane cylinder was opened followed by the reactor valve (V01). Both valves were shut after a predetermined amount of time. The amount of butane added to the reactor was gravimetrically measured. This

was done using a Mettler Toledo ML 3002 balance which had a 3200 capacity with 0.01g readability In all experiments the amount of butane added was 12.11 ± 1.19 wt%. The reactor setup was allowed to warm up to room temperature. Once the setup was at 25 °C, the reactor was connected to the nitrogen cylinder and pressurized to 4 MPa. The 4 MPa pressure difference between the nitrogen line and the batch reactor ensured that only the nitrogen gas entered the reactor. This was checked by measuring the mass of nitrogen by weight and by ideal gas law calculations for the volume of reactor and the final weight of the total reactor gravimetrically.

Once the temperature inside the reactor increased to 25 °C, the reactor was placed in the fluidized sand bath. The heat up time for the reactants to reach 400 °C was 6 minutes and the cool down period was 6 minutes. This was not counted as part of the duration of reaction time. After reaction, the micro reactor was vented and gases were collected in a gas bag. The procedure for dealing with the dissolved butane is described below. Liquids produced were extracted with methylene chloride and filtered through a 0.22 μm filter paper to obtain methylene chloride insoluble solids (coke) and maltenes. Pressurized reactors were weighed before and after reaction as well as after depressurization. This was the standard method to determine both liquid and gas yield gravimetrically.

Material balances were challenging because it was noticed only later that at least 6 hours were required for dissolved butane to completely bubble out of the bitumen matrix. Since the coke and asphaltenes would not contain any butane and were found on a bitumen basis, material balances were reported as coke, asphaltene content and (maltenes + gas), where the maltenes + gas fraction was found by difference. One could determine the solubility of butane in bitumen at room temperature in literature used during the vapor extraction (VAPEX) process and find the mass of liquids by quantifying butane solubility. But this process does not take place at elevated temperatures like 400 °C and thus does not account for butane cracking also taking place during pyrolysis. Hence it was decided to

report mass balances in this manner. The asphaltene content in the Cold Lake bitumen feed that was used was determined in accordance with the standard test method. Precipitated asphaltenes were dried overnight in a vacuum oven at 75 °C.

The liquids which contained 2-4 % methylene chloride and residual butane were devolatilized for 12 hours at 50 °C. This allowed for all methylene chloride to be completely removed just like methylene chloride was removed in every neat bitumen batch study. Viscosity analysis, refractive index and ^{1}H-NMR analysis gave true values of undiluted pyrolysis liquids.

5.2.3 Analysis

The pyrolysis gas was analysed by gas chromatography (GC) on an Agilent 7890A equipped with a flame ionization detector (FID) and a thermal conductivity detector (TCD). Separation was performed on a HapSep R column 2.44 x 0.003m (8 ft x 1/8 inch). Carrier gas used for analysis was helium with a constant flow of 25ml/min. The injector temperature was set at 200 °C. The temperature program used was injection of sample at 70 °C and hold for 7 minutes, then ramping at 10 °C/min to 250 °C and holding for 2 minutes, followed by ramping at 30 °C/min to 300 °C and holding for 8 minutes.

Viscosity analysis of bitumen feed and bitumen diluted with solvent was performed using an Anton Paar RheolabQC viscometer. The RheolabQC was initially factory calibrated with a Newtonian viscosity standard specimen (blended hydrocarbons) whose kinematic viscosity was measured using a capillary viscosimeter of the Ubbelohde type, which was traceable to the national standard of the viscosity. The sample measuring cup used was C-CC17/QC-LTC and an average sample of 4 grams was used during analysis. The shear rate used for all viscosity measurements was 10 s^{-1}.

Refractive Index (RI) measurements were performed using an Anton Paar refractometer Abbemat 200. RI measurements were determined relative to air

using the sodium D-line (589 nm). The refractometer was factory calibrated with official standards from the national metrology institute of Germany and the refractive index results are measured to ±0.0001 nD. In our experiments, all measurements were made at 30°C. The instrument had been able to control temperature values to an accuracy of ± 0.05 °C.

CHNOS analysis was performed on a thermo Scientific Flash 2000 CHNS-O Organic Elemental analyzer.

In order to visually distinguish the coke formed at different reaction times, images of coke and asphaltenes were taken using a Carl Zeiss Discovery V.20 stereomicroscope. This lens had a zoom range of 20:1, was capable of a magnification of 345X. The maximum resolution of the camera was 1000 {line pairs (LP)}/mm. A resolution of 10 lines per millimeter implies 5 dark lines alternating with 5 light lines or 5 line pairs per millimeter (5LP/mm). Images were taken using reflected light at 20X and 25X magnifications. Analysis of the mesophase was done using a Zeiss Axio observer inverted microscope. Cross polarized light was used to capture images of the mesophase. The lens used was an EC EPIPLAN 5x/ 0, HD 422030-9960 lens.

The micro carbon residue (MCR) values were determined by thermogravimetric analysis (TGA), using a Mettler Toledo Model TGA/DSC1 LF FRS2MX5. This instrument was equipped with the ultra-micro balance cell and DTA sensor. The resolution of the balance was 0.1/1 μg. The instrument was capable of measuring simultaneous heat flow and weight change of samples. The micro carbon residual percentage analysis was carried out with nitrogen as carrier gas. All micro carbon residue measurements were determined in accordance with the standard test method ASTM D4530.

The ^{1}H Nuclear Magnetic Resonance (NMR) spectra were obtained using a Nanalysis 60 MHz NMReady-60 spectrometer. The instrument was pre calibrated

with deuterated chloroform (D-chloroform). 0.2g of oil was dissolved in 1 ml of D-chloroform, placed in 5 mm NMR tubes and analysed using the following parameters: spectral range 14 ppm; digital resolution: 0.03 H; number of scans per sample: 16; active scan time: 4.7 seconds. The average scan time was 14.7 seconds and 4000 points were recorded per scan. All spectra obtained were analysed using Mnova NMR software. Exported data was baseline corrected using a multipoint baseline correction method. All points were picked using this method to baseline correct the spectrum obtained. Peak integration was performed on the baseline corrected spectrum using aliphatic and aromatic hydrogen ranges. The spectral widths were determined from literature and integration was performed over that specific range. The ranges are mentioned in section *5.3.4 ^{1H-NMR} product analysis*

5.3 Results and Discussion

5.3.1 The Induction Period of Coke Formation

Based on the temperature, pressure and time exposed to the atmosphere, the characteristics (viscosity, refractive index, micro carbon residue and asphaltene content) of the feed change notably. This was clearly seen in Chapter-3 when we compared the asphaltene content, MCR and carbon, hydrogen content of the aged and fresh bitumen (Table 3-1). It was therefore important that the feed be characterized (Table 4-1) and the induction period of coke formation for this feed be determined (Figure 5-2). Different bitumen feeds have different induction periods.

When bitumen is pyrolysed, coke, gas and pyrolysis liquids are products formed in different proportions as a function of pyrolysis time. When batch reactor pyrolysis of neat bitumen was done, four regimes were observed during which bitumen properties changed. The induction period of the Cold Lake bitumen sample we used was found to be 80 minutes (Figure 5-1). The prevailing view about the formation of coke was that coke was formed by a series of polymerization and condensation steps from the lightest to the heaviest

fractions.[9][10] During pyrolysis, there is cracking leads to formation of free radicals. As explained in *section 2.3 Thermal Cracking,* this leads to hydrogen disproportionation and radical addition that causes formation of heavier products. However, later studies showed that the aromatic fragments initially form lower molecular weight and more aromatic compounds while remaining soluble in the matrix.[7]   This occurs during the induction period. Only when these higher aromatics start to combine to form higher molecular weight species, does a phase separation step (mesophase formation) occur after which coke is formed. The induction period of the bitumen in our study was 80 minutes.
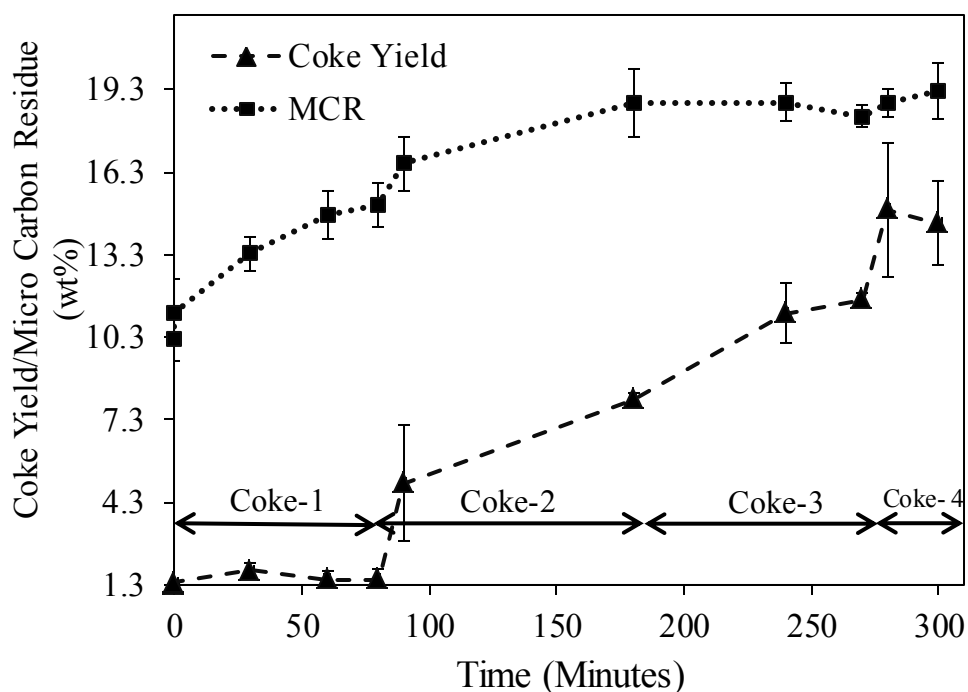
Figure 5-1: Coke yield (-▲-) and Micro Carbon residue (..■..) of thermally treated bitumen at different times

Coke, (defined as methylene chloride insoluble solids) was filtered and analyzed under a stereomicroscope under reflected light. Based on the pyrolysis time, there seemed to be four major classifications of coke structurally:

1) Neat bitumen had 1.3 ± 0.05 percent by weight solids in the matrix. This was consistently seen during the induction period (Time regime: 0-80 minutes). These were brownish platelet type of structures when vacuum filtered. This is seen in figures 5-2A-a and 5-2A-b. The solids (Coke-1) were easily filterable through a 0.22 µm filter paper.

2) After the induction period of coke formation (Time regime: 80-180 minutes) the platelet type of structure continued to be observed but the color of the coke (Coke-2) darkened (Figure 5-2A-c). This darkening may be attributed to the development of carbonaceous residue over the solids. The difference can be seen in comparing Figure 5-2A-a/b to Figure 5-2A-c. Coke-2 was easily filterable through a 0.22 µm filter.

3) For coke-3 (Time regime: 180-270 minutes), filtration of coke was difficult if not impossible because of plugging. If fine coke formed was around the size range of the filter pore size, it would explain why filtration was difficult. In order to visually see the structure of the coke, a droplet of unfiltered pyrolysis liquids was diluted 50 times in methylene chloride to remove any liquids and it was analyzed under the stereomicroscope (Figure 5-2-d).

4) When bitumen was pyrolysed for 270-300 minutes, multinuclear fused aromatic structures were observed. This is described as Coke-4 and is seen in Figure 5-2A-e. Sufficient pyrolysis time allowed for these structures to form. This was easily filterable through a 0.22 µm filter.

| a) Solids (0 mins) Coke-1 | b) 60 minutes Coke-1 (solids) | c) 120 minutes Coke-2 |
| d) 240 minutes Coke-3 | e) 300 minutes Coke-4 | Pentane Asphaltenes |
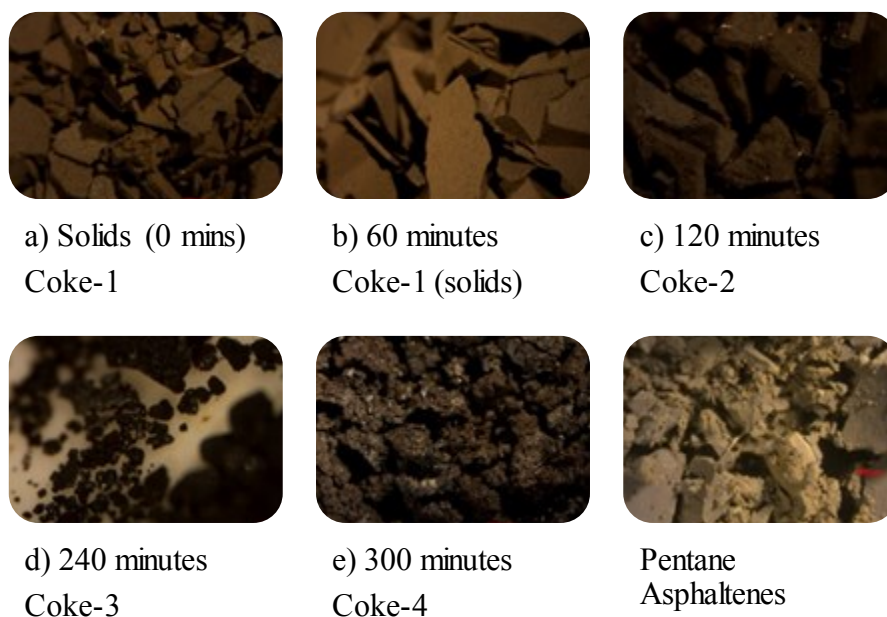
Figure 5-2A: Structural variation of coke based on pyrolysis time. All images were taken with a stereomicroscope at 20X magnification. Except for 3a-d (25X)
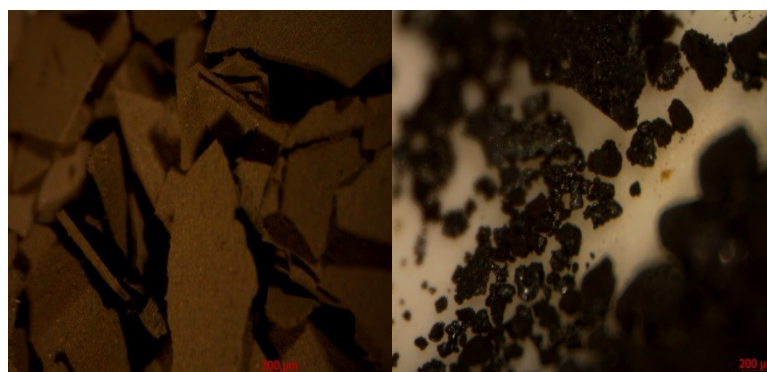
Figure 5-2B: Coke at 60 minutes (solids) versus fine coke (240 minutes)

As bitumen was heated to 400 °C and quenched at different pyrolysis times, an increase in the Micro Carbon Residue (MCR) was continuously observed. Even for a zero minute heat up, the MCR increased from 10.23 ± 0.8 to 11.2 ± 1.18 wt%. There seemed to be a local minimum at extended pyrolysis times but this observation was based on average values and is not statistically significant. Thermal conversion caused hydrogen disproportionation that ultimately caused

coking. Experimental studies from literature have shown that hydrogen disproportionation starts taking place at 200 °C.[11][12] It was certain that the higher temperature (400 °C) coupled with increased pyrolysis time caused hydrogen disproportionation the effect of which is discussed in Section 5.3.3 and Section 5.3.4 . This caused a reduction in the liquid yield (Table 5-1). This was observed in our previous work as well (Chapter -3).

Table 5-1: Product Yields (wt%) during thermal treatment of Cold Lake bitumen at 400 °C at different times

Time (mins)	Coke		Liquids		Gas	
	x	s	x	s	x	s
Feed	1.3	0.05	98.7	0.4	-	-
0ᵃ	1.41	0.03	97.56	0.5	1.02	0.48
30	1.84	0.28	97.46	0.36	0.69	0.3
60	1.51	0.28	94.1	0.29	4.13	0.22
80	1.51	0.35	93.2	0.65	5.29	0.35
90	4.97	2.11	88.8	1.7	3.37	2.39
180	8.02	0.27	84.2	1.3	7.7	1.07
240	11.16	1.1	82.2	1.04	6.6	0.2
270	11.67	0.23	81.46	1.87	6.86	1.65
280	14.93	2.419	78	3	7.1	3.44
300	14.43	1.51	74.77	3.7	10.8	4

ᵃ – Refers to a zero minute heat up from room temperature to 400 °C and quenching.
X = average value, s = sample standard deviation

Wiehe observed an asphaltene maximum just before the onset of coking.[7] During the induction period the wt% of asphaltenes start increasing. At the end of the induction period the asphaltene concentration started decreasing since the asphaltenes are not soluble in the bitumen matrix anymore and turn to coke.[7] It was of interest to check the variation of the asphaltene content as a function of pyrolysis time to probe not just its relationship on coke make but also observe if there was any effect on the physical properties of the pyrolysis liquids.

5.3.2 Viscosity and Ashphaltene content of pyrolysis products

Viscosity determination was one of the analyses performed on the pyrolysis liquids. The viscosity trend with pyrolysis time was complex. A zero minute reaction time at 400 °C caused a 47.6% reduction in viscosity. A reaction time of 30 minutes at 400 °C caused a 98.4% reduction compared to bitumen feed viscosity. The reaction time was within the induction period where no coke make was observed. The viscosity trend did not stop here when pyrolysis time was extended. After a constant reduction in viscosity, there were two viscosity maxima (Figure 5-3). An ashphaltene content determination at different times showed a complex and superficially correlated trend with the viscosity. There were two important deviations. First, the marked decrease in the viscosity from 0-30 minutes that was not accompanied by a change in the asphaltenes content. Second was the lag in viscosity maximum (90 min) that was observed after the asphaltene maximum (80 min). The latter was repeated at 270 min, where the increase in asphaltenes content preceded the increase in viscosity.
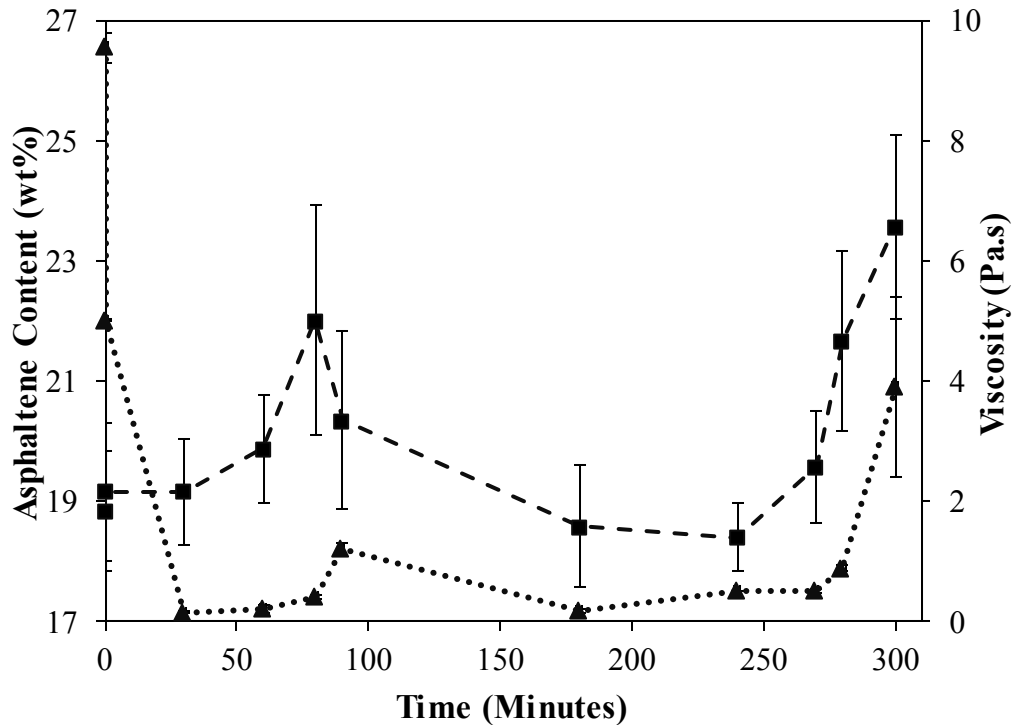
Figure 5-3: The effect of pyrolysis time on resulting asphaltene content (■) and viscosity (▲) of pyrolysis liquids.

Critically analyzing data collected (coke yield, viscosity and asphaltene content), there seem to be 7 regimes in bitumen pyrolysis. This has been summarized qualitatively in Table 5-2.

Table 5-2: Viscosity, Coke and Asphaltene regimes in bitumen pyrolysis

	Regime (minutes)	Viscosity	Ashphaltenes	Coke Make	MCR
I	Neat bitumen - 0	↓	↑	X	↑
II	0 - 30	↓	constant	X	↑
III	30 - 80	↑	↑	X	↑
	90 (End of Induction period)	↑	↓	↑	↑
IV	90 - 180	↓	↓	↑	↑
V	180 - 240	constant	constant	↑	↑
VI	240 - 270	constant	↑	↑	↑
VII	270 - 300	↑	↑	↑	↑

Much like what literature indicated there was an ashphaltene increase (Figure 5-3) during the progression of the induction period (Figure 5-1). The increase in asphaltene content did not affect the viscosity during the induction period (Regimes I II and III). This questions the removal of asphaltenes from the bitumen matrix as part of a pretreatment step especially from a visbreaking standpoint. A slight increase in the viscosity (1.91 ± 0.4 Pa.s) was observed right after the induction period (regime IV) but then dropped to 0.5 ± 0.025 Pa.s (Regime V) before increasing significantly in regime VI to 3.89 ± 1.5 Pa.s.

A viscosity increase after constant reduction was also observed when Cold Lake bitumen was visbroken at different times by Wang et al.[8] The main focus on the study was conformation and understanding of the conventional crude oil visbreaking time-temperature relation and its application to predict low temperature visbreaking performance. The relation did not hold true for low temperatures but at all temperatures studied but a) a significant viscosity decrease

was seen at low pyrolysis times and b) a viscosity maxima were observed just like in Figure 5-3 after a marked decrease in the viscosity when bitumen was pyrolysed at short times (0- 30 mins) for temperatures in the range of 260 °C - 400 °C.

It is important to note that the reaction network of bitumen pyrolysis is complex. Not only is there conversion of aggregates (which includes asphaltenes) to coke but since the propagation kinetics is free radical in nature there is simultaneous maltene to asphaltene conversion taking place. In our case the asphaltene content is the easiest measure of the aggregate content. Regimes I and II seem to be ideal from a visbreaking perspective. There is a significant reduction in viscosity whether or not there is an aggregate increase. As the end of the induction period is reached, the mean viscosity increases with a corresponding increase in the asphaltene content. When coking starts, there is carbon rejection and the foremost conversion taking place is the phase separation step (any aggregate to mesophase formation followed by coke formation). When coke is formed the highest molecular weight species are rejected and this results in a corresponding viscosity decrease since all viscosity values reported are cokeless viscosities, i.e the coke was removed by filteration before the viscosity was determined.

Ideally this would have continued until all asphaltenes are converted to coke but this was not the case. In regime V and VI, there is a second monotonic increase in the ashphaltene content and can be explained by the higher rate of maltene → ashphaltene conversion compared to asphaltene → coke conversion. A direct measure of this can be seen by the decrease (~10% in both cases) in the maltene weight fraction which occurs when the two asphaltene maxima are observed. This is not observed during the other time regimes of bitumen pyrolysis where the maltene weight fraction shows a monotonic decrease (Table 5-3).

Factors that govern bitumen viscosity can be both physical and chemical. Lesueur's[13] perspective on asphaltene content influencing viscosity are worth

mentioning and can be applied to this study. Asphaltenes have a maximum packing density corresponding to the minimum volume fraction (Φ_m). Due to the natural aggregation tendency of asphaltenes the aggregates may trap molecules within the aggregates or in association with the aggregates, which increase the volume of the asphaltenes. The effective volume fraction of asphaltenes (Φ_{eff}) is higher because of this factor.

Table 5-3: Yields of Maltenes and Asphaltenes during pyrolysis of Cold Lake bitumen at 400 °C and the corresponding effect on viscosity of pyrolysis liquids

Time (Mins)	Maltenes (wt%)		Asphaltenes (wt%)		Viscosity (Pa.s)	
	x	s	x	s	x	s
Feed	79.86	1.01	18.84	1	9.55	0.25
0	78.4	1.59	19.16	1.15	5	0.02
30	79.13	1.03	19.15	0.87	0.15	0.03
60	74.22	0.78	19.9	0.9	0.2	0.07
80	71.2	2.32	22.0	1.91	0.4	0.04
90	69.74	2.6	20.34	1.48	1.2	0.1
180	65.61	0.32	18.58	1.03	0.18	0.03
240	63.83	0.66	18.4	0.55	0.5	0.01
270	61.9	1.3	19.57	0.923	0.5	0.03
280	56.33	2.71	21.67	1.5	0.87	0.04
300	51.2	3.4	23.57	1.53	3.9	1.5

X = average value, s = sample standard deviation

Also as pointed out previously, the maltene fraction decreases sharply at points of asphaltene maxima than it does during the progression of other pyrolysis times. The viscosity of bitumen is thus increased relative to the vanishing-shear viscosity of the maltene fraction ($\mu_{0,malt}$) that follows Roscoe's law given by:

$$\frac{\mu}{\mu_{0,malt}} = \left(1 - \Phi_{eff}\right)^{-2.5}$$

...5-1

No solids were taken out before pyrolysis of bitumen. All viscosity values reported were after removal of coke and the particulates (solids) present. The solids content in the feed was 1.5 ± 0.05 wt%. These solids can act as nucleation sites for mesophase formation, and, by doing so the presence of solids affects the apparent length of the induction period before the onset of coking, as well as the size of the coke which ultimately depends on the ability of the mesophase to coalesce.[14][15] As seen in figure 5-2A, the nature of the coke changed during continued thermal conversion. These changes were seen in the rheological behavior as well as the ease of filtration according to a previous study.[16]

In the interest to quantify to what extent solids affect viscosity, a collegue from our research group found the viscosity of bitumen with and without the presence of solids. Cold Lake bitumen was visbroken at 340 °C for one hour. The viscosity of the unfiltered sample was 55 % higher than that of the filtered bitumen.[8] The bitumen was from the same barrel and thus the reaction time was well within the induction period. It is important to note that solids do have an impact on the absolute viscosity values alongside playing a role in induction period extension.[14]

5.3.3 Refractive Index and H/C Ratio

The refractive index and H/C ratio of samples was measured to track the nature of changes in the composition of pyrolysis products during thermal treatment. A lower refractive index is indicative of a product with more aliphatic character, i.e both paraffinic and naphthenic.[18] With increased pyrolysis time and with free radical addition the H/C ratio decreases because of formation of higher fused aromatic structures. The trend is seen in Table 5-4.

The solubility of coke precursors (Figure 5-4) in the matrix was expressed as solubility index (SI) which is an expression of coke formation tendency. This took into account the refractive index of the pyrolysis liquid and the Hydrogen/Carbon (H/C) ratio of the pyrolysis liquids.

Solubility Index (SI) = Refractive Index (RI) x (H/C ratio of pyrolysis

Products)

Table 5-4: Refractive index and Hydrogen/Carbon ratio of products after thermal treatment of Cold Lake bitumen at different times

Time	RI (at 30 °C)		H/C Ratio	
	x	s	x	s
Feed	1.5788	0.0032	0.121833	0.0001
0[a]	1.5801	0.0032	na	na
30	1.5852	0.0031	0.11816	0.000212
60	1.5982	0.0067	0.114099	0.001403
180	1.6558	0.0031	0.099832	4.85E-05
240	1.663	0.0031	na	na
280	1.6654	0.0034	0.097421	0.000294
300	1.6758	0.0048	0.093977	0.003039

na = not analysed, x = average, s = sample standard deviation
[a] – Refers to a zero minute heat up from room temperature to 400 °C and quenching.

With an increase in pyrolysis time, solubility of coke precursors like any aggregates, asphaltenes or mesophase decreases thus forming coke. A monotonic decrease in the solubility index indicates that any coke precursor (asphaltene, mesophase) become inherently less soluble in the bitumen matrix and thus the liquid is more likely to coke because of hydrogen deficiency. The MCR provides support to the observed solubility index trend (Figure 5-1).
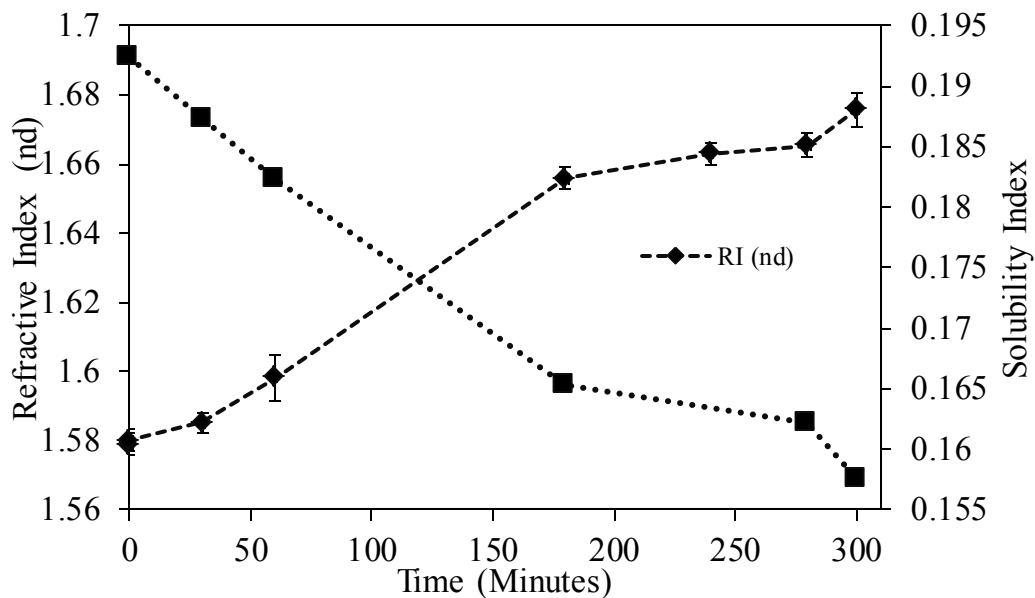
Figure 5-4: Refractive Index and Solubility Index variation with pyrolysis time

As a single test, the liquid that was pyrolysed for 200 minutes at 4 MPa in batch-mode was analysed under cross polarized light to probe for mesophase formation. Figure 5-5 shows mesophase formation in the lower left corner.

Figure 5-5: Mesophase formation at 200 minutes during pyrolysis when pyrolysis liquids were observed under cross polarized light (200X magnification)

5.3.4 ^{1}H-NMR product analysis

Pyrolysis of bitumen yielded two asphaltene maxima (Figure 5-3). Neat bitumen and pyrolysis liquids were subjected to a ^{1}H-NMR analyses to track the migration of hydrogen during bitumen pyrolysis.

Two specific values were quantified:

1) The total aliphatic hydrogen present in the matrix as a function of pyrolysis time. The ppm range of values integrated was over 0.5-4.5 ppm.

2) The methyl group percent in the aliphatic fraction was also quantified as a function of pyrolysis time. The ppm range of values integrated was over 0.5 - 1 ppm.[19]

The cut-off between aliphatic and aromatic hydrogen was taken as δ = 6.3 ppm, with lower shift-values being aliphatic and higher shift values being aromatic. Olefinic hydrogen overlaps the cutoff, as does hydrogen attached to some heteroatom functional groups.[20]

Table 5-5: The aliphatic hydrogen percentage and percentage of methyl groups present in the aliphatic hydrogen during neat bitumen pyrolysis at 400 °C with increase in time.

Time (min)	Aliphatic Hydrogen %		Methyl Group %	
	x	s	x	s
0	91	1	15.6	0.5
60	89.1	1.7	3.4	0.4
180	84.2	4.2	5.4	0.75
280	79.6	0.4	10.52	0.62
300	79.6	2.4	11.35	2.7

x= average, s= standard deviation

Neat bitumen has an initial aliphatic hydrogen per cent of 91 ± 1 % and with pyrolysis time the aliphatic hydrogen percent drops to 79.6 ± 2.4 % over a reaction time of 5 hours (Figure 5-6). The methyl group concentration in the

aliphatic region however showed a different trend. Initially the methylic concentration was 15.6 ± 0.5 %. After pyrolysis for 60 minutes the methyl concentration dropped to 3.4 ± 0.4 %. This however increased to 11.35 ± 2.7 % after 5 hours of pyrolysis.
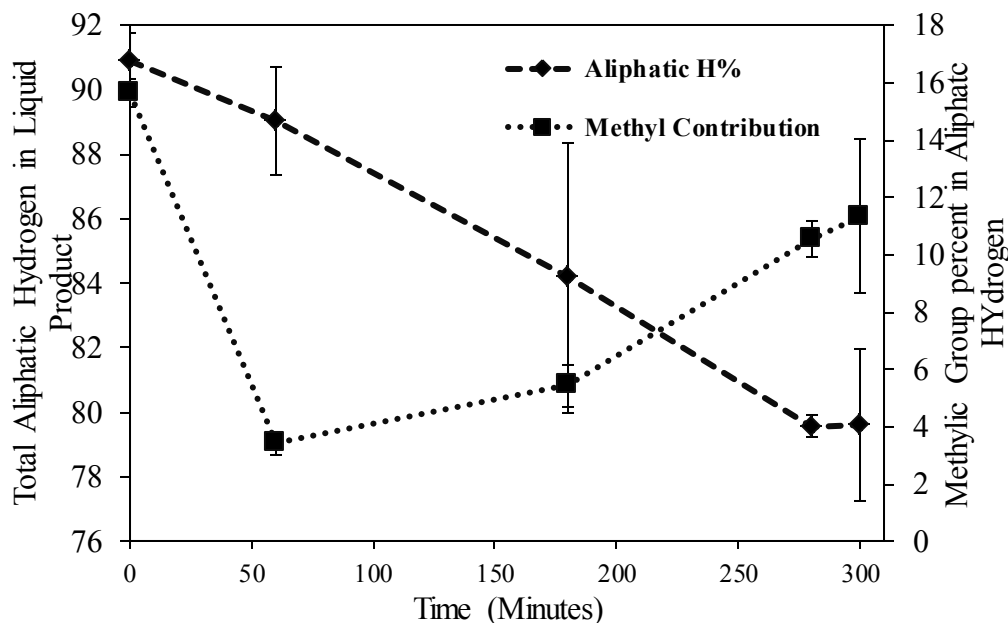
Figure 5-6: Variation of the total Aliphatic Hydrogen in the liquid product and the methyl group contribution to the aliphatic hydrogen with pyrolysis time

Hydrogen disproportionation causes the total aliphatic hydrogen decrease. The sudden initial drop of methyl group hydrogen content is due to the thermodynamically favorable cleavage of the aliphatic C-H bonds. The methyl group concentration increases and reaches a statistically constant value. Based on these results it was postulated that there is an equilibrium that governs the way in which free radicals (either H• or •CH$_3$) are terminated. At short contact times, termination by H is favored (where kinetics dominates), but if given a long enough time, the CH$_3$ content increases and methyl concentration dominates how radicals are terminated.

Wiehe[17] in his description of closed reactor data versus open reactors points out a couple of things that can be applied to understand this behavior. In closed

reactors the solubility relationship of light gases is a contributing factor in the mechanism of coke formation and induction period variation. In closed reactors the pressure and small gas space forces the volatile products to remain in the liquid phase. Previous studies have shown that with an increase in pressure the coke make decreases for open reactors.[6] This may be attributed to light gas interaction with free radical addition to enable coke suppression. According to Wiehe[17] the induction period is lowered because holding the volatile liquids in the liquid phase produces a solvent (light gases) with much lower ability to dissolve asphaltene cores. But at longer pyrolysis times, the high quantity of light gases (poor solvent) present in the system dissolves more asphaltene cores because of higher transferrable hydrogen in the system. This causes suppression of coke and would explain the methyl concentration increase with time.

There are opposing forces at work since light gases are also asphaltene precipitants. Does their ability to transfer methyl groups (transferable hydrogen) cause induction period extension or reduction? We investigated this by adding a light gas (*n*-butane) to the batch reactor system before pyrolysis.

5.4 Role of Butane in Induction period extension – reduction

Liquefied *n*-butane was added to bitumen and pyrolysed at different times to investigate its effect on coke make specifically. Three pyrolysis times were chosen. A) Within the induction period (60 minutes) B) After the induction period (120 minutes) and C) Extended pyrolysis time (300 minutes). The butane concentration in the reaction mixture of butane: bitumen was kept at 12.11 ± 1.19 wt%. Coke make and asphaltene content was calculated on a bitumen basis.
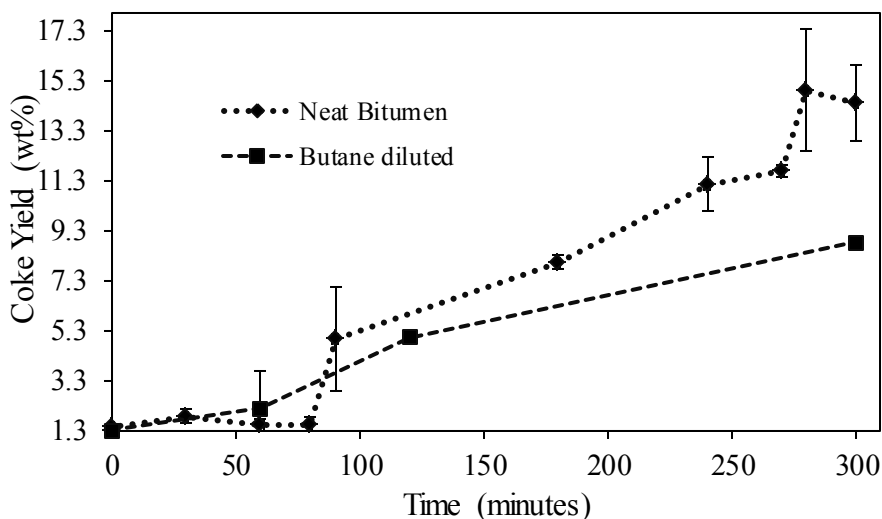
Figure 5-7: Comparison of coke yields when bitumen is diluted with 12.11 ± 1.19 wt% of butane and pyrolysed at 400 °C

Butane seemed to reduce the induction period (60 minutes) when 12.11 ± 1.19 wt% of butane was added. When an average of 12.11% of butane was added to bitumen and pyrolysed for 60 minutes, 2.19 ± 1.48 % of coke was produced. There was no significant change even at 120 minutes of pyrolysis. The surprise came when bitumen was diluted with butane and pyrolysed for 5 hours.

Table 5-6: Product Yields when bitumen was diluted with butane and pyrolyses at different times

Time (mins)	Coke (wt%)	s	Butane Added (wt%)	S	Asphaltenes (wt%)	s	Maltenes +Gas (wt%)	s
60	2.2	1.5	12.5	1.8	23.7	2.23	74.1	0.8
120	5.03	0.11	10.8	0	21.8	0.7	73.2	0.7
300	8.8	0.17	13.1	0.8	22	0.75	69.2	0.6

There was a 38% suppression compared to neat bitumen coking. Results from chapter-3, (Figure 3-7) describe the importance of reaction probability (concentration of solvent) and not just probability (rate constant). *n*-Butane is however, an asphaltene precipitant. By diluting bitumen with a high amount of butane, the probability of aggregation increases and thus a higher coke make may be explained by increased aggregation of species. One experiment was performed

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where when bitumen was diluted with 67.2 ± 1.1 wt% butane and the coke make was 24 ± 0.6 % for a pyrolysis time of 280 minutes. Neat bitumen when pyrolysed for the same reaction time had 14.93 ± 2.4 wt% of coke (Table 5-1). With higher concentration, butane does more harm than good even at extended pyrolysis times. The coke make is sensitive to the butane added. The two main results from this part of the study was 1) butane concentration should be kept low and 2) the most coke suppression was seen at long pyrolysis times.

5.4.1 Effect of butane dilution on product quality

The addition of butane as a solvent before pyrolysis caused changes in the coke make (Figure 5-7), but also affected the product quality. It must be noted that butane solubility in bitumen is high. At conditions of 35°C and 0.318 MPa butane was allowed to come into contact with Peace River bitumen. The solubility was reported as a mass fraction. It was observed that a mass fraction of 0.72 was soluble at these conditions. The saturation pressure was reported to be 0.334 MPa.[21] Multiple experiments were performed with propane that showed a constant increase in the solubility with increase in pressure.

Table 5-7: Asphaltene and Viscosity data for bitumen diluted with butane at different concentrations and pyrolysed

Time (minutes)	Butane Added (wt%)	s	Asphaltenes (wt%)	s	Viscosity (Pa.s)	s
60	12.5	1.82	23.7	2.2	0.7	0.22
120	10.8	0.02	21.8	0.7	0.63	0.2
300	13.1	0.83	22	0.8	1.33	0.15

Table 5-8: Refractive Index (R.I) and Micro Carbon Residue (MCR) data for bitumen diluted with butane at different concentrations and pyrolysed

Time (minutes)	Butane Added (wt%)	s	R.I (nd)	s	MCR (wt%)	s
60	12.5	1.82	1.5941	0.005	12.49	0.9
120	10.8	0.02	1.604	0.014	12.93	1.3
300	13.1	0.83	1.6599	0.004	17.25	0.85

Comparison of product quality is summarized and discussed in the two points below:

1) For a reaction time of 60 minutes, butane diluted bitumen had a higher asphaltene content (23.7 ± 2.2 wt%) and a higher viscosity (0.7 ± 0.22 Pa.s) compared to neat bitumen which had an asphaltene content of 19.9 ± 0.9 wt% and a viscosity of 0.2 ± 0.07 Pa.s (Table 5-3 and Table 5-7). This is probably because butane promoted mesophase formation and aggregation. Aggregates increase in size when butane is added and any aggregating species that can be seen under cross polarized light, be it asphaltenes or not can be responsible for this viscosity change. In this reaction time, the only significant difference was lower viscosity for the neat bitumen. There was no statistically significant difference in the refractive index and micro carbon residue between butane diluted and neat bitumen.

2) At extended pyrolysis times (300 minutes) there was a 66% reduction in the viscosity of butane diluted bitumen compared to neat bitumen. The asphaltene content however was not meaningfully different, again pointing to the fact that there is a poor correlation between the viscosity and asphaltene content. There was however a reduction in the MCR content 17.25 ± 0.85 wt% for butane diluted bitumen versus 19.24 ± 1 wt% for neat bitumen.

^{1}H-NMR analysis yielded interesting results. For all pyrolysis times, the mean aliphatic hydrogen content of butane diluted bitumen was higher than that of neat bitumen (Figure 5-8). The data was statistically significant for extended reaction times (300 minutes).
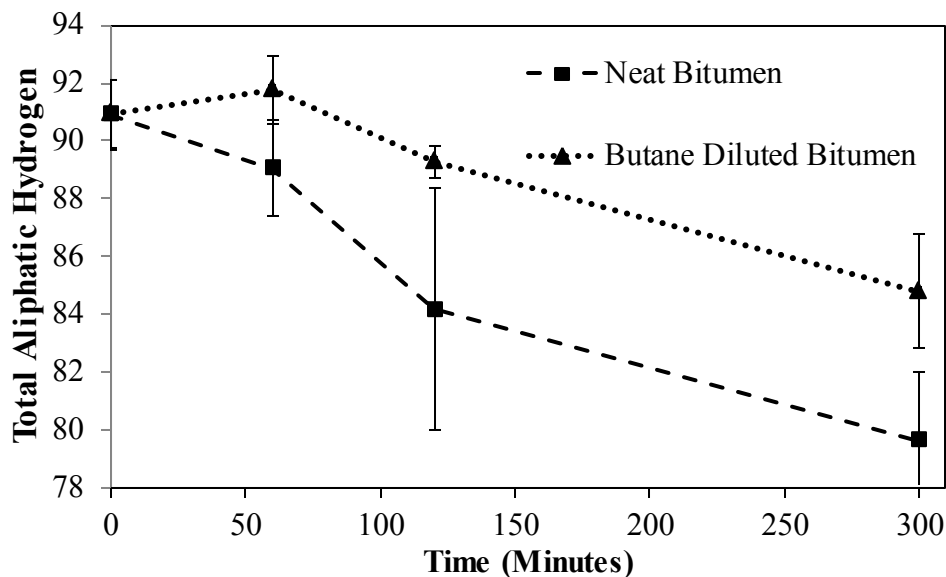
Figure 5-8: Total aliphatic hydrogen percent as a function of time in the liquid product for neat bitumen and bitumen diluted with butane before pyrolysis

Butane was able to increase the total aliphatic hydrogen of the pyrolysis products during all times investigated. After pyrolysis for 5 hours neat bitumen had a total aliphatic content of 79.6 ± 0.4 % compared to butane diluted bitumen that had a total aliphatic content of 84.8 ± 2 %. The meaningful difference in the total aliphatic content, the NMR results indicate that butane can act as a hydrogen transfer solvent. The hypothesis made in chapter -3 was it was through methyl radical donation. Hence the methyl group percent that made up the total aliphatics was calculated and compared (Figure 5-9).
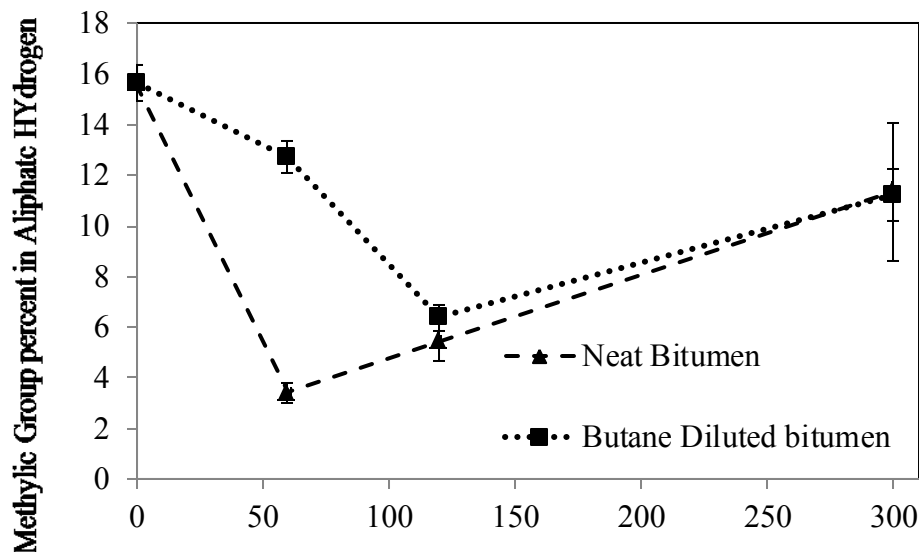
Figure 5-9: Methyl group contribution in the aliphatic hydrogen for neat bitumen and bitumen diluted with butane and pyrolysed.

There reduction in methyl group content was 78.2% when neat bitumen was pyrolysed for 60 minutes. When butane was added to the system and pyrolysed for 60 minutes the reduction in the methyl content was 7.8 %. After 120 minutes a 60% reduction in the total methyl content was observed. Butane was able to moderate the extent of methyl group cleavage during pyrolysis at low pyrolysis times. With extended pyrolysis time, even though there is more transferable hydrogen in the system, the methyl group content reaches a constant value in both cases. This is because with neat bitumen more and more light gases are formed until the reaction is moderated. This was also seen in Chapter-3 (see *3.3.4 Role of light gases in bitumen pyrolysis*). The constant value reached after 300 minutes again points to an equilibrium that governs how free radicals may be terminated.

5.5 Conclusions

Batch reactor pyrolysis of bitumen and butane diluted bitumen at varying reaction times yielded the following observations:

a) Four major regimes observed in coke make during pyrolysis of Cold Lake bitumen. In the first three regimes, there was no coke make and this is just

mineral matter present in the bitumen. This remained the same both quantitatively and visually. Filtration problems were encountered when bitumen was pyrolysed in the time frame of regime three (Coke-3). Visually, Coke-4 had a defined structure and this was easily filterable through a 0.22 μm filter paper.

b) The viscosity trend with pyrolysis time was complex. Two orders of magnitude of viscosity decrease from ~9.55 Pa.s to ~0.2 Pa.s was possible by heating Cold Lake bitumen to 400 °C for 30 minutes. There were two local viscosity maxima when pyrolysis time was increased.

c) An ashphaltene content determination at different times showed a complex and superficially correlated trend with the viscosity. There were two important deviations. First, the marked decrease in the viscosity from 0-30 minutes that was not accompanied by a change in the asphaltenes content. Second was the lag in viscosity maximum (90 min) that was observed after the asphaltene maximum (80 min). The latter was repeated at 270 min, where the increase in asphaltenes content preceded the increase in viscosity.

d) With increased pyrolysis time the coke formation tendency increased. The solubility index of the total liquid decreased. This in turn affected the ability of the bulk liquid to keep the coke precursors in solution.

e) With increasing pyrolysis time, the total aliphatic hydrogen content of the liquids decreased (Figure 5-6). The methylic hydrogen content went through a sharp decrease initially with increased pyrolysis time and increased at extended pyrolysis times.

f) Solvents may play a role in induction period extension or reduction. This depended on the type of solvent and its nature to react with the coke

precursors in the matrix. *n*-Butane was a poor solvent at shorter reaction times but was able to cause a 38% reduction in the coke make at extended pyrolysis times.

g) Coke make was sensitive to amount of butane added. Liquid quality (viscosity, refractive index, total aliphatic hydrogen content) was better when low butane amounts were added and longer pyrolysis time was allowed so as to allow transferable hydrogen to cause a meaningful difference in the product quality.

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Chapter - 6 Conclusions

6.1 Introduction

In the two years of research, observations were made that have helped contribute to knowledge in this specific area of science. The overall objective was to investigate pyrolysis behavior of bitumen at low temperatures, because it held the potential of higher liquid selectivity, and to understand how solvents influence coking.

6.2 Major Conclusions

The major conclusions from this work are listed as follows:

a) The mere presence of a solvent was important in coke suppression. The coke yield was halved at 20% solvent concentration, irrespective of the hydrogen transfer capabilities of the solvent.

b) It was observed that the better the H-transfer properties of the solvent, the more the coke suppression at high solvent concentrations (50% and greater).

c) Lighter products produced during bitumen pyrolysis may also serve as a solvent and by manipulation of VLE, the coke yield could be influenced (suppressed). The production of light gases was not primarily determined by over cracking of light products exposed to longer pyrolysis conditions.

d) From an industrial standpoint, ways to suppress coke and improve liquid yield during visbreaking have been suggested. They are: 1) Co-feed light hydrocarbons to suppress coking by methyl radical interactions. 2) Operate at lower temperatures and higher pressures to cause a higher concentration of lighter products in the liquid phase.

e) The overall hydrogen availability was as important as was the solubility limit of coke precursors in the liquid. If there was enough hydrogen that could be abstracted, the probability that this would keep the coke precursors soluble is higher. The more time given, the more meaningful the difference in coke make because of the more transferable hydrogen in the system.

f) Four major types of coke make was observed during pyrolysis of Cold Lake bitumen. In the first two regimes, there was no separate coke make and the coke was just mineral matter present in the bitumen. Filtration problems were encountered when bitumen was pyrolysed in regime three. This was not encountered in the last stage of coke formation. After 270 minutes of pyrolysis coke had a defined agglomerated structure.

g) For a zero minute reaction time, in a SDA-Visbreaking sequence even though there was no statistical difference in the refractive index, micro carbon residue data and ^{1}H-NMR data, the liquids from visbreaking-SDA had a higher aliphatic character.

h) The viscosity trend with pyrolysis time was complex. An order of magnitude viscosity decrease from ~9.55 Pa.s to ~0.2 Pa.s was possible by heating the feed to 400 °C for 30 minutes. There were two local maxima when pyrolysis time was increased. The viscosity behavior was interpreted based on the literature. The most plausible explanation for the rapid decrease in the viscosity during low temperature visbreaking, was a decrease in the effective volume fraction (Φ_{eff}) that was occupied by the colloidal fraction. A decrease in Φ_{eff} could result from disaggregation or the release of colloidally trapped material.

i) An ashphaltene content determination at different times showed a complex and superficially correlated trend with the viscosity. There were two important deviations. First, the marked decrease in the viscosity from 0-30 minutes that was not accompanied by a change in the asphaltenes content. Second was the lag in

viscosity maximum (90 min) that was observed after the asphaltene maximum (80 min). The latter was repeated at 270 min, where the increase in asphaltenes content preceded the increase in viscosity.

j) Based on the asphaltene-viscosity relationship with time, in a SDA-Visbreaking sequence, the most meaningful difference in the product quality will be seen when the reaction time is equal to or less than the induction period of coke formation of the feed. In our sample of Cold Lake bitumen this time is just before 80 minutes. This gives the best case of hydrogen transfer from asphaltenes to enrich the aliphatic hydrogen content of the liquid product.

k) The reactivity of the oilsands bitumen to thermal conversion is comparable to that of a young crude oil, which has not been subjected to high temperature and pressure over geological time. As seen in literature this is not a new observation, but the experimental observations noticed were supported by literature that dated back to 1926. The final implication is that oilsands derived bitumen should not be treated like a residuum despite its distillation profile suggesting so.

6.3 Future Work

a) In the coke suppression studies, we investigated the individual effects of different solvents and their ability to suppress coke. There is literature that explains the reduction in the rate significantly especially when reactive H-donors are added to the system during pyrolysis. This effect of rate reduction however is not well known and this can give insight to understanding how the lower rates can be overcome when mild pyrolysis is coupled with solvent addition.

b) Visbreaking coupled with Solvent deasphalting needs to be investigated in much greater detail since the initial results look promising.

c) Physical effects have indirectly always played a role in coke suppression. If one can understand and decouple the viscous component of bitumen from the elastic component, this might help in understanding how to process bitumen better rather than subjecting it always to high temperatures and pressures.

6.4 Presentations and Publications

The following is the list of publications and conference presentations during the two years of research:

1) Zachariah, A., Wang, L., Yang, S., Prasad, V., de Klerk, A. Suppression of coke formation during bitumen pyrolysis, *Energy Fuels*, **2013**, *27* (6), 3061–3070.

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