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Low Temperature Visbreaking

By

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Dedication

To my parents for all their support and sacrifices

Abstract

In industrial visbreaking processes, the conversion typically takes place at ~450 ℃ and the extent of conversion is limited by the coking propensity of the feed. Some of the older literature on bitumen upgrading reported that it was possible to substantially upgrade the straight run product at lower temperatures. In this study, the efforts were made to explore the thermal cracking behavior of oil sands bitumen at low temperature. Four temperatures were performed: 340 ℃, 360 ℃, 380 ℃ and 400 ℃.

In this study, a new hypothesis formulated - light gases formed during visbreaking could also suppress coke formation which was investigated by varying the pressures or batch/semi-batch operations. All the reactions occur during visbreaking depend on three operating variables: pressure, time and temperature. The inverse relationship between time and temperature broke down at low temperatures.

Keywords: Visbreaking, mild thermal cracking, light gases, time, temperature, inverse relationship.

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1. Introduction to oil sand bitumen pyrolysis

1.1 Background

Oil sand bitumen is considered as an energy resource with high viscosity, high molecular weight, high Conradson carbon residue (CCR), and low hydrogen and carbon (H/C) ratio. These are the major constraints that limit the production and processing of oil sand bitumen. Thermal conversion is the oldest of all refining processes, which currently commercially employed for the upgrading of heavy oils and bitumen. (1) The thermal conversion generally involves thermal cracking of the molecular bonds and the chemistry follows a free radical mechanism. (2, 3) Over the past decades, implementations have been carried on coking and residue hydroconversion processes for bitumen upgrading. Coking is a severe thermal cracking process that disproportionates the bitumen into a carbon-rich coke fraction and lower-boiling point lighter fractions which are suitable as feedstock for other refinery units. (2, 3) Residue hydroprocessing is a hydrotreaing pyrolysis process that reduces the sulfur and metal contents and improves the H: C ratio of product. (2, 3) However, visbreaking is also considered as one of thermal conversion technology found for bitumen upgrading. Subjecting to mild or severe operating temperature, visbreaking is a relative mild form of thermal cracking that was originally used to reduce viscosity and the pour point of liquid product to meet No. 6 fuel oil specifications (a high viscosity residual fuel). (3, 4, 5)

Since the demands of low value residual fuels (i.e. No. 6 fuel) continue to decrease, visbreaking has become an important refining process for bitumen. This is due to the mild cracking conditions used in visbreaking that favor a high yield of lighter liquid products with less gas and coke production. (4) From both economic and environmental points of view, the society became more conscious about how to use carbon more efficiently. Therefore, the emphasis of bitumen upgrading was shifted from production of fuel oils to maximizing the production of lighter liquid product with higher value. In the following applications, the mild pyrolysis of bitumen to increase the yield of lighter liquid product is considered in the present work.

As we know, in order to increase the yield of lighter liquid product, mild pyrolysis has to be operated at higher conversion. Practically, coke formation is one of the significant limitations in achieving the maximum conversion. Therefore, coke suppression is an important step in maximizing the yield of lighter liquid product. It was found that solvents can reduce free radical addition reactions through dilution and by free radical termination with hydrogen transfer agents. (2) Unexpectedly, a new insight was generated about coke suppression, namely, that light gases formed during pyrolysis have impact on coke suppression. (2)

Furthermore, our goal in this work is not only to increase in the production of lighter liquid product, but also to increase in the value of liquid product by monitoring the viscosity changes with processing time and temperature. Canadian oil sands bitumen production is geographically remote from the market, since pipeline transport is hindered by the high viscosity of the bitumen (~10^4 mPa·s at 40 ℃). (6) The methods to reduce the viscosity of bitumen are of interests to many refineries throughout the world. As in all cracking processes, the reactions are time-temperature dependent, and there is a trade-off relationship between reaction temperature and processing time. (3) The same conversion could be achieved under less severe operation conditions in terms of the inverse relationship of time and temperature. (3, 7) Since if the operation conditions are too severe, the yields of coke and light gases will increase due to an increase in reaction rate of coke formation through long-chain free radicals recombination and lighter product overcracking.(8) Plus, the resulting liquid products will be unstable, and polymerization will occur during storage and pipeline transportation which could cause filter plugging and sludge formation.(3) Consequently, it was postulated that at lower temperatures there may be an improvement in selectivity and product quality beyond that predicted from typical visbreaking operating experience at higher temperatures.

1.2 Objective/Purpose

The objective of this study was to explore the thermal cracking behavior of oil sands bitumen in the temperature range 320-400 ℃, which is below the typical minimum industrial operating temperature of 430 ℃. It was postulated that at lower temperatures there will be an improvement in liquid yield compared to the yield at the same level of conversion at higher temperatures.

1.3 Scope of Work

Three experimental investigations were performed:

1. The concentration of light products generated during bitumen pyrolysis was manipulated by pressure and batch/semi-batch operation to evaluate the impact of self-generated light gas products on coke suppression. Due to lack of knowledge in low temperature oil sand bitumen pyrolysis, trial experiments were conducted in batch conditions at 400 ℃ with initial pressure of 1MPa; and in semi-batch conditions at 400 ℃ with constant pressures of 1 MPa, 2 MPa, 4 MPa and 8 MPa. 4 MPa was selected for the experiments at different subsequent temperatures and times. This work is described in Chapter 3.

2. In accordance with the fundamentals of thermal cracking technology, the thermal conversion of all the reactions occurring during visbreaking depends on three operating variables: temperature, time and visbreaking pressure. Chapter 3 has investigated the effect of pressures on mass balances in visbreaking. The experiments under constant conditions of 4 MPa and 400 ℃ were conducted to investigate the impact of time on the

thermal cracking behavior of oil sands bitumen, by monitoring the variations in viscosity with processing time. This work is described in Chapter 4.

3. As mentioned previously, besides pressure and time, temperature is also one of the factors that impact visbreaking. Chapter 4 only carried out investigations on one temperature at 400 ℃. However, as noted before, was that lowering temperature could suppress coke formation. Based on the results in Chapter 4, a new hypothesis was formulated, namely, that the inverse proportionality between temperature and time to describe visbreaking conversion becomes invalid at lower temperatures. Thus, under constant pressure of 4 MPa, the experiments were performed at 340 ℃, 360 ℃ and 380 ℃ for different reaction times to verify the new hypothesis. In addition, it demonstrated an overall overview about the relationship between viscosity and temperature and time. This work is described in Chapter 5.

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2. Literature Review on Thermal Conversion of Oil Sands Bitumen

Abstract

In this chapter, the approach is to investigate the current knowledge regarding thermal cracking, as well as chemical and physical behaviors of oil sands bitumen. After presenting brief description of three main classes of thermal conversion technologies, visbreaking and its previous investigations will be discussed more specifically in this chapter.

Keywords: thermal cracking, oil sands bitumen, visbreaking, chemical and physical behaviors

2.1 Introduction

Upgrading of bitumen to the distillate products is an extensively process that required to reduce the molecular weight and boiling point of the components in the feedstocks. (1) The chemistry of this transformation from bitumen to lighter products is extremely complicated, partly because bitumen is composed of an exceeding large number of organic molecules, including hydrocarbon, heteroatomic groups and metals. (2) They are ranged from the simplest organic molecule, methane to large polymeric molecules with molecular weight exceeding 15,000. (3) Thermal conversion is a method that involves breaking apart molecules with heat. By subjecting high temperatures, the molecular weight of the substance been cracked could be reduced as the molecular bond is broken. The higher the temperature is, the faster the reactions will happen. This is also called thermal cracking since large hydrocarbons are made to crack and break down into small molecules. Thermal conversion is the oldest of all refining processes. The current process industrially employed for the upgrading of heavy oils and bitumen is thermal conversion. (4) Conversion takes place through thermal cracking (Pyrolysis) of the molecules and the chemistry follows a free radical mechanism. Free radicals are formed during pyrolysis reactions due to the homolytic scission of the covalent molecular bonds. Also, essentially all the mechanisms of thermal cracking involve the formation and reactions of radical species. Consequently, since most of the chemical reactions in the bitumen thermal conversion are thermally driven, there is no selectivity in bond cleavage. The most common bonds during primary upgrading are carbon-carbon (C-C), carbon-sulfur (C-S) and carbon-hydrogen (C-H). The bond dissociation energies of most common bonds are shown in Table 2-1. (2) However, the most important reaction that leads to a significant reduction in molecular weight is probably the cleavage of C-C bond. (1) In addition, the reaction mechanism of the hemolytic scission of C-C bond is free radical in nature, and proceeds with radical chain reactions. (1, 2)

Table 2-1: The bond dissociation energies (2, 5)

Chemical Bond	Energy, KJ/mol
C-C (aliphatic)	355.64
C-H (n-alkanes)	410.03
C-H (aromatic)	462.33
C-S*	322.17
C-N (in amine)	351.46
C-O (in methoxy)	343.09

*Estimated from methyl sulfide and methyl radical formation from dimethyl sulfide with additivity data of Benson. (2, 5)

Thermal conversion of bitumen to lighter fractions is mainly due to the radical chain reactions. Even though the individual step of radical chain reactions is simple, the overall radical chain reactions are complex, especially for the extremely complex mixture of bitumen. In order to explore the thermal cracking behaviors of bitumen, depth knowledge of overall radical chain reaction kinetics is required.

The scheme of the reactions of components of bitumen in the thermal cracking reactions is as following: (2)

Initiation: $R-R' \xrightarrow{k_{in}} R^{\bullet}+R'^{\bullet}$

Propagation:

Hydrogen abstraction $\beta_j^{\bullet} + R_jH \xrightarrow{k_{ij}} \beta_jH + R_j^{\bullet}$

β-Scission $R^{\bullet}-C-C-\beta_j \xrightarrow{k_i} R-C=C+\beta_j^{\bullet}$

Radical addition $R_i^{\bullet}+C=C-R_k \xrightarrow{k_a} R_i-C-C^{\bullet}-R_k$

Radical rearrangement $R^{\bullet} - C - C - \beta_j \overset{k_s}{\rightarrow} R_i^{\bullet}$

Termination: $R_i^{\bullet} + R_j^{\bullet} \overset{k_t}{\rightarrow} R_i - R_j$

Where $R - R'$ represents bitumen and R and R' are alkyl groups containing chains of carbon atoms maybe branched (i.e. Methyl, ethyl, etc.). $R^{\bullet}$, $R'^{\bullet}$ and $\beta_j^{\bullet}$ are alkyl radicals. $R - C = C$ represents olefins. Initially, free radicals are formed by hemolytic scission, which have unpaired electron. Then free radicals extract hydrogen from bitumen. Hence, β-scission performed on produced material to form olefins and alkyl radicals. Radical addition is the reverse kinetic of β-scission. In addition, as free radicals are highly reactive, radicals are rearranged to become more stable. The kinetic is finalized with termination, in which the radicals are recombined to form product.

Since the demand of market for heavy residual fuel oils is decreasing, the “bottom of the barrel” has become more of a problem for refiners due to the difficulties in processing heavy crudes. Historically, the heavy residual fuel oils have been burned to produce electric power and to supply the energy needs of heavy industry. (6) However, since the market is strictly controlled by more severe environmental restrictions, natural gas becomes more competitive rather than heavy residual fuel oils. Thus more heavy residuals in the crude are, more difficult in economically disposing them.

Thermal conversion is one of the main processing technologies for upgrading of the petroleum feedstocks throughout the world. This accounts for approximately 58 % of worldwide-installed capacity of residue upgrading. (7) There are other technologies also used for residue upgrading- such as residue hydroconversion, catalytic cracking and hydrocracking. (6) There are two main classes of thermal conversion technology are commercially used for bitumen: thermal viscosity reduction (visbreaking) and coking.(8) Visbreaking is a mild pyrolysis process that was originally developed to reduce the viscosity sufficiently for fuel oil applications, which accounts for one quarter of the world residue upgrading capacity. (8, 9) 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. Coking is a prolonged pyrolysis process that disproportionates the bitumen into light gases, liquid product and solid coke. (9)

2.2 Visbreaking

Since its introduction in 1920's, visbreaking process has been extensively used for residue (i.e. vacuum residues) upgrading refinery and other heavy streams to produce gas, naphtha, distillates and visbroken residue. (10) Visbreaking is a thermal process (non-catalytic) that was originally developed to reduce the viscosity for fuel oil applications. Visbreaking not only reduces viscosity but also results in cracking conversion to produce lighter product. As the society became more sensitive about the use of carbon, the industries have shifted their emphasis from the production of fuel oil to the increased production of lighter liquid products that have higher value.

However, visbreaking is a relative mild pyrolysis process that was used to reduce the pour points liquid product to meet No. 6 fuel oil specifications. Since the demand for residual fuel oil (i.e. No. 6 fuel oil), a low-value product is decreasing, there is a higher demand in lighter liquid product. Over the past decades, implementations have been carried on the investigations of coking and residue hydroconversion. (11) Visbreaking has also been investigated at high temperature of 430 ℃ in many literatures. Although visbreaking can reduce viscosity, the conversion of bitumen to lighter liquid product is limited. Consequently, coking must be prevented in order to maximize the production of lighter liquid products.

As there is a significant amount of vacuum residue left behind (about 40 % of the total crude processed), significant investments in the refining processes have become inevitable due to the changing patter of the market demand. (12-13) Visbreaking accounts for about 33 % of the total residue processing capacity. (13) The mild cracking conditions used in visbreaking favors high yield of lighter liquid product with less gas and coke formation. (10) An improvement could be achieved to maximize the production of lighter liquid product with higher value in a less severe reaction conditions. There are very few literatures on this investigation.

2.2.1 Process description

The visbreaking process is not very complicated. The general process description is as follows. The residue, before entering the visbreaker furnace, is preheated to the desired temperature through the preheat exchangers. The furnace is specially designed for mild pyrolysis and the main operating variables (time, temperature and pressure) are controlled to produce the desired products according with free radial mechanism. Afterwards, the material is then passed through a soaking zone and the product is quenched with gas oil. Finally, the quenched stream goes into a distillation column for product fractionation.

2.2.2 Types of visbreaking

There are two types of visbreaking technologies that currently employed industrially: (10)

- Coil visbreaking: it is a high-temperature cracking process for a pre-determined and relatively short processing time in a heater.
- Soaker visbreaking: it is a low-temperature with long processing time process, where most of conversions occur in a reaction vessel or soaker.

The following shows the simplified setup of coil and soaker visbreaking units in Figure 2-1 and Figure 2-2.

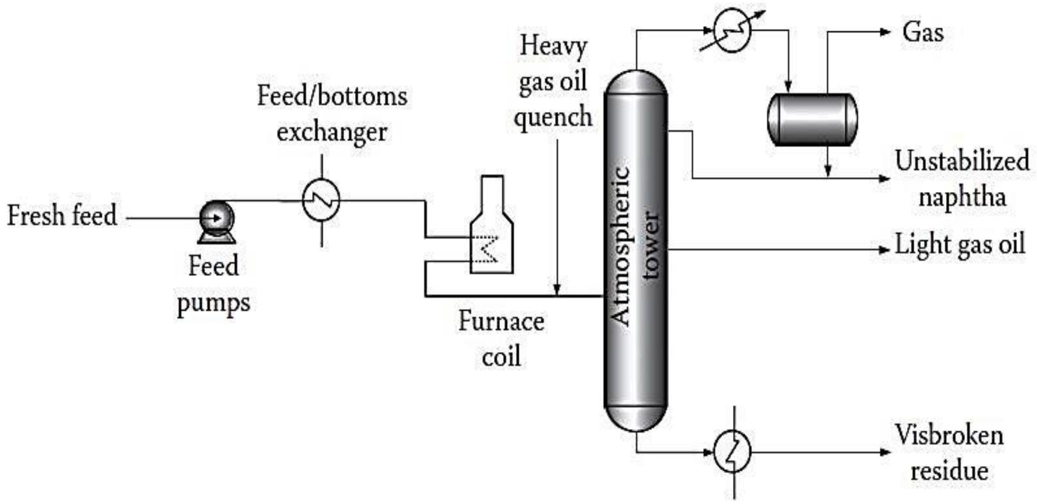

Figure 2-1: The process scheme of coil visbreaker. [10]

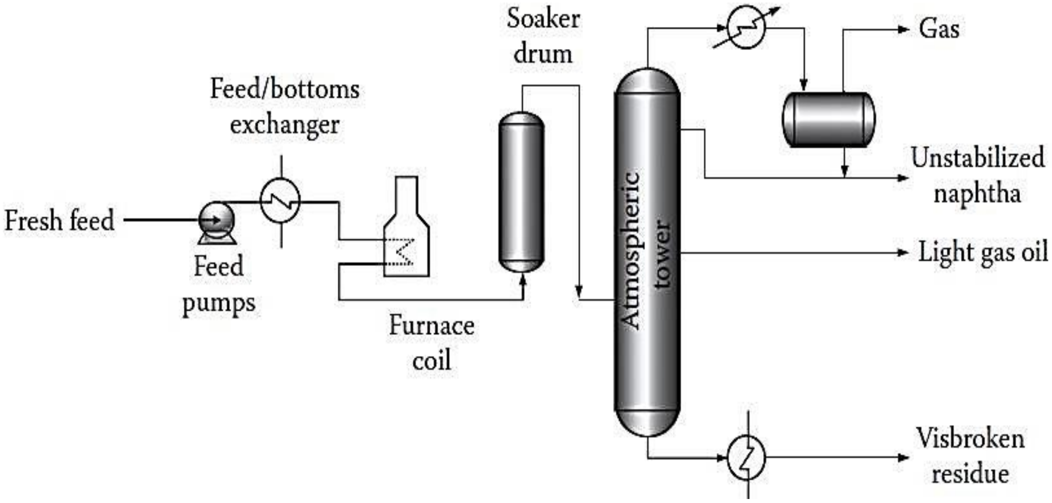

Figure 2-2: The process scheme of soaker visbreaker. [10]

2.2.3 Current investigations on visbreaking

One of the main objectives of visbreaking is to reduce the amount of residual oil produced in the atmospheric or vacuum distillation of crude oil, thus increasing the production of more valuable products. (10) In order to maximize the production of lighter liquid product, the formation of coke needs to be suppressed.

Mild pyrolysis has to be operated at higher conversion in order to achieve an increment in the production of lighter liquid products. Practically, the maximum conversion is significantly stoichiometrically constrained by coke formation due to the balance of H: C ratio between the feed and product. Consequently, the coke can be suppressed by hydrogen addition to increase the H: C ratio and avoid carbon rejection to form coke. This strategy has been employed in many technologies, such as in residue hydorconversion to obtain an overall increase in the H: C ratio of product, either through direct hydrogenation with H_2 or indirect hydrogen addition using solvent with hydrogen transfer capability. The latter approach has been practice in direct coal liquefaction. (9, 15) In some literatures, they have investigated visbreaking combined with hydrogen-donor solvent, (9, 16, 17) hydrothermal conversion, (18) as well as Aquaconversion in which self-generated hydrogen during visbreaking. (19)

To date, visbreaking has drawn great attentions from the researchers throughout the world. Many published literatures have investigated different aspects of visbreaking. Some of the early investigations on the topics of visbreaking of Cold Lake bitumen , (20) Athabasca bitumen, (21) and Utah tar sand bitumen (22) have focused on the development of thermal cracking reaction pathways, kinetics and models, as well as the characterization of the cracked products after thermal visbreaking. (6, 20-25) All the reactions in thermal cracking depend on three operating variables: time, temperature and pressure. (11, 26-28) Some attempts were approached by performing thermal visbreaking of bitumen (i.e. Athabasca bitumen, (27) Inner Mongolia oil sand bitumen (11)) and characterizing the yield of coke, gas and liquid products and monitoring the viscosity changes of liquid product. However, most investigations performed were at single temperature above 400 ℃ with insufficient information. There are very few literatures on the mild pyrolysis temperature range of 320 ℃ to 400 ℃ for different processing time.

2.3 Hydroconversion

The term hydroprocessing, also termed as hydroconversion, is used to denote those processes used to reduce the boiling range of the feedstock; in addition to remove substantial amounts of impurities such as metals, sulfur, nitrogen, and high carbon forming compounds through hydrotreating the cracked product.(6) Residue hydroconversion is a process that combines pyrolysis and hydrogenation. As presently practiced, different hydroprocessing technologies are employed industrially: fixed-bed processes-such as Residfining, Atmospheric Residue Desulfurization (ARDS), Vacuum Residue Desulfurization (VRDS), and

Resid Hydordesulfurization (Resid-HDS); (6) moving-bed processes- such as Chevron's OCR system, Shell's Hycon system, and Axens/IFP's Hyvahl system; ebullated-bed processes- such as H-Oil and LC-fining. (30)

The selection of the most economic method of processing the crude oil is a very complex matter; the advantage of hydroprocessing is to reduce the sulfur and metal contents of the vacuum reduced crude and improves the H: C ratio of the products by directly adding hydrogen. The disadvantage of the residue hydroconversion is, the products after hydroprocessing are very aromatic and may require sever hydrotreating operations to be suitable for fuel oils applications. The feed conversion level that can be achieved is 25 to 65 % in residue hydroprocessing processes. (6)

2.4 Coking

Coking processes are capable of converting heavy feedstocks into a solid coke and fractions of light compounds which are suitable as feedstocks to other refinery units for further conversion to produce higher value transportation fuels.

From a chemical reaction viewpoint, coking can be considered as an extensive thermal cracking process in which one of the end products is a carbon-rich fraction (i.e., coke). As presently practiced, different technologies have been applied for coking units: delayed coking, flexicoking, fluid coking.

Coking was used primarily to pretreat vacuum residuals to prepare suitable feedstocks for a catalytic cracker. In this way, it could reduce the coke deposition on the cracker catalyst and thereby allowed overall increase cracker efficiency. In addition, this also reduces the net yield of low-value residual fuel in refinery. From the view of feedstocks, it reduces the yield of metal content of the catalytic cracker feedstocks. However, one of the drawbacks of coking for high-sulfur crude oils are that delayed coking produces a fuel-grade coke with high sulfur content. This coke is very difficult to sell. But there is an alternative that hydroprocess the feed before feed to the coker, therefore it will reduce the sulfur level of the coker feed to make low-sulfur coke. From both viewpoints of operating and capital cost, flexicoking is more expensive than delayed coking, but flexicoking is able to produce low-heating fuel gas from coke to supply refinery energy needs and elemental sulfur production. Currently there is a market for this. However, there is a disadvantage of fuel gas production from coke in the flexicoking process, which is the fuel gas produced cannot be transported very far because the energy required for compression does not make it economical.

In recent years coking has also been used to prepare hydrocracker feedstocks and to produce a high quality “needle coke” from stocks such as heavy catalytic gas oils and decanted oils from the fluid catalytic cracking unit. (31- 32)

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3. The Effects of Pressure and Batch/Semi-batch Operations on Coke Suppression

Abstract

Coke formation can be reduced through mild pyrolysis (400 ℃) by adding solvents with hydrogen transfer capabilities.(1) Additionally, the concentration of self-generate light products during bitumen pyrolysis was manipulated by pressure and batch/semi-batch operations. The following chapter explains the experiments conducted in two types of operations: batch at 1 MPa and semi-batch over four pressures of 1 MPa, 2 MPa, 4 MPa and 8 MPa. Mild pyrolysis (400 ℃) of bitumen was investigated to establish ways in which coke formation can be suppressed. As anticipated, 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

As stated in the first chapter, the main purpose of the present work is to maximize the lighter liquid product yield and value due to the high value petroleum product demands of the market. Visbreaking is a form of thermal cracking that was originally developed to reduce the viscosity sufficiently for the fuel oil applications. Mild cracking conditions used in visbreaking favors a high yield of light liquid product with less gas and coke formation. As the society became more sensitive about the use of carbon, the industries have shifted their emphasis from the production of fuel oil to the increased production of lighter liquid products that have higher value.

As we know, in order to increase the yield of lighter liquid product, mild pyrolysis has to be operated at higher conversion. Practically, the maximum conversion is constrained by coke formation. How much pyrolysis conversion can be performed before carbon rejection by coke has to take place is stoichiometric limited due to the balance of H: C ratio between feed and product. Therefore, coke can be suppressed by hydrogen addition. As the H: C ratio increases, it decreases the need for carbon rejection. This strategy is employed in many aspects, such as direct coal liquefaction, (2) visbreaking with hydrogen-donor solvents (3) (4), and Auqaconversion(5).

Previous studies also have outlined that co-feeding a liquid solvent with bitumen will suppress coke formation during visbrekaing (1). Solvents can reduce free radical addition reactions through dilution and by free radical termination with hydrogen transfer agents.

In the present study it was found that not only direct hydrogen transfer agent addition can suppress coke but also other factors could suppress coke formation. Our working hypotheses were:

a) Coke formation could be suppressed by reduce the production of light gases during bitumen pyrolysis. Since light gases have higher H: C ratios than liquid products, over-cracking of lighter liquids at longer residence time was cited as one of the main reason for increased light gas production.(6) We believed if less light gases are produced, the need to produce coke through hydrogen disproportionation in order to balance the H: C ratio of feed and product will diminish. This hypothesis was investigated in this chapter and new hypothesis is outlined.

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. The characterization of bitumen is shown in Table 3-1.

Table 3-1. Characterization of the Cold Lake bitumen used as feed material [a]

Description	Fresh Cold Lake bitumen	
	x	s
Micro carbon residue (wt %)	15.0	0.7
Asphaltene content (wt %)	13.4	1.0
Mineral matter (wt %)	0.89	0.1
Elemental analysis (wt %)		
carbon	82.6	0.1
hydrogen	10.3	0.1
nitrogen	0.6	0.1
sulfur	4.7	0.1
oxygen (by difference)	2.6	0.3
Viscosity (mPa.s)		
at 40 °C	91864	3563
at 60 °C	9671	280

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

The solvent used to remove the liquid products from the micro-reactor and dilution is methylene chloride 99.9 %, supplied by Fischer Scientific. Praxair supplied nitrogen 99.999 % as compressed cylinder gas.

3.2.2 Equipment and Procedure

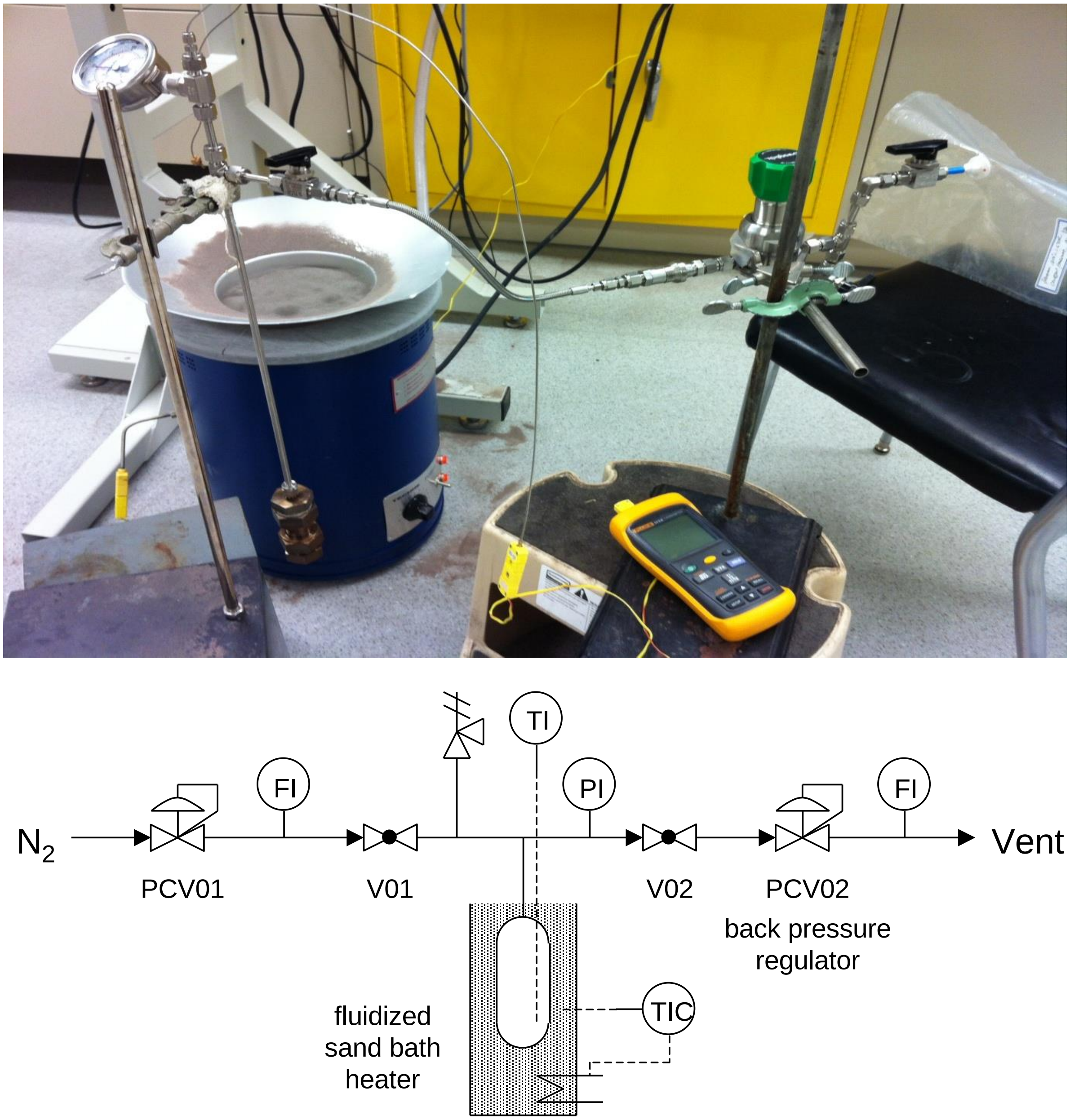

Figure 3-1. Semi-batch/batch of bitumen pyrolysis setup

All pyrolysis experiments were performed in a batch reactor that was operated 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 indirectly monitored by adjusting the temperature of the heated fluidized sand bath and air flow rate. During batch mode operation the reactor was purged and pressurized with nitrogen and then the system was closed before the reactor was placed in the heated fluidized sand bath. During semi-batch mode operating the same procedure was followed, but the pressure inside the reactor was controlled by adjusting the back pressure regulator.

For a typical experiment the reactor was filled with 8 g material (bitumen), 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 ℃ was 5 minutes. Two groups of experiments were performed: 1 MPa and 400 ℃ in batch mode for 1½ hours and 1,2,4,8 MPa and 400 ℃ in semi-batch mode for 1½ hours. The duration of each run was measured from the time the reaction temperature was reached. The cooling-down time at the end of the experiment was also 5 minutes. The reactor was then depressurized. The light gaseous products were collected in a gas bag and afterwards analyzed. After depressurizing and cleaning the reactor, the reactor and product were weighed. The weight of product was determined by the difference between before and after the reaction product was removed from the reactor. 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. Methylene chloride was removed from the pyrolysis product in a rotary evaporator. 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 HapSep 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 $ml \cdot min^{-1}$. The injector temperature was set at 200 ℃. The temperature program used started at 70 ℃ for 7 minutes, then ramping at 10 $°C \cdot min^{-1}$ to 250 ℃ and holding for 2 minutes, followed by ramping at 30 $°C \cdot min^{-1}$ to 300 ℃ 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-C17/QC-LTC and on average 4 g of the samples was required for analysis. The temperature during viscosity measurement was controlled by the fluid circulator.

Fourier transformed infrared (FT-IR) spectroscopic analysis was carried out to identify the compositions of the liquid product. FT-IR analysis was carried out using an ABB MB3000 Fourier equipped with a MIRacle^{TM} Reflection Attenuated Total Reflectance (ATR) diamond crystal plate and pressure clamp. The spectra were collected at a resolution of 4 cm^{-1} and 120 scans over the spectral region 4000-500 cm^{-1}.

Micro carbon residual percentage and mineral matter analyses were performed using a Mettler Toledo thermogravimetric analyzer (TGA/DSC 1). This instrument is equipped with the ultra-micro balance cell and DTA sensor. TGA/DSC 1 simultaneously measures heat flow in addition to weight change. The micro carbon residual percentage analysis was carried out with nitrogen as carrier gas; and the mineral matter analyses were carried out with air as carrier gas. Its main use is to characterize the materials with regard to their compositions. For the micro carbon residual percentage analysis, the TGA/DSC 1 analyzer is programmed to increase the temperature from room temperature to 600 ℃; and for the analysis of mineral matter, the temperature ramps up to 900 ℃ while the analysis is performed.

A Mettler Toledo ML 3002 balance (3200 g capacity with 0.01 g readability) was used for weighing of reactors, samples and products.

3.2.4 Calculations

For the gas GC analyses, the data were extracted in the external standard (ESTD) report. The mole % of each component was calculated using the following equation (3-1)

$$Mole\ \%\ of\ compound\ x = \frac{Response_x \cdot RF_x}{\sum_{x=1}^{n}(Response \cdot RF)} \times 100\ \% \tag{3-1}$$

$Response_x$ is the area of peak that stands for the compound *x*. Response factors (*RF*) are obtained from the calibration for the known compound x. The mole % of compound *x* does not include nitrogen due to high concentration of nitrogen in the product gas as nitrogen is the pressurizing gas. The thermal conductivity detector could not provide accurate value on nitrogen. Therefore, the mole % of compound *x* is the normalized value without nitrogen.

- Mass balance calculations

In order to carry out mass balance calculations, the reactant gas was assumed to be an ideal gas. Thus, the ideal gas law can be utilized.

$$PV = nRT \tag{3-2}$$

$$V = \pi \cdot (D/2)^2 \cdot L \tag{3-3}$$

$$m = n \cdot Molecular\ weight\ of\ the\ gas \tag{3-4}$$

$$mass\ \% = \frac{mole\ \% \cdot mole_{total} \cdot Molecular\ weight\ of\ the\ gas}{mass_{total}} \tag{3-5}$$

Where *P* is the pressure (Pa), *V* is volume (m3), *n* is mole, *R* is universal gas constant (8.314 J.mol-1.K-1), *T* is temperature (K), *m* is the weight of the reactant gas, *D* is the inside diameter of the reactor (m), and *L* is the length of the reactor (m).

Mass balance in batch mode: At room temperature, the reactor is pressurized with nitrogen to the desired pressure P. Volume is the reactor's volume, calculated in equation (3-3). The mole of nitrogen in the reactor will be calculated in equation (3-2). In batch mode, the mole of nitrogen remains the same before and after the reaction. After cooling the reactor from the reaction, the pressure after the reaction is known, and the volume is the reactor's volume. Temperature is the temperature after cooling, measured by the thermocouple. The mole of gas after reaction in the reactor can be calculated with the known parameters in equation (3-2). The difference of the gas mole before and after the reaction is the mole of gas without nitrogen. The mole % of gases can be calculated in equation (3-1) with the GC analyses. As the number of moles of nitrogen and its molecular weight are known, the mass of nitrogen can be calculated in equation (3-4). The total mass of gas in equation (3-5) excludes the mass of nitrogen. The mass % of the components in the gas products can be calculated in equation (3-5). With the total mass of gas, the mass of the components in the gas products can be determined.

$$Nitrogen\ Initial = Nitrogen\ Out + Nitrogen\ Remaining \qquad (3\text{-}6)$$

Mass balance in semi-batch mode: Followed the same procedure as calculated in batch mode, the mole of nitrogen and the mole of gas mixture in the reactor before and after the reaction are calculated, respectively. The unknown parameter is the mole of the continuous flowing gas during the reaction. As the mass flow rate of gas is known, the mass balance cannot be calculated with the flow rate. The total mole of continuous gas flowing out is set as the unknown variable. Since all the mole % of gas mixture in the reactor and continuous gas is provided with GC calculations in equation (3-1), all the parameters can be interpreted in terms of the unknown variable. Therefore, the mass of gas can be calculated in the excel spreadsheet with “Solver”. An example of the spreadsheet employed for the calculation can be found in Appendix A.

$$P_x = KH_x \cdot C_x \qquad (3\text{-}7)$$

The amount of coke is measured by weighing after filtration and the amount of raw product removed from the reactor, is subtracted from the amount of coke, which is the amount of liquid product. The amount of gas produced during the reaction is considered in mass balance calculations. The concentration of dissolved gas in the liquid phase is calculated in equation (3-7) of Henry's law.

3.3 Results and Discussions

3.3.1 Initial approaches

According to the working hypothesis outlined in the introduction, the lighter products in a closed system will run the risk of over-cracking to produce light gases. (6) The increasing production of light gas due to over-cracking of liquid, which will cause coke formation, because the H: C ratio of the liquid is decreased. However, based on the reported observation from our group, (1) a new hypothesis was formulated. It was postulated that lighter products are beneficial in coke suppression and that continuously removing such light products from the reaction system will promote over-cracking to increase the production of light gases. Eventually, the coke formation will increase through hydrogen disproportionate.

3.3.2 Studies on coke suppression

In order to place the current investigation in context, it is necessary to briefly discuss some of the work performed by a colleague. Ashley Zachariah (1) has investigated three types of solvents with hydrogen transfer capabilities in coke suppression. Three types of solvents are hydrogen donor-tetralin, hydrogen shuttler- mesitylene and naphthalene with weak hydrogen transfer abilities. Both Tetralin and mesitylene are capable of transferring hydrogen (H•) to a free radical (B•) formed during bitumen pyrolysis; however, by terminating the free radical species, tetralin itself does not become a free radical, but mesitylene becomes a free radical after donating hydrogen (H•). Naphthalene is a poor hydrogen transfer agent, and it is barely capable of transferring hydrogen (H•). However, 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 at a ratio of 4: 1 solvent to bitumen. 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 order to verify the effect of dilution in coke suppression, pyrolysis at different concentrations of solvent was performed to compare the coke formation. As the ratio of solvent to bitumen increased from 1:1 to 4: 1, there is not significant decrease in coke formation. We believed dilution is important in coke suppression especially for naphthalene with weak hydrogen transfer capability, but even at lower concentration for naphthalene, coke suppression was significant. Therefore there is at least one more mechanism that actively affects coke suppression.

As reported in Ashley Zachariah's work, for the bitumen pyrolysis diluted with strong hydrogen transfer agents tetralin and mesitylene, gas yields decreased as concentration of solvents increased. The gas yield for bitumen diluted with naphthalene remained constant. In addition, the gas yield of bitumen pyrolysis is the same as that of bitumen pyrolysis diluted with naphthalene. Therefore, 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.

3.3.3 Investigations on new hypothesis

In accordance with the investigations, a new hypothesis is formulated: coke formation can be suppressed by varying the pressures and batch/semi-batch operations. The difference in these two hypotheses is what the dominant mechanism is: 1. over-cracking of products due to longer residence time; 2. over-cracking of products and increased coke formation due to a lack of moderation by hydrogen transfer. In order to verify the new hypothesis, two types of experiments were performed to test which mechanism is dominant during bitumen pyrolysis: batch and semi-batch systems. As explained in the equipment and procedure, a batch system is a closed system, in which pressure increases as temperatures increases; conversely, a semi-batch system is a semi-open system with pressure controlled at constant level. Based on the experiments, two sets of experiments were conducted: semi-batch at different pressures; batch and semi-batch.

As outlined in the new hypothesis, light gas products could act as hydrogen transfer media in the reaction system to suppress coke formation. In order to verify this hypothesis, pyrolysis at four different pressures were performed under semi-batch mode at 400 ℃: 1 MPa, 2 MPa, 4 MPa and 8 MPa. As the pressure increased, it exploited vapor liquid equilibrium (VLE) to maintain a higher liquid phase concentration of light gas products using a semi-batch reactor. Consequently, as pressure increases, coke formation will be suppressed due to more light gas products that will be dissolved into liquid phase. The pressure in the reactor was kept constant by a back pressure regulator. The vapor phase material in excess was released to maintain a constant pressure (Figure 3-1). The assumption was the light gas products govern the vapor mixture pressure and the concentration of the light gas products in vapor phase does not vary very much. Therefore, under this assumption, the concentration of light gas products in the liquid phase for a given pressure will remain constant.

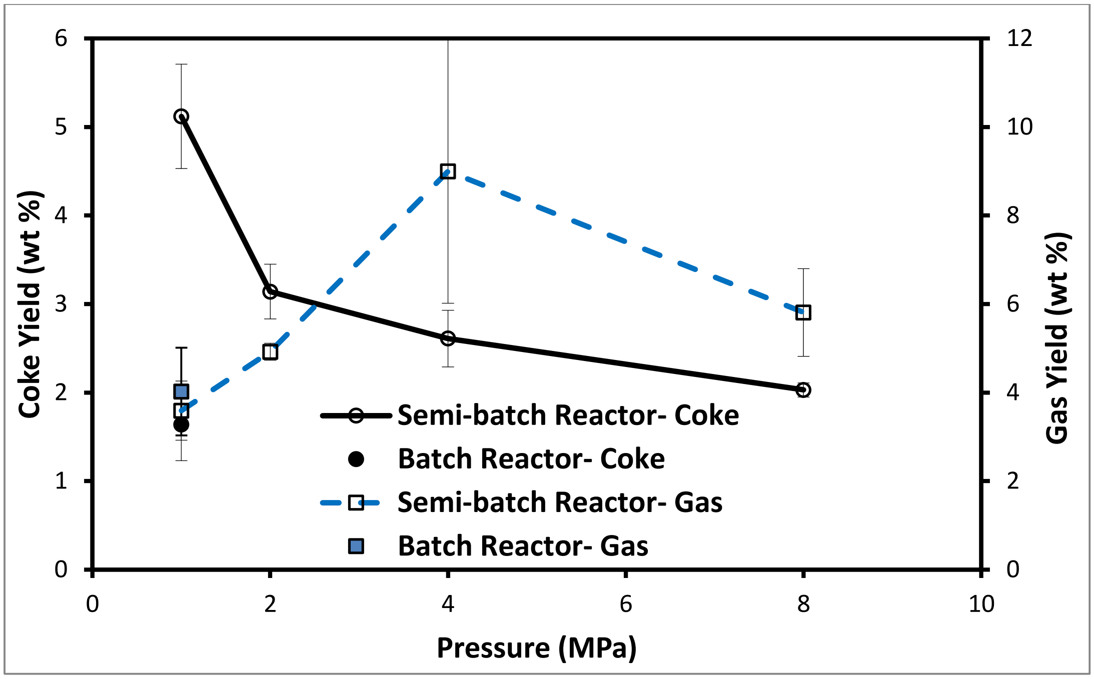

Figure 3-2. Coke yields (batch●, semi-batch ○) and gas yields (batch ■, semi-batch □) obtained after pyrolysis of fresh Cold Lake bitumen at 400 °C for 90 min in batch and semi-batch reactors at different pressure conditions

As shown in Figure 3-2, it was found that as the pressure was increased, the coke yield decreased. It supported the new hypothesis, which stated that the light products produced by pyrolysis acted as the hydrogen transfer solvent. (1) The coke yield decreased from 5.12 % ± 0.6 to 3.14 % ± 0.3 from 1 to 2 MPa, and the difference is statistically significant at 99 % confidence. The coke yield decreased monotonically with an increase in pressure and the change in coke suppression was statistically significant at 90% confidence, but a further increase in pressure had less effect on coke yield. Based on the comparison conducted between different pressures, it can be concluded that this behavior mimicked that of hydrogen transfer solvents stated in Section 3.3.2. Consequently, a little solvent can make a big difference in coke suppression, but the solvent concentration became less significant in further suppression of coke formation as the rate of coke suppression was reduced with an increase in pressure.

The coke yield decreased with an increase in pressure only supported the hypothesis that light gas products became hydrogen transfer solvents; however, it did not formulate which mechanism is dominant during bitumen pyrolysis. Therefore, coke yield is only one aspect of the impact of pressure on reaction selectivity. Besides coke yield, there is another aspect that needed to be considered is the yield of light gases produced during pyrolysis. As shown in Figure 3-2, the yield of light gas produced increased as the pressure increased. However, this is not a monotonic increase. The experiment at 4 MPa pressure was repeated four times, and it was not clear why the highest gas yield was obtained at 4 MPa, or why the standard deviation for the experiments at 4 MPa was much higher than usual. Overall, there is a directional increase in the yield of light gas products with an increase in pressure, which supports the hypothesis that an increase in vapor phase residence time leads to over-cracking.

Based on the data at different pressures, it is not sufficient to verify the new hypothesis. Since over-cracking of the lighter liquid product will cause an increase in the gas yield, which decreases the H: C ratio of the liquid product and forms coke. (6) However, there is a monotonic decrease in coke yield with an increase in gas yield. This indicates at least one more mechanism has impact on coke suppression.   Sachanen pointed out that the influence of pressure depends on the composition of the matrix, which means to some extent is determined by pressure through VLE. (3) Therefore, the pressure is not an independent factor that has impact on the mechanisms of bitumen pyrolysis. It is highly sensitive to the composition of the matrix. If Sachanen is correct about the influence of pressure through VLE, the outcome of the batch system would be different from the semi-batch system because the composition of the matrix is completely different.

A comparison was conducted between batch and semi-batch systems. One set of experiments was performed in batch operation, where the pressure, initially at 1 MPa, was allowed to develop autogenously in a closed system. In a closed system, all the light gas products formed during pyrolysis remain in the reactor and the concentration of light gas products in the liquid phase is governed by VLE. At the end of the reaction the pressure inside the reactor reached 2.2 MPa. As investigated previously, the lighter products produced during pyrolysis performed the role of hydrogen transfer solvents, therefore, as observed in Figure 3-2, coke yield was lower in the batch reaction than in any of the semi-batch reactions. Surprisingly, the gas yield was approximately the same as that found during pyrolysis in semi-batch mode at 1 and 2 MPa. Since batch mode represents longest residence time, according to the previous hypothesis investigated based on pressures, it will lead to over-cracking of light products. However, 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.

Table 3-2. Liquid yields obtained after pyrolysis of fresh Cold Lake bitumen at 400 °C for 90 min 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

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

Overall, the results indicated that even though operating pressure and VLE may play a role, that there is another aspect that influences the yield distribution. As shown in Table 3-2, the liquid yield obtained from pyrolysis in batch mode 94.34 wt% was meaningfully higher than the highest liquid yield obtained in semi-batch mode pyrolysis at 8 MPa. The difference was statistically significant at 95 % confidence.

3.4 Conclusion

Based on the previous studies on impact of direct solvent addition on coke suppression, another approach was followed to adjust the hydrogen availability by employing pressures and the method of operation (batch/semi-batch) to manipulate the light gas product concentration in fresh bitumen. The following observations were made:

a) The coke yield could be manipulated through pressure in the semi-batch pyrolysis. As the pressure increased, the coke yield decreased with an increase in the light gas product concentration in the liquid phase due to vapor liquid equilibrium.
b) The coke yield in batch mode is lower than the value in any semi-batch mode. Since the difference in batch and semi-batch modes is that batch mode is a closed system, which remained all the self-generated light gases in the system.
c) Based on the results, it can be concluded that light gas products formed during bitumen pyrolysis was not an irreversible product and served as hydrogen transfer solvent, which mimicked the behavior of solvent in coke suppression.
d) The yield of light gas products increased due to light product over-cracking because over-cracking of lighter liquid product causes an increase in the gas yield.
e) However, the light gas yield was not primarily determined by over-cracking of the light products exposed to pyrolysis conditions for longer. Since in a closed system, it represents longest residence time but the light gas products yield in a closed pyrolysis was not much different from that in an open pyrolysis.

f) Consequently, the liquid yield in a closed pyrolysis increased due to high H: C ratio of total reacting mixture. However, the liquid yield in an open pyrolysis system remained almost constant due to the trade-off between light gas products over-cracking and coke suppression.

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4. The Effects of Time in Bitumen Visbreaking

Abstract

Visbreaking of fresh Cold Lake bitumen at the operating temperature of 400 ℃ was investigated to explore the thermal cracking behavior of oil sands bitumen at low temperature (below the normal operating temperature of 450 ℃), by characterizing the product yields and viscosity changes with process time. The experiments were performed in a semi-batch mode at constant pressure of 4 MPa for different reaction time. 90 min is considered to be the break-down point of processing time at 400 ℃ since: 1. the yield of coke remained constant up to 60 min and the solid yield could be considered to be composed of mineral matter and associate carbon; 2. the viscosity decreased significantly from 0 min to 60 min and reached the minimum value before 90 min, where viscosity increased. Consequently, the results indicate that significant viscosity reduction is possible at short reaction time at 400 ℃ without significantly affecting the liquid yield or the coking propensity.

Keywords: Visbreaking, pyrolysis, bitumen, coke, reaction time, viscosity

4.1 Introduction

Canadian oil sands bitumen production is geographically remote from the market. Pipeline transport is hindered by the high inherent viscosity of the bitumen (~10^4 mPa·s at 40 °C) (1) and methods to reduce the bitumen viscosity are of interest.

Visbreaking is a mild thermal cracking process that was originally devised to reduce the viscosity of fuel oil without causing fuel oil instability. Significant conversion typically takes place at ~450 °C and the extent of conversion is limited by the coking propensity of the feed.(2) The Conradson carbon residue (CCR) of oil sands bitumen is high, of the order of 13 wt% on the total bitumen.(1) The high CCR value of bitumen limits the usefulness of visbreaking to upgrade straight run bitumen. Yet, some of the older literature on bitumen upgrading reported that it was possible to substantially upgrade the straight run product at lower temperatures, because the bitumen behaved like a young crude oil, despite its heaviness.(3)

The objective of this study was to explore the thermal cracking behavior of oil sands bitumen at 400 °C, which is below the normal operating conditions employed in industrial visbreaking.

4.2 Experimental

4.2.1 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. The bitumen samples used in this Chapter's experimental investigations were from the same barrel as that in Chapter 3. The characterizations of the bitumen samples are described in Table 3-1.

Methylene chloride and nitrogen, with the same features as described in section 3.2.1, were also used in this chapter's experimental investigations.

4.2.2 Experiment and procedure

Figure 3-1, as described in section 3.2.2, is the same experimental setup used in this chapter's investigations. All pyrolysis experiments were performed in a batch reactor that was only operated in 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 indirectly monitored by adjusting the temperature of the heated fluidized sand bath and air flow rate. The reactor in the semi-batch mode was purged and pressurized with nitrogen, but the pressure inside the reactor was controlled by adjusting the back pressure regulator while the reactor was placed in the heated fluidized sand bath.

For a typical experiment the reactor was filled with 8 g material (bitumen), 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. In this case, the reactor was pressurized to the pressure that was higher than the desired pressure, before connecting with the back pressure regulator. Since the back pressure regulator with the connections could be purged with the excess nitrogen. The heat-up time from room temperature to 400 ℃ was 6 minutes. All the experiments were performed at the constant conditions of 4 MPa and 400 ℃ for 0 min, 10 min, 20 min, 30 min, 60 min, 90 min, and 120 min. The duration of each run was measured from the time the reaction temperature was reached. 0 min indicates the reaction was stopped as the desired temperature reached. The cooling-down time at the end of the experiment was also 6 minutes. The reactor was then depressurized. The light gaseous products were collected in a gas bag and afterwards analyzed. After depressurizing 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. Methylene choloride was removed from the pyrolysis product by rotary evaporator. The pyrolysis liquid product was dried on the stove overnight for viscosity measurement. Material balances for the experiments were typically in the range 97-103 %. All experiments were performed at least in triplicate.

4.2.3 Analyses

All the equipment mentioned in section 3.2.3 was used in this chapter's investigations. In addition, viscometer was used to analyze the liquid products.

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. The temperature during viscosity measurement was controlled by the fluid circulator. The viscosity was measured at two temperatures 40 ℃ and 60 ℃.

4.2.4 Calculations

GC calculations and mass balances were conducted in the same way that explained in section 3.2.4.

4.3 Results and discussions

4.3.1 Background

As mentioned in chapter 3, visbreaking at mild cracking conditions could sufficiently reduce the production of residual fuels, which are low grade fuel oils, thus increasing the production of more valuable products. It favors a high yield of lighter product but less coke and gas.(4) The results investigated in chapter 3 verified that light gas products produced during pyrolysis at 400 ℃ , which is lower than the normal visbreaking temperature of ~ 450 ℃, acted as hydrogen transfer solvents in coke suppression. However, as one of the oldest processes for upgrading of heavy fuel oils, visbreaking was originally developed to reduce viscosity for fuel oil applications.

Since its introduction in 1920s, visbreaking has been extensively employed for upgrading of heavy petroleum. It has become more important in refinery as the demand for residual fuel oil, a low-value product continues to decrease. This is not only due to its capacity to improve the selectivity of lighter liquid production, but also to reduce the viscosity of pyrolysis visbroken residue. The market of Canadian oil sand bitumen production is geographically controlled due to the high viscosity of bitumen. Visbreaking is capable of reducing the viscosity of bitumen; therefore it needs less diluent (middle distillate) to bring its viscosity down to a marketable level for pipeline transportation, and that the middle distillate can be saved for producing more valuable refinery products. (4)

As in all cracking processes, the reactions are time and temperature dependent, and there is a trade-off relationship between reaction temperature and processing time. (6) As outlined in the working hypothesis in section 3.1, lowering the reaction temperature will suppress coke formation. Therefore, processing time and reaction temperature have significant impact on visbreaking. In this chapter, the temperature of 400 ℃ was investigated at different processing times by maintaining constant pressure in order to eliminate the impacts of the pressure and reaction temperature. The results of the investigations at different temperatures are described in chapter 5.

4.3.2 Mass balance analyses

The liquid, coke and gas yields obtained after pyrolysis of the bitumen at 400 ℃ for different reaction times in semi-batch reactors at constant pressure of 4 MPa are shown in Table 4-1. Reactions were performed for times of 0 min, 10 min, 20 min, 30 min, 60 min, 90 min and 120 min, respectively, with the reaction time being counted from the time the reactor reached 400 ℃. The reaction time of 0 min means the reaction is stopped immediately once the reactor reaches 400 ℃ (the heat-up time from room temperature to 400 ℃ is 6 min). The yield of liquid decreased from 97.8 wt% to 95.8 wt% from 0 min to 20 min, and then remained fairly constant up to 60 min. Thus, the liquid yield decreased from 60 min to 120 min. The yield of coke remained constant from 0 min to 20 min, and gradually increased to 1.7 wt% ± 0.44 at 60 min. The yield of gas increased from 0.91 wt% to 2.9 wt% from 0 min to 20 min, and then remained approximately constant at 3.0 wt% up to 60 min. As the yield of coke remained approximately constant from 0 min to 20 min, there is a trade-off between the gas yield and liquid yield. Additionally, from 20 min to 60 min, the yields of gas, coke and liquid stayed constant. However, there is a meaningful difference in the coke yield between 60 min and 90 min with 95 % confidence.

Table 4-1. Liquid, coke and gas yields obtained after pyrolysis of fresh Cold Lake bitumen at 400 ℃ for different reaction times in a semi-batch reactor at a constant pressure of 4 MPa [a]

Time	Liquid %		Coke %		Gas %	
	x	s	x	s	x	s
0	97.8	0.18	1.2	0.004	0.91	0.19
10	96.6	0.38	1.2	0.003	2.1	0.38
20	95.8	0.35	1.2	0.004	2.9	0.35
30	96.1	0.51	1.4	0.004	2.5	0.50
60	95.3	0.79	1.7	0.44	3.0	0.38
90	88.1	3.3	2.6	0.32	9.3	3.1
120	89.5	0.94	5.6	1.1	4.9	0.20

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

4.3.3 Viscosity analyses

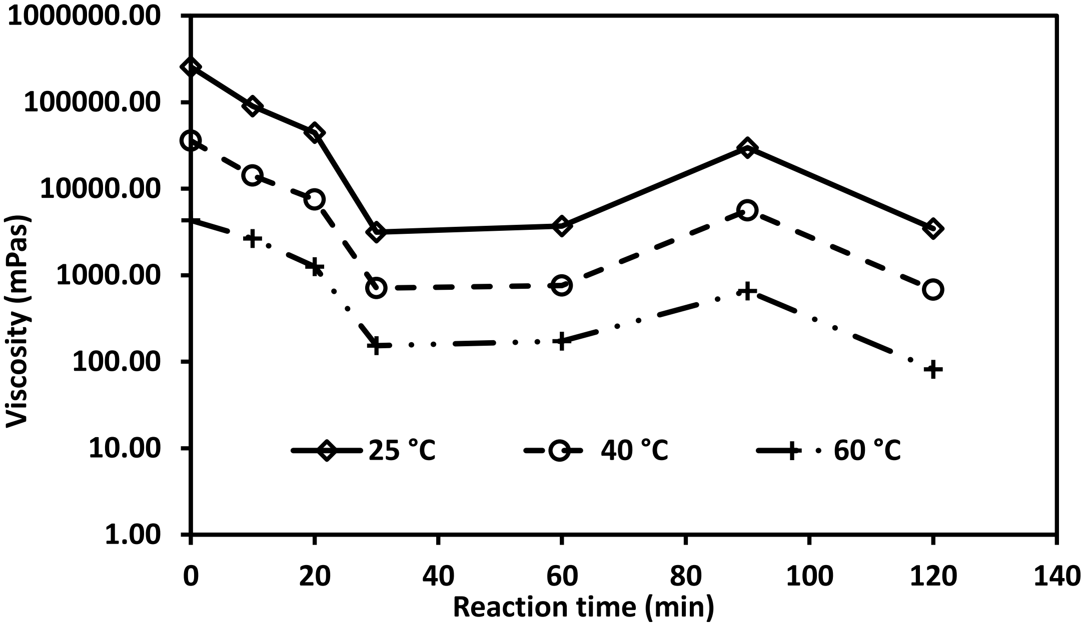

Figure 4-1. Viscosity distribution of pyrolysis product of 400 ℃ at constant pressure (4 MPa) at reaction times of 0 min, 10 min, 20 min, 30 min, 60 min, 90 min and 120 min

As listed in the characterization of Cold Lake bitumen in Table 3-1, the viscosity of Cold Lake bitumen is 9671 mPa.s at 60 ℃. As the reaction time increases, a significant decrease in viscosity compared to fresh Cold Lake bitumen was observed up to 30 min, after which the viscosity remained constant up to 60 min. Consequently, the viscosity measured at 40 ℃ was reduced by 99 % compared to the value of fresh bitumen from 0 min to 60 min without coke formation. Afterwards, there was an increase in the coke yield from 60 min to 90min, the viscosity increased slightly from 761 mPa.s to 5616 mPa.s at 40 ℃. The viscosity was measured on the liquid product after extracting the solid yield.

The increment in viscosity is due to the formation of heavy components. Therefore, 90 min was considered to be a break-down point in processing time at 400 ℃ since before reaching 90 min, the viscosity reached its minimum value and at 90 min, coke formation initiated.

Table 4-2: Visbreaking Time-Temperature Relationship (Equal Conversion Conditions) (4)

Time, min	Temperature	
	℃	℉
1	485	905
2	470	878
4	455	850
8	440	825

Akbar (5) proposed a visbreaking time-temperature relationship (under equal conversion conditions, where conversion represents product yield), which indicated that there is a trade-off between reaction time and temperature as shown in Table 4-2. In order to achieve equal conversion, at higher reaction temperature, it requires shorter process time; at lower reaction temperature, it requires longer process time. The relation indicated that at 400 ℃, equal conversion could be achieved at the equivalent process time of approximately 51 min. As listed in Table 4-3, viscosity reduction up to 1.3 x 10^3 mPa.s (60 ℃) is achieved at a reaction time of 20 min. The viscosity of product pyrolyzed for 20 min reaction time is measured at 97 ℃ is 65 mPa.s, which is comparable to or lower than values reported in the literature shown in Table 4-3. The viscosity (100 ℃) at 405 ℃ for a reaction time of 51 min was reported to be 5 x 10^2 mm^2s^{-1} by Shen et al. (7), as 80 % viscosity reduction compared to the value (100 ℃) of bitumen was achieved at 51 min shown in Figure 4-2. This is significant, since a similar viscosity reduction could be achieved with shorter reaction time at 400 ℃. Moreover, the viscosity could be reduced further by increasing the processing time to 30 min and stayed fairly constant up to the break down point.

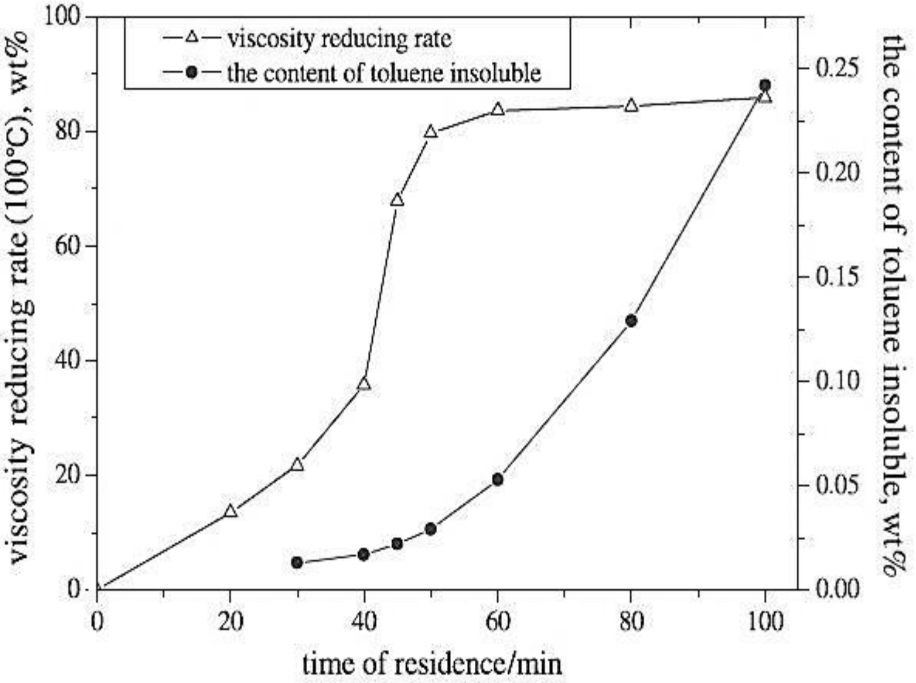

Figure 4-2. Effect of residence time on viscosity reduction rate and the content of toluene insoluble (7)

Table 4-3. Viscosity comparison between our data and literature data

Our Data (mPa.s)		**Literature Data ($mm^{2} \cdot s^{-1}$)**
400 ℃		405 ℃
20 min (60 ℃)	20 min (97 ℃)	51 min (100 ℃)
1.3 x 10^{3}	65	5 x 10^{2}

Ash analysis using TGA/DSC, provided in Table 3-1 indicates that fresh Cold Lake bitumen contains 0.89 wt % mineral matter; this is 75 % of the initial yield of coke (approximately 1.2 wt %). Thus, up to 60 min, the solid yield can be considered to be composed of mineral matter with associated carbon. (8) The coke yield only increases (with statistical significance) at processing times of 90 min and larger. Thus, it is reasonable to conclude that coking starts to occur significantly past 60 min. Also, the liquid, coke and gas yields remain constant at times greater than 20 min, while the viscosity at the reaction time of 20 min is reduced significantly by 92 % compared to the value of fresh bitumen. The results suggest that viscosity reduction is possible at relatively short reaction times at 400 ℃ without initiating coking, and also without substantially changing the liquid yield.

4.4 Conclusions

Through experimental investigations on relationships between reaction time and viscosity at 400 ℃, the following observations were made:

a) For a reaction time of 0 min to 20 min, the yield of coke remained constant, and there is a trade-off between the yield of liquid and gas.

b) There is no coke formation up to 60 min as the yield of coke remained constant at 1.2 wt%. In accordance with the analyses on mineral matter of bitumen, the solid yield could be considered to be composed of mineral matter and associate carbon.

c) The rate of viscosity reduction is slowing down from 0 min to 30 min and reaching steady at 60 min.

d) From 20 min onwards to higher reaction time up to 60 min, the yield of liquid, gas and coke remains constant.

e) At the processing time of 90 min and higher, the yield of coke increases dramatically with a meaningful difference at 95 % confidence.

f) 90 min is the break-down point of processing time at 400 ℃ where the coke yield and viscosity increase.

g) Overall, based on the results, it suggests that the viscosity reduction is possibly achieved at relatively shorter reaction time at 400 ℃ without initiating coking, and also without substantially changing the liquid yield.

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5. Inverse Relationship between Time and Temperature in Bitumen Visbreaking

Abstract

Visbreaking of fresh Cold Lake bitumen at operating temperatures of 340 ℃, 360 ℃, 380 ℃ and 400 ℃ was investigated to verify whether the inverse relationship between time and temperature is valid in low temperature visbreaking of oil sands bitumen. Each temperature was performed in semi-batch mode under constant pressure of 4 MPa for different reaction time. As described in Chapter 4, 90 min is considered to be a break-down point for 400 ℃. Based on the inverse relationship between time and temperature proposed in the literature, the break-down points of reaction time for each temperature that are equivalent to 90 min at 400 ℃ are calculated and investigated in terms of mass balances and viscosity changes. Consequently, in accordance with the variations in the coke yield and viscosity with time and temperature, the thermal conversion of bitumen failed to follow the inverse relationship of the reaction time and operating temperature at low temperatures.

Keywords: Visbreaking, break-down point, viscosity, reaction time

5.1 Introduction

5.1.1 Background

Lowering temperature can suppress coke formation since at low temperature, it slows down the reaction rate of free radicals, and hence it gives time to free radicals to recover from recombination by reduction in mass transfer. (1)

Temperature is one of factors that have impact on bitumen visbreaking. However, along with the temperature, time also plays a role as there is an inverse relationship between time and temperature. (2) The relationship between time and temperature is thermally driven in terms of the Arrhenius Equation, where the selectivity is based on the activation energy required for homolytic scission of bonds. As the temperature increases, higher conversion can be achieved. Since at high temperature, there is large amount of energy that there is no selectivity. However, at low temperature, there is limited amount of energy that the homolytic scission required lowest activation energy first occurs. Same idea can be employed on the factor of time.

5.1.2 Working hypotheses

Based on the results described in Chapter 4, at 400 ℃, there is no coke formed up to 60 min. Thus, the solid yield can be considered to be composed of mineral matter with associated carbon. In addition, the viscosity of pyrolysis liquid product at 60 min is reduced significantly compared to the value of fresh bitumen. Therefore, 90 min is considered as the break-down point of bitumen thermal conversion at the processing temperature of 400 ℃ as viscosity increased and coke formed. A hypothesis is formulated: Coke formation could be suppressed by lowering the operating temperature. (1) For the same level of cracking conversion in visbreaking, there is a inverse relationship between the operating temperature and the processing time. (2) 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. (3)

Since there is no coke formed up to the break-down point of reaction time, another hypothesis is formulated: the thermal conversion of bitumen does not follow the inverse relationship of temperature and time. In this chapter, three more reaction temperatures 340 ℃, 360 ℃ and 380 ℃ for different reaction time. Additionally, the break-down points of reaction time for each temperature that are equivalent to 90 min at 400 ℃ are calculated with the inverse relationship of temperature and time.

5.2 Experimental

5.2.1 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. The bitumen samples used in this chapter's experimental investigations were from the same barrel as that in Chapter 3. The characterizations of the bitumen samples are described in Table 3-1.

Methylene chloride and nitrogen, with the same features as described in section 3.2.1, were also used in this Chapter's experimental investigations.

5.2.2 Equipment and procedure

The experimental set-up used in this chapter's investigations is the same as that described in section 3.2.2 and Figure 3-1. All pyrolysis experiments were performed in a reactor that was only operated in 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 indirectly monitored by adjusting the temperature of the heated fluidized sand bath and air flow rate. The reactor in the semi-batch mode was purged and pressurized with nitrogen, but the pressure inside the reactor was controlled by adjusting the back pressure regulator while the reactor was placed in the heated fluidized sand bath.

For a typical experiment the reactor was filled with 8 g material (bitumen), 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. In this case, the reactor was pressurized to a pressure that was higher than the desired pressure, before connecting it to the back pressure regulator, so that the back pressure regulator with the connections could be purged with the excess nitrogen. The heat-up time from room temperature to 400 ℃ was 6 minutes. All the experiments were performed at the constant conditions of 4 MPa. Three temperatures were performed except 400 ℃: 340 ℃, 360 ℃ and 380 ℃ for different reaction times. The break-down points of reaction time were calculated to be 1440 min, 577 min, and 232 min for 340 ℃, 360 ℃, and 380 ℃, respectively. The duration of each run was measured from the time the reaction temperature was reached. 0 min indicates the reaction was stopped as the desired temperature was reached. The cooling-down time at the end of the experiment was also 6 minutes. The reactor was then depressurized. The light gaseous products were collected in a gas bag and analyzed afterwards. After depressurizing 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. Methylene chloride was removed from the pyrolysis product by rotary evaporation. The pyrolysis liquid product was dried on the stove overnight for viscosity measurement. Material balances for the experiments were typically in the range 97-103 %. All experiments were performed at least in triplicate.

5.2.3 Analyses

All the equipment mentioned in section 3.2.3 was used in this chapter's investigations. In addition, viscometer was also used to analyze the liquid products in this chapter.

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. The temperature during viscosity measurement was controlled by the fluid circulator. The viscosity was measured at two temperatures 40 ℃ and 60 ℃.

5.2.4 Calculations

GC calculations and mass balances were conducted in the same way that explained in section 3.2.4.

5.3 Results and discussions

5.3.1 Background

As mentioned in Chapter 4, the reactions are time and temperature dependent. There is a trade-off relationship between processing time and operating temperature. (2, 4) Chapter 4 only investigated the impact of the time factor in bitumen visbreaking at a temperature of 400 °C. A hypothesis was formulated on the relationship between time and temperature: thermal conversion of bitumen failed to follow the inverse relationship between process time and reaction temperature.

The meaning of the inverse relationship between time and temperature, is since bitumen visbreaking is thermally driven, at high temperature, there is large amount of energy available for all the reactions happen at the same time, under this circumstances, there is no selectivity; at low temperature, there is insufficient energy for all the reaction happen, therefore, as the temperature increases, the energy accumulates until reaching the level of energy for certain type of reaction happen, in this case, there is selectivity.

Therefore, in order to verify the hypothesis formulated, three more temperatures lower than 400 ℃ were investigated for different process time in this chapter, which are 340 ℃, 360 ℃ and 380 ℃.

5.3.2 Mass balance analyses

The material balances of bitumen pyrolysis at temperatures of 340 ℃, 360 ℃, and 380 ℃ and 400 ℃ for different processing times are shown in Table 5-1. Based on the inverse relationship between time and temperature proposed in the literature, (2, 4) higher temperatures need shorter reaction time and lower temperatures need longer reaction time. As investigated at 400 ℃ in Chapter 4, the viscosity at reaction time of 60 min was reduced by 99 % compared to the value of fresh bitumen. Also, the coke yield remained constant up to a reaction time of 60 min. Thus, the solid yield was considered to be composed of mineral matter with associated carbon according to the mineral matter analyses obtained in Table 3-1. Thence, 90 min was considered to be the break-down point for 400 ℃. Furthermore, there is no coke formed up to 90 min for 400 ℃. Three other temperatures were investigated: 340 ℃, 360 ℃ and 380 ℃. Different reaction times were investigated at each temperature. The break-down points of reaction time at these temperatures in were calculated to be 1440 min, 577 min, and 232 min, respectively.

As shown in Table 5-1, the coke yield remained constant up to 480 min, 240 min and 120 min for temperatures of 340 ℃, 360 ℃ and 380 ℃. At 340 ℃, there was a trade-off between the yields of liquid and gas from 0 min to 60 min. Onwards from 60 min to 480 min, the yields of liquid and gas remained constant. At 360 ℃, as the time increased from 0 min to 20 min, the yields of liquid and gas remained fairly constant. Thus, from 20 min to 30 min, the yield of liquid decreased as the yield of gas increased. Afterwards, from 30 min to 240 min, the yields of gas and liquid remained approximately constant. At 380 ℃, as the reaction time increased from 0 min to 20 min, the liquid yield decreased while the gas yield increased. Subsequently, the yields of gas and liquid remained constant up to 120 min. Consequently, there was no coke formation up to the break-down points of reaction time for each temperature, after which coke was formed. As the reaction time increased, there was a trade-off between the yields of liquid and gas; thus, the yields of liquid and gas stayed constant until the break-down points of reaction time. Therefore, the thermal conversion of bitumen does not follow the inverse relationship of time and temperature.

Table 5-1. Mass balances of pyrolysis at temperatures of 340 ℃, 360 ℃, 380 ℃ and 400 ℃ for different processing time

Time	Liquid %		Coke %		Gas %	
	x	s	x	s	x	s
			T=340 ℃			
0	99	0.006	1.24	0.005	0.25	0.001
60	98	0.002	1.24	0.002	0.62	0.0008
120	98	0.19	1.24	0.002	0.78	0.19
240	98	0.45	1.24	0.003	0.91	0.5
480	98	0.13	1.28	0.08	0.33	0.07
1440	97	0.33	1.35	0.06	1.2	0.4
			T=360 ℃			
0	98	0.50	1.41	0.29	0.79	0.26
10	98	0.55	1.2	0.07	0.99	0.49
20	98	0.33	1.2	0.07	0.91	0.4
30	97	0.33	1.16	0.07	1.45	0.32
60	97	0.54	1.2	0.07	1.54	0.47
240	97	0.07	1.25	0.0009	1.54	0.07
577	96	0.43	1.28	0.07	2.69	0.36
			T=380 ℃			
0	97	0.5	1.41	0.08	1.49	0.57
10	98	0.14	1.25	0.003	0.95	0.14
20	97	0.006	1.24	0.002	1.74	0.003
30	97	0.29	1.12	0.002	1.78	0.29
60	97	0.07	1.28	0.07	1.66	0.07
120	96	0.2	1.29	0.07	2.37	0.25
232	96	0.32	1.45	0.19	2.52	0.14
			T=400 ℃			
0	98	0.18	1.2	0.004	0.91	0.19
10	97	0.38	1.2	0.003	2.1	0.38
20	96	0.35	1.2	0.004	2.9	0.35
30	96	0.51	1.4	0.004	2.5	0.50
60	95	0.79	1.7	0.44	3.0	0.38
90	88.1	3.3	2.6	0.32	9.3	3.1
120	89.5	0.94	5.6	1.1	4.9	0.20

5.3.3 Viscosity analyses

In order to determine the break-down point of reaction time, the viscosity is another important parameter, along with the yield of coke. Figure 5-1 shows the viscosity measurements of liquid product obtained at different reaction times for 340 ℃, 360 ℃, 380 ℃ and 400 ℃. As described in Chapter 4, the viscosity of liquid product collected at 400 ℃ continuously decreased until 60 min. Thus, the viscosity slightly increased at 90 min and decreased at 120 min. The viscosity measurements were also performed on the temperatures of 340 ℃, 360 ℃ and 380 ℃. As shown in Figure 5-1, the reduction in viscosity at these temperatures is similar to that at 400 ℃ described in Chapter 4.

However, the behaviors in viscosity changes at 340 ℃, 360 ℃ and 380 ℃ are slightly different from that at 400 ℃ described in Chapter 4. For temperatures of 340 ℃, 360 ℃ and 380 ℃, the viscosity initially decreased and an increase in viscosity was observed right before the break-down point of reaction time. Afterwards, the viscosity decreased again at the break-down point of reaction time. Consequently, at the temperature of 400 ℃, the viscosity increased with initial coke formation at the reaction time break-down point of 90 min. However, at the other three temperatures, an increase in viscosity was found before the break-down points without forming coke. Although the viscosity measurement is regardless of coke formation since the coke yield was extracted from the liquid product, the cause that coke formed is due to the formation of heavy components; as heavy components are forming in process, the viscosity will increase.

Considering from the aspect of same conversion can be obtained in the relationship between time and temperature, (4) therefore, it also proves that the relationship between time and temperature in thermal conversion of bitumen is invalid at low temperatures.

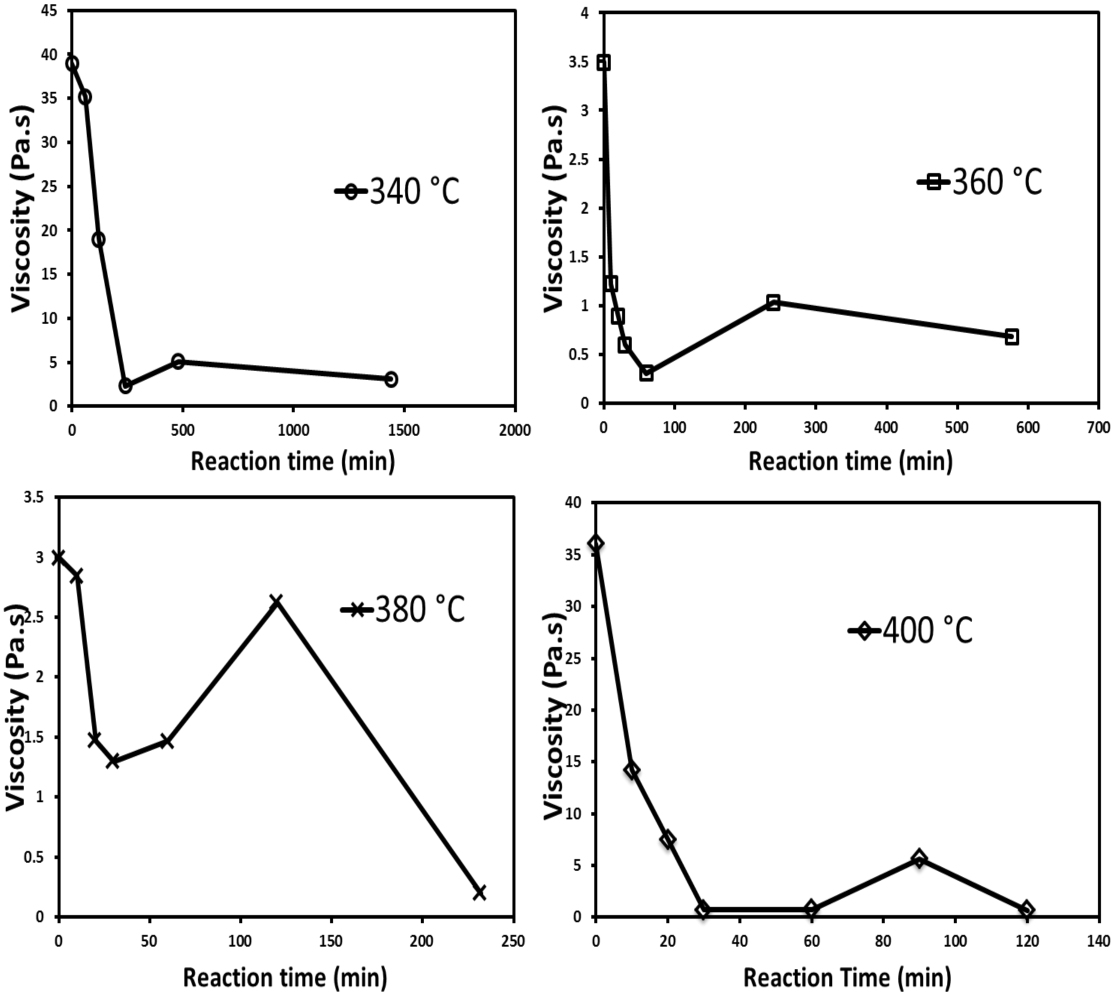

Figure 5-1. The viscosity measurements of pyrolysis liquid products obtained at different reaction time for 340 ℃, 360 ℃, 380 ℃ and 400 ℃

Shen et. al (6) reported that the general mechanism of visbreaking involves the cleavage of molecular bond and the rupture of ring structures of heavy oils to form large numbers of smaller molecular weight and less viscous species. As explained by Quignard and Kressmann (8), all of the reactions occurring during visbreaking proceed by thermal activation and free radical steps: Initiation step-the free radicals formed through homolytic scission of bonds, and the most common bonds during primary upgrading is carbon-carbon (C-C), carbon-sulfur (C-S) and carbon-hydrogen (C-H). (9) ; propagation step-the free radicals experience reactions of hydrogen transfer, decomposition and creation of new low molecular weight free radicals, isomerization, cyclizaiton, condensation/polymerization; recombination step, free radicals recombine together. These reactions depend on pressure, time and temperature, and their effect has been studied in previous chapters; in this chapter, the effect of time and temperature on viscosity was investigated.

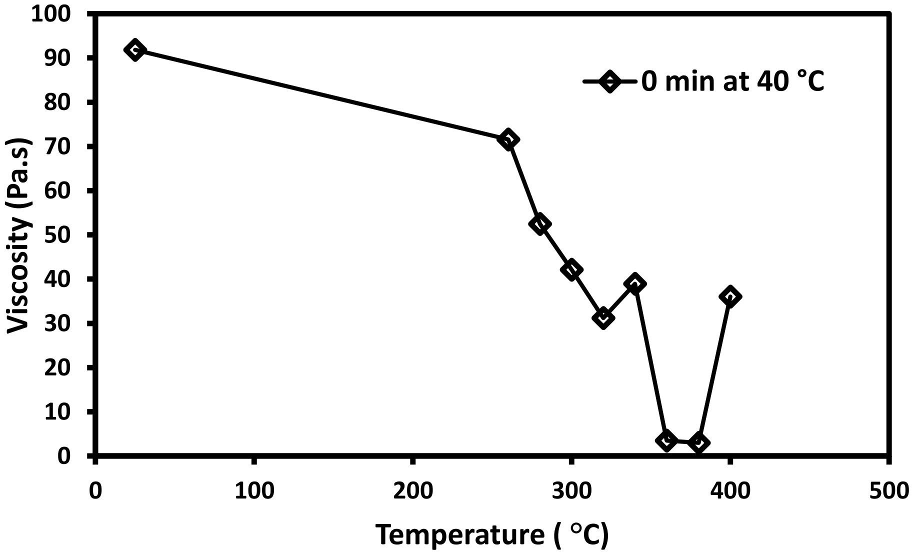

Figure 5-2: The viscosity of liquid product obtained under 0 min of reaction time for different temperatures measured at 40 ℃

In Figure 5-2, it shows viscosity changes with reaction temperatures. The viscosity of fresh bitumen measured at 40 ℃ was 91863.5 ± 3562.7 mPa.s. As the temperature increased, the viscosity did not decrease monotonically, but it followed a general decreasing trend, which mimic a similar viscosity behavior investigated for the coal –slurry-gas mixture in preheater. (10) As described in Section 5.1.1, all the reactions in bitumen visbreaking are thermally driven. The thermal conversion of bitumen involves with thermal cracking of molecular molecules and followed with free radicals chemistry. As the temperature increased, bitumen broke into small and simple molecules. Large amount of alkanes formed and followed with free radicals formation by homolytic scissions of bonds. Since formation of free radicals decreases viscosity; free radicals addition increases viscosity. Hence, as the temperature increased, the viscosity decreased smoothly. Until the viscosity reached the minimum, free radicals reacted with alkanes and free radicals addition became dominant. Then the viscosity increased at 340 ℃. As the temperature continued increasing, homolytic scission of bonds became dominant instead of free radicals addition, the viscosity decreased afterwards. This is repeated in a cycle, which mimicked the viscosity behaviors in coal-liquefaction preheater. (10) Initially, the viscosity decreased smoothly as the temperature increased until reaching a minimum point. Afterwards, swelling and agglomeration occurred lead to an increase in viscosity. Then depolymerization decreased the viscosity.

5.4 Conclusions

Through experimental investigations on relationships among reaction time, operating temperature and viscosity, the following observations were made:

a) Based on the inverse relationship between time and temperature, the break-down points of reaction time that equivalent to 90 min at 400 ℃ were calculated to be 1440 min, 577 min and 232 min for 340 ℃, 360 ℃ and 380 ℃, respectively.

b) There was no coke formation up to the break-down points of reaction time for 340 ℃, 360 ℃ and 380 ℃.

c) In accordance with the effect of time and temperature on the thermal conversion of bitumen, it verified that the conversion did not follow the inverse relationship between time and temperature.

d) At the reaction temperatures of 340 ℃, 360 ℃, and 380 ℃, as the reaction time increased, the viscosity decreased monotonically and an increase in viscosity was observed before the break-down point of reaction time without coke formation. This is due to the formation of heavy components, which also proves the relationship between time and temperature invalid at low temperatures.

e) Consequently, it was postulated that at lower temperatures there is an improvement in selectivity and product quality beyond that predicted from typical visbreaking operating experience at higher temperatures.

f) The behavior in viscosity reduction of bitumen visbreaking, changing with the reaction temperature, is similar to the behaviors investigated in direct coal liquefaction.

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6. Conclusions and Significance

6.1 Introduction

The research was funded by Helmholtz-Alberta initiative as part of the Theme 1" Advanced Processes for Bitumen and Coal Upgrading and Conversion Technologies". The objective was to investigate the thermal cracking behavior of oil sands bitumen during pyrolysis. Especially, investigations were carried out on visbreaking by characterizing the yield of liquid, coke, gas and changes in viscosity with processing time.

6.2 Major conclusions

a) Based on the investigations by employing pressures and the method of operation (batch/semi-batch), it can be concluded that light gas products formed during bitumen pyrolysis were not irreversible products and served the function of a hydrogen transfer solvent.

b) The coke yield could be manipulated through pressure in semi-batch pyrolysis, since the light gas product concentration in fresh bitumen depended on the pressure and the method of operation (batch/semi-batch). As the pressure increased, the concentration of light gas products in the liquid phase increased with less coke formation.

c) The yield of light gas products increased as pressure increased at 400 ℃ due to lighter product over-cracking. However, the light gas yield was not primarily determined by over-cracking of the light products exposed to pyrolysis conditions for longer times. A closed system represents the longest residence time; however, the light gas products yield in a closed pyrolysis was not much different from that in an open pyrolysis system.

d) The liquid yield in a closed pyrolysis system increased due to high H: C ratio of total reacting mixture. However, the liquid yield in an open pyrolysis remained constant due to the trade-off between light gas products over-cracking and coke suppression.

e) Besides the factor of pressures, time also has impact on visbreaking. Investigations were carried out at 400 ℃ for different processing time to study the effects of time on the yield of liquid, coke, gas, and viscosity changes. For a reaction time of 0 min to 20 min, the yield of coke remained constant, and there was a trade-off between the yield of liquid and gas.

f) There was no coke formation up to 60 min as the yield of coke remained constant. In accordance with the analyses on mineral matter, the solid yield could be considered to be composed of mineral matter and associate carbon.

g) There was significant reduction in viscosity from 0 min to 20 min. This means there is a meaningful reduction in viscosity without coke formation.

h) From 20 min onwards to higher reaction time up to 60 min, the yield of liquid, gas and coke remained constant while the viscosity was reduce by 99 % from 0 min to 60 min compared to the value of fresh bitumen. Meanwhile, the viscosity kept fairly constant from 30 min to 60 min.

i) At the processing time of 90 min and higher, the yield of coke increased dramatically with a meaningful difference at 95 % confidence.

j) There was an increase in the viscosity at the reaction time of 90 min due to heavy components formed.

k) 90 min is considered to be the break-down point in processing times at 400 ℃ where coke formed and viscosity increased.

l) Overall, related the results with literature, it suggests that the viscosity reduction is possibly achieved at relatively shorter reaction time at 400 ℃ without initiating coking, and also without substantially changing the liquid yield.

m) The last factor that was considered in present work was temperature. Based on the inverse relationship between time and temperature, the break-down points of reaction time that equivalent to 90 min at 400 ℃ were calculated to be 1440 min, 577 min and 232 min for 340 ℃, 360 ℃ and 380 ℃, respectively.

n) There was no coke formation up to the break-down points of reaction time for 340 ℃, 360 ℃ and 380 ℃. Initially, there was a trade-off between the yields of gas and liquid and then remained constant. At higher reaction time, the yield of coke increased.

o) As the reaction time increased up to the break-down points, the viscosity continuously decreased; afterwards, there was slightly increment in viscosity due to heavy components formed but without coke formation for the temperatures of 340 °C, 360 °C and 380 °C.

p) In accordance with the effect of time and temperature on the thermal conversion of bitumen, it verified that the conversion did not follow the inverse relationship between time and temperature.

q) At lower temperatures there may be an improvement in selectivity and product quality beyond that predicted from typical visbreaking operating experience at higher temperatures.

6.3 Significance of the present work

Applying this work for the industrial uses can be beneficial from two perspectives: First, from the market demand aspect - as the demand in heavy residual fuel oil decreases while high demand in lighter liquid fuel oil. And second, from pipeline transportation point of view by reducing the viscosity could drop the price of oil fuels as less diluent needed.

However, application of this work in the larger industrial scale is premature. First of all, it should still be confirmed whether it is economically efficient on the energy consumption rather than diluent addition. An economic estimates need to be conducted before employing in industrial applications. Furthermore, the stability of the liquid product needs to be confirmed. Since the stability standard of the liquid product for pipeline transportation from Canada to United States is two weeks. This is significant due to this could cause huge economic loss if the pyrolysis liquid product cannot be stable while transportation.

6.4 Future work

One of the potential areas that can be considered for more investigation in the future is to analyze the specific component in light gases formed during pyrolysis plays the important role of solvent in coke suppression. As based on the results investigated, the light gases could dissolved in the bitumen acting as solvent to suppress coke formation; however, not all the components in the light gases have this kind of function.

Another potential area of study might be whether there are other mechanical factors that have impact on coke suppression and viscosity changes. The investigation could be carried out on applying shear force during pyrolysis.

6.5 Presentations and Publications

The nature of the project required regular formal updates on progress, as well as opportunity to present aspects of the work to a broader audience at conferences.

Wang, L., Prasad, V., de Klerk, A. *Catalytic conversion of light olefins to liquid synthetic fuels*. Poster session presented at: 3rd HAI annual meeting, Edmonton, Canada, May 9-11, 2012.

Wang, L., Yang, S., Prasad, V., de Klerk, A. *Low temperature pyrolysis of bitumen*. Poster session presented at: HAI 2rd Science Forum, Potsdam, Germany, September 10-11, 2012.

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

Wang, L., Yang, S., Prasad, V., de Klerk, A. *Low temperature visbreaking of bitumen*. Poster session presented at: 4th Faculty of Engineering Graduate Research Symposium (FEGRS 2013), Edmonton, Alberta, June 19-20, 2013.

Wang, L., Yang, S., Prasad, V., de Klerk, A. *Visbreaking of oil sands bitumen at low temperature*. Presented at: 246th ACS National Meeting, Indianapolis, Indiana, September 8-12, 2013.

Wang, L., Yang, S., Prasad, V., de Klerk, A. *Low temperature visbreaking*. Presented at: HAI 3rd Science Forum, Edmonton, Canada, September 29-20, 2013.

Appendices

A. Appendix I: Additional data used for mass balance calculations of batch and semi-batch operations in Chapter 3, 4 and 5

Table A-1. Mass balance of batch operation at 1MPa and 400 ℃ for 1½ hours

Components	Normalized Mole %	Normalized Mole composition	Moles	Actual Mole Composition	Actual mole %	KH (CP, M/Kpa)	C (mol/L)	Dissolved in Liquid (mol)	Mass (g)	Molar Mass (g/mol)	Dissolved in Liquid (g)
CH4	31.379	0.3138	0.00255975	0.1580	15.8008	0.000014	0.002322719	1.784E-05	0.041345	16.04	0.00028613
CO2	4.164	0.0416	0.00033967	0.0210	2.0967	0.000335637	0.007389176	5.675E-05	0.017442	44	0.00249695
ethylene	0.491	0.0049	0.00004002	0.0025	0.2470	0.000047	0.000121917	9.363E-07	0.001149	28.05	0.00002626
Acetylene	0	0	0	0	0	0.00041	0	0.000E+00	0.000000	26.04	0
Ethane	15.359	0.1536	0.00125294	0.0773	7.7342	0.000019	0.001542966	1.185E-05	0.038032	30.07	0.00035633
Propylene	2.000	0.0200	0.00016313	0.0101	1.0070	0.000048	0.000507506	3.898E-06	0.007028	42.08	0.00016401
Propane	11.725	0.1172	0.00095647	0.0590	5.9041	0.000015	0.00092989	7.142E-06	0.042495	44.1	0.00031494
i-butane	2.103	0.0210	0.00017155	0.0106	1.0590	0.000011	0.00012231	9.393E-07	0.010025	58.12	0.00005459
n-butane	5.625	0.0562	0.00045886	0.0283	2.8325	0.000011	0.00032715	2.513E-06	0.026815	58.12	0.00014603
cis 2-butene	0.462	0.0046	0.00003769	0.0023	0.2327	0.000011	2.68717E-05	2.064E-07	0.002126	56.106	0.00001158
i-pentane	4.191	0.0419	0.00034185	0.0211	2.1102	0.0000081	0.000179472	1.378E-06	0.024764	72.15	0.00009945
n-pentane	12.660	0.1266	0.00103275	0.0637	6.3749	0.0000081	0.000542188	4.164E-06	0.074813	72.15	0.00030043
n-hexane	0.282	0.0028	0.00002299	0.0014	0.1419	0.000006	8.93933E-06	6.865E-08	0.001987	86.18	0.00000592
i-hexene	1.943	0.0194	0.00015854	0.0098	0.9786	0.000006	6.16534E-05	4.735E-07	0.013704	86.18	0.00004081
H2	0	0	0	0	0	4.837117473	0	0.000E+00	0.000000	2.02	0
Ar	6.138	0.06138	0.00050073	0.0309	3.0909	1.38203E-05	0.000448534	3.445E-06	0.020142	39.95	0.00013762
N2	N/A	N/A	0.00804252	0.4964	49.6448	6.41658E-06	0.003344775	2.569E-05	0.225990	28.01	0.00071952
CO	1.479	0.01479	0.00012066	0.0074	0.7448	0.000335637	0.002624858	2.016E-05	0.003944	28.01	0.00056465
SUM	100	1	0.01620012	1	100			0.00015745	0.325813		0.00500570

Continued:

	N2		
mass	0.225912021	Gas (no N2) mole	0.008157605
mole	0.008068286	Total Gas mass	0.33
KH	6.41658E-06	Total Gas mole	0.016200122
C (mol/L)	0.003355492	Dissolved in Liquid (Incl. N2)	0.005725218
Dissolved in Liquid	2.57702E-05	Dissolved in Liquid (Excl. N2)	0.0050057
In Gas	0.008042516	Calculated Gas mass	0.325812514
mole %	49.64478916	Calculated/Actual	0.987310649

Table A-2. Mass balance summary of batch operation at 1 MPa and 400 ℃ for 1½ hours

Runs	N2 (g)	Weight of Bitumen (g)	Weight of Product (g)	Liquid (g)	Coke (g)	Actual Gas (No N2) (g)	Calculated Gas (No N2) (g)	Mass In	Mass Out	%Difference
1	0.225912021	8.01	7.68	7.57	0.11	0.33	0.325812514	8.01	8.0058125	99.94772178
2	0.222432	8.06	7.71	7.55	0.16	0.35	0.246251624	8.06	7.9562516	98.71279931
3	0.223734556	8.01	7.8	7.64	0.16	0.21	0.281174898	8.01	8.0811749	100.8885755
AVE	0.224026192	8.026666667	7.73	7.586667	0.143333	0.296666667	0.284413012	8.026666667	8.014413	99.84969886
SD	0.001758245	0.028867513	0.06244998	0.047258	0.028868	0.075718778	0.039879165	0.028867513	0.0629042	1.091195162

Table A-3. Mass balance of semi-batch operation at 400 ℃ and 1 MPa for 1½ hours

Components	Normalized fraction	Moles	Molar Mass (g/mol)	Mass (g)	Gas In moles	Gas In mole fraction	KH (CP, M/Kpa)	C (mol/L)	Dissolved in Liquid	Gas in Mass (g)	Dissovled in Liquid mass (g)	Gas Out moles	Gas out Mass(g)
CH4	0.34189	0.0022841	16.04	0.03664	0.0007312	0.10483	0.000014	0.00066	5.14E-06	0.011729	8.25E-05	0.0015601	0.025
CO2	0.03994	0.0002668	44.00	0.01174	0.0000854	0.01225	0.000335637	0.0018	1.44E-05	0.003758	6.34E-04	0.0001822	0.0080
ethylene	0.01040	0.0000695	28.05	0.00195	0.0000222	0.00319	0.000047	6.74E-05	5.25E-07	0.000624	1.47E-05	0.0000475	0.0013
Acetylene	0	0	26.04	0	0	0	0.00041	0	0	0	0	0	0
Ethane	0.17225	0.0011508	30.07	0.03460	0.0003684	0.05281	0.000019	0.00045	3.52E-06	0.011078	1.06E-04	0.0007860	0.024
Propylene	0.03762	0.0002513	42.08	0.01058	0.0000805	0.01153	0.000048	0.00025	1.94E-06	0.003386	8.17E-05	0.0001717	0.0072
Propane	0.13329	0.0008905	44.1	0.03927	0.0002851	0.04087	0.000015	0.00028	2.15E-06	0.012572	9.48E-05	0.0006082	0.027
i-butane	0.02218	0.0001482	58.12	0.00861	0.0000474	0.00680	0.000011	3.37E-05	2.62E-07	0.002758	1.52E-05	0.0001012	0.0059
n-butane	0.07816	0.0005222	58.12	0.03035	0.0001672	0.02397	0.000011	0.00012	9.24E-07	0.009716	5.37E-05	0.0003567	0.021
cis 2-butene	0.00719	0.0000480	56.106	0.00269	0.0000154	0.00220	0.000011	1.09E-05	8.50E-08	0.000862	4.77E-06	0.0000328	0.0018
i-pentane	0.03295	0.0002201	72.15	0.01588	0.0000705	0.01010	0.0000081	3.68E-05	2.87E-07	0.005084	2.07E-05	0.0001503	0.0108
n-pentane	0.04066	0.0002716	72.15	0.01960	0.0000870	0.01247	0.0000081	4.54E-05	3.54E-07	0.006274	2.55E-05	0.0001855	0.013
i-hexene	0.01017	0.0000679	86.18	0.00585	0.0000217	0.00312	0.000006	8.42E-06	6.56E-08	0.001874	5.65E-06	0.0000464	0.0040
n-hexane	0.00895	0.0000598	86.18	0.00515	0.0000191	0.00275	0.000006	7.41E-06	5.77E-08	0.001650	4.98E-06	0.0000409	0.0035
H2	0	0	2.02	0	0	0	4.837117473	0	0	0	0	0	0
Ar	0.06435	0.0004299	39.95	0.01717	0.0001376	0.01973	1.38203E-05	0.00012	9.56E-07	0.005498	3.82E-05	0.0002936	0.012
N2	N/A	0.0151612	28.01	0.42466	0.0048366	0.69339	6.41658E-06	0.0020	1.56E-05	0.135474	4.37E-04	0.0103191	0.29
CO	0	0	28.01	0	0	0	0.000335637	0	0	0	0	0	0
SUM	1			0.24009						0.212336	1.62E-03	0.0148822	0.45

Continued:

	N2				
mass	0.424949374	Gas (no N2) mole	0.006680761	Total mass of Gas (Inc. N2)	0.666980502
mole	0.015176763	Total Gas mass	0.25	Total mass of Gas (Excl. N2)	0.242031128
KH	6.41658E-06	Gas In mole	0.006975364		
C (mol/L)	0.002002133	N2 in reactor mole	0.004852231		
Dissolved in Liquid	1.55966E-05	N2 in gas in reactor mole	0.004836635		
In Gas	0.004836635	Total mass of N2	0.424949392		
mole %	69.56241457	Total mole of N2	0.015171346		
Gas In (No N2) mole	0.002138729	Mass In	8.464949374		
Gas Out (No N2) mole	0.004563046	Mass Out	8.456980502		
N2 Out (X) mole	0.010319114				
Gas Out (Y) mole	0.01488216				

Table A-4. Mass balance summary of semi-batch operation at 400 ℃ and 1 MPa for 1½ hours

Runs	N2 (g)	Weight of Bitumen (g)	Weight of Product (g)	Liquid (g)	Coke (g)	Actual Gas (No N2) (g)	Calculated Gas (No N2) (g)	Mass In	Mass Out	%Difference
1	0.424949	8.04	7.79	7.33	0.46	0.25	0.242031128	8.04	8.032031	99.900885
2	0.441242	8.16	7.89	7.52	0.37	0.27	0.265449144	8.16	8.155449	99.94423
3	0.446547	8.03	7.68	7.27	0.41	0.35	0.346417859	8.03	8.026418	99.955391
AVE	0.437579	8.076666667	7.786666667	7.373333	0.413333	0.29	0.28463271	8.076667	8.071299	99.933502
SD	0.011255	0.072341781	0.105039675	0.130512	0.045092	0.052915026	0.054773665	0.072342	0.07293	0.0287931

Table A-5. Coke and gas yields obtained after pyrolysis of fresh Cold Lake bitumen at 400 ℃ for 1½ hours in batch and semi-batch reactors at different pressure conditions

Pressure (MPa)	Avg. coke yield (wt %)		Avg. gas yield (wt %)		St.Dev. coke yield (wt %)		St.Dev. gas yield (wt %)	
	batch	semi-batch	batch	semi-batch	batch	semi-batch	batch	semi-batch
1	1.64	5.12	4.02	3.59	0.41	0.59	0.99	0.67
2		3.14		4.92		0.31		0.19
4		2.61		9.00		0.32		2.98
8		2.03		5.81		0.08		0.99

B. Appendix II: Additional data on viscosity and TGA results in Chapter 4 and 5

Table B-1. Viscosity measurement at 40 ℃ of pyrolysis product obtained at 340 ℃ and 4 MPa for different processing time

40 ℃/Time (min)	AVE	STD
0	39.0	1.4
60	35.2	0.31
120	19.0	0.042
240	2.29	0.023
480	5.08	0.20
1440	3.08	0.19

40 ℃	AVE	STD
60 without filter	54.4	0.21
60 with filter	35.2	0.31

TableB-2. Viscosity measurements at 40°C of pyrolysis product at 360°C, 380°C and 400°C

T	0min		10min		20min		30min		60min		90min		120min		232min		240min		577min	
	x	s	x	s	x	s	x	s	x	s	x	s	x	s	x	s	x	s	x	s
360	3.49	0.039	1.22	0.080	0.89	0.037	0.60	0.036	0.31	0.0068							1.03	0.034	0.68	0.031
380	3.00	0.076	2.84	0.035	1.47	0.046	1.30	0.034	1.47	0.0081			2.62	0.072	0.20	0.004				
400	36.0	0.32	14.2	0.20	7.51	0.11	0.71	0.046	0.76	0.064	5.6	0.22	0.68	0.074						

Table B-3. Viscosity measurements at 60°C of pyrolysis product at 360°C, 380°C and 400°C

T	0min		10min		20min		30min		60min		90 min		120min		232min		240min		577min	
	x	s	x	s	x	s	x	s	x	s	x	s	x	s	x	s	x	s	x	s
360	0.47	0.034	0.31	0.048	0.28	0.035	0.20	0.041	0.033	0.014							0.3	0.004	0.21	0.006
380	0.31	0.041	0.26	0.037	0.12	0.042	0.11	0.0098	0.34	0.031			0.61	0.042	0.09	0.02				
400	4.3	2.1	2.7	1.1	1.3	0.11	0.15	0.026	0.17	0.012	0.66	0.031	0.082	0.041						

Table B-4: Viscosity of fresh bitumen and after drying from dissolving in the methylene chloride

Fresh Bitumen Feed		
Runs	40	60
1	95972.3	9351.2
2	89985.6	9871.8
3	89632.6	9789.7
AVE	91863.5	9670.9
STD	3562.7	279.9
After drying		
Runs	40	60
1	104535.2	10732.1
2	109628.3	10857.4
3	103704.7	11315.1
AVE	105956.1	10968.2
STD	3207.2	306.9

Table B-5. TGA results for 340 ℃

Time (min)	MCR %	
	x	s
0	9.1	1.2
60	10	0.13
120	10	0.59
240	9.0	0.17
480	10	1.1

Table B-6. TGA results for 360 ℃

Time (min)	MCR%	
	x	s
0	9.3	1.9
10	10	0.69
20	9.8	0.056
30	9.7	0.47
60	9.6	0.27
240	11	0.29
577	10	0.29

Table B-7. TGA results for 380 °C

Time (min)	MCR%	
	x	s
0	9.34	0.59
10	8.84	1.4
20	9.82	2.1
30	10.1	1.3
60	11.3	3.8
120	11.8	0.15
232	12.2	1.5

Table B-8. TGA results for 400 °C

Time (min)	MCR %	
	x	s
0	12.28	0.14
10	12.24	0.57
30	13.47	2.1
60	15.46	1.3
90	17.96	0.63
120	17.3	1.6

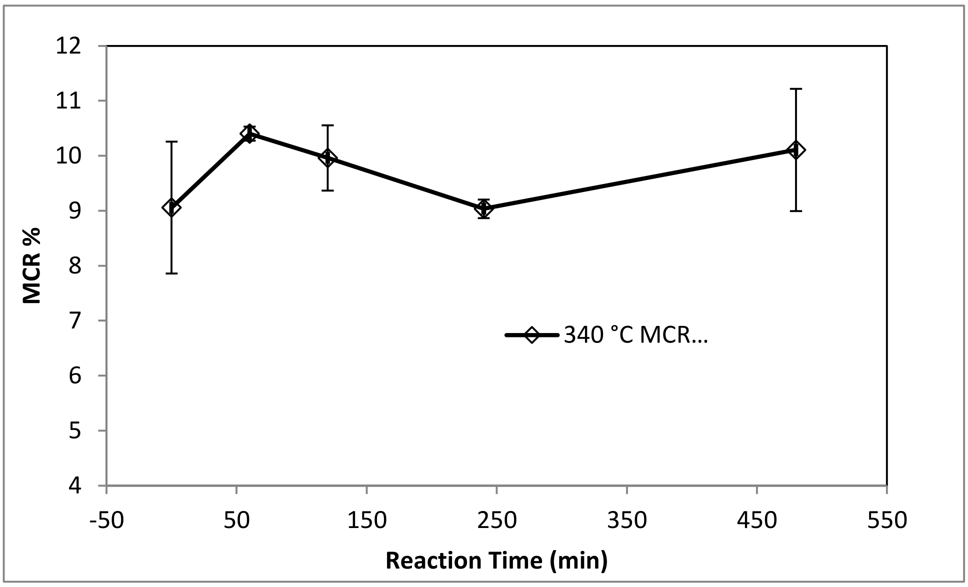

Figure B-1. TGA results of pyrolysis product at 340 ℃

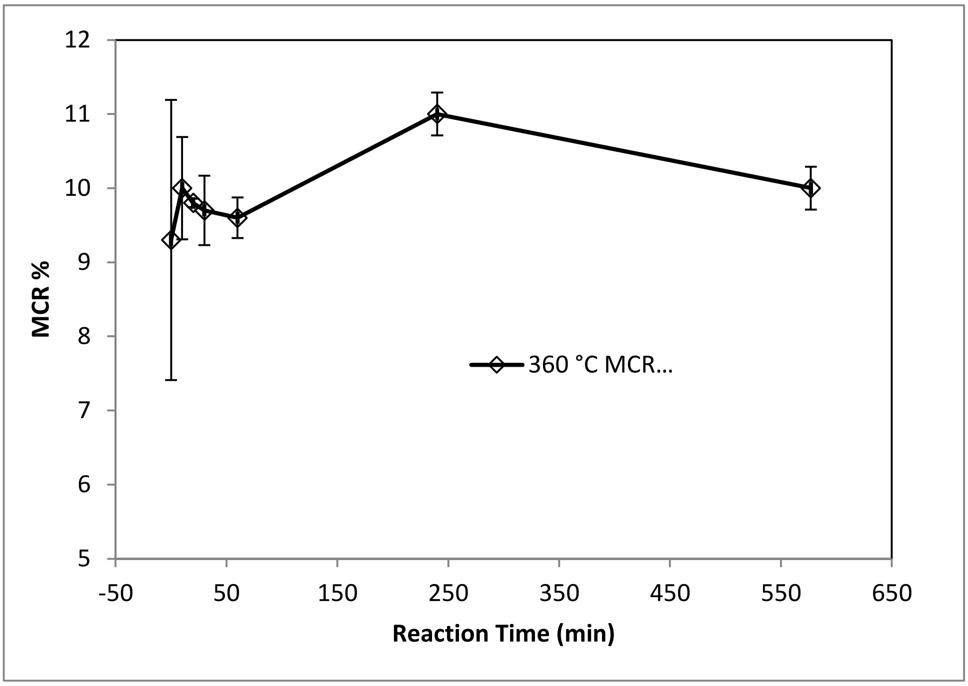

Figure B-2. TGA results of pyrolysis product at 360 ℃

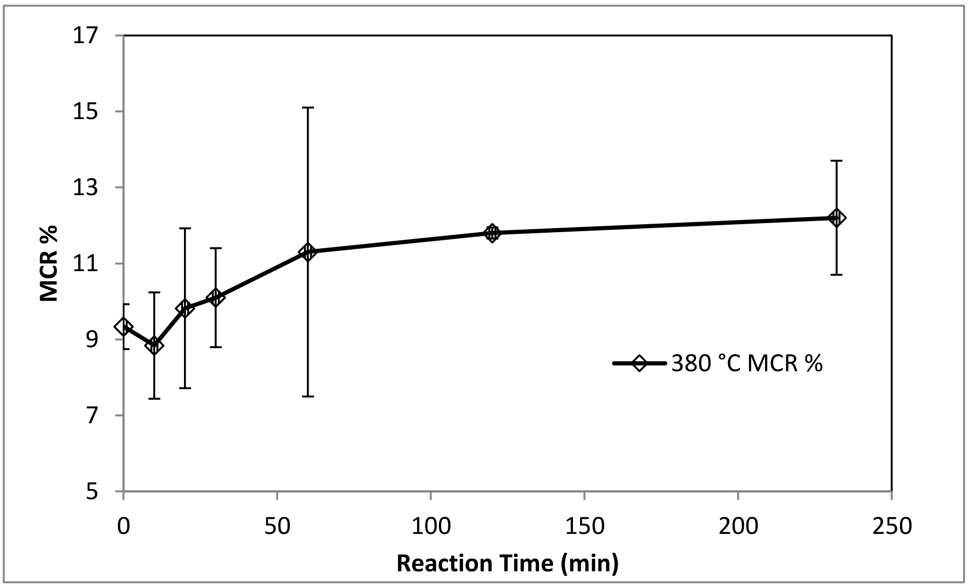

Figure B-3. TGA results of pyrolysis product at 380 ℃

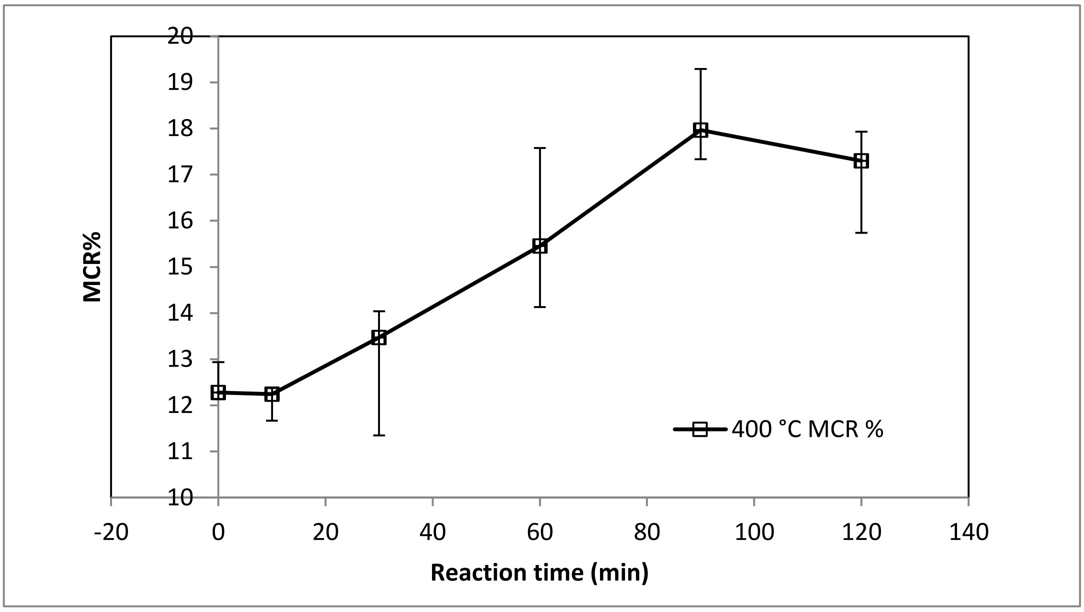

Figure B-4. TGA results of pyrolysis product at 400 ℃