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Modeling Mild Thermal Cracking of Heavy Crude Oil and Bitumen with VLE Calculations

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M.A.Sc. in Chemical Engineering

Thesis Submitted in the Partial Fulfillment of the Requirements for the Master of Applied Science in Chemical Engineering

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Abstract

The current shortage of crude oil from conventional sources has increased interest in developing unconventional resources such as oil sands. Heavy crudes and bitumen are found in Northern Alberta and their exploration, processing, and transport to market pose challenges in the use of these resources. Part of the solution to these challenges involves the reactive thermal processing of heavy crudes and bitumen. This thesis focused on mild thermal cracking reactions, and two studies regarding these reactions were presented.

The first was an experimental study performed in a pilot-scale semi-batch reactor. The three crude oils were heated to 350, 400, 425, and 450°C at 1240 kPa. A five-lump reaction model combined with a process simulator with VLE calculations was fitted with the experimental data obtained. The goodness of fit between the model predicted values and experimental values for the Hardisty (MBL), Albian Heavy Synthetic (AHS), and Christina Lake Dilute Bitumen (CDB) were determined to be 0.99, 0.99, and 0.98, respectively. Moreover, 80, 85, and 89% of the optimized model's predicted values had less than 10% error for MBL, AHS, and CDB, respectively.

The second study described the implementation of a mild thermal cracking reaction model to the development of a train car fire-model for the assessment of safety aspects in the design of train cars used to transport crude oil. Case studies were conducted using the UniSim® depressuring utility and a previously developed mild thermal cracking reaction model to demonstrate the effect of compositional change. Three crude oils with varying properties and representative of the types of crudes transported by rail in Canada were used here: MBL, AHS, and CDB. The case studies conducted showed the performance of a train car fire-model to be dependent on the crude oil characteristics: up to -57% and -99% difference in model predicted variables for AHS and CDB, respectively, when compared to MBL. Furthermore, the model's performance was also shown to be affected by the compositional change of a given crude oil due to mild thermal cracking reactions: up to 42% difference in model predicted variables when compared to the base case.

Sommaire

La pénurie actuelle de pétrole brut provenant de sources conventionnelles a accru l'intérêt pour le développement de ressources non-conventionnelles comme les sables bitumineux. Les pétroles bruts lourds et le bitume se trouvent dans le nord de l'Alberta et leur exploration, traitement et transport vers le marché posent des défis dans l'utilisation de ces ressources. Une partie de la solution à ces défis implique le traitement thermique réactif des pétroles bruts lourds et du bitume. Cette thèse a porté sur les réactions légères de craquage thermique, et deux études concernant ces réactions ont été présentées.

La première était une étude expérimentale réalisée dans un réacteur semi-continu à l'échelle pilote. Les trois pétroles bruts ont été chauffés à 350, 400, 425 et 450 ° C à une pression de 1240 kPa. Un modèle de réaction à cinq composants, incorporé à un simulateur de procédé avec des calculs d'équilibre liquide-vapeur, a été optimisé pour représenter les données expérimentales obtenues. La qualité de l'ajustement entre les valeurs prédites du modèle et les valeurs expérimentales pour le Hardisty (MBL), l'Albian Heavy Synthetic (AHS) et le bitume dilué Christina Lake (CDB) a été déterminée à 0,99, 0,99 et 0,98, respectivement. De plus, 80, 85 et 89% des valeurs prédites du modèle optimisé présentaient une erreur inférieure à 10% pour MBL, AHS et CDB, respectivement.

La deuxième étude a décrit la mise en œuvre d'un modèle de réaction de craquage thermique léger à l'élaboration d'un modèle de feu de wagon pour l'évaluation des aspects de sécurité dans la conception des wagons utilisés pour le transport du pétrole brut. Des études de cas ont été menées à l'aide de l'utilitaire de dépressurisation UniSim® et d'un modèle de réaction de craquage thermique léger développé précédemment pour démontrer l'effet du changement de composition. Trois pétroles bruts aux propriétés variables et représentatifs des types de bruts transportés par chemin de fer au Canada ont été utilisés ici: MBL, AHS et CDB. Les études de cas ont montré que la performance d'un modèle de feu de wagon dépendait des caractéristiques du pétrole brut: jusqu'à -57% et -99% de différence dans les variables prédites du modèle pour AHS et CDB, respectivement, par rapport à MBL. De plus, la performance du modèle a également été affectée par le changement de composition d'un pétrole brut donné en raison de réactions de craquage thermique légers: jusqu'à 42% de différence dans les variables prédites du modèle par rapport au cas de base.

Statement of Contribution and Collaborators

I, André Guerra, hereby declare that I am the sole author of this thesis. I developed and wrote the code for all the models developed in MATLAB® and VBA. I also created the process simulations used in this work. Benoit Duhoux wrote one of the scripts in MATLAB® and one subroutine in VBA, which were implemented in the models I developed.

The experimental work was conducted at CanmetENERGY-Ottawa in the Partial Upgrading Development Lab (PUDL) pilot plant. Plant operation and sample gathering were performed by me with the help of CanmetENERGY engineer Samantha Bryson and combustion technologists Steve Montero and Chris Mallon. Chemical analysis of samples was performed by the characterization lab at CanmetENERGY-Ottawa. High temperature simulated distillations were performed at CanmetENERGY-Devon.

Two chapters are manuscripts for future publication, which contain the names of all contributing authors.

My thesis supervisor was Arturo Macchi from the Department of Biological and Chemical Engineering from the University of Ottawa; he provided comments and corrections for the work presented. Dr. Robert Symonds and Dr. Robin Hughes from CanmetENERGY-Ottawa also provided technical guidance and editorial suggestions.

Acknowledgements

I would like to express my deepest gratitude to my supervisor Dr. Arturo Macchi for providing invaluable advice and support during my graduate studies. Arturo, you pushed me at times when it was necessary, yet you gave me the freedom and trust to work independently. I greatly appreciate your mentorship.

I would like to thank Dr. Robin Hughes at Natural Resources Canada CanmetENERGY-Ottawa for allowing me to be part of, and contribute to, his research group. The experience was invaluable and much appreciated.

Dr. Robert Symonds, at CanmetENERGY-Ottawa, thank you for all your guidance and patience throughout my graduate degree. I learned a great deal from you, and I enjoyed working together.

Samantha Bryson, Steve Montero, and Chris Mallon at CanmetENERGY-Ottawa, thank you for all your hard work. You were instrumental in enabling me to complete this project on time.

A special thanks to Benoit Duhoux. Benoit took the time to introduce me to MATLAB® and to teach me how to integrate a MATLAB® script to process simulators.

My family: Luis Antonio (father), Paula (mother), and Júlia (sister). Thank you all for your support and love. It would have been difficult to accomplish this without all of you with me.

Thank you to all my friends for making the endless time spent on campus enjoyable.

Finally, I'd like to thank my girlfriend Kelly Ann. Your constant encouragement and love kept me motivated and sane throughout this ***unsteady***-state process.

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Nomenclature

Notation	Definition	Units
[G]	Gas mass percentage	wt%
[GLN]	Gasoline mass percentage	wt%
[LGO]	Light Gas Oil mass percentage	wt%
[R]	Residue mass percentage	wt%
[VGO]	Vacuum Gas Oil mass percentage	wt%
A_i	Arrhenius pre-exponential factor of the ith reaction	1/min
E_{ai}	Activation energy of the ith reaction	J/mol
k_i	Kinetic parameter of the ith reaction	1/min
R	Gas constant	J/mol K

List of Acronyms

Acronym/Abbreviation	Definition
AFFTAC	Analysis of Fire Effects on Tank Cars
AHS	Albian Heavy Synthetic
BBM	Black-Box Model
BLEVE	Boiling Liquid Expanding Vapour Explosion
C	Coke
CDB	Christina Lake Diluted Bitumen
D	Distillate
DOT	Department of Transportation
EoS	Equation(s) of State
G	Gas (-C-5)
GBM	Grey-Box Model
GLN	Gasoline (IBP-150°C)
I	Intermediate
IBP	Initial Boiling Point
LGO	Light Gas Oil (150-350°C)
LPG	Liquefied Petroleum Gas
MBL	MBL Hardisty
P	Product
PNA	Polynuclear Aromatic
PR	Peng-Robinson
PRV	Pressure Relief Valve
R	Residue (500+°C)
SAGD	Steam Assisted Gravity Drainage
SSE	Summation of Squared Errors
TBP	True Boiling Point
TC	Transport Canada
VGO	Vacuum Gas Oil (350-500°C)
WBM	White-Box Model

Chapter 1 – Introduction

1.1 Petroleum Chemistry Overview

Petroleum occurs in the solid (absorbed/mixed with sand, stone, or clay), liquid, and gaseous phases. The characteristic that gives petroleum its major value is its ability to burn. This family of combustible minerals is called "caustobolites" [1]. There is a physical distinction between coal caustobolites and petroleum caustobolites, however, all caustobolites contain hydrogen, carbon, oxygen, and most often sulfur and nitrogen. These occur in different ratios in different types of caustobolites. Petroleum is a complex mixture of hydrocarbons and other carbon compounds. These compounds include, paraffinic, aromatic and naphthenic hydrocarbons, asphaltenes, resins, and ash. Table 1-1 lists the common elemental composition of petroleum.

Table 1-1: Typical elemental content of petroleum [1]

Component	Typical Content [wt.%]
Carbon	84-87
Hydrogen	12-14
Oxygen	1-2
Sulfur	1-2
Nitrogen	1-2

Petroleum contains large molecular weight compounds such as resins and asphaltenes, which often contain heteroatoms (e.g.: sulfur, nitrogen, oxygen). However, these elements are found in smaller structures as well. Ash is the incombustible component of petroleum [1]. Asphaltenes and resins are large, complex molecules, which are soluble in petroleum at reservoir conditions. Moreover, these compounds are characterized as soluble in aromatic solvents (i.e.: toluene) and insoluble in paraffinic solvents (i.e.: n-heptane).

Petroleum is further characterized based on its physical properties such as density, viscosity, pour point, boiling point, and organic solvent solubility. The physical properties of petroleum allow for oil obtained from different locations in the world to be compared and ranked based on value and the desired product properties of the petroleum processing industry. This report focuses on heavy crude oil and bitumen. These can be naturally occurring, or processed petroleum fraction equivalents, which have higher than average density and viscosity.

1.2 Bitumen and Heavy Crude Oil

1.2.1 Market Demand

The increased demand for light crude products and depleting reserves of sweet light crude oils have increased the refining industry’s interest in processing “bottom of the barrel” fractions [2]. These are heavy petroleum remains (bottoms) from atmospheric or vacuum distillation towers used in the refining of light petroleum. The heavy fractions can be converted into lighter petroleum products. Conversion products have increased market value as they can be used for fuel blending or as raw material in the petrochemical industry, in similar ways as products from light crude refining are used. The conversion of heavy crudes, or heavy fractions, improves the crude’s transportability and value [3], and can increase the profitability of an entire refinery [4]. To achieve this conversion, processes involving carbon rejection and hydrogen addition are used to increase the oil’s hydrogen-to-carbon ratio [3], [4].

Heavy crude contains a greater amount of long chain hydrocarbons, asphaltene, and resin, which increase its density and viscosity [5]. Figure 1-1 shows the density and viscosity associated with different types of crudes. Figure 1-1 was adapted from *Upgrading Oilsands and Heavy Oil* by M. Gray [5].

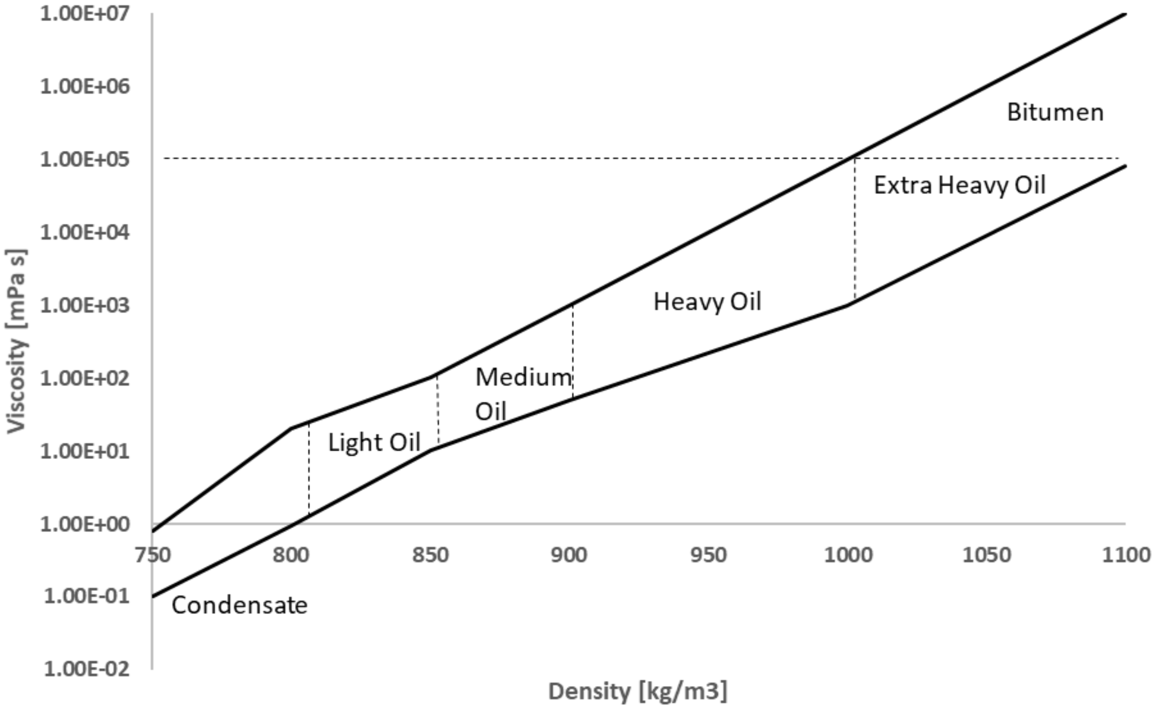

Figure 1-1: Viscosity and density of different grades of crude oil at standard conditions and 15°C (Adapted* [5]*)

1.2.2 Physical and Chemical Characteristics

Bitumen is a naturally occurring mixture of hydrocarbons found mixed in rocks and soil. Its constituent compounds contain high levels of sulfur and nitrogen, and some heavy metals (i.e.: vanadium and nickel) [5]. In its natural form, bitumen is too viscous and dense to flow at pipeline temperatures (7-11°C) [5]. There are two main deposits of bitumen in the world: Canada and Venezuela. The Canadian reservoirs are almost entirely found in the northern region of the province of Alberta, and they rank as the third largest oil source in the world [6]. The main Canadian deposits of bitumen are in the Cold Lake, Athabasca, and Peace River regions. Alberta Energy's website illustrates the Albertan resources [6]; Figure A 1 of the Appendix shows the three major reserves in Alberta. The Canadian Oil Sands proven reserves were 166 billion barrels in 2014, and the total oil production reached 2.3 million barrels per day [6].

Heavy petroleum crude is naturally occurring, or partly processed, petroleum that has a high content of heavy molecular weight components, such as long chain hydrocarbons, asphaltenes, or resins. This molecular content contributes to its "heavy" denomination and leads to different physical properties compared to its "lighter" counterparts. Heavy crude is characterized by its higher than average density and viscosity. The crude's density and viscosity are used to grade and price the oil. The American Petroleum Institute (API) gravity scale was developed to index and grade the petroleum based on its specific gravity (or density) [5]. Heavy oils have API gravities below 20 [2]. Table 1-1 compares the physical properties of light crude with two types of bitumen.

Table 1-2: Comparison between the physical properties of light crude and bitumen at standard conditions[5]

Property	Light Crude	Cold Lake Bitumen	Athabasca Bitumen
API Gravity at 15°C	40.8	10.0	9.0
Metals, [ppm]	3.2	220.0	280.0
Kinematic Viscosity at 40 ºC, [$m^2/s \times 10^{-6}$]	4	5000	7000

Canadian bitumen has a lower hydrogen content than light crude petroleum. Bitumen is "heavier" as it has a higher content of heteroatoms, aromatics, asphaltenes, and resins, which are high density unsaturated molecules. This leads to a lower overall hydrogen-to-carbon ratio, lower API and higher viscosity (Table 1-2). Moreover, the sulfur content in bitumen (>4wt%) is as high as four times the sulfur content of lighter crudes. The high sulfur content proves cumbersome for heavy petroleum processing units. Sulfur can deactivate certain catalysts required for bitumen processing.

1.2.3 Upgrading Processes

Upgrading refers to the conversion of heavy crudes to lighter ones. The upgrading technologies applied to heavy crude feedstock include catalytic and thermal carbon rejection processes. As their names suggest, these processes upgrade crude by catalytic action and exposure to high temperatures, respectively [7]. The objective of these processes is to cleave carbon-carbon (C-C) bonds in long hydrocarbon chains of the heavy crude feedstock, and to increase hydrogen-to-carbon ratio. This process converts the heavy crude feed into lighter and more valuable products (lower average molecular weight). This thesis focuses on the thermal cracking technologies. The technologies that use this type of carbon rejection mechanism include visbreaking, delayed coking, fluid coking, and flexi-coking.

Table 1-3. Characteristics of different thermal cracking processes [7]

Technology	Summary
Visbreaking	- Mild thermal cracking (400-450°C) - Low conversion (up to 10%) - Main purpose is to reduce viscosity of feedstock
Delayed Coking	- Moderate thermal cracking (480-520°C) - Coke yield (30%) - Continuous process - Coke builds up in the delayed coker vessel and is switched to another vessel once the first has filled with coke
Fluid Coking	- Severe Thermal cracking (480-565°C) - Fluidized bed with solids used for heat transfer to the oil feedstock - Coke forms on the surface of solid particles, which is burned off in regeneration; particles are cycled between a fluid coking bed and a combustion bed making the process continuous - Produces less coke than fluid coking (20% coke yield)
Flexi-coking	- Severe Thermal cracking (480-565°C) - Fluid bed with coke gasification - Burning the sulphur rich coke in fluid coking can release hydrogen sulphide and sulphur dioxide in the process (safety hazard) - Gasification of coke (with steam) is an alternative for the removal of coke from the solid particles and contributes to syngas production (CO + H_2)

The upgrading of heavy crude oil and bitumen can be classified by the extent to which it is upgraded – which is determined by its final product's physical properties. Fully upgraded bitumen has physical properties comparable to those of light-medium crudes extracted from natural reservoirs. Upgraded crude whose specifications approach that of light crude is referred to as synthetic crude oil. Partial upgrading, on the other hand, improves the feedstock's properties towards that of natural light-medium crudes, but its properties will not improve enough to reach those of synthetic crude oil (fully upgraded).

1.3 Thermal Cracking

1.3.1 Thermodynamics and Kinetics

Thermal cracking is a spontaneous reaction at increased temperatures, which causes conversion of heavy crude to lighter products by breaking or "cracking" bonds [5]. It is an endothermic reaction whose activation energy depends on the bond to be broken. Table 1-4 lists the activation energies necessary to break different types of bonds found in heavy petroleum. From the table, it is evident that sulfur, oxygen, and nitrogen removal is thermodynamically favorable in thermal cracking. Moreover, the cleavage of carbon-carbon bonds of alkanes is also favoured over other carbon-carbon bond types.

Table 1-4: Estimated activation energy for breaking bonds found in petroleum [5]

Chemical Bond	**Energy (kJ/mol)**
C-C (aliphatic)	344 ± 4
C-H (primary)	411 ± 4
C-H (secondary)	398 ± 4
C-H (aromatic)	464 ± 8
C-S	307 ± 8
C-N	342 ± 8
C-O	344 ± 4

Thermal cracking is a non-catalytic process, and is based on a radical mechanism [5], [8]. Equations 1.1-1.4 represent the three phases of a radical mechanism: (1.1) initiation, (1.2 and 1.3) propagation, and (1.4) termination.

Initiation

$$\text{alkane} + \text{heat} \rightarrow 2\ \text{Radicals} \tag{1.1}$$

Propagation

$$\textbf{(H abstraction)}\ \text{alkane} + \text{Radical} \rightarrow (\text{Radical} + \text{H}) + \text{Radical} \tag{1.2}$$

$$\textbf{(}\boldsymbol{\beta}\textbf{ scission)}\ \text{Radical} \rightarrow \text{Radical} + \text{Olefin} \tag{1.3}$$

Termination

$$\text{Radical} + \text{Radical} \rightarrow \text{Products} \tag{1.4}$$

Thermal cracking operating conditions depend on the type of thermal cracking reactions that the process considered targets. These can be separated into mild, moderate and severe processes [7]. Pyrolysis, visbreaking, and coking are the main types of thermal cracking used in the petroleum industry. Each of these processes has specific operating conditions. Pyrolysis is performed at low pressures (2-3 bar), but at high temperatures (900+ºC), which classifies it as a severe thermal cracking process [8]. Visbreaking is a mild cracking process with an operating temperature range of 400-450ºC, but it operates at higher pressures (10-15 bar) [2], [7]. Finally, coking conditions are intermediate to visbreaking and pyrolysis. However, coking conditions further depend on the type of coking process: (i) delayed coking (5-15 bar, 450-550ºC) or (ii) fluid coking (2-3 bar, 480-590ºC) [7]–[9].

1.3.2 Coke Product and Coking Processes

Coke is a carbon-rich (85 wt% carbon) solid product from thermal cracking of heavy crudes [7]. It is formed through the condensation of aromatic and poly-nuclear aromatic molecules, and through the heating of asphaltenes and resins in heavy petroleum [7]. As previously mentioned, asphaltenes and resins are soluble in different types of organic solvents and are soluble in liquid petroleum under reservoir conditions. Thus, they are classified as solubility classes of compounds

– they have similar (but not identical) structures and solvent solubility. During thermal cracking processes, the reactions that convert heavy molecules to lighter ones cause the molecular composition of the oil to change due to the difference in physical properties between the original crude and the products formed. A net accumulation of paraffinic liquid products can change the solubility of asphaltenes in the bulk liquid phase and cause them to precipitate, leading to the formation of a mesophase and, ultimately, coke [10], [11].

Coking processes take advantage of the formation of coke during thermal cracking in the upgrading of heavy crude. The crude components involved in the formation of coke have a large percentage of the heteroatom content in the crude. This leads to the formation of a solid coke product rich in heteroatoms, and light liquid and gas products with lower heteroatom content [7].

Although the different types of coking processes are based on similar principles, the unit operations are different altogether. In the fluid coking process, heavy crude is fed into a fluidized particle bed, in which the particles are hot enough to heat up the crude to cracking temperatures and to induce coke formation. Coke deposits on the surface of the fluidized bed particles. The fluid coking bed is connected to a fluidized bed combustor, where the coked particles are transported to and the coke is burned. This heats up the particles, which are recycled back to the fluid coking bed to provide heat to the heavy crude. This occurs in a continuous process. Delayed coking also operates continuously, but it utilizes a swing between two coking drums. The heavy crude is heated, in a furnace, to temperatures where thermal cracking can occur. However, the temperature is not so great as to immediately initiate coking reactions. At delayed coking conditions, the crude will experience coking at a relatively slower rate. The unit operation allows for the crude heated in the furnace to travel to coking drums, where the coking process takes place – hence, “delayed” coking. This ensures that no coking occurs in the furnace, which prevents interruptions in operation to de-coke the furnace. Two coking drums are used to swing the process to one drum, while the other is cleaned of coke deposits.

1.4 Visbreaking Upgrading Technology

1.4.1 Overview

Visbreaking is a heavy crude oil processing technology that uses thermal energy to chemically upgrade heavy crude components into lighter products. It is characterized by mild temperature range of operation (400-480°C), and is normally operated at pressures between 10-20 bar [7]–[9], [12]. The visbroken product has a reduced bulk viscosity and pour point in comparison to the process' feedstock properties. This type of upgrading process is common in European refineries, given that it is selective to diesel product, and European market's diesel demand [13]. Due to its main requirement of a heat source, visbreaking is a "simple" and relatively portable technology that can readily be deployed in remote locations.

1.4.2 Application Opportunities

Steam Assisted Gravity Drainage (SAGD) is an enhanced oil recovery technology that uses steam injection into the ground to facilitate the extraction of bitumen. SAGD facilities are often found in remote areas, and their operation requires the extracted bitumen to be blended with diluents to achieve reduced viscosity and to allow for its transport. Visbreaking technology's simplicity and portability make it a viable option for on-site processing of bitumen prior to transport. The product's lower viscosity and pour point decrease the amount of diluent required before transport, which contributes to a reduction in operation costs. Moreover, the smaller diluent volume requirement leads to an increased transportation capacity from the SAGD facility to the processing destination.

Additionally, a SAGD facility offer a process integration opportunity. These facilities often have excess process heat available, for example from their steam production. This excess heat may be heat-integrated to provide the visbreaking process with the necessary energy to drive the thermal cracking reactions. The potential reduction in diluent requirement, increase in transportation capacity, and process heat integration can contribute to improved process economics.

1.4.3 Hydrotreatment of Upgraded Product

1.4.3.1 Hydrogen Requirement

The thermal cracking products in the visbreaking process are chemically unstable due to their higher composition of unsaturated hydrocarbons, such as olefins and diolefins [9]. These are straight chain hydrocarbons with one and two carbon-carbon double bonds, respectively. These components can react to form undesired by-products, which may precipitate out of the liquid phase [9]. It follows that to stabilize their reactivity, unsaturated hydrocarbons must be hydrogenated to their saturated forms (paraffins). Hydrogen gas is not naturally available and is usually required at high pressures for hydrotreatment; Sanchez and Ancheyta [14] suggest the H-Oil process (a hydrocracking technology) operating pressure to be 165-200 bar. Although the operating pressure for olefin hydrotreatment may not be as high as the H-Oil process, the hydrogen requirement for the visbreaker process can still represent considerable costs.

An estimation of the hydrogen requirement for a hydrotreatment process is largely dependant on the type of hydrotreatment process (e.g.: olefin hydrotreatment, hydrodesulfurization, etc.), the operating pressure, and the feedstock for hydrotreatment (e.g.: naphtha, kerosene, etc.). To illustrate this variability, Parkash [15] has reported the hydrogen requirement for Naphtha hydrodesulphurization at 2090 kPa (303 psia) to be 283 m^3 of hydrogen per m^3 of crude oil (45 scf/bbl), and the hydrogen requirement for kerosene hydrotreating at 9300 kPa (1350 psig) to be 98.75 m^3 of hydrogen per m^3 of crude oil (555 scf/bbl).

Given the uncertainty of estimations, and the potentially high cost due to extreme operating conditions, alternative hydrogenation methods can lead to increased viability to the implementation of a visbreaker process unit.

1.4.3.2 Methane as a Hydrogen Donor

Recent studies point towards the possible use of methane as a hydrogen donor to fulfill the hydrogen requirement to stabilize the visbroken product. Although the hydrogen-carbon bond in methane has one of the highest bond energies in a hydrocarbon (see Table 1-4), the use of bi-functional metal-modified zeolite catalysts has been shown to effectively activate the hydrogen [16], [17]. This type of novel technology has the potential to reduce energy intensive hydrogen production such as steam-methane reforming. Moreover, the methane hydrogen-donor-catalyst system proposed allows for the carbon atom to be incorporated into the unsaturated hydrocarbon, preventing its release as carbon dioxide [16]. Thereby, increasing hydrocarbon yield and reducing process emission.

1.5 Crude Oil Transport and Safety

The transport of crude oil and other flammable liquids by rail requires special attention by regulators to prevent accidents such as the 2013 Lac-Mégantic, QC, derailment, or the Heimdal, N.D., derailment in 2015. In the event of a derailment of a train transporting crude oil, some train cars may rupture and spill oil, while others remain intact. The spilt oil can catch on fire, forming a pool-fire. The intense and sustained fire can expose intact train cars to a large heat flux. As a result, the crude oil in the intact train car will undergo phase change and chemical reactions (mainly thermal cracking), which can lead to system pressurization. In the case that the train car is properly vented and allows for depressurization, the crude oil system will vaporize and exit through a pressure relief valve. However, if the pressurized system is not properly relieved of the built-up pressure, a Boiling Liquid Expanding Vapour Explosion (BLEVE) may occur. Due to the intense heat provided by a pool-fire and the associated material stress, the train car's shell may rupture. The section of the train car shell above the liquid level is especially vulnerable to failure as heat is not dissipated to phase change as it occurs in areas of the shell below the liquid level. In a BLEVE, the shell failure causes a rapid system depressurization, in which a large portion of the liquid content vapourizes and instantly feeds near-by fires resulting in an explosion.

The study of mild thermal cracking kinetics performed in this thesis also focuses on the transportation of crude oil by rail. Transport Canada is currently working with CanmetENERGY, and other governmental departments in Canada and the United States, to examine what occurs inside a crude oil train car that is exposed to a sustained heat source. This is an attempt to prevent events such as Lac-Mégantic in 2013, by examining and understanding the behaviour of crude oil in accident conditions. To ensure safety is maintained in the transportation of crude by rail.

1.6 Thesis Objectives

As presented in the introductory sections of this thesis, thermal cracking reactions are at the core of heavy crude oil processing, and visbreaking in particular. The accurate modeling of these reactions is crucial for the improvement and operation of current processes, and to the research and development of new processes related to the thermal upgrading of unconventional heavy crude. The main purpose of this thesis is to study the reaction kinetics and develop a reaction model of the thermal cracking of crude oil. The objectives set out by this work are outlined as follows:

1. Develop a mild thermal cracking model with VLE calculations to determine reacting phase composition

2. Collect experimental data of mild thermal cracking reactions and use it to determine the kinetic parameters of the model developed in objective 1
3. Use the reaction model developed in objectives 1 and 2 to determine the effect of composition change and crude oil properties on the performance of a train car transporting crude oil when it is exposed to a fire

1.7 Thesis Outline

The work presented in this thesis is divided into five chapters. Two of these chapters are manuscripts being prepared for future publication in refereed journals.

Chapter 1 is an introduction into the topics of heavy petroleum chemistry and processing, in the context of crude upgrading *via* thermal action.

Following the introduction, an overview and background analysis on the topic of thermal cracking reaction modeling is presented in **Chapter 2.** This Chapter will present the modeling paradigms of black, grey and white box models, it will overview the current literature models and identify some of their limitations, and it will suggest an improved kinetic model.

Chapter 3 is presented as a manuscript that details the development of a mild thermal cracking reaction model with VLE calculations. This work uses a modified partial upgrading pilot plant from CanmetENERGY-Ottawa to collect mild thermal cracking experimental data to be used in a kinetic analysis.

Given the capabilities of the improved kinetic model, its implementation to a case scenario was demonstrated in **Chapter 4**. This Chapter is a manuscript examining the use of the mild thermal cracking reaction model to examine the effect of compositional change due to reactions on the pressure relief system of a train car transporting crude oil. The train car and crude oil specifications were provided by Transport Canada.

Finally, **Chapter 5** contains this thesis' conclusions and suggested future directions for research.

Chapter 2 – Thermal Cracking Reaction Modeling

2.1 Black, Grey and White Box Models

Mathematical models can be thought of as boxes, which give a certain output in response to a specified input. How the "box" utilizes the inputs to reach the output values is dependant of what is inside the box. The contents of the box are mathematical relationships that either fundamentally or empirically link the inputs to the outputs. The box models can be classified into three categories: black, grey, and white-box models. The black-box model (BBM) is the simplest type of model. Compared to grey and white-box models (WBM), BBMs have the least number of relationships between inputs and outputs. A BBM is progressively improved to a grey-box model (GBM) by the addition of more mathematical relationships. The WBM is the complete mathematical representation of all the relationships between inputs and outputs.

2.2 Literature Models

Thermal cracking reaction models proposed in literature differ in many aspects: crude feedstock, lumping methods (see Chapter 3), reaction pathways/network, and experimental development. Figure 2-1 summarizes some of the models available in the literature. The two-lump model is the simplest one, where the feedstock is represented as one single reactant lump and it is cracked into one product lump.

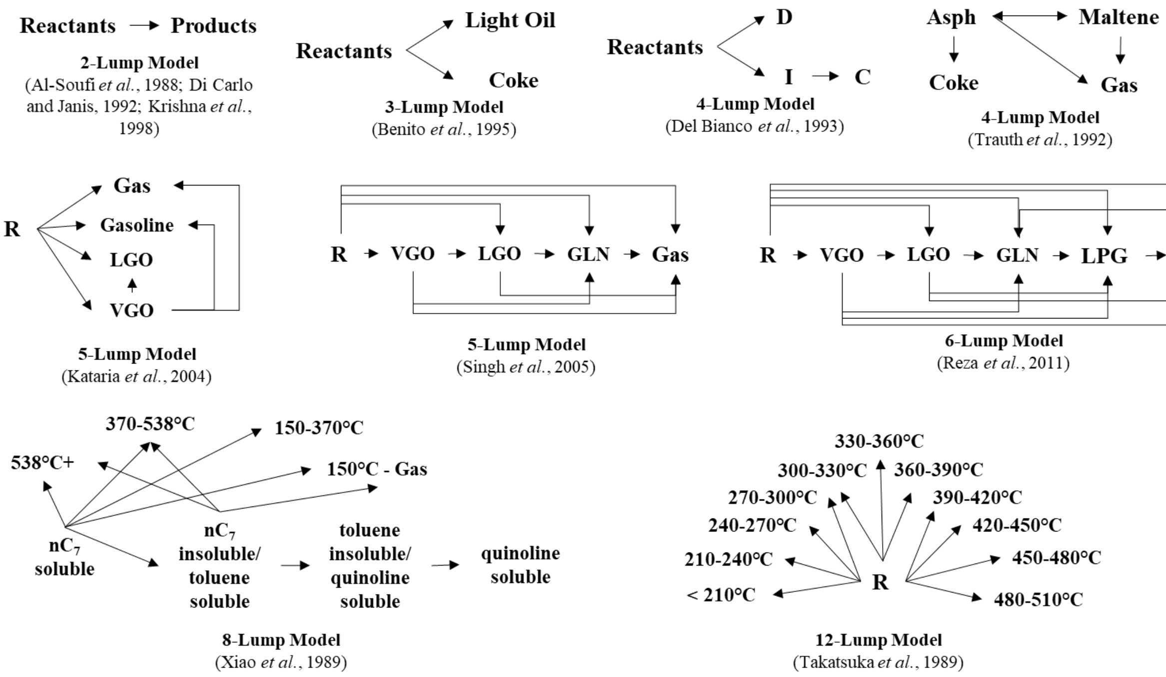

Figure 2-1: Visual representation of a selection of literature thermal cracking kinetic models [2], [18], [27], [19]–[26] ***(Adapted from Ancheyta*** [9]***)***

Models were improved from the two-lump BBM with a higher number of lumps to represent the reactants and products, and by the creation of more representative reaction pathways. The further specifications "lightened" the black-box models into a grey-box models. However, due to the complexity of crude oil systems, some assumptions remain, which contribute to their continued limited applicability.

This work identifies two aspects of model limitations: the characterization of crude oil systems, and the thermodynamic calculations (VLE) necessary. These factors are not independent and together contribute to model limitations. Firstly, crude oil components are defined based on normal boiling points. As such, the crude oil system is defined on an overall composition basis. The overall system composition is determined by high temperature simulated distillations (e.g.: ASTM D2887), which produce an equivalent TBP curve of the sample [28]. Moreover, as discussed in Chapter 1, mild thermal cracking reactions are assumed to occur almost solely in the liquid phase.

This poses a problem, as the reactive system's concentration is not equal to the overall system composition but to the liquid phase composition. Models that fit experimental data, characterized on an overall system basis, straight to the kinetic model confound the VLE that the system experiences at reaction conditions into the kinetic parameters that are developed. Such models are suited for product yield predictions (i.e.: overall composition at the end of the process) but are not suited for predicting the reactive system composition through time – something that is necessary for industrial scale operations to study and understand the state of the system during process operation. This leads to the second aspect of limitation for literature models, the thermodynamic calculations (VLE).

In mild thermal cracking, the reactive sub-section in the crude oil system is the liquid phase. As such, the relative amounts of each reactant must be determined in the liquid phase, at reaction conditions (temperature and pressure), so that these concentrations may be fit to the reaction model for the development of representative kinetic parameters. Due to the difficulties presented above, crude oil systems can only be characterized on an overall basis. Aguilar and Ancheyta [4] addressed this issue in their reactor development. Their work presented the idea of implementing a VLE calculation in between each iteration of the reactor model to determine the proportion of the system that was in the liquid phase and its composition. The reactor model would then apply the reaction model to the liquid phase composition only and combine the mixed phase products to the vapour phase present from the previous iteration. Figure 2-2 is an adapted representation of the iterations in their model. The objective was to obtain a more representative visbreaker reactor simulation, and to determine the effect of VLE on reactor output. Their work concluded that the addition of the VLE component to the reactor model affected conversions at higher temperatures and higher residence times, namely soaker visbreaker reactors [4], [9]. Experimental studies aimed at developing reaction kinetics use batch reactors systems sustained at high temperatures and are comparable to soaker visbreaker conditions. Aguilar and Ancheyta's conclusion demonstrates the necessity for the VLE component in kinetic models to which experimental data obtained from batch reactors is applied.

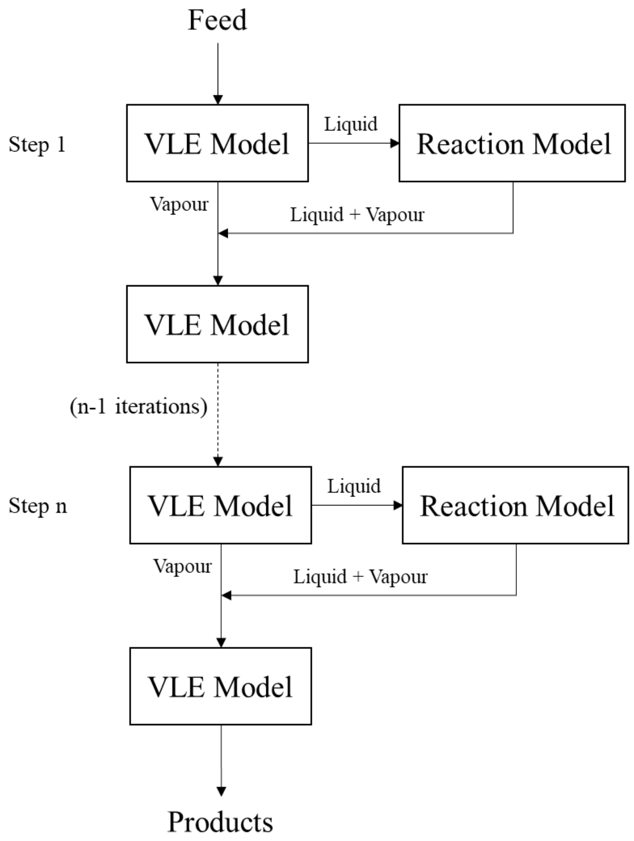

Figure 2-2: Representation of the iterative implementation of VLE calculations to determine the reactive system (liquid phase) composition as suggested by Aguilar and Ancheyta [4], [9]

2.3 Process Simulator Integration with a Kinetic Model

2.3.1 Motivation

The implementation of a thermodynamic model (VLE) for crude oil systems is a difficult task. As previously mentioned, crude oil components are so varied and complex that lump pseudo-component are used to represent them and to simplify reaction modeling. This simplification is unfavourable to the accuracy of thermodynamic models. Even the simpler equations of state (cubic EoS or Peng-Robinson) require component-specific information, such as activity coefficients. Given the variability of crude components, this type of information is almost always unavailable. One approach to solve this problem is to represent the thermodynamic constants and properties of an entire lump with one of the component species for which this information is available. For instance, the GLN lump can be represented by n-octane. This type of approach introduces inaccuracy to the model as the lump's physical properties are averaged to that of one single component species. Moreover, this approach may be considered satisfactory for the lumps with lower boiling points (Gas, GLN, LGO) as information may be available for simpler (alkane/alkene) low boiling point hydrocarbons. It is difficult to represent the higher boiling point lumps using this method. These lumps are composed of polynuclear aromatic (PNA) hydrocarbons, whose physicochemical properties (molecular weight, heteroatom content, saturation level, etc.) can greatly vary between types of crude oil. Moreover, it is highly desirable for models that use the lumping method to use narrow boiling point range definitions of pseudo-components to represent crude oil systems. This prevents the same loss of information that occurs with averaged thermodynamic properties [29].

In addition to product yield predictions, one of the most desirable capabilities of a crude oil processing reactor model is the predictability of product properties such as density, viscosity, heat capacity, and distillation curve [9]. The integration between a model and a process simulator presented here can help address this necessity with a higher level of confidence as the process simulator's predictive performance is industry proven and continuously improved.

Finally, an important aspect of model applicability is its adaptability. The thermodynamic equations used in a model can add or detract from the model's applicability due to their specific strengths and weaknesses. Petroleum systems are often modeled in process simulators using the Peng-Robinson or Soave-Redlich-Kwong cubic equations of state [30], [31]. However, thermodynamic models with higher complexity have been increasingly used in the oil and gas industry, such as the Cubic Plus Association equations set (CPA) [32]. The process simulator integration approach presented here introduces the possibility to interchange the thermodynamic equation set as desired without requiring major changes to the overall model, as would be required if the equations were manually implemented in the model.

2.3.2 Integration Approach

2.3.2.1 Model to Process Simulator Connection

The kinetic model presented in this work was developed in MATLAB® and used Microsoft's Component Object Modeling (COM) connection to communicate with the UniSim® Design Suite R450 process simulator, where thermodynamic calculations were performed. It is note-worthy that this integration can be done with Aspen HYSYS® process simulator. The choice to use UniSim® is mainly attributed to the slower performance of the computationally heavy Aspen HYSYS® application. Furthermore, a variable data type incompatibility between MATLAB® and UniSim® prevented the direct transition of arrays. A MS Excel® VBA routine was implemented for the conversion of double-type arrays (used by MATLAB®) to a variant-type array, which is the data-type required by UniSim®'s simulation file. The COM objects defined in the MATLAB® code access the simulation case file to read and input values to the process streams. This input-output capability allowed for the integration of VLE to the kinetic model.

2.3.2.2 Crude Characterization and Batch Mass Conservation

The process simulation used by this work required two aspects to be addressed: the characterization of the crude oil system, and a set of equations used to represent the VLE observed in experimental data used for the kinetic studies. The first aspect was addressed using UniSim®'s crude assay characterization tool. The process simulation case was provided with bulk properties (density, kinematic viscosity at 40°C, and the TBP curve data) of the crudes considered: MBL, AHS, and CDB. The process simulation characterization created pseudo-components to represent the crude assay as described by the input data. The oil assay characterization tool will produce increasingly accurate simulated assays with more physicochemical information provided. The VLE representation was performed by the Peng-Robinson (PR) thermodynamic fluid package (set of equations) applied to the pseudo-components created by the assay characterization described. PR is the recommended fluid package when handling crude oil assays [33]. A validation of the VLE is presented in Chapter 3.

The experimental system used in this work (described in Chapter 3) uses a semi-batch reactor with a sweeping nitrogen blanket in the head of the reactor. The equations presented in Chapter 3 are batch reactor mass balances. As previously presented, the system to which the reaction mass balances are applied to is the liquid phase (the reacting system). Since the only mass to leave the reactor is in the vapour phase, and is unavailable to react, the batch reactor set of equations can still be used to represent the reactions that occur in the remaining liquid mass. However, to do so the model must track the mass that remains in the liquid phase throughout the time iterated solution of the mass balances in conjunction with the VLE.

The process simulator uses flow basis models. To implement the batch mass balances and to record the system's mass through each iteration, the model successively updated the inlet stream with the mass flow rate and composition of the output stream from the previous iteration. This allows for the batch of liquid mass available in the reactor to be modeled using flow streams without previously unavailable mass being introduced to the system between iterations through unchanged mass flow rates.

2.4 Effect of VLE Calculations to a Mild Thermal Cracking Reaction Model

This work implemented the iterative VLE calculations suggested by Aguilar and Ancheyta [4] to the five-lump mild thermal cracking kinetic model presented by Singh *et al.* [2] to test the effect that VLE calculations on the model's predictions. Two versions of the model were developed in MATLAB®, one that only executed the reaction model and one that implemented the VLE calculations to the reaction model through an integrated process simulation file, as described in section 2.3. The VLE was used to define the reacting system composition, which is the liquid phase (see section 2.2). The component lump masses that should experience the greatest effect of the VLE implementation are the lumps that experience the most volatility at reaction conditions. In this case, the affected lumps are VGO, LGO, and GLN. The mass percentage of all lumps through a 100-minute reaction period were compared between the two MATLAB® models (Reaction and Reaction-VLE). These comparisons are shown in Figure 2-3.

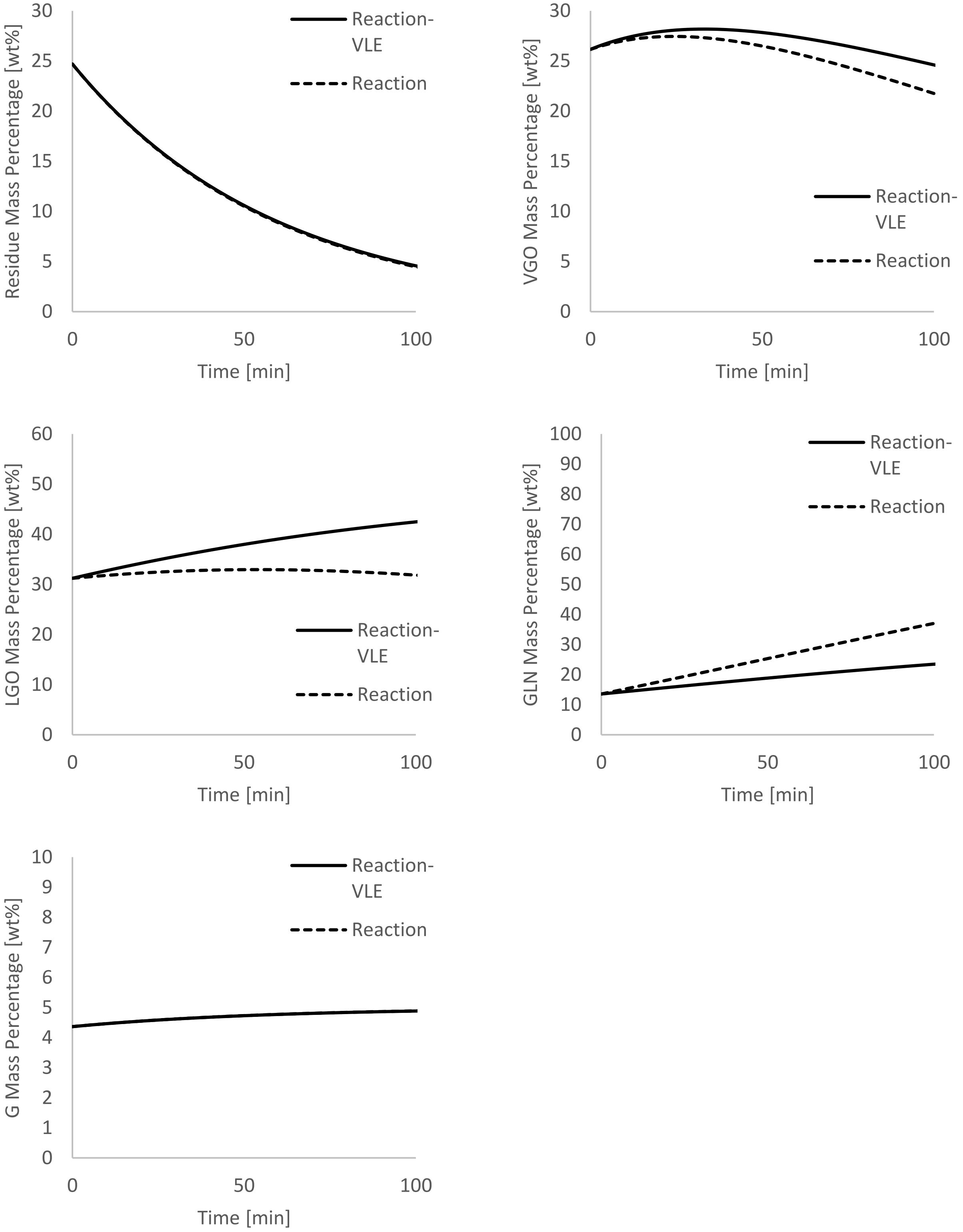

Figure 2-3: Mass percentage for each component lump for a 100-minute reaction residence time for the Reaction and Reaction-VLE models

It is evident from Figure 2-3 that the effect of VLE on the model increases with simulated time (reaction residence time). This can result in considerable modeling limitation when simulating a system in which thermal cracking occurs for a longer period.

2.5 Current Models' Applicability and the Improved Model's Potential Benefits

The fact that this work's intent is to identify the limitations with current literature models does not diminish their inherent applicability. The extent of the model's applicability is dependent on the feedstock used, the reaction conditions, and experimental system used to conduct the kinetics studies [34]–[36]. It is important to acknowledge that current literature models have strived to best represent the system. Some of the attempts to do so include small scale experiments to maximize conditions control, short residence times to minimize the effect of VLE, and the development of increasingly complex reaction networks to better represent the reactions that take place (see section 2.2).

The improved model suggested is intended to extend the applicability of models like the ones presented in section 2.2. As previously mentioned, the implementation of VLE in the kinetic model introduces the ability to predict the reacting system's composition through time and allows for the kinetic constants experimentally derived to be more representative of the reactions only (no VLE confounding factor). Arguably, an even more important benefit of the suggested model's VLE capabilities is the possibility for more complex systems, such as pilot plants, to be used in kinetic studies. The VLE component can be modified to represent a more complex system like other pilot plants or process configurations (see section 3.1.2.3).

Chapter 3 – Five-lump mild thermal cracking reaction model of heavy crude oils with VLE calculations to determine reacting phase composition

This chapter will be prepared as a manuscript for submission to a refereed journal

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Abstract:

When exposed to heat, crude oil undergoes chemical reactions whose rates and severities depend on the temperature and pressure of the system. The broad term for the set of reactions that occurs is thermal cracking. Thermal cracking primarily involves the breaking of carbon-carbon bonds in hydrocarbon chains of the component molecules in crude oil. This breaking of bonds results in the break-down of large hydrocarbon chains (heavier and higher boiling point) to smaller hydrocarbon chains (lighter and lower boiling point). Mild thermal cracking reactions are considered in this work. This type of reactions occurs at a temperature range approximately between 350-450°C and occurs almost exclusively in the liquid phase. There have been models proposed in the past for these types of reactions. However, the proposed models have a limitation in that they assume the overall system to be reactive, and not the liquid phase alone. The objective of this work is to implement a VLE calculation to a reaction model and present the rates of reaction constants optimized to the reaction model for three crude oils: Hardisty (MBL), Albian Heavy Synthetic (AHS), and Christina Lake Diluted Bitumen (CDB). The reaction model obtained can be valuable for visbreaking and partial upgrading process simulations. Experimental study was performed in a pilot-scale semi-batch reactor. The three crude oils were heated to 350, 400, 425, and 450°C at 1240 kPa. A five-lump reaction model incorporated to a process simulator with VLE calculations was optimized to fit the experimental data obtained. The goodness of fit between the model predicted values and experimental values for MBL, AHS, and CDB were determined to be 0.99, 0.99, and 0.98, respectively. Moreover, 80, 85, and 89% of the optimized model's predicted values had less than 10% error for MBL, AHS, and CDB, respectively.

Keywords: Visbreaking, partial upgrading, bitumen, heavy crude, thermal cracking, reaction kinetics, pilot scale.

3.1 Introduction

In today's petroleum industry, the market value of heavy and extra heavy crude oils is increasing due to a shortage of conventional crudes. Their raw value alone, however, does not completely justify their exploration. The result is a need for the development of new technologies and optimization of current processes to further increase the market value of heavy crudes [37]. Crude oil upgrading refers to the conversion of heavy crudes (higher carbon-to-hydrogen ratio and boiling point) to lighter ones (lower carbon-to-hydrogen ratio and boiling point). Upgraded crudes have increased market value due to improved transportability and more desirable chemical properties. Upgrading technologies applied to heavy crude feedstock include catalytic and thermal carbon-rejection processes [7]. This work focuses on the latter type. Visbreaking (viscosity breaking) is an upgrading technology that modifies crude oil via heat exposure, and it is characterized by relatively mild temperatures.

When exposed to heat, crude oil undergoes chemical reactions whose rates and severities depend on the temperature, pressure, residence time, and feedstock properties of the reacting system [34]–[37]. The broad term for the set of reactions that occurs is thermal cracking. Thermal cracking primarily involves the breaking of carbon-carbon bonds in hydrocarbon chains of the component molecules in crude oil, thereby reducing the bulk carbon-to-hydrogen ratio of the crude. Thermal cracking is sub-divided into mild, moderate, and severe. Mild thermal cracking occurs at a temperature range approximately between 400-450°C, and occurs almost exclusively in the liquid phase [4], [24], [29], [37]. Models have been proposed in the past for this type of reaction, an extensive review of the literature models has been presented elsewhere [38]. The development of these models has focused on, and are differentiated by, their crude oil component definition techniques. These include lumping methods to define reactants and products, number of lumps used, and the reaction pathways between reactants and products. However, these models lack the capability to predict the liquid and vapour phase compositions in the reacting mixture. These compositions can be important to represent online compositions in an upgrading process, which can be used for studying or optimizing such processes. This work thus adds VLE calculations to an existing model and presents the associated kinetic constants for three crude oils: MBL Hardisty (MBL), Albian Heavy Synthetic (AHS), Christina Lake Diluted Bitumen (CDB).

3.1.1 Crude Oil Components

3.1.1.1 Lumping Method

Crude oil components are highly complex mixtures of hydrocarbons, which may vary in composition depending on the type of crude oil (e.g.: light, medium, heavy, extra heavy, bitumen) and the geographic location where the crude was sourced. Normally, crude oils are characterized by their true boiling point (TBP) curve [7]. TBP curves provide a mass distribution according to boiling points and are determined using simulated distillations (e.g.: ASTM D86, D1160). Due to the large number of components, it is inefficient to model all possible reactions in a reactive crude oil system. As a result, these systems are normally simplified and modeled using pseudo-components or lumped components with a reduced total number of components and reactions. The objective of lumping components is to group hydrocarbon molecules with similar physical and chemical properties and model them as one component. There are continuous and discrete lumping methods, which are described elsewhere [39], this work used a discrete lumping technique, and defines the lumped components by its boiling point range, i.e.: the temperature the components in the lump first begins to vaporize to the temperature where the entire lump is found in the vapour phase.

3.1.1.2 Molecular Characterization

A further complexity of crude oil models is that their components can be characterized based on their molecular structure using analyses such as SARA and PIONA. SARA analysis characterizes the oil assay into groups: Saturates, Aromatics, Resins, and Asphaltenes. The PIONA analysis characterizes the oil assay into Paraffin, Iso-paraffin, Olefin, Naphthene, and Aromatic groups. Virtual Materials Group (VMG) has presented a two dimensional slate method of characterization that defines components based on carbon number (equivalent to boiling point) and molecular structure by PIONA analysis [40]. Although the inclusion of molecular characterization can represent an increased level of accuracy in the modeling of crude oil components, it dramatically increases the number of unknowns to be solved by adding reactants, products, and reaction pathways between them. The solution to such a highly underspecified system can be less accurate than that of a simpler system due to an associated larger number of local optimums. Local optimums can hinder the search for a global optimum. Molecular characterization was thus not implemented in this work.

3.1.1.3 Number of Lumps

When comparing kinetic models, the number of lumps used is associated with the model's ability to realistically predict the reactions taking place. Models that use a larger number of lump components are better able to represent the reactions present. However, the larger number of component lumps increases the complexity of the model and decreases its solution efficiency. Larger number of lumps creates an increasingly underspecified system, which has a larger number of possible solutions. A system defined by five component lumps has been shown to be adequate for the prediction of mild thermal cracking reaction behaviour [25], [38], [41].

3.1.1.4 Coke Product

Moderate thermal cracking (485-550°C) leads to the formation of solid carbon material – coke. The formation of coke can begin at lower temperatures, but the rate of formation is considerably lower [37], [38], [42]. Most coke formation occurs near, and within, the temperature range of moderate thermal cracking. Moderate thermal cracking conditions can produce upwards of 30 wt% yield of coke [7]. It is noteworthy that the extent of coke formation does not only depend on temperature but also feedstock properties. Feedstock with higher asphaltene content are associated with the formation of coke [11], [43]–[45]. Since this work focuses on mild thermal cracking, the production of coke has not been included in the model presented here.

3.1.2 Reaction Models

3.1.2.1 Black and Grey-Box Models

Literature reaction models differ in terms of: (i) lumping methods, (ii) crude feedstock properties, (iii) reaction pathways, and (iv) experimental development of kinetic parameters [9]. The simplest models are referred to as Black-Box Models (BBM), which use two lumps to represent the system, i.e.: reactant and product lumps. The problem with BBMs is that all physical and chemical phenomena that occur are represented together in one step. The simplicity of the BBM makes it easier to solve, but it reduces its applicability and accuracy. BBMs are improved into Grey-Box Models (GBM) by explicit representation of more aspects of the system being modelled, i.e.: chemical components, molecular composition, reaction pathways and/or kinetics. Ideally, a perfect mathematical model where all aspects of the system are modeled is referred to as a White-Box Model (WBM). The goal to improve a given GBM is to progressively add to the model more aspects of the system and effectively create “lighter” Grey-Box Models.

3.1.2.2 Literature Thermal Cracking Model Limitation

Current literature thermal cracking models use TBP data as input and predict TBP data as their output. The TBP curve outputs provided by the model represent the overall system composition at the desired reaction time. As a result, these models are well suited for predicting process yields given a TBP feedstock characterization and process conditions. However, such models cannot be used to predict the system's liquid and vapour phase compositions. The model's suggested kinetic parameters are not only representative of the reactions that take place, but also of the phase changes that occur in the process of bringing the system up to, and down from, reaction conditions. For that reason, the kinetic parameters associated with these models could be classified as *pseudo*-kinetic parameters. Figure 3-1 is a general representation of models that have this type of limitation.

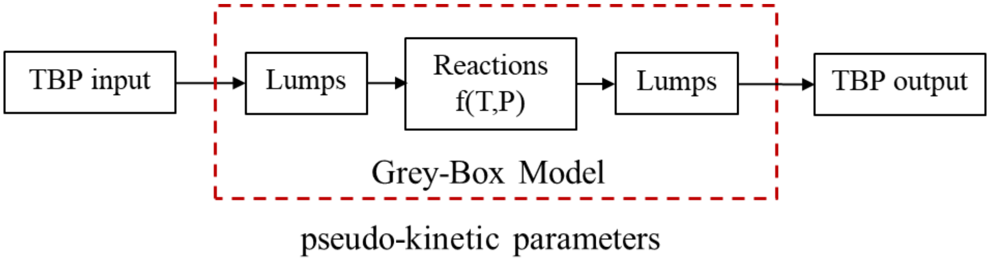

Figure 3-1: Generic representation of a thermal cracking grey-box model designed for process yield predicitons

For the development of intrinsic kinetic parameters for a reaction model, the essential piece of information necessary is the reacting system's chemical composition at reaction conditions. The biggest challenge with modeling reactive crude oil systems is determining the reacting system's composition. As previously mentioned, mild thermal cracking reactions are assumed to occur predominantly in the liquid phase. This means that an accurate mild thermal cracking kinetic model must implement a vapour-liquid equilibrium (VLE) model to determine the liquid phase (reacting system) composition. An iterative approach to implementing a VLE model to a visbreaker reactor model has been proposed by Aguilar and Ancheyta [4] to improve process yield predictions. A similar iterative approach is presented here, but it is implemented in the reaction model to which experimental data is fit to improve the kinetic parameter estimation of the reaction model studied.

3.1.2.3 Suggested Improvement to Literature Grey-Box Models

This work proposes a reaction model for mild thermal cracking of crude oil that uses VLE calculations to determine phase compositions. Figure 3-2 is a visual representation of the proposed kinetic model and can be contrasted with Figure 3-1 for visualization of the added VLE capabilities.

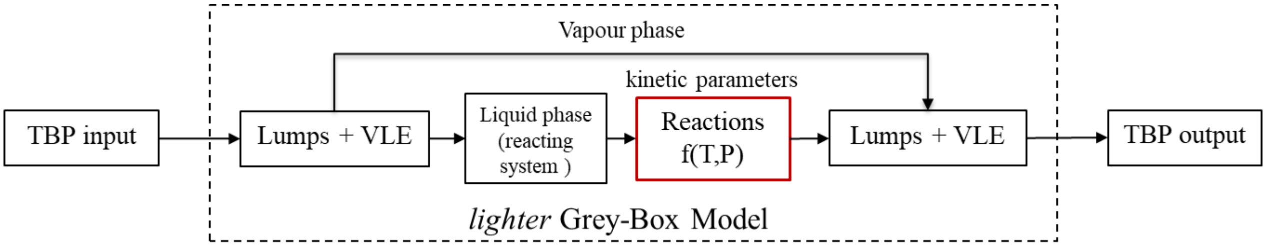

Figure 3-2: Proposed thermal cracking grey-box model featuring the implementation of VLE

The proposed model uses an iterative approach between the VLE and reaction mass balances to solve the system. In each iteration of the solution, represented by the dashed line box in Figure 3-2, the model follows these steps. Pre-reaction, the VLE is used to determine the composition of the liquid phase. The liquid phase composition is applied to the reaction mass balances to determine the reaction product yields. Reaction products are distributed across both liquid and vapour phases, depending on the lump definition each falls under. The model combines the new products to the previous step’s vapour phase components (unreacted), and the VLE re-calculate system’s liquid and vapour compositions. This completes one iteration of the solution procedure. When the system has been solved for the desired number of iterations, the output is the overall system composition, which is equivalent to its TBP.

The implementation of VLE calculations in the proposed reaction model has two main advantages to its applicability. The first is the capability for predicting overall system composition and liquid and vapour phase compositions at reaction conditions. This may be important to the study, or optimization, of thermal cracking process units. Secondly, it allowed for the use of a pilot-scale system, in which VLE is a non-negligible factor, to be used in this kinetic study.

3.2 Kinetic Model

3.2.1 Reaction Network

The model proposed here uses a reaction network similar to the one presented by Singh *et al.* [2] to represent the reactions that occur in the system. This reaction network was selected as it models mild thermal cracking reaction in a crude oil system and its number of lumps and their boiling point definitions are conducive to obtain a representative model with the desired complexity. The crude oil's lumped components were defined based on their boiling point temperatures and are identified in Table 3-1. The initial boiling point (IBP) for the three crude oils examined in this work ranged between 34-37°C.

Table 3-1: Crude oil component lump names, abbreviations, and boiling point definitions

Lump Name	Lump Abbreviation	Boiling point definition
Gas	G	$-C_5$
Gasoline	GLN	IBP-150°C
Light Gas Oil	LGO	150-350°C
Vacuum Gas Oil	VGO	350-500°C
Residue	R	500+°C

Mild thermal cracking reactions have been experimentally observed to follow pseudo-first-order kinetics [2], [4], [7], [18], [24], [42], [46]. Each of the reaction pathways in the model presented by Singh *et al.* [2] (Figure 3-3) were approximated as first-order Arrhenius kinetics.

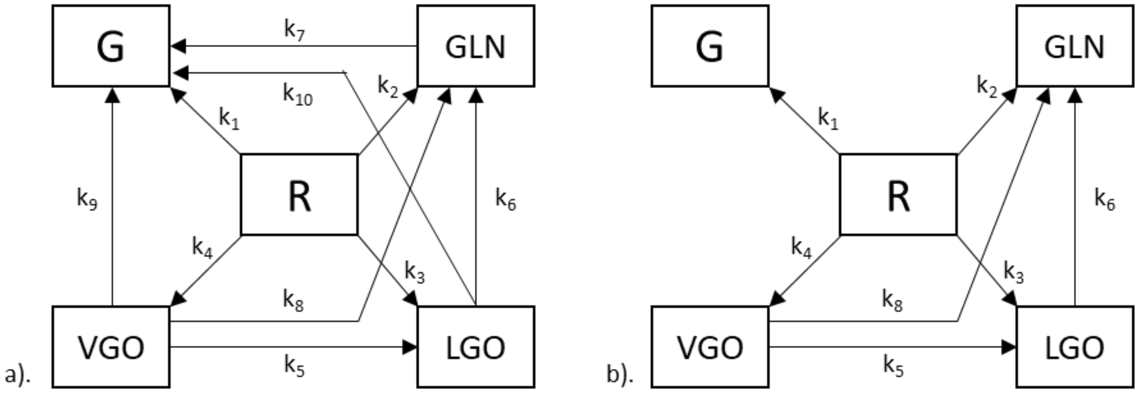

Figure 3-3: Five lump kinetic network (a), and the simplified kinetic network (b) presented by Singh et al. [2]

Singh *et al.* [2] used experimental data to simplify their original reaction network by determining reaction paths that had negligible observed rates of reaction and a Delplot analysis to determine if lumps were made through primary or secondary conversion [2], [47]. They were able to determine that 7 of the 10 reactions in the network in Figure 3-3a were enough to represent their experimental data [2]. Namely, k_7, k_9, and k_{10} were determined to be negligible reaction pathways. Due to different feedstock crude oil used, this work used the original reaction pathways (Figure 3-3a).

The change in system component masses with respect to time of the kinetic network (Figure 3-3a) can be represented using the following mass balance equations for a batch reactor (closed) system:

$$\frac{d[G]}{dt} = k_1[R] + k_7[GLN] + k_{10}[LGO] + k_9[VGO] \tag{3.1}$$

$$\frac{d[GLN]}{dt} = k_2[R] + k_8[VGO] + k_6\,[LGO] - k_7[GLN] \tag{3.2}$$

$$\frac{d[LGO]}{dt} = k_3[R] + k_5[VGO] - (k_6 + k_{10})[LGO] \tag{3.3}$$

$$\frac{d[VGO]}{dt} = k_4[R] - (k_5 + k_8 + k_9)[VGO] \tag{3.4}$$

$$\frac{d[R]}{dt} = -(k_1 + k_2 + k_3 + k_4)[R] \tag{3.5}$$

where, [R], [VGO], [LGO], [GLN], and [G] are mass concentrations in units of $wt\%$ and k_n are the kinetic constants of the n^{th} reaction pathway. In the model presented here, each component $wt\%$ is based on the reacting system, i.e.: the liquid phase, as a result the weight percentage is based on the liquid phase $\left(\frac{kg_{lump\ liquid}}{kg_{total\ liquid}} x100\%\right)$.

3.2.2 Model Implementation

As previously discussed, the lumping of components is necessary for handling crude oil composition and for the practical application of reaction kinetics. The lumping of components requires the thermodynamic properties and characteristics of the components to be averaged within a given lump. For increased accuracy in thermodynamic modeling, narrow lump definitions (boiling point ranges in this case) are desirable. This minimizes the effects of averaging component properties [29]. To this end, the proposed model uses a process simulator as the source of VLE calculations. The process simulation uses the crude assay characterization tool to model the desired crude oil with narrow boiling point ranges (5-20°C) and to calculate the VLE based on a chosen of equations of state. This work used the Peng-Robinson (PR) model, but the process simulator file allows for the interchange of PR with other thermodynamic models as required by the system under consideration.

The model presented in this work was developed by implementing the mass balances presented in the previous section in a MATLAB® program. The ordinary differential equation solver *ode45* available in MATLAB® was used to solve the system of equations 3.1-3.5. The MATLAB® program was incorporated with a process simulation created in Honeywell's UniSim® Design Suite R450 through Component Object Model (COM) communication between the two applications. The MATLAB® program communicated with the process simulation file in each time-step of the system's solution to determine the composition of the reacting system (the liquid phase), to which the reaction mass balances were applied. A detailed description of the combined approach was presented elsewhere (Chapter 2).

3.3 Experimental Methods

3.3.1 Partial Upgrading Development Laboratory (PUDL)

The experimental program was completed at the Natural Resources Canada CanmetENERGY-Ottawa research complex in conjunction with the Fluidized Bed Conversion and Gasification research team. The experiments were conducted in a crude oil processing pilot plant – the Partial Upgrading Development Laboratory (PUDL). Figure 3-4 is a process flow diagram of the pilot plant and its components.

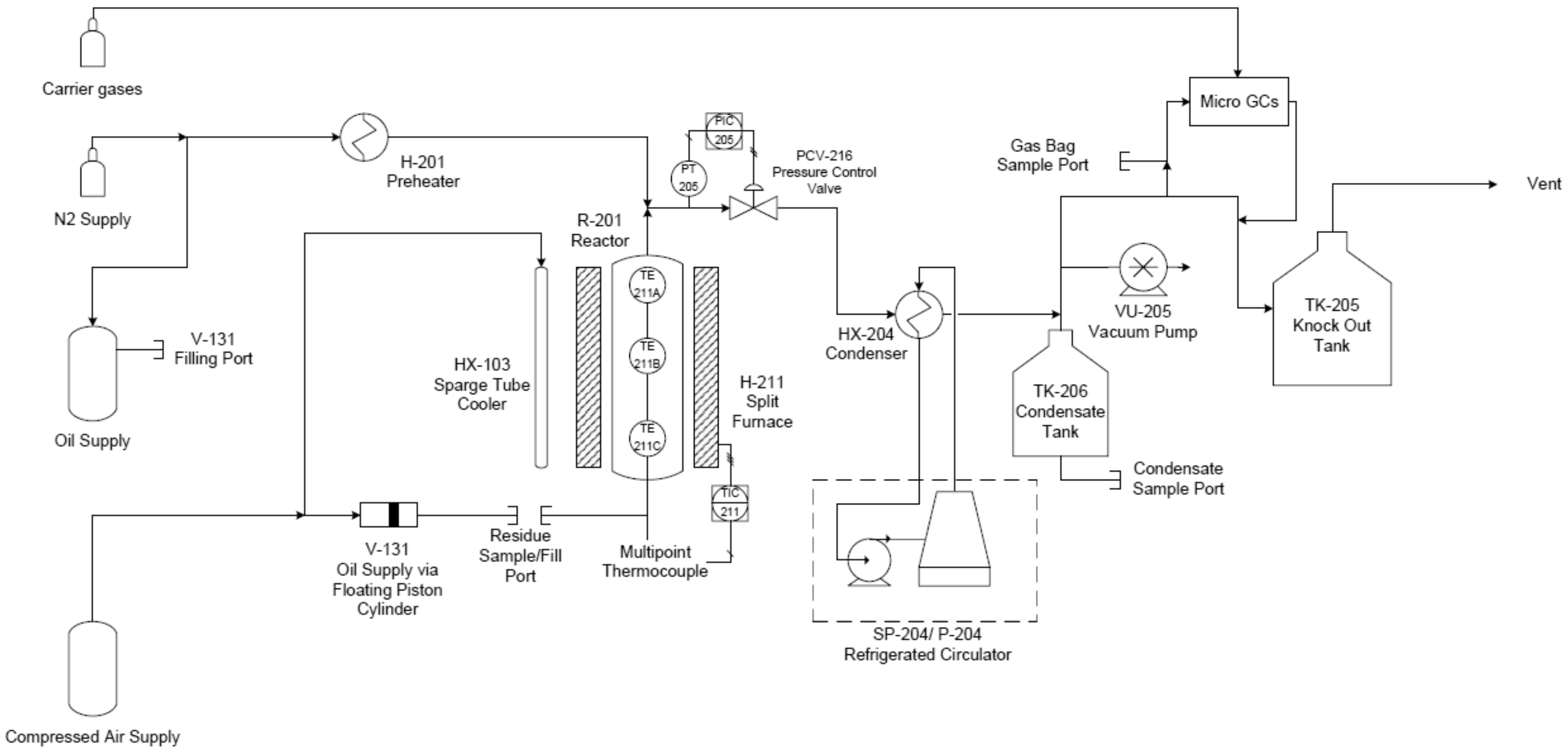

Figure 3-4: CanmetENERGY Partial Upgrading Development Lab (PUDL) process flow diagram

3.3.2 Experimental Program and Analysis Methods

Three crude assay samples were used in the experimental program – MBL Hardisty (MBL), Albian Heavy Synthetic (AHS), Christina Lake Diluted Bitumen (CDB). These are a medium crude, a partially upgraded heavy crude, and a diluted bitumen, respectively. These samples have different characteristics and their properties are presented in Table 3-2. The system was operated at 350, 400, 425, and 450°C, and reactor pressure was maintained at 1240 kPa. These conditions are within the reported operating ranges for visbreaking technology [7]–[9], [12]. Although mild thermal cracking reactions typically begin near 400°C, experimental runs at 350°C were performed to examine the lower temperature range reaction rates. Reactor temperatures were achieved using a three-zone electric furnace (H-211). The system was maintained at pressure by a pressure relief control valve (PCV-216). The reactor operated in a semi-batch format with a sweeping nitrogen stream blanketing the top section of a vertical reactor (R-201). The nitrogen flow carried off any of the evolved gases to down stream sections of the pilot plant for cooling, condensing, and Micro Gas Chromatography (Micro GC) analysis of the component gas species. Micro GC analysis was conducted online in two-minute intervals. Reaction products samples collected included liquid residue from the reactor (R-201), condensate (hydrocarbons condensable at 30°C) from a collection tank (TK-206), and off-gases mass flow measurement combined with gas characterization by Micro GC analysis (Agilent 3000A Micro GC).

Table 3-2: Physical characteristics of the three crude oils used in experimental runs

Parameter	**MBL**	**AHS**	**CDB**
Density [kg/m^3]	867.5	940.6	927.0
Kinematic Viscosity at 40°C [m^2/s x10^{-6}]	8.26	70.99	88.29
Heat of combustion [cal/g]	10718	10314	10283
Micro Carbon Residue (MCR) [wt%]	4.69	13.9	11.7

Residue and condensate liquid samples were characterized by the CanmetENERGY-Devon laboratory in Alberta. The samples' boiling point distributions were determined using ASTM D7169, which characterizes crude oil components up to a boiling point of 720°C [48]. The boiling point distribution is equivalent to a TBP curve, and the distribution of each sample was combined into lumps as defined in section 3.2.1. All characterized samples were combined into an overall lump composition to represent the system composition at each reaction residence time. Different residence times were tested to allow for kinetic analysis and development of reaction kinetic constants. The raw experimental data for all experimental runs conducted are presented in Appendix B.

Reaction residence times of 0, 10, 20, and 30 minutes were used for lower temperatures runs (350 and 400°C) and 0, 5, 10, and 15 minutes were used for higher temperature runs (425 and 450°C). Shorter residence times were used for higher temperature runs to better capture the changes in component masses due to the faster rates of reaction expected at these temperatures. The zero-minute residence time experimental runs were conducted to account for changes in mass between component lumps due to reactions and/or phase change that may occur during the heating process up to the experimental run's reaction temperature. Moreover, once residence time was reached, the reactor was cooled to below 350°C. This temperature is low enough to stop any further feedstock conversion, and allows for the assumed negligible conversion during the remaining quenching time [42]. The reactor was quenched by delivering compressed air through a sparge tube directly onto the reactor surface. The reactor contents were cooled to temperatures below 350°C within two to four minutes after the end of an experimental run. This cooling rate is lower than rates achieved in thermal cracking kinetics studies that use molten salt baths for heating and cold-water baths for quenching [2], [24], [46], but given the difference in experimental scale it was considered high enough to minimize reactions during system cooling.

To ensure that all mass in the system was accounted for, a mass balance was conducted for each test run completed. The collected samples were weighted, and their total mass was compared to the mass of crude oil initially charged into the reactor. The collected masses ranged between 95-100% of the charged mass. The deviations in mass balance are attributable to minor losses of mass during collection of samples. Moreover, the GC gas analysis was conducted in two-minute intervals, which can underestimate the mass of gases evolved and may have contributed to this discrepancy.

3.4 Results and Discussions

3.4.1 Validation of Process Simulation VLE

An experimental validation was performed to ensure that the UniSim® process simulation file used to model the VLE of the experimental system (PUDL) was accurate to the system's observed VLE. In addition to the experimental runs intended for kinetic studies as presented earlier, each crude oil tested was also run at 300°C. The mild thermal cracking reactions were assumed to be negligible at this temperature, which made these test runs adequate for VLE comparison. The liquid residue sample weights of each 300°C test run was compared to the model's predicted liquid weights. The model's VLE predicted liquid mass was calculated to be 6.1 to 31.7% lower than the experimental liquid residue mass. This lower predicted mass indicates that the VLE model overestimated the extent of the loss of liquid mass due to VLE. This range includes all three crudes considered: MBL, AHS, and CDB.

This discrepancy was identified to be due to the process simulation's representation of PUDL's nitrogen sweep stream. The continuous flow nitrogen stream carries any crude oil vapourized mass away from the head section of the vertical reactor. The vapour in the head space of the reactor is highly diluted by nitrogen, which sustains low partial pressures of crude oil species in the vapour phase and forces further vapourization of the liquid crude mass. The sweep nitrogen stream was removed from the process simulation and the percentage differences between experimental liquid mass and model predictions were re-calculated to be between 3.6 and 6.1% lower than the experimental liquid residue mass.

Although the physical system has a sweeping nitrogen stream, the VLE validation demonstrated that its inclusion in the process simulation would overestimate the mass vaporization that takes place inside the reactor. Thus, to best represent the PUDL system, the model developed here does not include a sweeping nitrogen stream in the UniSim® process simulation. Moreover, the VLE was assumed to behave similarly for all temperatures considered in this work (350-450°C).

3.4.2 Experimental Data Optimized to Reaction Model

A MATLAB® routine was created to optimize the reaction model's predicted lump masses to the experimental data collected. The optimization function *fmincon* in MATLAB® was used to conduct the optimization with a user-made objective function that calculated the summation of squared errors (SSE) between model predictions and experimental values for each lump at the corresponding residence time (equation 3.6). The function *fmincon* is efficient and allows for constraints to be used to facilitate the optimization of a nonlinear multivariable system. The optimization procedure was performed for each temperature considered and with each of the three crude oils examined (MBL, AHS, and CDB) to obtain optimum reaction rate constant values for each crude at each condition.

$$SSE = \sum \frac{\left(y_{i,t,T,m} - y_{i,t,T,exp}\right)^2}{y_{i,t,T,exp}} x100\% \qquad \textbf{3.6}$$

$y_{i,t,m} \rightarrow model\ lump\ i\ wt\%\ at\ residence\ time\ t\ at\ temperature\ T$

$y_{i,t,exp} \rightarrow experimental\ lump\ i\ wt\%\ at\ residence\ time\ t\ at\ temperature\ T$

The values of the reaction rate constants reported by Singh *et al.* [42] were used as initial guesses for the optimization procedure in this work. Moreover, the boundary $\{10^{-9} \leq k_i \leq 1\}$ was implemented as a constraint on the reaction rate constants to restrict the optimization procedure and to prevent longer running time. Similar reaction models have reported rate constant values below $10^{-9}\frac{1}{min}$ as negligible reaction rates, and no rates of reaction to have been reported over the value of $1\frac{1}{min}$ [2], [38], [49].

The SSE was used as the objective function as it is well suited for quantifying the discrepancies between model predicted values and the experimental data. The coefficient of determination (R^2) was not used as the objective function for optimization as it fails to account errors that occur in similar magnitude on the negative and positive sides. However, once optimized using the SSE, the coefficient of determination was used as a measure of agreement between the optimized model's predictions and the experimental data.

3.4.3 Optimized Reaction Model

The reaction model presented in section 3.2 was optimized as described in the previous section. The model's optimized reactions rates for each of the ten reaction pathways in Figure 3-3a are presented in Table 3-3-Table 3-5 for each of the crude oils considered.

Table 3-3: Reaction rate constants of the optimized reaction model for the mild thermal cracking of MBL

Crude Oil	**MBL**			
Temperature [°C]	**350**	**400**	**425**	**450**
Reaction rate constants	$[\boldsymbol{min^{-1}}]$			
k_1	3.31E-09	1.00E-09	9.51E-06	1.18E-02
k_2	3.51E-07	2.93E-03	9.63E-06	1.20E-03
k_3	3.26E-04	2.67E-09	1.34E-03	2.76E-08
k_4	9.06E-04	2.83E-03	1.04E-02	4.21E-09
k_5	1.83E-03	3.31E-03	2.67E-02	2.02E-01
k_6	2.70E-03	8.61E-09	8.04E-02	2.42E-07
k_7	4.14E-02	1.01E-09	8.98E-02	1.65E-07
k_8	2.55E-07	5.50E-08	1.91E-05	3.25E-08
k_9	3.75E-09	1.00E-09	2.10E-05	1.02E-08
k_{10}	4.30E-09	1.00E-09	7.54E-04	1.52E-02

Table 3-4: Reaction rate constants of the optimized reaction model for the mild thermal cracking of AHS

Crude Oil	**AHS**			
Temperature [°C]	**350**	**400**	**425**	**450**
Reaction rate constants	$[\boldsymbol{min^{-1}}]$			
k_1	1.00E-09	6.55E-06	8.59E-06	8.25E-03
k_2	1.00E-09	3.29E-03	1.72E-05	1.27E-03
k_3	1.00E-09	1.68E-04	9.14E-03	2.38E-02
k_4	2.29E-04	3.34E-04	1.08E-04	1.67E-05
k_5	1.00E-09	1.55E-03	6.42E-04	8.85E-05
k_6	1.02E-09	4.33E-05	2.99E-02	9.46E-05
k_7	5.91E-02	3.42E-02	1.35E-01	1.16E-02
k_8	1.00E-09	1.06E-04	4.07E-05	3.43E-02
k_9	1.00E-09	1.61E-05	1.53E-05	6.56E-03
k_{10}	1.01E-09	5.82E-05	5.73E-05	1.03E-03

Table 3-5: Reaction rate constants of the optimized reaction model for the mild thermal cracking of CDB

Crude Oil	**CDB**			
Temperature [°C]	**350**	**400**	**425**	**450**
Reaction rate constants	$[\boldsymbol{min^{-1}}]$			
k_1	5.27E-07	1.15E-03	1.23E-06	4.33E-06
k_2	7.69E-07	1.94E-06	3.95E-06	6.09E-06
k_3	1.11E-03	5.04E-03	9.15E-06	1.57E-02
k_4	1.00E-03	3.36E-05	1.28E-02	9.68E-05
k_5	1.46E-05	1.95E-03	2.22E-02	3.62E-03
k_6	4.31E-04	1.94E-05	1.18E-05	2.77E-05
k_7	2.64E-01	9.62E-01	4.25E-04	4.57E-05
k_8	3.57E-06	4.96E-06	1.01E-02	1.66E-01
k_9	1.93E-06	2.03E-04	3.03E-06	4.40E-03
k_{10}	9.63E-06	5.25E-04	9.68E-02	2.51E-05

The rate of reaction constants and temperature data presented above was fit to a first order Arrhenius model. The activation energies and Arrhenius pre-exponential factors for each crude oil examined is presented in Table 3-6.

Table 3-6: Activation energy and Arrhenius pre-exponential factor for the ten reaction pathways of the optimized mild thermal cracking reaction model between 350 and 450°C

Crude Oil	**MBL**		**AHS**		**CDB**	
	$\boldsymbol{E_a}$ $[\boldsymbol{kJ/mol}]$	$\boldsymbol{A_o}$ $[\boldsymbol{1/min}]$	$\boldsymbol{E_a}$ $[\boldsymbol{kJ/mol}]$	$\boldsymbol{A_o}$ $[\boldsymbol{1/min}]$	$\boldsymbol{E_a}$ $[\boldsymbol{kJ/mol}]$	$\boldsymbol{A_o}$ $[\boldsymbol{1/min}]$
k_1	540.74	3.93E+35	551.47	1.57E+37	49.98	5.39E-2
k_2	251.44	1.45E+15	490.06	1.02E+33	78.41	2.73
k_3	-215.92	5.31E-23	666.17	1.85E+47	6.85	3.20E-3
k_4	-320.86	1.85E-29	-85.87	2.59E-11	-23.06	7.53E-06
k_5	168.63	1.36E+11	464.64	1.17E+31	241.89	5.56E+15
k_6	-184.91	1.42E-19	527.53	9.06E+35	-117.97	3.24E-14
k_7	-295.30	4.73E-28	-33.71	1.06E+04	-337.14	8.37E-29
k_8	3.39	5.58E-07	605.18	9.22E+41	412.46	2.68E+28
k_9	148.11	7915.45	550.10	1.68E+37	213.64	1.43E+12
k_{10}	596.45	2.64E+40	511.07	1.99E+34	139.87	2.04E+7

As previously mentioned, the model was optimized using the SSE between model prediction and experimental data. The goodness of fit between the optimized model's predictions and the experimental data is presented here in the form of parity plots, which include the data's coefficient of determination as a quantification of the fit. Figure 3-5 to Figure 3-7 are parity plots for each crude oil examined in this work (MBL, AHS, and CDB). Error lines representing positive and negative 10% error are shown in each plot.

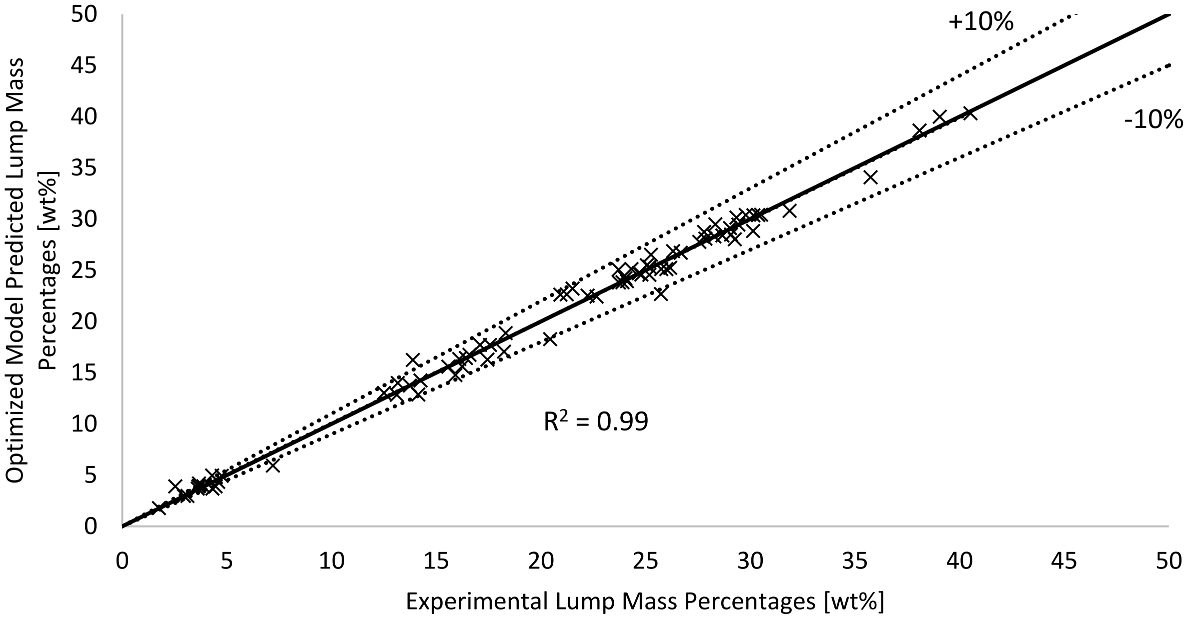

Figure 3-5: Parity plot for the MBL model lump mass percentage predictions versus experimental data with +/-10% error lines

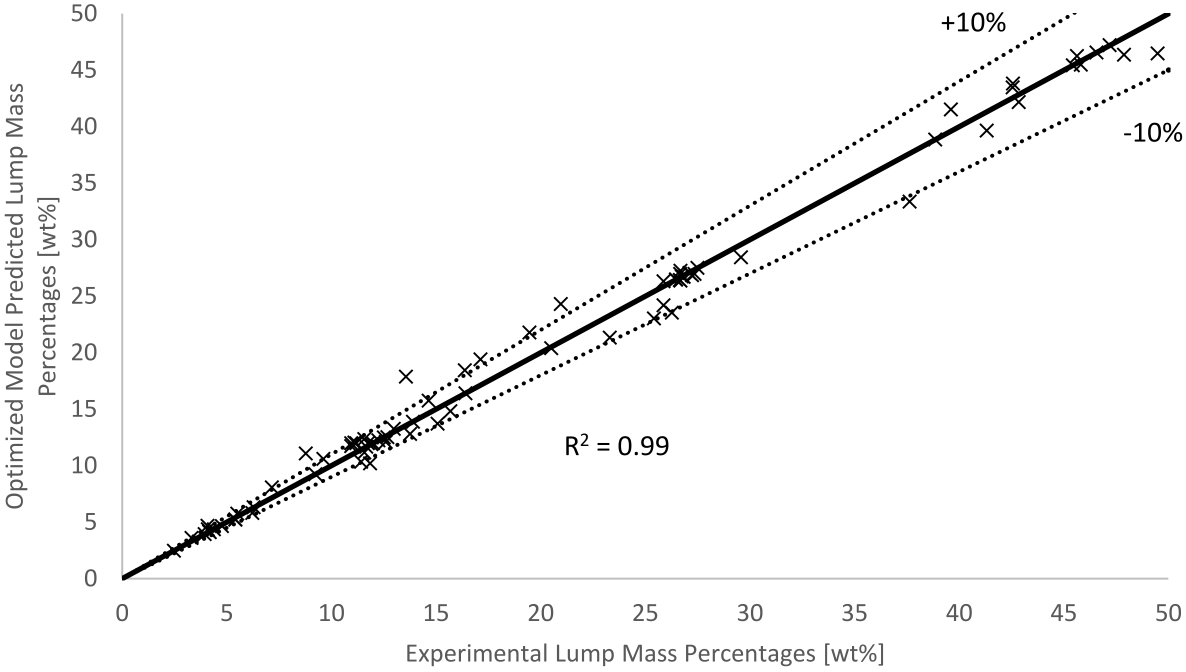

Figure 3-6: Parity plot for the AHS model lump mass percentage predictions versus experimental data with +/-10% error lines

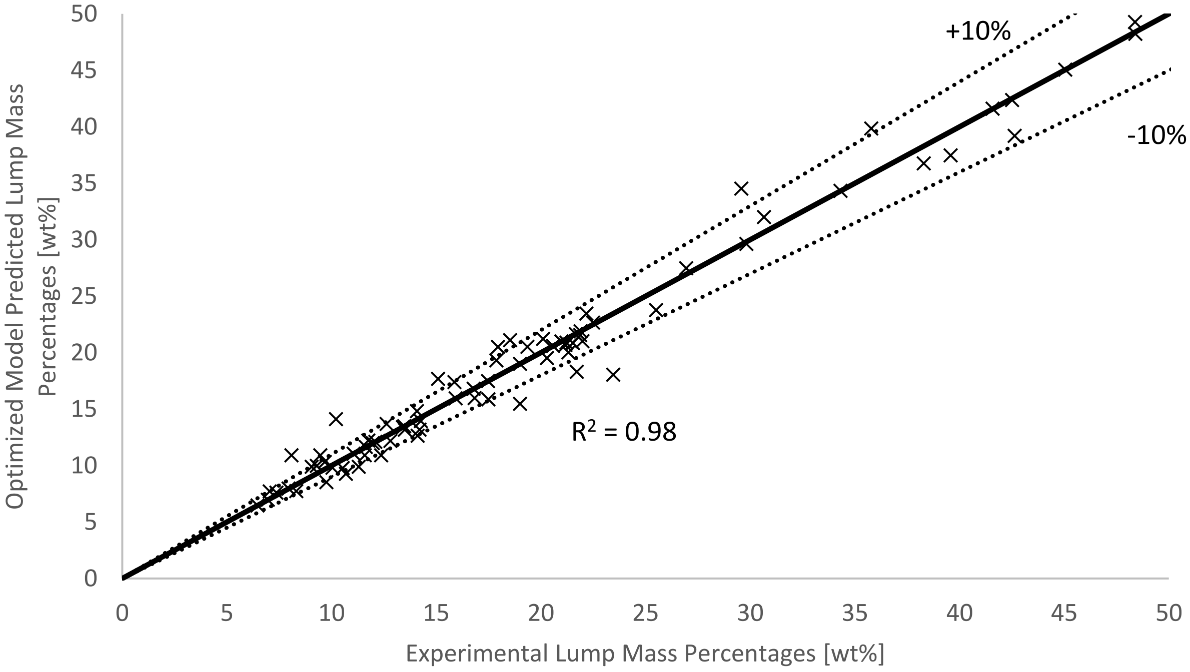

Figure 3-7: Parity plot for the CDB model lump mass percentage predictions versus experimental data with +/-10% error lines

The optimized models for the three crude oils examined are shown to have a high level of agreement with experimental data. MBL, AHS, and CDB were determined to have coefficients of determination (R^2) of 0.99, 0.99, and 0.98, respectively.

Another measure of the performance of the optimized models has been presented by Singh *et al.* [38] as the percentage of model predicted values to have a percentage error below a certain value. Table 3-7 presents the percentage of model predicted values that have $\leq 5\%$, $\leq 10\%$, $\leq 15\%$ and $\geq 25\%$ error with respect to their corresponding experimental value.

Table 3-7: Percentage of model predicted lump masses that have lower than 5, 10, 15% and higher than 25% SSE for MBL, AHS, and CDB

Error	$\leq 5\%$	$\leq 10\%$	$\leq 15\%$	$\geq 25\%$
	Percentage of model predictions (%)			
MBL	73.75	88.75	95	1.25
AHS	62.50	85	95	2.50
CDB	52.50	80	90	2.50

As shown on Table 3-7, a high percentage of model predicted values (80-88.75%) have less than 10% error. Moreover, only 1.25-2.5% of model predicted vales have an error greater than 25%. This level of error can be considered acceptable in the optimization of a complex system such as the one presented in this work.

Figure 3-8 presents the predicted mass percentage trends from the model presented above in direct comparison to the experimental data obtained for the AHS crude. Each component lump in the system is presented separately. These plots show the temperature dependence of the rates of reaction as different trends in consumption or production of the lumps observed at each experimental temperature (350-450°C). As expected, lumps defined by lower boiling points (i.e.: GLN and G) increase in mass percentage with time and temperature as they are produced. This is contrasted by higher boiling point lumps (i.e.: R and VGO), which decrease in mass percentage with time and temperature as they are mostly consumed. Middle boiling point lumps (i.e.: VGO, LGO, and GLN) have a lower observed change in mass percentage, especially at lower reaction temperatures. This is attributable to their simultaneous consumption and production. The model and experimental data for the AHS crude were discussed here and presented in Figure 3-8, as the other two crudes (MBL and CDB) considered in this work were observed to follow the same general trends discussed above.

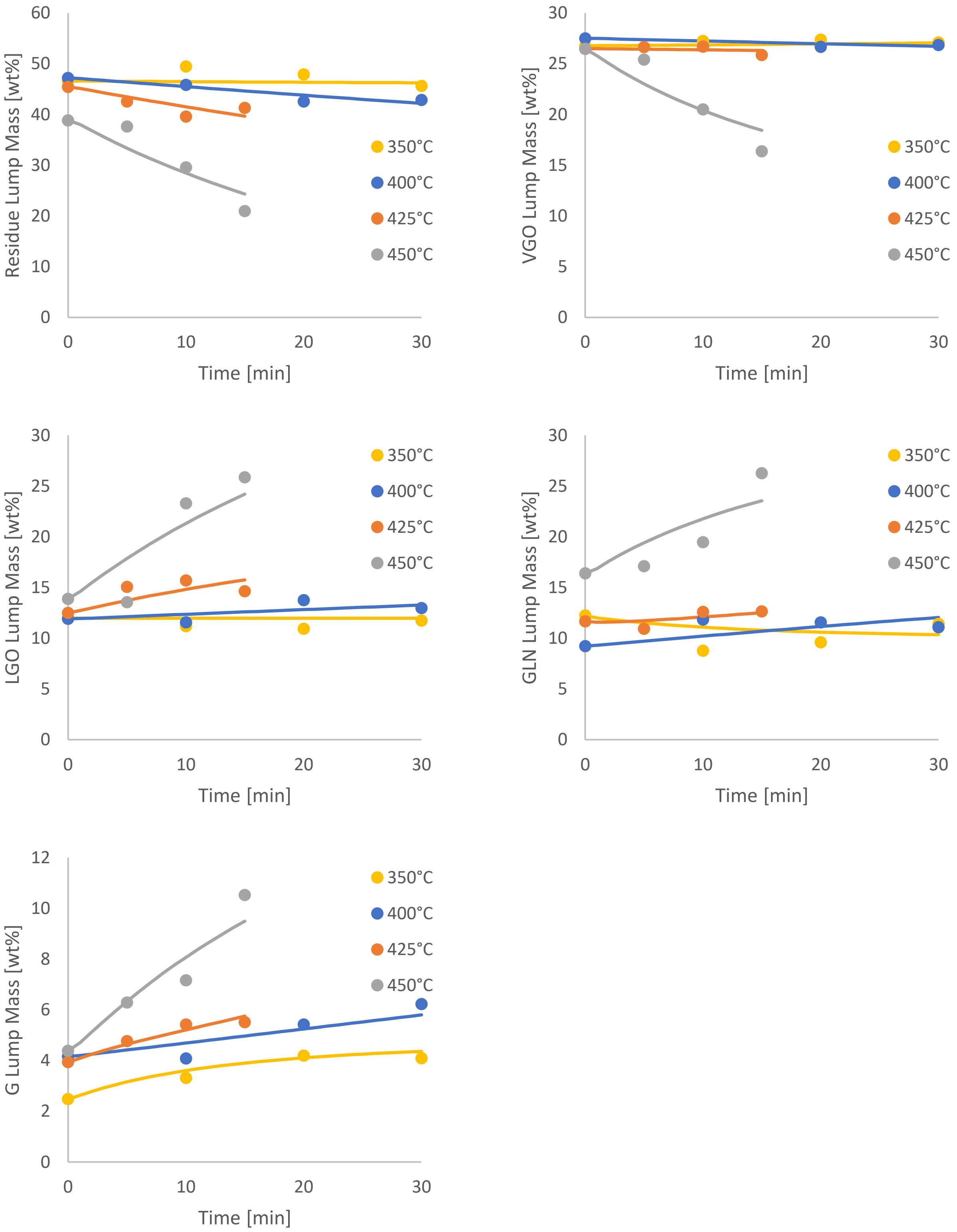

Figure 3-8: Model mass percentages predictions for all lumps through residence time (lines) compared to experimental data (points) for the AHS crude

3.4.4 Model Parameters Interpretation

The previous section presented the activation energies for the reaction pathways modeled in this work (see Table 3-6), and for each crude oil, some had negative values. The Arrhenius reaction model assumes there is an increase in rates of reaction as temperature is increased. A negative activation energy indicates the opposite, i.e.: the rate of reaction decreases as the temperature increases.

This work considers a complex system of parallel and serial reactions, it simplifies them to be represented as first order reactions and uses the Arrhenius model to represent their temperature dependence. These simplifications are necessary to allow efficient modeling of mild thermal cracking reactions; however, these may be the source of counter-intuitive results such as negative activation energies. Some of the potential reasons to the negative activation energies are discussed here.

Unlike some literature models, which use a starting material defined to only contain a "residue" lump, this work used crude oils that contain an initial distribution of all the lumps defined. This results in the simultaneous consumption and production of multiple lumps through residence time. Moreover, the reaction pathways used in this model (Figure 3-3a) are a set of competing reactions. It is possible that a change in temperature causes the pathway of rate control to change to an alternate pathway. This shift can cause a behavior that does not follow the Arrhenius model and can result in negative activation energies [50].

The reactions are modeled as a system of elementary first-order reactions between species, and the species are represented as lumps defined by their boiling point. These assumptions may obscure some of the compositional changes that may occur within a given lump. The composition of a given lump may change during residence time in a way other than described by the lump's definition (boiling point) and the reaction pathways modeled. For instance, molecular changes may occur to the hydrocarbon species in a given lump, which can affect the rates of the reactions modeled.

Given these reasons, the activation energies presented can be referred to as “observed negative”. Moreover, provided that the assumptions made in this work are justifiable and that a high degree of fit between model predictions and experimental data was achieved, the observed negative activation energies can be considered representative of the reactions experimentally observed as far as the model describes them.

The discussion above highlights that the assumptions and methods used to develop models such as the one presented here effectively create a mathematical model whose parameters, although based on physical phenomena, lose their physical representation. For instance, the negative activation energies previously discussed. The analysis and interpretation of the model parameters, as they relate to the physical phenomena they are intended to represent or as they relate to each other, is thus inappropriate.

3.4.5 Coke Formation

In the experimental program presented in this work, small amounts of solid or sludge material was observed to form in the high temperature reaction runs (450°C). This solid or sludge mass may be the first stages in the formation of coke. In all experimental runs, the mass of all products collected (post reaction mass) was compared to the total mass of crude oil charged into the system (pre-reaction mass). The mass balance on all experimental runs were determined to be high enough (95-100%) to not warrant the consideration of coke as a major product in the reactions and its inclusion in the reaction model.

3.5 Conclusions

This study reported optimized sets of rates of reaction constants for the mild thermal cracking of three types of crude oil: a medium crude (MBL), an upgraded heavy crude (AHS), and a diluted bitumen (CDB) for reactions at 350, 400, 425, and 450°C. The reactions were represented by a five-lump model with ten reaction pathways.

The reaction model presented in this study implemented a process simulation in UniSim® R450 to perform VLE calculations. This was necessary to determine the reactive system, the liquid phase, to which the reaction model was applied. The optimization of the reaction model resulted in a high level of agreement between model predictions and experimental values. The coefficient of determination (R^2) for MBL, AHS, and CDB, were 0.99, 0.99, and 0.98, respectively. Moreover, 89, 85, and 80% of the optimized model's predicted values had less than 10% error for MBL, AHS, and CDB, respectively. These were considered a low associated error due to the complexity of the reaction model optimized.

Finally, this study implemented VLE calculations in a process simulator in the context of the development of reaction model kinetic constants. The ability of the model to communicate with a process simulation file also introduces the capability to determine liquid and vapour phase compositions and physical properties through time. This may be valuable for the simulation and product property predictions of processes where mild thermal cracking occurs, such as partial upgrading of bitumen and heavy crudes.

Chapter 4 – Crude oil train car fire-model: A physical and reactive study on the pressure relief system for safety considerations

This chapter will be prepared as a manuscript for submission to a refereed journal

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Abstract:

Rail continues to be an important mode of transportation of crude oil and its derivatives from sources, to refineries, and to end consumers. Multiple rail accidents in the recent past have raised concerns about the safety measures and regulations enforced on the transportation of dangerous goods by rail, such as crude oil and its refined products. Government regulators seek to assess the safety features of new and current train car designs through physical models such as Analysis of Fire Effects on Tank Cars (AFFTAC). When exposed to heat, crude oil undergoes thermal cracking reactions. Thermal cracking is a carbon rejection reaction that changes the overall properties and composition of the crude oil. Current models, such as AFFTAC, do not include a reaction model. This work attempted to demonstrate the value of using the depressuring utility in UniSim® R450 process simulation software and of considering the compositional change due to thermal cracking reactions in a train car fire-model. Case studies were conducted using the depressuring utility and a previously developed mild thermal cracking reaction model to demonstrate the effect of compositional change. Three crude oils with varying properties and representative of the types of crudes transported by rail in Canada were used here. The case studies conducted showed the performance of a train car fire-model to be dependent on the crude oil characteristics. Furthermore, the model's performance was also shown to be affected by the compositional change of a given crude oil due to mild thermal cracking reactions. It was concluded that current train car fire models will benefit from the implementation of a reaction model to represent the system's compositional changes.

Keywords: Crude oil, safety, train, accident, explosion, pool fire, thermal cracking, Lac-Mégantic, derailment, AFFTAC.

4.1 Introduction

The current political and social climates have proved resistive to the transport of crude oil by pipelines. As a result, a large portion of the required transport of crude oil and other flammable liquids between sources, refineries, and final market destinations continues to be met through transport-by-rail. Figure 4-1 presents the volume of crude oil exports by rail as reported by Transport Canada.

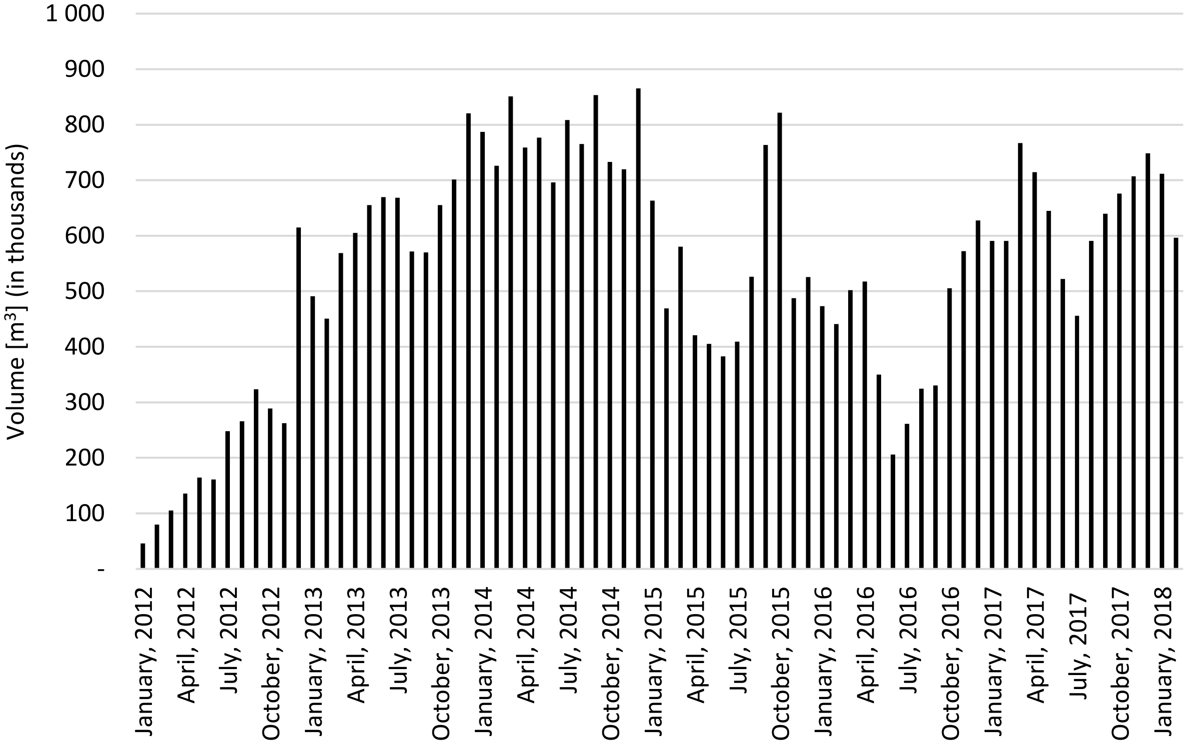

Figure 4-1: Canadian Crude Oil Exports by Rail - Monthly Data [51]

The volume of crude transported by rail has periods of sharp declines over the years presented, which may be partly attributable to feedback responses to accidents and periodic lows in the market price of a barrel of crude. However, the overall trend in Figure 4-1 indicates that crude-by-rail has a strong overall presence and it can be expected to follow this trend in the near future. The transport of crude oil and other flammable liquids by rail requires special attention by regulators to prevent accidents such as the 2013 Lac-Mégantic, QC, derailment, or the Heimdal, N.D., derailment in 2015. The accident in Lac-Mégantic killed 47 people and displaced thousands due to fires in the town centre [52]. A derailment involving crude oil may result in a pool fire and a Boiling Liquid Expanding Vapour Explosion (BLEVE). Ruptured tank cars can create a spill, which if ignited becomes a pool fire. Moreover, the crude inside intact train cars exposed to the intense heat flux from pool fires pressurizes as it is contained by the train car shell. If the heat stress on the shell causes it to rupture, the boiling liquid will quickly vapourize and expand due to the pressure drop. This vapour will feed near-by fires causing a violent explosion – a BLEVE. To reduce the risk of BLEVEs, train car design must include a proper depressurization system.

Table 4-1 summarizes rail occurrences as reported by the Transportation Safety Board of Canada. Some of the noteworthy entries are highlighted on the table. There is a somewhat constant number of overall accidents, accidents involving dangerous goods, and fatalities over the reported years. This data supports the importance of assessments of safety measures regarding the transportation of dangerous goods.

The transport of dangerous goods by rail is regulated by Transport Canada (TC) in Canada and by the Department of Transportation (DOT) in the United States. An agreement has been made between TC and DOT to update the regulations of the transport of crude and ethanol by rail in North America [52]. The updated regulations for train cars is the TC117 in Canada and the DOT117 in the US, which by 2025 must be used for the transport of all flammable liquids by rail [53].

Currently, the software used for simulating train car designs for approval by regulatory bodies is the Analysis of Fire Effects on Tank Cars (AFFTAC). AFFTAC's capabilities are implemented by a two-dimensional model that includes prediction of heat exchange between the thermal masses (i.e.: tank car shell, jacket, liquid and vapour lading), the pressure relief valve position, venting of lading through valve, tank volume, tank wall burst strength [54]. Together these factors help regulators determine whether a tank car design is appropriate for given test case scenarios.

One limitation of the AFFTAC model is that it neglects reactions between the species present in the lading of the train car. Crude oil undergoes thermal cracking reactions when exposed to heat [2], [7], [12], [24], [37], [38], [42]. The crude oil in train cars can experience these reactions if exposed to a considerable heat source such as a fire. These reactions cause the composition of the crude oil to change and consequently its physical properties. The reacted crude may have considerably different physical responses to heat and increased pressures associated with a train car fire. It follows that the reactions are an important aspect to be considered when simulating the crude oil system's behaviour inside a tank car exposed to a heat source.

This work will present train car fire-model simulations with case studies. These will show the impact of composition change due to mild thermal cracking reactions on the performance of a train car exposed to a fire. Moreover, these simulations will consider three different crude oils, which will elucidate the effect of lading properties on the train car fire-model. This information will be beneficial to regulators interested in validating current train car fire models, such as AFFTAC, and exploring possible improvements to existing simulation software.

Table 4-1: Summary of rail occurrences between 2007 and 2016 (Reproduced from [55]***)***

Year	**2007**	**2008**	**2009**	**2010**	**2011**	**2012**	**2013**	**2014**	**2015**	**2016**
Accidents	**1334**	**1199**	**1055**	**1116**	**1072**	**1049**	**1099**	**1237**	**1201**	**1035**
Main-track collisions	9	7	5	4	3	6	4	9	4	5
Main-track derailments - 1-2 cars*	76	67	39	41	49	35	52	46	42	38
Main-Track Train Derailments - 3-5 cars	25	16	6	11	17	9	13	15	8	7
Main-Track Train Derailments - 6 or more cars	59	46	22	30	44	23	19	41	27	18
Crossing accidents	221	223	188	180	171	192	184	185	165	133
Non-main-track collisions	105	92	95	94	89	101	94	114	96	73
Non-main-track derailments - 1-2 cars (a)*	467	446	395	457	404	424	437	523	534	441
Non-Main-Track Train Derailments - 3-5 cars (a)	138	101	89	93	91	77	89	90	87	59
Non-Main-Track Train Derailments - 6 or more cars (a)	36	42	25	26	27	29	25	34	26	27
Collisions/Derailments involving track units	30	27	50	36	34	25	41	34	53	36
Employee/Passenger accidents	18	12	12	9	11	7	8	12	15	16
Trespasser accidents	97	71	71	81	66	71	57	54	50	70
Fires/Explosions	**25**	**12**	**20**	**30**	**23**	**17**	**11**	**36**	**32**	**35**
Other accident types	28	37	38	24	43	33	65	44	62	77
Reportable incidents	223	216	209	188	233	238	224	218	216	188
Dangerous goods leaker**	88	64	78	68	79	93	94	63	33	30
Main-track switch in abnormal position	7	13	4	5	10	5	7	6	13	7
Movement exceeds limits of authority	106	111	106	101	118	120	98	129	142	133
Runaway rolling stock	13	16	13	5	16	13	14	11	14	9
Other reportable incidents	9	12	8	9	10	7	11	9	13	9
Main-track accidents (b)	258	209	170	166	201	135	184	212	223	209
Million main-track train-miles (MMTTM) (c)	84.5	83.1	72.2	77.6	78.4	80.1	78.5	76.5	74.3	74.7
Main-track accidents/MMTTM	3.1	2.5	2.4	2.1	2.6	1.7	2.3	2.8	3.0	2.8
Accidents involving dangerous goods	**191**	**153**	**133**	**141**	**121**	**120**	**145**	**174**	**145**	**108**

Main-track derailments	35	23	11	13	20	6	11	25	12	10
Crossing accidents	6	4	3	7	1	4	5	5	4	4
Non-main-track collisions	41	33	32	26	21	21	26	37	33	19
Non-main-track derailments	101	85	81	88	73	88	98	97	92	67
Other accident types	8	8	6	7	6	1	5	10	4	8
Accidents with a dangerous goods release	3	3	3	3	3	2	7	4	6	1
Accidents Involving Runaway Rolling Stock	40	27	31	25	27	33	39	23	29	33
Fatalities for reportable occurrences	**84**	**74**	**71**	**81**	**71**	**81**	**125**	**56**	**46**	**66**
Crossing accidents	26	28	19	24	25	33	30	21	15	19
Trespasser accidents	55	45	52	55	43	44	43	32	30	47
Other occurrence types	3	1	0	2	3	4	52	3	1	0
Serious injuries for reportable occurrences	**59**	**65**	**50**	**64**	**52**	**73**	**39**	**53**	**50**	**56**
Crossing accidents	23	37	21	28	22	32	27	29	18	24
Trespasser accidents	24	20	15	19	21	22	10	21	17	20
Other occurrence types	12	8	14	17	9	19	2	3	15	12

Data extracted March 31, 2017.

Federally regulated railway occurrences.

a. Data from 2005 to 2007 have been adjusted in light of clarifications to industry of TSB's reporting requirements.

b. Accidents which occurred on main-track or spurs, excluding crossing and trespasser accidents.

c. Main-track train-miles are estimated (Source: Transport Canada).

*New TSB regulations came into effect on July 1, 2014. Under the new reporting requirements all derailments are reportable.

**Under the new reporting requirements the minimum reporting threshold for incidents (200 litres) involving the release of low vapour pressure flammable liquids has been harmonized with Part 8 of the Transportation of Dangerous Goods Regulations.

4.2 Train Car Model

4.2.1 Thermal Cracking

Crude oil undergoes mild thermal cracking reactions in a temperature range of 400-450°C [2], [7]. Thermal cracking is a thermal carbon-rejection reaction, which breaks carbon-carbon bonds and thereby decreases the crude’s carbon-to-hydrogen ratio, boiling point, and viscosity [3]–[5], [7]. In the case of a train car exposed to a heat source, as the temperature gradually increases, mild thermal cracking is the first set of reactions that will occur. As such, this should be the first set of reactions to be considered when modeling the system. Mild thermal cracking occurs predominantly in the liquid phase under the conditions pressurized train car (approx. 12 bar) [2], [4], [7], [24], [29], [37]. As a result, vapour-liquid equilibrium (VLE) is an important aspect of a model that implements mild thermal cracking reactions.

Crude oil is composed of a complex mixture of hydrocarbons. Lumping techniques are used to simplify the system’s components and allow for efficient reaction modeling. A five-lump mild thermal cracking reaction model that implements VLE calculations has been presented elsewhere (Chapter 3). This reaction model was developed using three crude oils commonly transported by rail in Canada: Hardisty MBL (MBL), Albian Heavy Synthetic (AHS), and Christina Lake Diluted Bitumen (CDB). These three crude oils have a wide range of properties. MBL is a medium crude, AHS is an upgraded heavy crude, and CDB is a diluted bitumen. Reaction kinetic parameters obtained experimentally are highly dependant on the characteristics of the feedstock (crude oil) used [34]–[36]. This model is appropriate to model the reactions that occur in the train car that may be carrying one of the three crude oils, or another crude with similar properties (Table 4-2).

Table 4-2: Physical characteristics of the three crude oils considered in this study

Parameter	**MBL**	**AHS**	**CDB**
Density [kg/m^3]	867.5	940.6	927.0
Kinematic Viscosity at 40°C [m^2/s x10^{-6}]	8.26	70.99	88.29
Heat of combustion [cal/g]	10718	10314	10283
Micro Carbon Residue (MCR) [wt%]	4.69	13.9	11.7

4.2.2 Process Simulation

Honeywell's UniSim®'s depressuring utility is a simulation tool designed to dynamically model the behaviour of a vessel exposed to a fire as it pressurizes and pressure relieves [33]. As such, it is an adequate tool for modeling a crude oil train car exposed to a fire. The utility allows for vessel specifications such as orientation, dimensions, relief valve characteristics, heat flux model, and vessel fill percentage. UniSim®'s depressuring utility can be used in conjunction with a mild thermal cracking reaction model to study the behaviour of crude oil lading in a train car exposed to a heat source (i.e.: pool fire) as the lading changes composition due to the reactions.

Normally, complex solutions are represented by one or two components with known properties (e.g.: gasoline represented by n-octane). This simplification can lead to decreased reliability in the model predictions. Process simulators such as UniSim® are designed to model complex solution systems like crude oils. UniSim® contains a crude oil assay characterization tool, which allows for confident physical modeling of crude oils given bulk properties of the crude oil. Moreover, process simulators are equipped with robust thermodynamic equations of state that can predict liquid-vapour behaviour of crude oil systems. The Peng-Robinson (PR) equation of state was chosen to model this system as it is generally recommended for crude oil systems [33]. Additionally, the UniSim® depressuring utility has the capability of predicting vapour and liquid phase properties.

4.3 Methods

4.3.1 Crude Oil Compositions and Reaction Model

The crude oil assay characterization tool in UniSim® was used to model the crude oil samples. The characterization tool required crude oil bulk properties: density, kinematic viscosity at 40°C, and the true boiling point (TBP) mass distribution of the crude. Based on this input, the process simulator created a representative assay modeled by hydrocarbon pseudo-components, which are defined by their boiling points. For each crude oil examined in this study, this composition is referred to as the original UniSim® characterization, and it refers to a composition where no mild thermal cracking reactions have occurred.

The case studies performed in this work used three crude oils transported in Canada: MBL, AHS, and CDB. Three compositions of each crude oil were defined. The first, is the original UniSim® characterization described above. The two other compositions were modified to represent the change in the original composition due to mild thermal cracking reactions. A five-lump mild thermal cracking reaction model was developed for MBL, AHS, and CDB in Chapter 3. The model was implemented at different temperatures and residence times to obtain crude oil compositions which represent the system at those conditions. The reaction model was applied to the original composition to obtain the 350°C, 0 min (composition 2) and the 450°C, 15 min (composition 3). The change in composition due to reactions progressively increases from composition 1 to 2 to 3, as the reaction conditions become more severe.

Table 4-3 lists all the compositions used in the simulated case studies for each crude oil. Each case study was initialized with one of the compositions in Table 4-3 and all cases were simulated with the same specifications discussed in the next section. It is important to note that each case study simulates the physical changes in the system, but no compositional change occurs during a simulated case. The effect of compositional change due to reactions will be observed when contrasting simulation runs between compositions 1 to 3 (Table 4-3).

Table 4-3: Matrix describing the compositions of each crude obtained by applying the mild thermal cracking reaction model with the listed temperature and residence time

	Crude Oil		
Composition	**MBL**	**AHS**	**CDB**
1	MBL Original	AHS Original	CDB Original
2	MBL 350°C, 0 min	AHS 350°C, 0 min	CDB 350°C, 0 min
3	MBL 450°C, 15 min	AHS 450°C, 15 min	CDB 450°C, 15 min

4.3.2 Depressuring Utility and Train Car Specifications

The depressuring utility in Honeywell’s UniSim® R450 was used to model the physical changes in the train car fire-model. The utility is initialized with one of the compositions described in the previous section. It also accepts vessel specifications as input to simulate the system’s physical behaviour. Table 4-4 presents the variables used to simulate the case studies presented in this work. Some of these values were provided by Transport Canada to represent a typical crude rail car in Canada. Moreover, the utility’s inputs can be modified to represent specifications of other rail cars.

Table 4-4: UniSim® R450 depressuring utility input variables

Input variable	**Value**	**Units**
Vessel orientation	Horizontal	-
Flat end volume	109.8	m^3
Diameter	3	m
Initial liquid volume	104.2	m^3
Heat transfer model constants		
C_1	5.78×10^7	kJ/h
C_2	0	kJ/s
C_3	0	kJ/h °C
C_4	0	°C
C_5	0	kJ/h
Heat loss model	(None)	-
Valve parameters		
Flow equation	Relief	-
Orifice diameter	75	mm
Discharge coefficient	1	
Set pressure	1240	kPa
Liquid flow equation	(No liquid flow)	-
Full open pressure	1356	kPa
Options		
Depressuring time	25	min
Time step size	0.5	s

The depressuring utility has a “fire” heat transfer rate model, which is presented as equation 4.1. A constant heat transfer rate was used in this work to represent the energy gain from a fire, which led to a linear increase in vessel temperature for all case studies performed (Figure 4-4). Additionally, the system is assumed to homogeneously increase in temperature. This was taken as the upper boundary case, or worse case scenario, where the heat transfer rate will have the fastest effect on the overall system.

$$Q = C_1 + C_2 t + C_3 (C_4 - T_{vessel}) + C_5 \left(\frac{v_{L,t}}{v_{L,to}} \right) \quad \textbf{4.1}$$

$Q - heat\ transfer\ rate\ [kJ/h\ ]$
$t - time\ [s]$
$T_{vessel} - vessel\ temperature\ (°\mathrm{C})$
$v_{L,t} - liquid\ volume\ at\ time\ t\ [m^3]$
$v_{L,to} - liquid\ volume\ at\ time\ t = 0\ [m^3]$

The depresuring utility can simulate a more realistic heat transfer model. One suggested method is to use Computer Fluid Dynamics (CFD) simulations to better understand the heat transfer on the overall train car system. The UniSim® depressuring utility's fire model (equation 4.1) constants C_1 to C_5 can then be used to fit such information to model a more realistic heat transfer into the system.

4.4 Results and Discussion

The case studies considered the pressure relief system performance by examining the simulated trends in vessel pressure, liquid level, and pressure relief valve (PRV) open percentage. The UniSim® depressuring utility can calculate the values many more variables associated with the system, including individual component mass composition and properties of both the vapour and liquid phases. The variables examined in this work were chosen to assess the safety performance of a train car design. Moreover, these variables are comparable to the outputs of an AFFTAC simulation.

4.4.1 Original Composition as a Base Case

The original composition obtained from the UniSim® assay characterization was used as a base case since it is generated to represent each crude oil, and it does not take into considerations changes in mass due to mild thermal cracking reactions. The trends in system pressure, PRV open percentage, and liquid level through time as the system experiences a linear increase in temperature from 350°C at 0 minutes, to 450°C at 25 minutes are presented in Figure 4-2 and Figure 4-3. The original composition simulations are represented by the grey trend lines. The linear increase in temperature of each case study is presented in Figure 4-4.

The following discussion addresses the original composition trends for MBL (plots A.1., B.1. in Figure 4-2 and C.1. in Figure 4-3) but is applicable to all crude oils case studies (MBL, AHS, and CDB), as they follow similar trends with different absolute values relative to each other. All three variables increased approximately linearly in the first 2-3 minutes of simulation. The linear increase in the liquid level (C.1.) of the system is substantial and suggests the liquid volume in the vessel to thermally expand as the temperature rises. This leads to the observed increase in system pressure (A.1.) and PRV opening percentage (B.1.) as the vapour mass is pressurized in the vessel's head space. After 5 to 6 minutes in the simulation, the liquid level stabilizes to a constant value and the PRV reduces its percentage opening. This indicates the thermal expansion of the liquid has reached its maximum and its effect on the system pressure is smaller. As a result, the system pressure is reduced momentarily and the PRV percentage opening partially closes. After the reduction in pressure, the system re-pressurizes in a non-linear trend, which can be attributed to the vaporization of crude oil components in the liquid phase. The components progressively vapourize as the temperature linearly increases and surpasses each component's boiling point at the vessel pressure (A.1.).

The liquid level did not reach the vessel's height for all the case studies performed in each of the three crude oils studied. This result is important for the safety assessment of a train car exposed to a fire as the PRV is often designed for vapour flow only and may be ineffective in relieving pressure if the liquid level rises to the top of the train car and pushes through the valve.

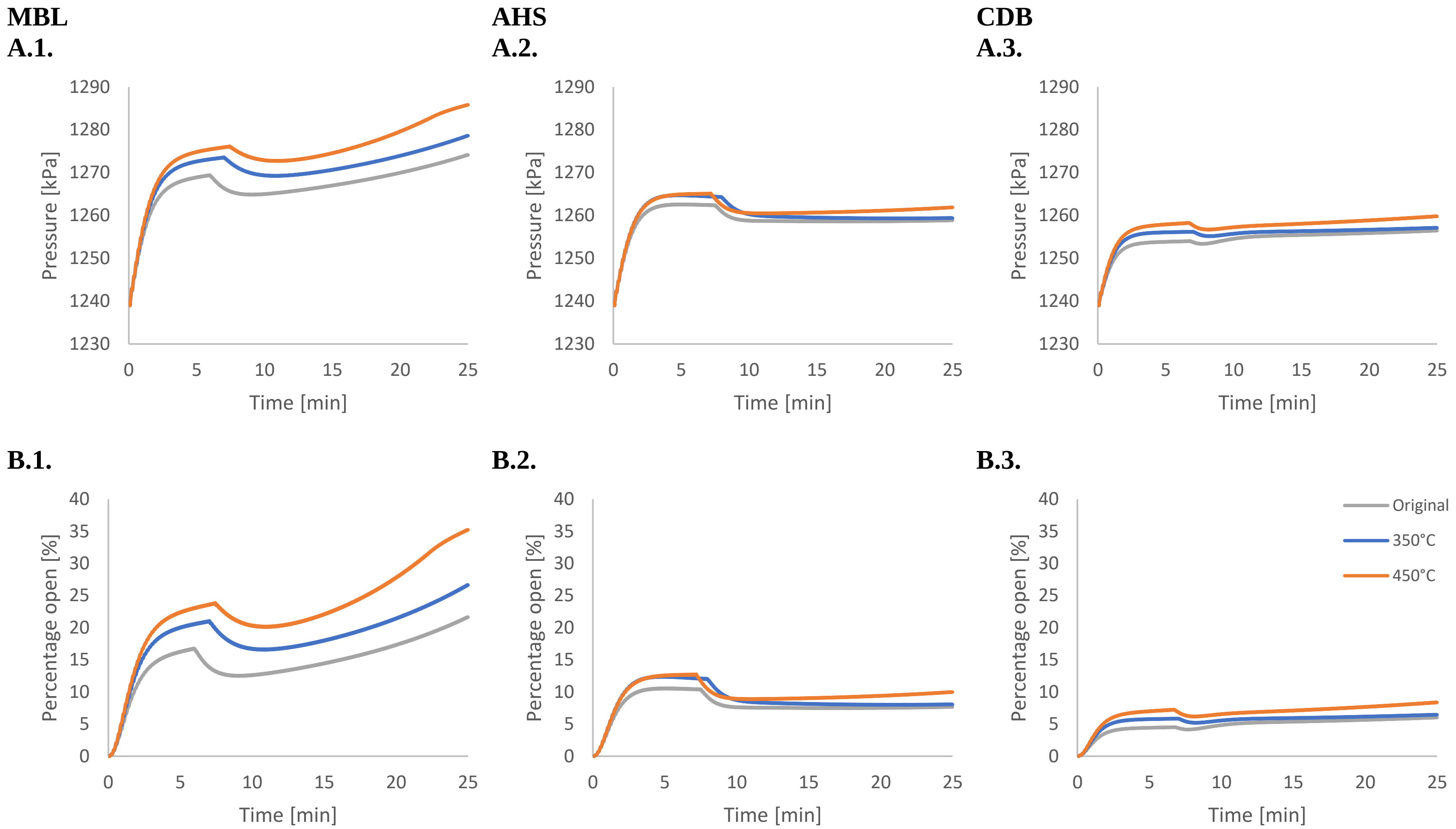

Figure 4-2: Depressuring utility vessel pressure (A) and PRV percentage open (B) for three compositions of each of the crude oils considered: MBL (1), AHS (2), and CDB (3)

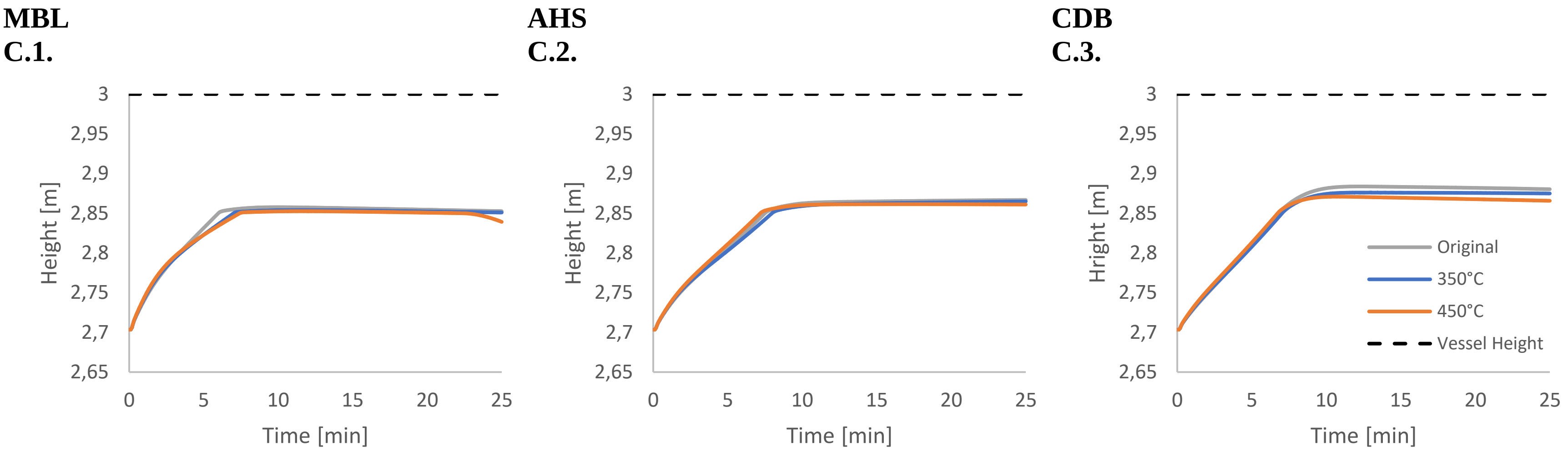

Figure 4-3: Depressuring utility vessel liquid level (C) for three compositions of each of the crude oils considered: MBL (1), AHS (2), and CDB (3)

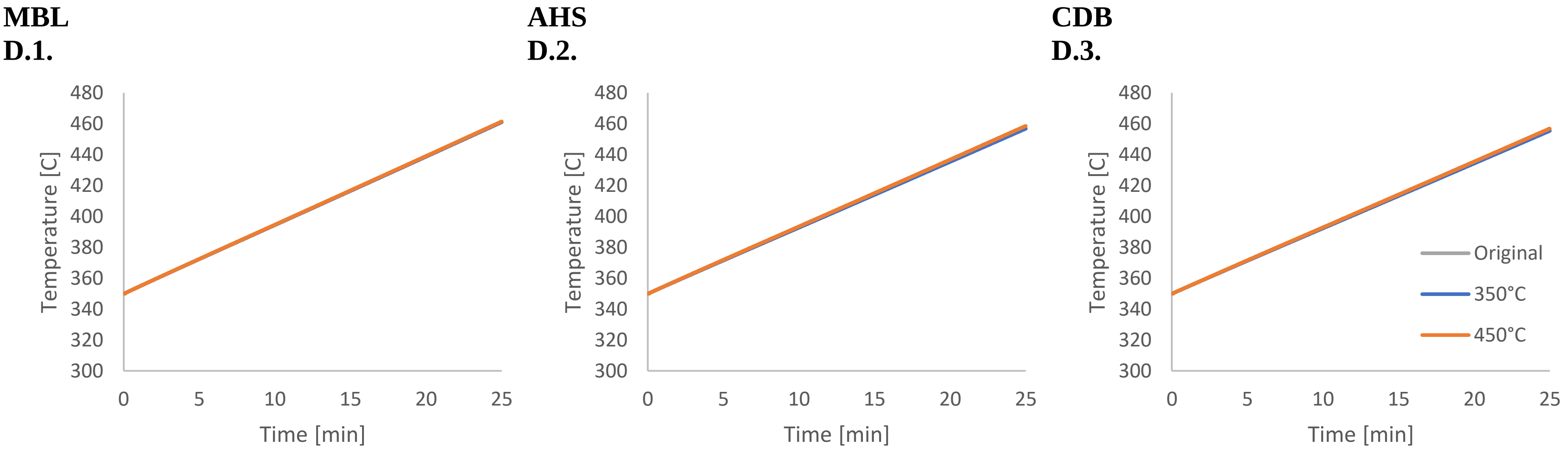

Figure 4-4: Temperature profiles (D) for three compositions of each of the crude oils considered: MBL (1), AHS (2), and CDB (3)

4.4.2 Effect of Composition Change Due to Reactions

The three compositions used for each crude demonstrate the effect of considering the mild thermal cracking reactions on the performance of the train car exposed to a fire. As expected, the train car simulations provided a "band of performance" for each of the depressuring variables simulated. This band defines the area where the value of the variable is most likely to occur, given the variability in composition due to reactions for the range of conditions defined in this study (Table 4-3). The area is contained by the trendlines for compositions 1, 2 and 3. Table 4-5 shows the average percentage differences between the predicted variable values for compositions 2 and 3 in comparison to the base case (composition 1) of each crude oil considered. As a result, the positive or negative average differences indicate the direction of change in trends as composition changes due to reactions. The pressure and PRV open percentage were shown to have higher values as the change in composition due to reactions increased, while the liquid level was shown to have lower values.

Table 4-5: Average percentage difference for the predicted pressure, PRV percentage opening, and liquid level for compositions 2 and 3 compared to composition 1 of each crude oil

Variable and Compositions	**Average Percentage Difference**		
	MBL	**AHS**	**CDB**
Pressure			
Composition 2	0.31%	0.10%	0.10%
Composition 3	0.61%	0.17%	0.24%
PRV Percentage Open			
Composition 2	23%	11%	15%
Composition 3	42%	18%	34%
Liquid Level			
Composition 2	-0.10%	-0.08%	-0.17%
Composition 3	-0.15%	-0.04%	-0.28%

4.4.3 Effect of Crude Oil Type

In Table 4-5, AHS and CDB simulations demonstrated smaller differences in variable predicted values when compared to the base case (composition 1). This indicates that the train car fire-model simulations for AHS and CDB were less affected by the change in composition due to reactions when compared to the MBL case study. The similarity in properties between AHS and CDB when compared to MBL (Table 4-2) may contribute to the similar effects observed in these crudes. MBL is a lighter crude oil that contains a higher proportion of lower boiling point components, which will more readily vaporize at the conditions considered in the case studies.

A further measure of the effect of crude oil type on the train car fire-model results is the average difference in values between the predicted variables for composition 1 case studies of AHS and CDB in comparison to the predicted values for composition 1 case study of MBL (Table 4-6). This comparison focuses on the differences between crude oils by examining case studies with compositions unchanged by the mild thermal cracking reaction model.

Table 4-6: Average percentage difference for the predicted pressure, PRV percentage opening, and liquid level between composition 1 of AHS and CDB compared to composition 1 of MBL

Variable	**Average Percentage Difference**		
	MBL	**AHS**	**CDB**
Pressure	-	-0.62%	-1%
PRV Percentage Open	-	-57%	-99%
Liquid Level	-	-0.02%	0.45%

The comparison presented in Table 4-6, indicates that both AHS and CDB composition 1 case studies resulted in lower average values of pressure and PRV percentage open compared to the matching MBL case. Additionally, the liquid level was shown to have the smallest difference in both AHS and CDB cases.

4.4.4 Comparison to AFFTAC

Unlike AFFTAC, the depressuring utility cannot model the vessel strength and assess its burst performance, and it does not include variable orientations for the train car. For instance, a derailed train car may be laying on its side when exposed to a fire, and the PRV may be in a region of the vessel below the liquid level. In this case, the model would require allowing liquid flow though the PRV, which the UniSim® depressuring utility does not. Additionally, the burst strength of the train car vessel is an important safety aspect for the assessment of train car designs, as it can clarify the cases in which a burst shell may occur.

UniSim®'s capability for modeling complex hydrocarbons solutions and other flammable liquids increases the model's ability to accurately predict the physicochemical properties of the multiphase system in comparison to models that use binary or ternary solutions to represent a complex solution. Additionally, the model presented here also can implement the effect of composition change due to mild thermal cracking reactions on the model predicted variables. These two features can beneficial to the safety assessment of train car designs.

4.5 Conclusions

The three case studies presented above enabled two major conclusions to be drawn. Firstly, the pressure relief performance of a train car exposed to a fire varies depending on the type of crude oil used as lading. The three types of crude (MBL, AHS, and CDB) used in each case study, demonstrated the difference in pressure relief performance variables. Notably, up to -1% average difference in predicted pressures in the train car, and up to -99% average difference in valve opening percentage patterns, when comparing AHS and CDB to the MBL case, confirm the effect of lading properties on the performance variables of the train car fire-model. This indicates that, for efficient and safe performance, the pressure relief system may require specific designs for each crude oil ladings considered for transport in new train cars if the ladings' physicochemical properties differ considerably. This may be an important consideration for train cars that may be used to transport different flammable liquids, e.g.: ethanol, distillates, crude oil, light boiling point petrochemicals.

Secondly, case studies performed demonstrated the effect of compositional change due to mild thermal cracking reactions on the performance of the train car fire-model for each crude oil considered. Each crude oil was simulated in three distinct compositions, representing the progressive change in composition due to mild thermal cracking reactions. The case studies determined the average percentage difference in predicted pressure, PRV percentage opening and liquid level between the base case (no reactions) and cases where composition change due to reaction occurred to be between -0.1 to 42% for MBL, -0.04 to 18% for AHS, and -0.17 to 34% for CDB. The highest differences were observed to be for the PRV percentage opening comparisons and the smallest differences for liquid level comparisons.

The differences in performance suggest that software, such as AFFTAC, used to approve or quantify the performance of new and existing train car designs would benefit from the consideration of lading composition change due to reactions that occurs during a fire. Either by implementing a reaction model in the simulation, or by presenting its output performance variables as a "performance band". As presented in this study, the band can be obtained by discretely simulating case studies with lading compositions associated with the product composition of a mild thermal cracking reaction model for increasingly severe conditions. The band identifies an area where performance variable values are most likely to fall, for the given train car design specifications and fire conditions.

Chapter 5 – Conclusions and Future Work Suggestions

5.1 Conclusions Summarized

The work presented in the previous chapters fulfilled this thesis' objectives. A mild thermal cracking reaction model was developed, its parameters determined using collected experimental data, and the reaction model was implemented in a train car fire-model to determine the effect of composition change due to reactions and crude oil properties on the performance of a train car exposed to a fire. An introduction and literature review were presented in Chapters 1 and 2. Chapter 3 was a model development and experimental kinetic study, which resulted in a model that predicts phase composition in a reacting crude oil system using VLE calculations, and kinetic parameters for the mild thermal cracking of three crude oils (MBL, AHS, and CDB) through a five-lump and ten-reaction pathway system. The three crude oil's experimental data were fit to the model developed with high level of agreement. The model's coefficient of determination for MBL, AHS, and CDB were 0.99, 0.99, and 0.98, respectively. Additionally, the model resulted in 89, 85, and 80% of predicted values within 10% error of the experimental data for MBL, AHS, and CDB, respectively.

Chapter 4 was intended to investigate safety aspects of the transport of crude-by-rail. The depressuring utility in UniSim® R450 was used in conjunction with the mild thermal cracking model developed in Chapter 3 to create a train car fire-model. Case studies on train car performance were conducted to evaluate the effect of crude oil property variations, and composition change due to reactions on train car performance variables when exposed to a fire. The results suggested that crude oils with considerable variance in properties and/or that experience compositional change due to reactions can affect the predictions of a train car fire-model's performance variables such as vessel pressure (up to 1% average difference), pressure relief valve position (up to -99% average difference), and vessel liquid level (up to 0.45% average difference).

5.2 Future Work

The mild thermal cracking reaction model developed in this work may be valuable in the context of partial upgrading of heavy crudes. More specifically, the MATLAB-UniSim® model connection presented here may be used to implement a UniSim® process simulation of partial upgrading technology such as visbreaking. For the modeling of higher temperature thermal cracking, the addition of a coke lump may be required for accurate representation of product mass distributions.

Moreover, an important aspect of partial upgrading of crudes is the stabilization of upgraded material by hydrogenation through hydrotreatment. The hydrotreating of thermally cracked hydrocarbon material requires further reaction modeling efforts. Due to the nature of hydrotreating unsaturated hydrocarbons, reaction kinetics may need to be developed in terms of molecular structure, i.e.: PIONA or SARA. Fukuyama and Terai [56] developed a hydrocracking model that may elucidate some considerations required for the partial upgrading and hydrotreating modeling. In their work, SARA defined reactants were used to predict the formation of boiling point defined lumps. Experimental work on the hydrotreatment of partially upgraded crude oils may also prove valuable for the determination of the hydrogen requirement in a partial upgrading process facility. The hydrogen requirement may have considerable effect on the economics and associated viability of partial upgrading technologies such as visbreaking.

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Appendix A

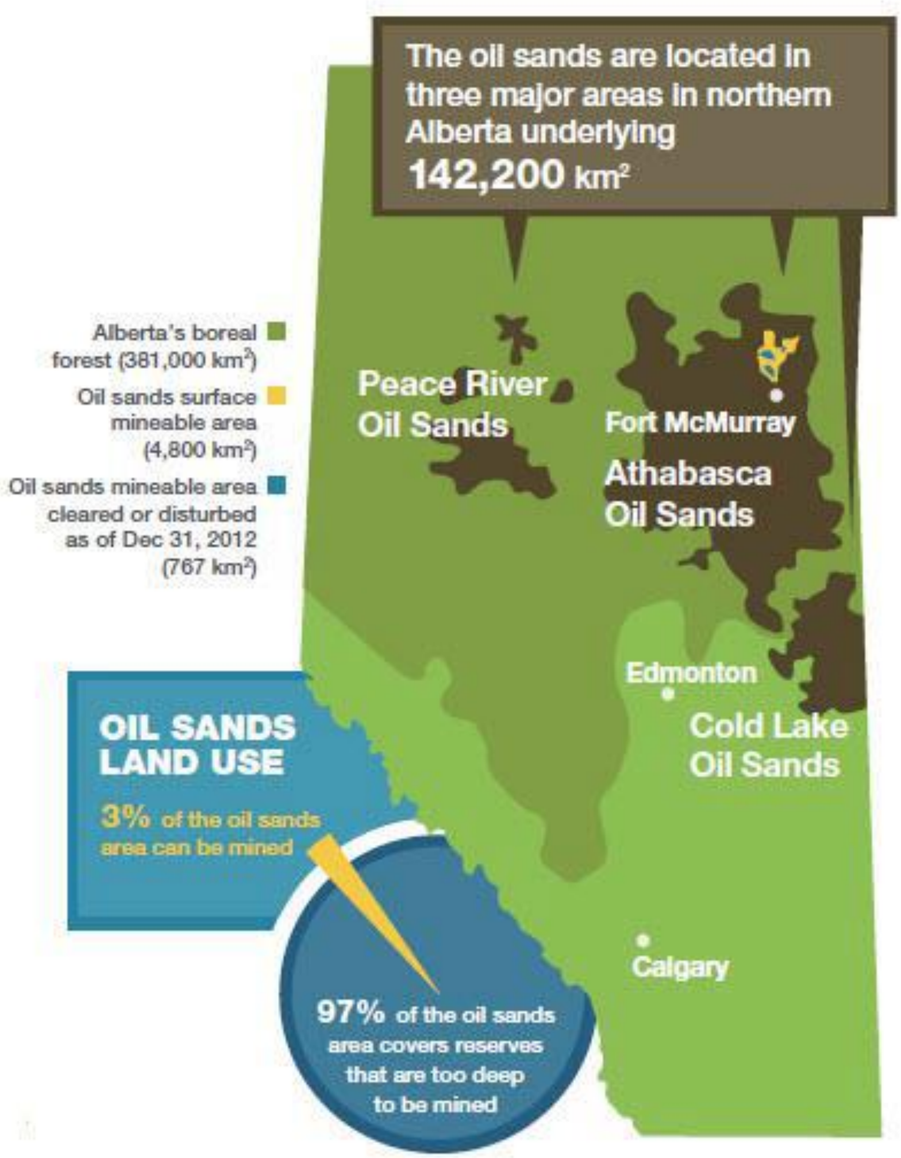

Figure A 1: Geographic map of Alberta's oil sands resources [6]

Appendix B

Table B 1: Mass percentages of each lump for all MBL experimental runs described in Chapter 3

350°C	**Time (min)**			
Lump	0	10	20	30
R	29.43	29.04	27.81	28.67
VGO	24.69	25.19	23.96	24.04
LGO	30.38	30.16	29.79	30.52
GLN	13.74	12.50	14.15	13.11
G	1.76	3.11	4.30	3.66
400°C				
Lump	0	10	20	30
R	26.68	26.18	23.89	22.24
VGO	23.72	25.75	25.99	24.33
LGO	30.14	28.33	29.34	31.88
GLN	15.58	16.10	18.24	17.09
G	3.88	3.64	2.54	4.45
425°C				
Lump	0	5	10	15
R	28.28	26.32	25.18	24.11
VGO	25.26	25.07	24.81	23.74
LGO	29.27	27.57	27.86	29.09
GLN	14.24	17.44	17.56	18.31
G	2.95	3.60	4.59	4.76
450°C				
Lump	0	5	10	15
R	16.42	16.24	15.91	13.16
VGO	21.51	20.45	16.59	13.89
LGO	35.76	38.09	39.06	40.53
GLN	22.66	20.93	21.23	25.74
G	3.66	4.29	7.20	6.69

Table B 2: Mass percentages of each lump for all AHS experimental runs described in Chapter 3

350°C	**Time (min)**			
Lump	0	10	20	30
R	46.56	49.48	47.89	45.63
VGO	26.74	27.24	27.36	27.11
LGO	11.99	11.18	10.95	11.75
GLN	12.24	8.78	9.62	11.42
G	2.47	3.31	4.19	4.09
400°C				
Lump	0	10	20	30
R	47.20	45.82	42.58	42.86
VGO	27.49	26.69	26.67	26.84
LGO	11.91	11.57	13.76	12.99
GLN	9.23	11.85	11.58	11.10
G	4.16	4.08	5.41	6.22
425°C				
Lump	0	5	10	15
R	45.43	42.56	39.61	41.32
VGO	26.46	26.65	26.69	25.87
LGO	12.50	15.08	15.69	14.64
GLN	11.67	10.95	12.60	12.67
G	3.94	4.77	5.41	5.50
450°C				
Lump	0	5	10	15
R	38.86	37.63	29.57	20.97
VGO	26.47	25.41	20.50	16.37
LGO	13.89	13.56	23.30	25.87
GLN	16.40	17.12	19.47	26.27
G	4.38	6.28	7.16	10.52

Table B 3: Mass percentages of each lump for all CDB experimental runs described in Chapter 3

350°C	**Time (min)**			
Lump	0	10	20	30
R	51.39	48.94	48.39	48.39
VGO	19.00	20.28	21.31	19.36
LGO	12.09	14.11	14.21	12.62
GLN	11.05	9.29	9.05	11.30
G	6.47	7.37	7.04	8.32
400°C				
Lump	0	10	20	30
R	45.05	42.51	35.78	39.57
VGO	21.89	21.89	20.10	21.22
LGO	13.47	16.84	21.71	17.95
GLN	11.64	8.09	12.37	11.59
G	7.95	10.68	10.04	9.67
425°C				
Lump	0	5	10	15
R	41.58	42.64	38.29	29.57
VGO	20.59	21.53	21.99	18.53
LGO	17.48	15.87	15.09	23.45
GLN	13.40	10.21	14.09	19.00
G	6.95	9.76	10.54	9.45
450°C				
Lump	0	5	10	15
R	34.31	30.66	29.82	26.94
VGO	20.98	17.48	14.26	13.49
LGO	16.79	17.87	21.67	25.51
GLN	15.94	21.17	22.49	22.17
G	11.98	12.81	11.76	11.89