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Kinetic modeling of catalytic in situ upgrading for Athabasca bitumen, deasphalting pitch and vacuum residue

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Kinetic modeling of catalytic in situ upgrading for Athabasca bitumen, deasphalting pitch and
vacuum residue

by

Francisco Javier Da Silva De Andrade

A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES
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Abstract

Due to their high viscosity, extra-heavy oils and bitumens are more difficult to recover than conventional oils, so they are mainly produced by Thermal Enhanced Oil Recovery (TEOR) methods. In the pursuit of a less energy demand process and relying on new developments in ultradispersed catalysts for hydroprocessing, in situ upgrading, is proposed as an economically feasible, environmentally friendly and novel alternative to produce upgraded oil with transportable specifications.

In this work, kinetic models for ultradispersed catalytic hydroprocessing for Athabasca bitumen, pitch and vacuum residue have been developed. These models can be used for predicting conversion and product yields which are essential for simulation, design and evaluation of this process at both surface and reservoir level. Results showed that residue (550+ °C) conversion fits a first-order reaction, with activation energies within the range of 50-200 kJ/mol depending on the feedstock. Kinetic models showed good agreement reporting average errors lower than 7.5%.

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Last but not least, I am profoundly thankful to my lovely wife for being my journey partner, my mother-in-law for her encouragement and help during this time, my parents for the values they taught me, and my relatives for their unconditional support.

With love to my journey partner Valentina....

*“I believe in intuition and inspiration.
Imagination is more important than
knowledge. For knowledge is limited, whereas
imagination embraces the entire world,
stimulating progress, giving birth to evolution.
It is, strictly speaking, a real factor in
scientific research”*

Albert Einstein (1879-1955)

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List of Symbols, Abbreviations and Nomenclature

Symbol	Definition
ATTP	Accelerated Transportation Technology and Policy
CHOPS	Cold Heavy-Oil Production with Sand
CISU	Catalytic In-Situ Upgrading
D	Distillates
DAO	De-Asphalted Oil
EOR	Enhanced Oil Recovery
G	Gases
GC	Gas Chromatography
GHG	Greenhouse Gases
IEA	International Energy Agency
HP	Hydro-Processing
HPAI	High Pressure Air Injection
k	Reaction Constant [h^{-1}]
MBPD	Millions of barrels per day
MCR	Micro Carbon Residue
N	Naphtha
OPEC	Organization of Petroleum Exporting Countries
r	Reaction Rate [h^{-1}]
R	Residue
SAGD	Steam-Assisted Gravity Drainage
SARA	Saturates, Aromatics, Resins and Aromatics
SDA	Solvent De-Asphalting
TBP	True Boiling Point
THAI	“Toe-to-Heel” Air Injection
u	Atomic Mass Unit
UD	Ultra-Dispersed
VAPEX	Vapor Extraction
VGO	Vacuum Gas Oil
VR	Vacuum Residue
y	Mass Fraction

CHAPTER 1: INTRODUCTION

Based on the World Population Report published by the United Nations, population is expected to grow by at least 30% by 2050 (United Nations, 2010), which brings as a consequence an increase of energy demand for the near future. The energy market is dominated by fossil fuels due to their relatively low cost, exploitation feasibility, safety, and availability, and it is projected to continue in this privileged position by at least half a century. As a consequence of the depletion of light oils, other energy sources will be exploited despite the technical difficulties and relatively higher costs implied, making them still more feasible than other alternatives.

Heavy oil, extra-heavy oil and bitumen are more difficult to recover than conventional oils so typically they are produced by means of Enhanced Oil Recovery (EOR) methods, mainly thermal methods. Since these technologies are energy intensive (e. g. SAGD requires from 2 to 4 barrels of water converted into steam per barrel of bitumen produced) Catalytic In-Situ Upgrading (CISU), based on new developments such as Ultra-Dispersed (UD) catalyst in Hydro-Processing (HP), is proposed as an alternative and novel process to recover and upgrade oil at the same time.

1.1 Background:

1.1.1 World Oil Reserves, Future Trends:

Because conventional oil reserves (heavy oils, light oils and natural gas liquids) have been declining over the last decade, unconventional reserves (Tight Oil, Extra-Heavy Oils, Bitumen and Kerogen) are being exploited more frequently around the world. Figure 1.1, a distribution of the world reserves classified by type, clearly shows that conventional oils currently represent

only 42% of technically recoverable reserves, and this number is expected to drop down to 26% in the near future (Gordon, 2013).

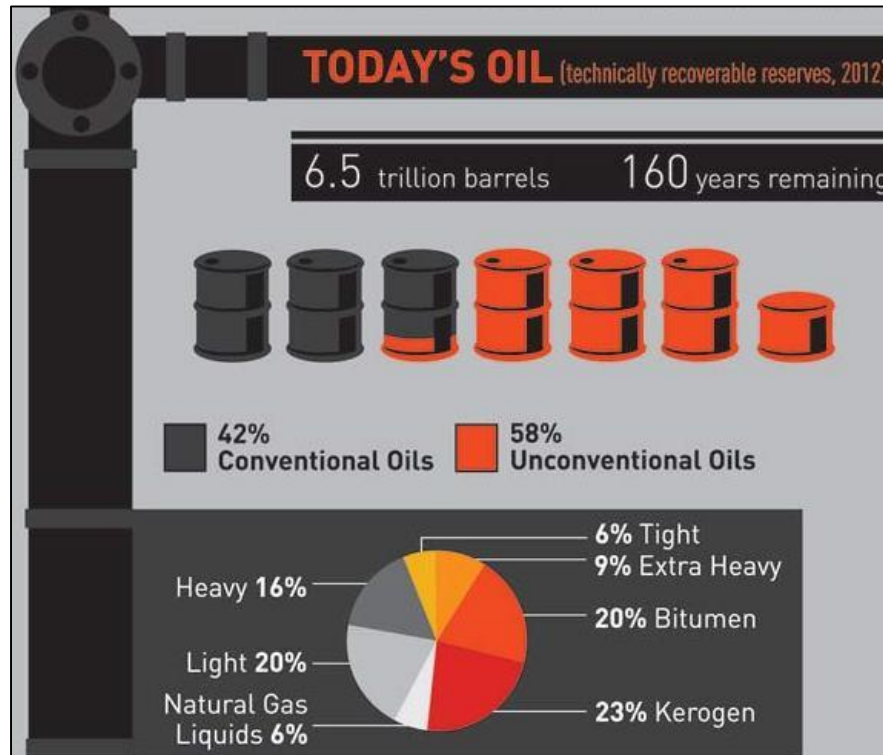


Figure 1.1: Worldwide reserves distributed by type (Gordon, 2013)

1.1.2 World Oil Demand, Future Trends:

Figure 1.2 shows four forecasted oil-demand scenarios. The first scenario assumes a future in which new policies related to the use of renewable energy have been implemented, energy-efficiency targets have been met, a significant reduction of greenhouse-gas emissions, and the compliance of international agreements about the use of fossil fuels. The second prediction assumes a continuation of the application of current policies (IEA, 2012).

One of the scenarios proposed by the Organization of Petroleum Exporting Countries (OPEC), called Accelerated Transportation Technology and Policy (ATTP) scenario, also

assumes the application of measures to diminish the impact of fossil fuels on the environment. Their other forecast, conventional Reference Case, is based on the assumption that current conditions will continue (OPEC, 2011).

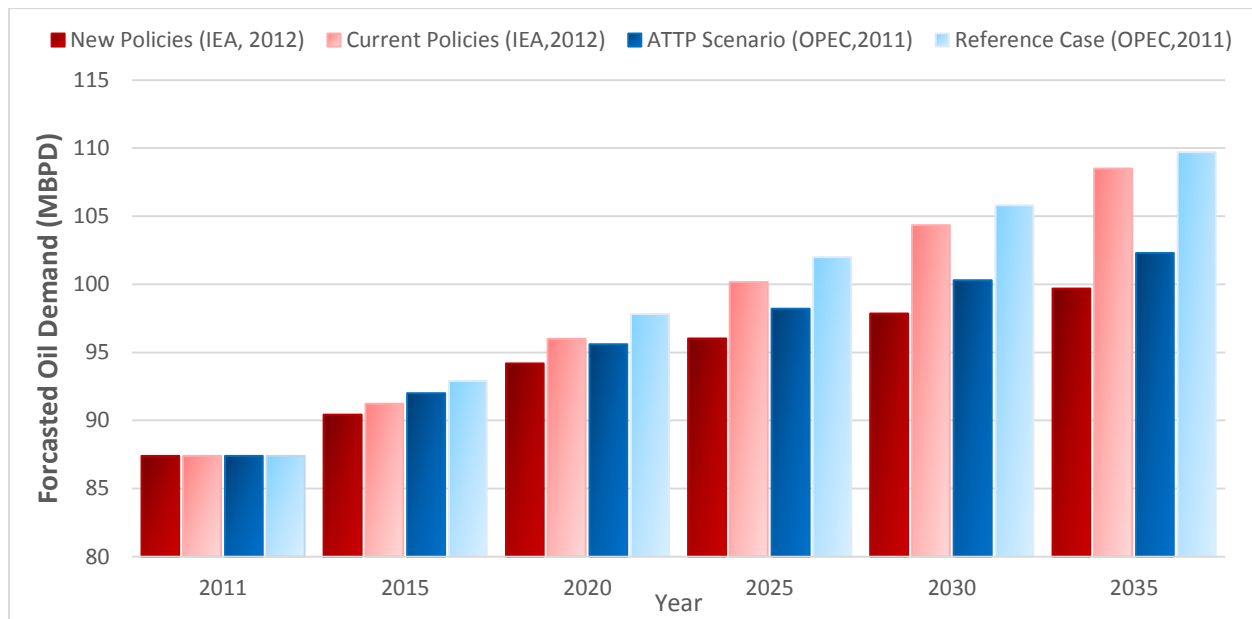


Figure 1.2: Forecasted oil demand for 2010-2035

All these scenarios conclude that there will be an increment in oil-demand; most conservative estimations suggest a growth of 0.6% annually while others provide figures close to 1% rate, which translated in absolute values represent an increment of at least 12 MBPD in the next 20 years.

1.1.3 Canada Oil Reserves and Market Position:

Canada's proven reserves have been estimated at 173.2 billion barrels. This places Canada as the country with the third highest oil reserves after Venezuela and Saudi Arabia (Xu and Bell, 2013). However, about 167 billion barrels are located in the three designated oil sands areas (Athabasca, Cold Lake and Peace River) in northern Alberta (CAPP, 2014). In 2012

Canada's oil production reached 3.1 MBPD, ranking it as the fifth highest oil producer in the world, after Russia with 10.3 MBPD, Saudi Arabia with 9.5 MBPD, United States with 6.5 MBPD and China with 4.1 MBPD (Xu and Bell, 2013). Figure 1.3 shows Canada's oil sands and conventional production from 2005 until 2014 and the forecasted production until 2030. Production from oil sands has been forecasted to grow from 1.9 MBPD up to 4.8 MBPD by 2030, increasing Canada total production from 3.5 to 6.4 MBPD (CAPP, 2014).

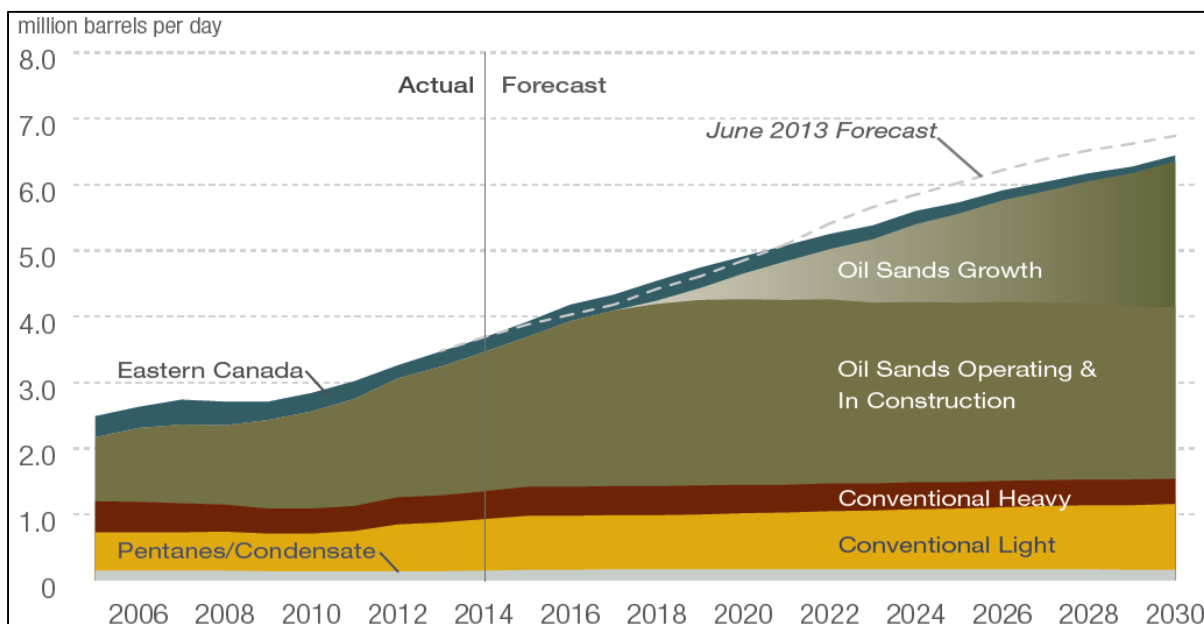


Figure 1.3: Canadian oil sands and conventional oil production

1.1.4 Actual Heavy Oil and Bitumen Recovery Methods:

Nowadays, two methods are mainly applied for recovering heavy oils, extra-heavy oils and bitumens: thermal methods (Cyclic Steam Stimulation, Steam Flooding, Steam-Assisted Gravity Drainage, etc.) or Surface Mining. Thermal EOR processes add heat to the reservoir to reduce oil viscosity making the oil more mobile (Shah et al., 2010). Their major disadvantages are the high cost of steam generation due to the use of natural gas as fuel, excessive carbon dioxide emissions, and high costs associated with water treatment (Pereira-Almao, 2012).

Surface mining has been applied extensively in Canada and in few reservoirs in Russia. Nonetheless, this method is limited to relatively shallow reservoirs. Regardless of its high recovery factors (as much as 90%), environmental concerns arise because large extension of wetlands needs to be drained, rivers diverted and all trees and vegetation stripped from the surface. In addition, this method uses large volumes of water and, in spite of recycling methods, most of the water ends up in tailing ponds (Shah et al., 2010).

1.2 Motivation:

Significant amounts of money have been invested in the oil industry during the last century. More than 700 refineries all over the world are currently operating to satisfy the demand of fuels. Installed oil pipelines exceed a million of kilometers targeting oil transportation from reservoir to refineries sites. It is neither technically practical nor economically viable to adapt these transportation networks to heavy oils, extra-heavy oils and bitumens; therefore, there is a need to upgrade them in situ to meet transportation systems such as viscosity, API gravity and many other specifications including sulfur, water, and sediments contents.

When working with heavy oils, extra-heavy oils and bitumens, due to their high viscosity and, therefore, very low mobility at reservoir conditions, the application of EOR methods is required, which mainly rely on energy addition with the objective of decreasing viscosity. On the other hand, to meet the criteria of pipeline specifications and transportability, the produced oil requires upgrading processes to improve its quality. These processes normally proceed via carbon rejection or hydrogen addition pathways, both demanding significant energy usage; hence, by combining recovery and upgrading processes thermal energy is applied once, leading in a substantial reduction of energy requirement and Greenhouse Gas emissions (GHG), greatly reducing the demand for water and natural gas (Pereira-Almao, 2012). Based on new

developments in ultradispersed catalytic hydroprocessing and the need of developing new recovery/upgrading processes with less energy demand and emissions, Dr. Pedro Pereira-Almao and coworkers (2013) from the Catalyst for Bitumen Upgrading Group (GBUG) at the University of Calgary, have patented a novel process for in situ upgrading of heavy, extra-heavy oils and bitumen via nanocatalysts.

Two main schemes have been proposed for this technology; they differ by its main separation stage and therefore the injection fluid. The first one (see Figure 1.4) uses vacuum distillation, where the partially upgraded bitumen coming from the in situ upgrading reservoir and the bitumen coming from other reservoirs are fed to the vacuum distillation column separating them into light hydrocarbons, Vacuum Gas Oil (VGO) and high boiling point hydrocarbons (550+ °C) called vacuum residue (VR). The blend of light hydrocarbons, VGO and a small fraction of VR (if feasible), comprises the transportable (produced) oil of the process.

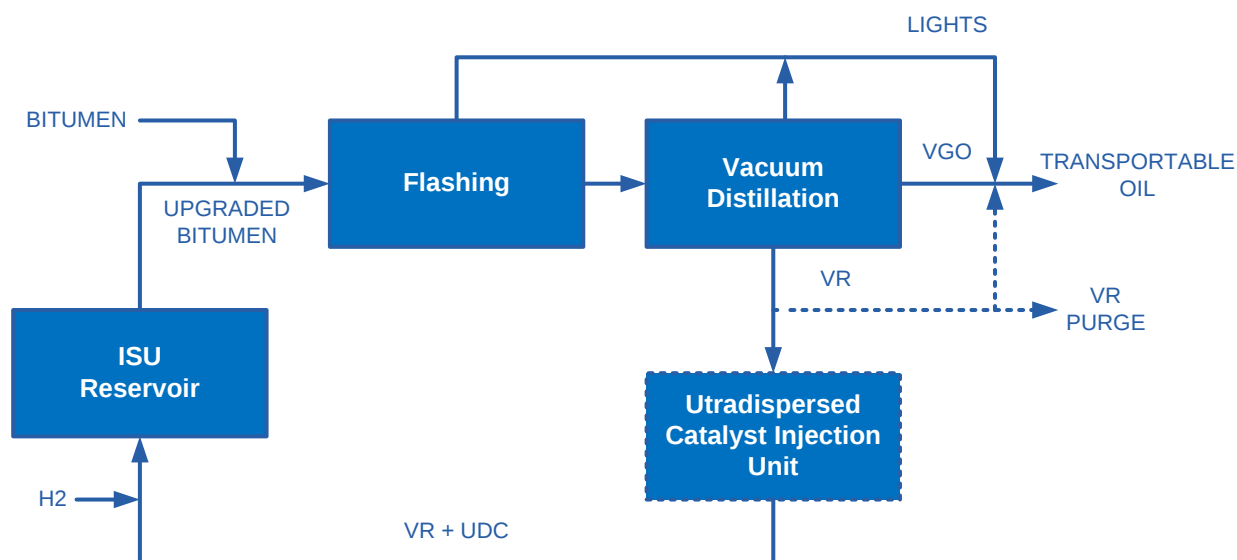


Figure 1.4: Catalytic In Situ Upgrading scheme based on Distillation

VR is then sent to the Ultradispersed Catalyst Injection Unit, where hydroprocessing nanocatalysts (Ni/Mo/W) are incorporated via decomposition of water-in-bitumen transient catalytic microemulsions, preparation that was patented by Pereira-Almao and coworkers (2007). Finally, VR is mixed with hydrogen and injected back to the reservoir acting as a heat and catalyst carrier to the reservoir. The nanocatalyst particles are retained in the porous medium without affecting its permeability, and this established catalyst zone remains active even after several pore volumes of hot fluid injection (Coy, 2013). An alternative scheme is proposed replacing the distillation unit by a Solvent De-Asphalting unit (see Figure 1.5), where deasphalting pitch plays the role of the vacuum residue and the produced oil will result from blending lights, De-Asphalted Oil and a small fraction of pitch (if feasible).

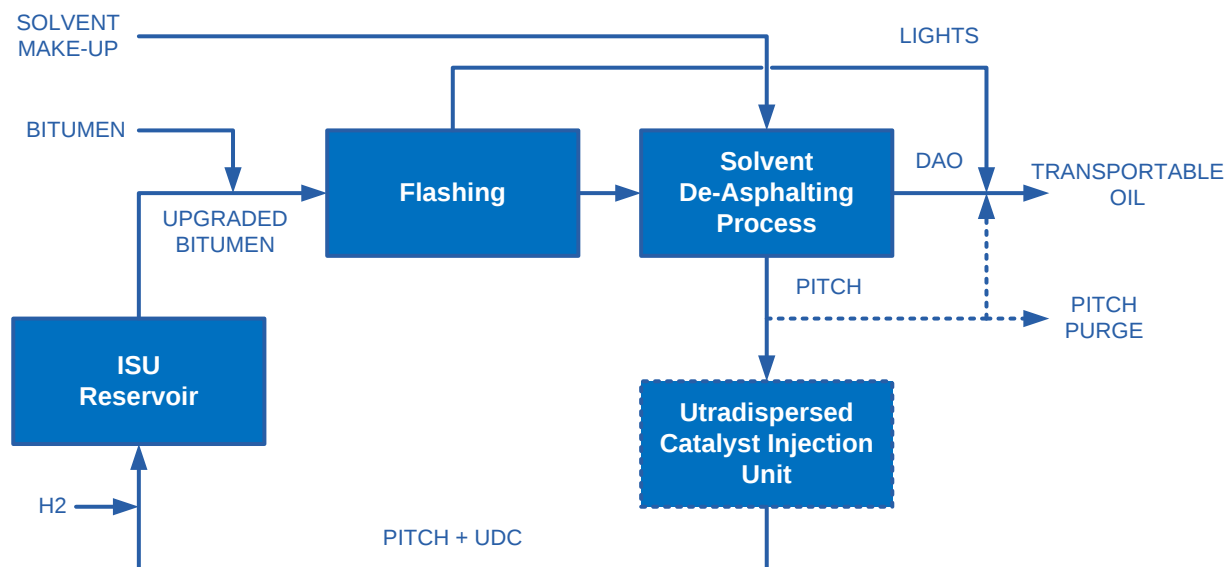


Figure 1.5: Catalytic In Situ Upgrading based on Solvent De-Asphalting

For studying distillation-based schemes, Industrial VR from Athabasca bitumen was supplied by Suncor Energy Inc. to carry out this set of experiments. For the SDA-based scheme,

producing pitch by performing laboratory scale solvent de-asphalting runs will demand long processing time due to its low production rate and may produce variability of the product properties due to the lack of fine process control inherent of this method. Building an in-house bench scale pilot plant to produce pitch from Athabasca was one of the challenges faced during this research. This unit significantly reduced pitch production time, and allowed the accurate control of variables such as temperature, pressure, and stirring, decreasing the variability of pitch properties. SDA pilot plants with this characteristics (capacity and design) have not been registered in North America.

A preliminary economic evaluation and environmental impact analysis was conducted by Pereira-Almao (2012), revealing that, when compared with conventional techniques, this catalytic in situ upgrading showed higher profitability due to its lower investment and operating costs, with reduced and “coke-free” emissions.

1.3 Objectives:

The main objective of this research is to develop kinetic models for catalytic in situ upgrading process of Athabasca bitumen, vacuum residue, and deasphalting pitch with ultra-dispersed catalyst and hydrogen within the range of conditions estimated to be viable for in situ upgrading in northern Alberta oil sand deposits. In order to achieve this macro objective, the following set of specific objectives was conceived and agreed for development:

- To redesign and optimize an SDA pilot plant unit at bench scale to produce pitch from Athabasca Bitumen.
- To prepare tri-metallic (Ni/Mo/W) ultra-dispersed catalysts in deasphalting pitch and vacuum residue obtained from Athabasca bitumen.

- To perform kinetic studies of catalytic ultradispersed hydroprocessing of deasphalting pitch and vacuum residue, both obtained from Athabasca bitumen, at reservoir conditions.
- To develop kinetic models for catalytic ultradispersed hydroprocessing of pitch and vacuum residue from Athabasca Bitumen at reservoir conditions.

1.4 Organization of the Thesis

This thesis is divided into 7 (seven) chapters, whose contents are described as follows:

- Chapter one presents the introduction, background and motivation of this research as well as the proposed objective of the investigation.
- Chapter two provides the literature review relevant to this work.
- Chapter three presents detailed descriptions of experimental activities carried out in this research, including: materials, characterization methods and processing unit (pilot plants).
- Chapter four contains the redesign and optimization of the Solvent De-Asphalting unit, as well as the tests results of unit validation and the Athabasca deasphalting pitch production results.
- Chapter five provides all the outcomes related to the reactivity test of ultradispersed catalytic hydroprocessing of Athabasca pitch and vacuum residue.
- Chapter six presents the results for the kinetic model of ultradispersed catalytic hydroprocessing of Athabasca bitumen, vacuum residue and pitch.
- Chapter seven contains the most important conclusions and recommendations reached from conducting the present research.

CHAPTER 2: LITERATURE REVIEW

This chapter provides an extensive literature review of the principles, concepts and theoretical basis, and a summary of previous findings in the field of catalytic in situ upgrading that was used in the development of the research presented in this work. It is divided in three major sections: petroleum fundamentals, in which all the essential concepts related to petroleum are presented; heavy, extra-heavy oil and bitumen recovery methods, which describes all methods that are used for recovering the heaviest crude oils; and finally, heavy, extra-heavy oil and bitumen upgrading processes, where the most important processes and technologies for oil upgrading are summarized, including the proposed Catalytic In-Situ Upgrading.

2.1 Petroleum Fundamentals:

2.1.1 *Definition of petroleum:*

Petroleum, also known as Crude Oil, is one of the most important substances consumed at present. It is used as a main source of energy for industry, heating, and transportation and it also provides raw materials for the petrochemical plants to produce polymers, plastics, and many other products. The word petroleum, derived from the Latin words *petra* and *oleum*, means literally *rock oil* and refers to hydrocarbons that occur widely in the sedimentary rock in the form of gases, liquids, semisolids and solids (Speight, 2007).

2.1.2 *Composition of Petroleum:*

Petroleum is not a uniform material; in fact, its chemical and physical (fractional) composition can vary not only with the location and age of the oil field but also with the depth of the individual well. Indeed, two adjacent wells may produce petroleum with markedly different characteristics. From a chemical stand point, petroleum is an extremely complex mixture of hydrocarbon compounds, usually with minor amounts of nitrogen-, oxygen-, and sulfur-

containing compounds as well as trace amounts of metal-containing species such as vanadium, nickel, iron and copper organometallics. The most valuable information from elemental analysis that can be obtained is on the carbon to hydrogen ratio (C/H) and sulfur content which are the most important variables that determine the quality of the oil (Riazi, 2005). The elemental composition of crude oils is surprisingly uniform even though their physical characteristics vary widely. The elemental composition of crude oils usually falls within the ranges shown in Table 2.1:

Table 2.1: Ranges of elemental analysis for crude oils (Speight, 2007)

Element	Mass Fraction (%)
Carbon	83.0-87.0
Hydrogen	10.0-14.0
Sulfur	0.05-6.0
Nitrogen	0.1-2.0
Oxygen	0.05-1.5%
Metals (Ni and V)	<1,000 ppm

Crude oils are mixtures of pure components, but these are extremely numerous and the difficulty to individually describe their components increases with the number of carbon atoms (Wauquier, 1995). The compounds present in petroleum can be classified into two general types: hydrocarbon and nonhydrocarbon constituents.

2.1.2.1 Hydrocarbon Constituents:

It is difficult to determine on the basis of the data obtained from synthesized hydrocarbons the identity or even the similarity of the synthetic hydrocarbons to those that

constitute many of the higher boiling fractions of petroleum. Nevertheless, it has been well established that the hydrocarbon components of petroleum are composed of paraffinic, naphthenic, and aromatic groups. Since olefins are more reactive than saturated hydrocarbons, they are naturally uncommon in crude oils, being usually produced through cracking reactions (Riazi, 2005); acetylenic hydrocarbons are even less frequent (Speight, 2007).

- **Paraffin Hydrocarbons:** these correspond to saturated hydrocarbons with straight or branched chains, but without any ring structure. The proportion of paraffin compounds varies for each crude oil, but within any crude oil, the amount of pure paraffinic hydrocarbons usually decreases with increasing molecular weight, although the proportion of paraffinic branches may increase.
- **Naphthene Hydrocarbons:** also known as cycloparaffins, this group corresponds to saturated hydrocarbon containing one or more rings, each of which may have one or more paraffinic side chains. Naphthene rings may be built up of a varying number of carbon atoms, and among the synthesized hydrocarbons there are individual constituents with rings having from three up to eight carbon atoms, being in the natural petroleum product 5 and 6 carbon atoms the most common. As the molecular weight of the crude oil increases, there is an increase in the amount of cycloparaffinic species in the fraction. Mono and bicyclic naphthenes are generally the most abundant type of cycloparaffins in the lower boiling point fractions.
- **Aromatics:** this group corresponds to hydrocarbons containing one or more aromatic rings, which may be linked up with naphthene rings or paraffinic side chain. Aromatic compounds are present in all crude oils, there is a general increase in the proportion of aromatic hydrocarbons with increasing molecular weight. However, aromatic compounds without the accompanying naphthene rings or alkyl-substituted derivatives seem to be present in

appreciable amount only in lower petroleum fractions, conversely these are relatively rare in heavier fractions. In the higher boiling point petroleum fractions, many polycyclic structures occur as naphthenoaromatic systems. The naphthenoaromatic hydrocarbons, together with the naphthenic hydrocarbon series, form the major content of higher boiling point petroleum fractions.

2.1.2.2 Nonhydrocarbon Constituents:

Crude oils contain appreciable amounts of nonhydrocarbon constituents (also called heteroatomic compounds). This family mainly comprises sulfur, nitrogen, and oxygen containing compounds and, in smaller amounts, organometallic compounds in solution in colloidal suspension and suspended inorganic salts. The heteroatomic compounds appear throughout the entire boiling range of the crude oil, but tend to be concentrated mainly in heavier fractions and in the non-volatile residues (Speight, 2007).

- Sulfur compounds: these compounds are among the most important heteroatomic constituents of petroleum. In general the higher the density of the crude oil, the higher the sulfur content. High sulfur content is generally considered harmful in most petroleum products, and their removal or conversion to hydrocarbons by extracting the sulfur atom is an important refinery practice.
- Oxygen compounds: the total oxygen content of a crude oil is usually less than 2% in weight, although larger amounts have been reported, but this may be related to a prolonged exposure to air either during or after production. However, the oxygen content of petroleum increases with the boiling point of the fractions; in fact, the non-volatile residuum may have oxygen contents up to 8% in weight.

- Nitrogen compounds: In general, the nitrogen content of crude oil is low and generally falls within the range 0.1% to 0.9%, although some crude oils may contain up to 2% nitrogen. Nitrogen distributes throughout the boiling ranges, but it has the tendency to be more abundant in high boiling point fractions and residua. An approximate correlation exists between nitrogen content and API gravity of crude oils, also there is an approximate correlation between nitrogen content and carbon residue: the higher the nitrogen content, the higher the carbon residue.
- Metallic constituents: these are found in every crude oil and their concentration have to be reduced to convert the oil into transportation fuel. Nickel and vanadium are generally orders of magnitude higher than other metals in petroleum, except when contaminated with coproduced brine (sodium, magnesium, and calcium) or corrosion products gathered during transportation or storage (iron). Distillation concentrates the metallic constituents in the residues, although some can appear in the higher boiling distillates, due at least in part to entrainment.

2.1.2.3 Compounds with undefined chemistry

Compounds present in heavy fractions of petroleum may be major in number and certainly more complex than in lighter fractions. This creates challenges for characterization of these fractions since it is impossible to completely isolate and analyze molecules by means of modern analytical methods, which leads to the use of definitions that refers to a family of compounds with similar characteristics rather than compounds with specific structures. One definition is based on SARA analysis, whose acronym stands for Saturates, Aromatics, Resins and Asphaltenes. SARA analysis divides crude oil components according to their polarizability and polarity. Saturates family comprises linear, branched and cyclic paraffins which are non-

polar. Aromatics, as shown previously, comprise hydrocarbons with one or more aromatic rings which are slightly polarizable. The remaining two fractions, resins and asphaltenes, have polar substituents (Fan, Wang et al., 2002).

- Resins: these have a molecular structure made up of condensed aromatic compounds with long cycloaliphatic chains, making them soluble in the oil medium. The average molecular weight of resins ranges from 500 u to 1,000 u. These molecules typically include heteroatoms such as sulfur, nitrogen, nickel and vanadium. The oil medium and resins are generally grouped together under the term malthenes (Wauquier, 1998).
- Asphaltenes: The most accepted asphaltene definition is based on its experimental solubility in different solvents: the fraction insoluble in a paraffinic solvent but soluble in an aromatic solvent is called asphaltene (Sheu and Mullins, 1995). The most common solvents used in this definition are pentane and heptane as paraffin and toluene as aromatic, and the paraffin-soluble portion which contains the oil medium plus resins is given the name of malthenes (Wauquier, 1995). The asphaltene content is mostly reported as n-pentane (or n-heptane) insoluble; however, strictly speaking, they must be calculated as the difference between weight percentage of n-pentane (or n-heptane) insoluble minus the weight percentage of toluene insoluble (Ancheyta, 2013).

Asphaltenes have very condensed flat aromatic structures, including between six and twenty aromatic rings. Initially it was believed that their average molecular weight was approximately 1,000 u to 100,000 u, however, recent finding due to the development of new techniques suggest that this value spans between 1,000 to 2,000 u or even lower. Their side chains are too small to make them soluble in very light oil mediums, so they are present in the form of micelles. However, their micellar size is several angstroms and

they are “peptized” (i.e. solubilized) by resins which give them solubility in the oil medium (Wauquier, 1998). Despite the fact that the molecular structure of asphaltene molecules is complex and they may change from one crude oil sample to another, two general models (see Figure 2.1) have been proposed (Ancheyta, 2013):

- Continental type: pericondensed structures in which asphaltene cores are constituted by more than seven aromatic rings, which form planar aggregates in asphaltene solutions.
- Archipelago type: asphaltenes are represented by small aromatic cores linked to other cores by means of bridging alkanes, i. e. presence of islands of small aromatic cores linked by alkyl and sulfur bonds.

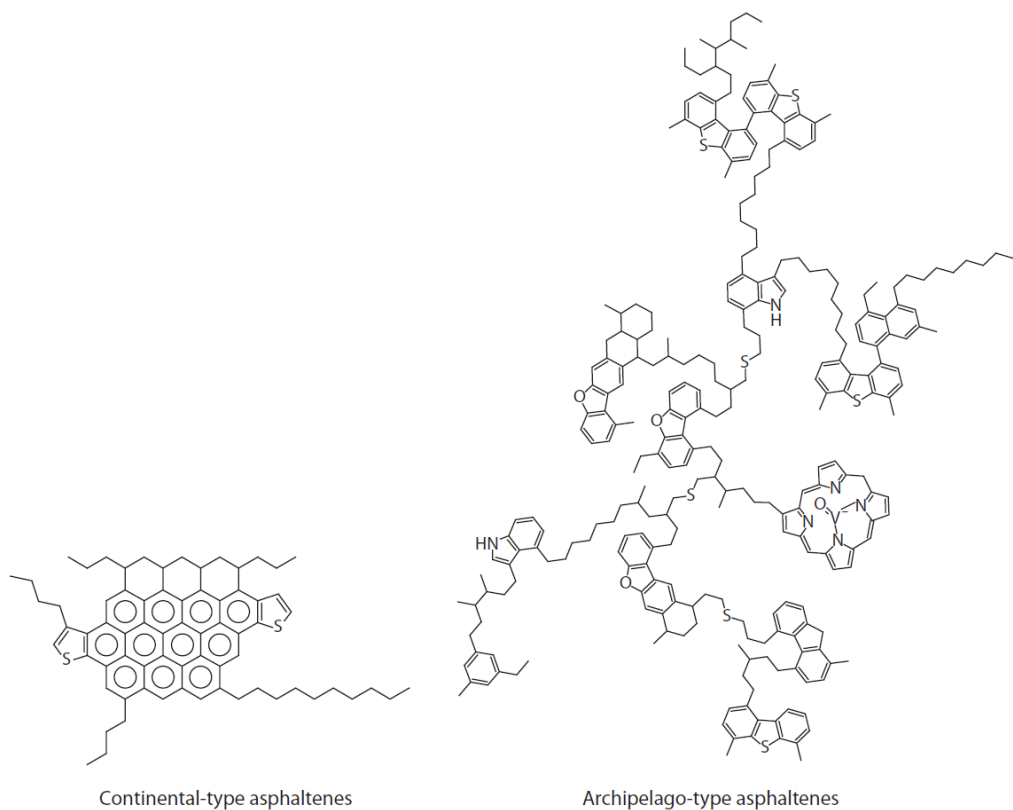


Figure 2.1: Average molecular structures for continental-type and archipelago-type asphaltenes (Ancheyta, 2013)

Due to their high viscosity, high density, high sulfur content, and tendency of aggregation and precipitation, asphaltenes represent an important issue for the oil industry. It is generally accepted that asphaltenes flocculation and further precipitation may take place because of either temperature, pressure or composition changes, presence of paraffinic diluents or electrokinetic effects (Leontaritis, 1989). Problems with asphaltenes deposition manifest all across the process from the production (upstream), transportation (midstream), and upgrading and refining (downstream). The most common problems at upstream levels were commented by Leontaritis, 1989:

- Formation damage: this may be caused due to asphaltene flocculation and deposition that take place either deep in the reservoir or near the wellbore.
- Well problems: asphaltene deposits on well tubing on the wellhead choke (which controls surface pressure and production rate) cause a blockage causing loss of production.
- Surface facilities: asphaltene deposition may cause equipment plugging and failure of safety and process monitoring and control devices.

During midstream operations, asphaltenes deposition and thickening appear when temperature decreases during transportation (Sheu, 2001). A general practice for heavy oil transportation is the use of light solvents, such as naphtha or condensate, however an excess of these fluids may produce asphaltene precipitation and pipeline plugging. In upgrading and refining operations, all the problems mentioned above related to instrumentation for the production side, apply to the refining side as well. Asphaltenes may deposit on distillation towers, separators, heat exchangers, pumps, and pipelines,

causing blockage or plugging or can deactivate or poison catalysts by entrainment in some units of the refinery.

2.1.3 *Petroleum Properties:*

Due to the complexity of performing compositional analysis, crude oils and their fractions are characterized instead by relatively simple analytical tests and these results are used with empirical correlations for predicting physical properties, phase behavior, reactivity, among others. The following properties are the most important used for characterizing crude oils and their fractions:

2.1.3.1 API Gravity:

The density of petroleum oils is expressed in terms of API gravity rather than specific gravity; it is related to the specific gravity in such fashion that an increase in API gravity corresponds to a decrease in specific gravity. The units of API gravity are °API and can be calculated from Equation 1 (Gary and Handwerk, 2001):

$$API = \frac{141.5}{sg @ 60^{\circ}F} - 131.5 \quad \textbf{Equation 1}$$

Where:

API: API gravity[° API]

sg: Specific gravity [*Dimensionless*]

2.1.3.2 Boiling Point Range:

The boiling point distribution of crude oils gives an indication of the quantities of the various products present. The most useful type of distillation is known as a True Boiling Point distillation (TBP) and, generally refers to a distillation performed in equipment that accomplishes a reasonable degree of fractionation. Despite the fact that there is no specific test

procedure called a TBP distillation, the ASTM D-2892 test is widely accepted. This corresponds to a laboratory technique in which the distillation is carried out using 15 theoretical plates at reflux ratio of 5:1 (Gary and Handwerk, 2001).

Advances in capillary Gas Chromatography columns (GC) and stationary phase technologies, together with either programmed temperature vaporization or on-column injection techniques, has allowed the development of High Temperature Simulated Distillation (HTSD, ASTM D-7169), which extends the boiling range distribution of hydrocarbon to a final boiling point of about 760 °C (1,400 °F), improving the accuracy of heavy oil TBP distillation curve over conventional test or extrapolations (Golden, Villalanti and Martin, 1994).

2.1.3.3 Viscosity:

Viscosity is the internal resistance of fluids to flow, so this property is used for defining if a crude oil is suitable for transportation. In order to assure flowing of petroleum in pipe distribution networks, it is common to set limits for oil API gravity and/or viscosity, which changes from one country to another. The National Energy Board of Canada established in 2008 a maximum viscosity of 350 cSt at pumping conditions and a maximum specific gravity of 0.94 (minimum 19 °API) for oil transportation purposes. As it can be seen in Figure 2.2, heavy oils (Low API gravity) generally exhibit high viscosity values thus, using API gravity or density as a secondary variable for regulating oil pipelining is justified.

The problem of determining the viscosity of heavy crude oils is not so critical since most of the time a viscometer is available, the problem arises when predicting the viscosity of blends of various crude oils (Ancheyta, 2013). Prediction of viscosity when mixing heavy oils with other fractions is a challenging task, and a proper mixing rule for such purpose is still needed (Centeno et al., 2011).

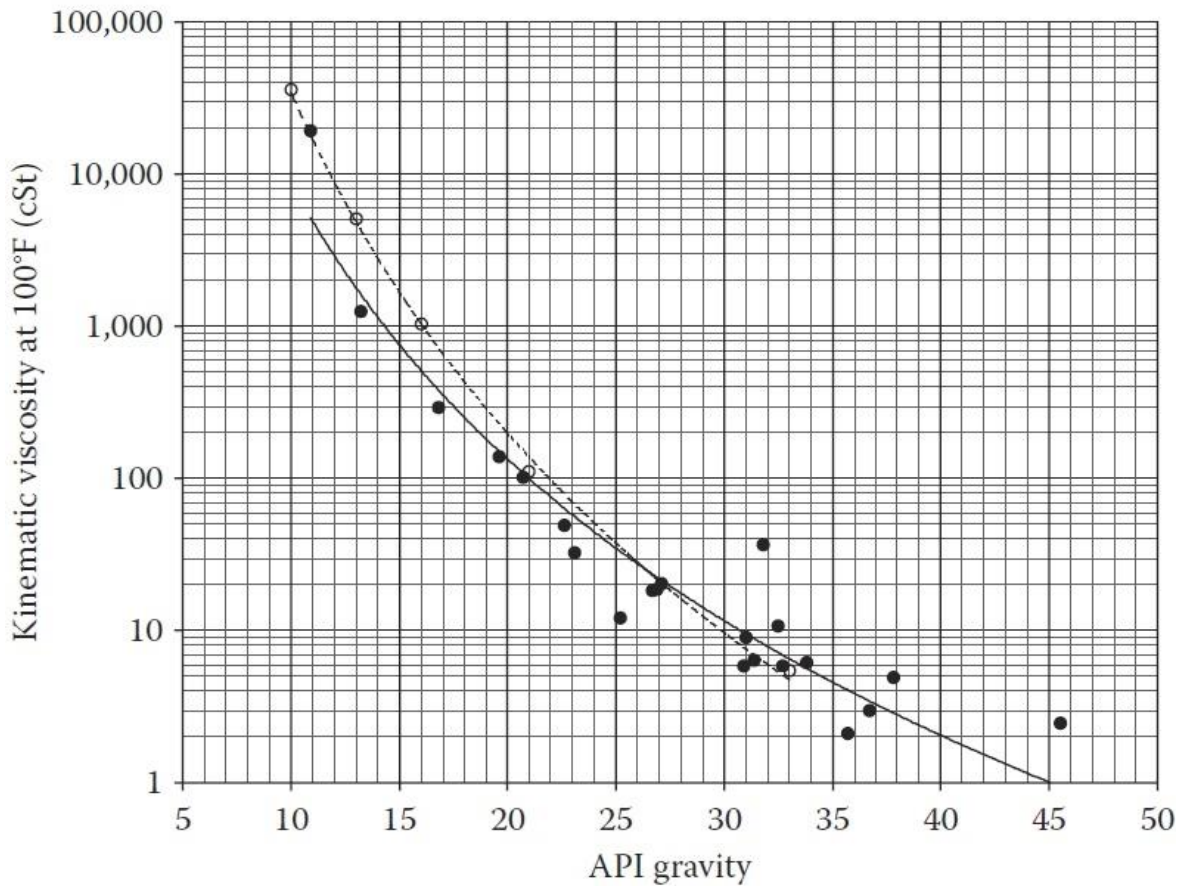


Figure 2.2: API gravity and viscosity of different crude oils. Mexican Oil (●) fitted by continuous curve, Oils from different countries (○) fitted by dashed curve (Ancheyta, 2013)

2.1.3.4 Petroleum Classification:

Several classifications for petroleum have been used based on different criteria such as sulfur content, use, price, etc. However, the most worldwide accepted classification is based on API gravity and viscosity (Ancheyta, 2013; Pereira-Almao, 2013):

- Light Crude Oil: API gravity of at least 30 °API.
- Medium Crude Oils: API gravity ranges between 21 and 30 °API.

- Heavy Crude Oil: API gravity ranges between 10 and 20 °API.
- Extra-Heavy Oils: API gravity less than 10 °API and viscosity lower than 10,000 cP at reservoir condition.
- Bitumens: API gravity less than 10 °API and viscosity higher than 10,000 cP at reservoir condition.

2.2 Heavy, Extra-Heavy Oil and Bitumen Recovery Methods:

All primary, secondary and tertiary methods have been applied for this purpose but, due to the high viscosity and density of these petroleums, primary and secondary methods have had limited success. This section will describe the different methods used for recovering heavy, extra-heavy oils and bitumens.

2.2.1 Primary and secondary recovery methods:

2.2.1.1 Surface Mining:

Surface mining has been operated extensively from open-cast mines in Canada since 1967, although heavy oils have been recovered by surface mining in Russia. After excavation, hot water and caustic soda (NaOH) is added to the mined material. The combination of hot water and agitation releases bitumen from the oil sand, and allows small air bubbles to attach to the bitumen droplets. The resulting bitumen froth can then be skimmed from the top (surface). Approximately four tonnes of material must be mined to produce one barrel of synthetic crude oil. In terms of recovery the process is very efficient and around 90% of the bitumen found in the deposit is recovered. However, this method is limited to shallow reservoirs, (less than 100 meters deep) and, the major drawback is its environmental impact, e. g. wetlands need to be drained,

rivers diverted, trees and vegetation stripped from the surface, and high water consumption requirement, between 2 to 4.5 barrels of water per barrel of oil produced (Shah et al., 2010).

2.2.1.2 Cold Production:

Where the oil viscosity is sufficiently low to flow at reservoir conditions, heavy oils can be produced from boreholes by primary cold production. Much of the oil in the Orinoco heavy-oil belt in Venezuela is currently recovered in this way, as are reservoirs offshore of Brazil. Horizontal and multilateral wells are drilled in order to contact as much of the reservoir as possible and diluents, such as naphtha, are injected to decrease fluid viscosity further. In order to lift the oil to the surface, electrical submersible pumps and progressive cavity pumps, are employed. Recovery factors are poor, typically in the range of 5-6%, although that may be increased up to 10% by the use of horizontal wells (Shah et al., 2010).

2.2.1.3 Water flooding:

Water flooding is usually used as a secondary recovery process but has also been successfully employed as a primary technique in some heavy oil fields. Water is injected in a well and pushes the oil towards the producing wells where submersible pumps help raise the oil to the surface. Eventually the water front will reach the production well and increasingly larger quantities of water will be produced, making the process less economical until the producer well becomes watered-out. Recovery factors of up to 20–40% have been achieved in light oil reservoirs, even up to 60%, but this decreases significantly with increasing oil viscosity due to channelling of the water flood front, resulting in poor sweep efficiency for all but the lightest heavy oils (Shah et al., 2010).

2.2.1.4 Cold Heavy-Oil Production with Sand:

Cold Heavy-Oil Production with Sand (CHOPS) modifies the more usual cold production technique where the completion zone of the well is designed to retain the crushed rock and sand which is carried to the well by the oil flow. This makes it easier to process the oil at the surface. Instead, CHOPS allows the sand to erode out of the well, thus extending highly permeable flow paths, or wormholes, through the reservoir to the well and thereby increasing production rates to 10 to 30 times those achieved in traditional cold production. Typically, over 12% of oil in place can be recovered, which is an improvement over traditional cold production.

A major issue with CHOPS, however, is the separation of sand which is both mechanically and economically intensive due to the special fluid handling equipment necessary. The disposal of the large amounts of sand produced is also a problem and waste management can account for 15–35% of operating costs (Shah et al., 2010).

2.2.2 *Tertiary recovery methods:*

Tertiary recovery methods, also known as Enhanced Oil Recovery (EOR), are usually considered as the third stage of production where the oil left behind by the low risk primary and secondary methods is extracted. The objective of these methods is to improve oil displacement and the sweep efficiency of the reservoir. As it can be seen in Figure 2.3, there are three major branches of EOR: miscible displacement, chemical flooding and thermal methods. A wider classification groups chemical and miscible flooding as non-thermal methods, which has been largely unsuccessful for heavy oil recovery (Farouq Ali, 2007), with some specific exceptions.

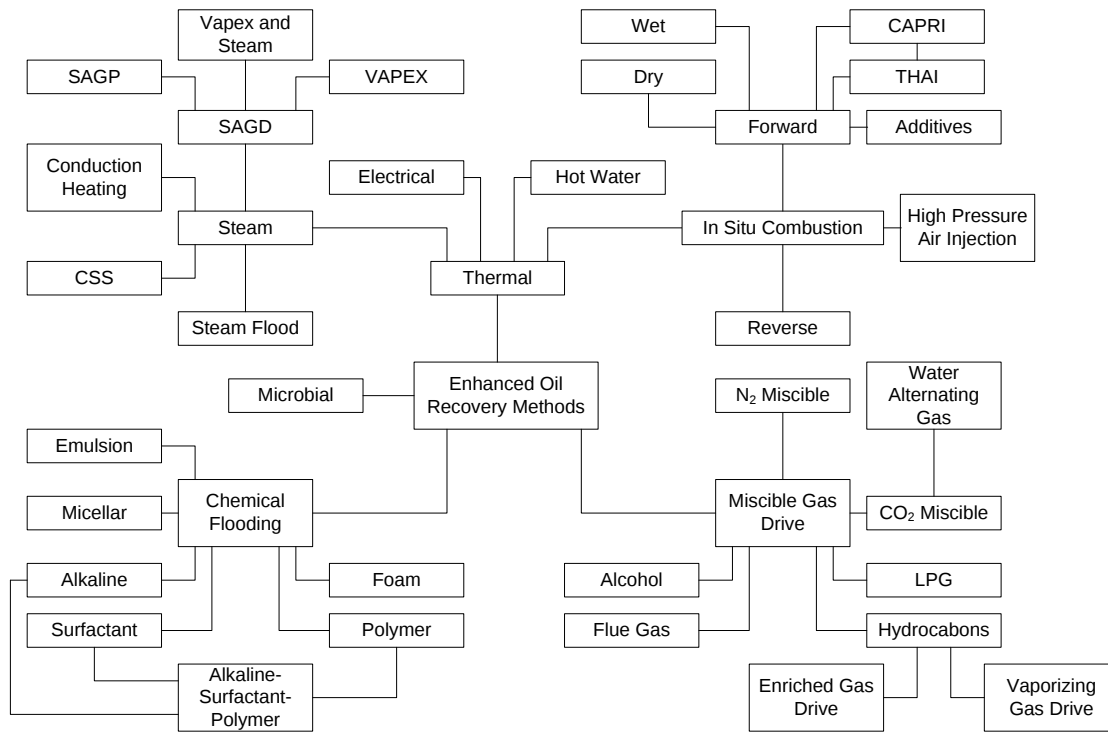


Figure 2.3: Enhanced Oil Recovery Technologies (Shah et al., 2010)

2.2.2.1 Miscible displacement:

The primary objective is to displace the oil with a fluid that is miscible at the conditions existing at the interface between the injected fluid and the oil bank being displaced (Green and Willhite, 1998). The main problem, though, is that the displacement efficiency decreases rapidly with increasing oil density and viscosity since fingering of the gases start occurring making the technique only economical for the lighter end of heavy oils (Shah et al., 2010).

2.2.2.2 Chemical Flooding:

Chemical flooding is a general term for techniques involving the injection of chemicals to decrease interfacial tension improving sweep efficiency. The three main chemical groups used are polymers, surfactants and alkaline flooding although; they can be combined to obtain the best characteristics of each one. Reservoir characteristics place particular restrictions, as carbonates

and clays absorb the chemicals. Recoveries up to 40% can be achieved but the technique is restricted by the high cost of the chemicals and is little used on large reservoirs, with the exception of China. More recent developments include the use of emulsions, foams and microbes, the latter producing surfactants *in situ* as a result of their normal biological processes (Shah et al., 2010). Polymer flooding is not cost-effective for processing heavy oils. At present, few if any surfactant floods have been successful, none in heavy oil formations. Alkaline or Emulsion flooding has been commercially successful in heavy oil reservoirs (Farouq Ali, 2007).

2.2.2.3 Thermal Methods:

Thermal processes add heat to the reservoir to reduce oil viscosity as well as vaporizing lighter components, making the oil more mobile. Thermal methods can be used for most oils but the high energy costs normally only makes them an economical choice for the hard to extract, high viscosity heavy oils and oil sands. The use of electrical heaters or hot water in a process analogous to water flooding have been used but, the two major groups use either steam or *in situ* combustion of a portion of the reservoir to heat the oil (Shah et al., 2010).

2.2.2.3.1 Steam Flooding:

This is a multi-well pattern drive process wherein steam is injected into the reservoir by using a system of injection and production wells. Steam injection rate is an important factor in this process, since a high rate can cause early steam breakthrough, while a low rate leads to excessive heat losses. In addition to lowering the viscosity, the injected steam provides the drive energy. The produced oil is characterized by a lower viscosity and higher API than the oil in-place. Recovery values are often lower than 50%. In case of very viscous oils, steam stimulation of producing wells before and during flooding may be required to lower the flow resistance. The

major drawback of this process is excessive heat loss, long payout and high cost in comparison with other thermal processes (Farouq Ali, 2007).

2.2.2.3.2 Cyclic Steam Stimulation (CSS):

This is a three-stage process starting with the injection of high pressure steam followed by the soak stage where the heat is left to distribute before the well is finally put into production. The oil production rate increases quickly to a high rate, staying at that level for a short time before gradually declining over several months. The cycle is then repeated when the oil rate becomes uneconomic. Steam to oil increases as cycles are repeated, typically spanning the range from 3:1 to 4:1 across the lifetime of the process. CSS is particularly attractive because it has quick payouts; however, recovery factors are low compared with other thermal techniques; typically 10–40% of the oil in place is recovered (Shah et al., 2010).

2.2.2.3.3 Steam-Assisted Gravity Drainage (SAGD):

In a typical SAGD process, two horizontal wells running parallel to one another about 5 m apart are employed. Steam is injected into the upper injection well, reducing the viscosity of the oil which drains into the lower production well along with condensed steam and is then pumped to the surface. Continuous injection causes a steam chamber to form and expand in the reservoir and for this reason the process performs better with bitumen and oils with low mobility, as steam channels are less likely to form.

SAGD is sensitive to operational and geometric reservoir parameters with high vertical permeability, being particularly crucial to the process' success. Recoveries of 40-60% have been reported along with high production rates. Large volumes of water are needed to run SAGD, requiring between two and ten barrels of water injected as steam for every barrel of oil produced. This water then has to be separated from the oil produced along with any formation water,

adding additional costs to the project. Furthermore, SAGD have been identified as contributor up to 60% of the total GHG emission from heavy oil extraction and processing (Shah et al., 2010).

2.2.2.3.4 In-Situ Combustion (ISC):

In this method, also known as fire flooding, air or oxygen is injected to burn portion (~10%) of the in-place oil to generate heat. Very high temperatures, in the range of 450-600 °C, are generated in a narrow zone. High reduction in oil viscosity occurs near the combustion zone. The process has high thermal efficiency, since there is relatively small heat loss to the overburden or underburden, and no surface or wellbore heat loss. In some cases, additives such as water or gas are used along with air, mainly to enhanced heat recovery. Severe corrosion, toxic gas production, and gravity override are common problems. *In situ* combustion has been tested in many places, however, few projects have been economical at commercial scale. The main variations of *in situ* combustion are (Thomas, 2008):

- Forward combustion: ignition occurs near the injection well, and the hot zone moves in the direction of the air flow.
- Reverse combustion: ignition occurs near the production well and the heated zone moves in the counter direction to the air flow.
- High Pressure Air Injection (HPAI): involves low temperature oxidation of the in-place oil (there is ignition).

2.2.2.3.5 THAI™ and CAPRI™ Processes:

THAI™ (Toe-to-Heel Air Injection) and CAPRI™ (Catalytic upgrading Process *In situ*) are variations of ISC, using a vertical injector well placed near to the top of the reservoir, with a horizontal production well placed near the base of the reservoir (Thomas, 2008). These are processes more robust and stable than conventional ISC, because they eliminate the tendency for

gas override and also have a ‘built-in’ guidance mechanism, by virtue of the combustion front propagating along the horizontal producer well from the ‘toe’ position to the ‘heel’. The objective is to add some control to the conventional ISC process since the combustion front propagates along the horizontal well, from the “toe” position, to the “heel”.

The horizontal producer well effectively self-seals as coke is formed as the combustion front progresses, closing off the “toe” and preventing gas bypass. Furthermore, compared to ISC, the path of the mobilized oil to the producer well is much shorter, increasing production rates. Experimental modelling has suggested recoveries up to 80-85% of oil in place may be feasible. The partially upgraded oil produced with THAI is thought to occur because of the thermal cracking reactions taking place in the coke and mobile oil zone. The reactants are comprised of water (steam), oil, combustion gases, and unconsumed oxygen. Pilot tests carried out in Christina Lake, Alberta, Canada have reported a partial oil upgrade from 7.9 °API up to 10.6 to 16.1 °API (Shah et al., 2010), however no indication of the stability of this oil has been provided.

CAPRITM process is basically a variation of THAITM process, in which the thermally cracked oil, captured by the horizontal well, can be upgraded to lighter fractions by utilizing an annular catalytic bed around the horizontal well (Thomas, 2008). In experimental laboratory studies, heavy crude from the Athabasca oil sand and Wolf Lake heavy oil have been upgraded by 8 and 10.5 °API respectively, using Nickel/Molybdenum and Cobalt/Molybdenum hydrotreating catalyst. However this process will have to overcome some significant challenges before it can be economically viable, oil production is significantly affected by coke deposition in the catalyst zone (Moore et al., 1996), and quick catalyst poisoning/deactivation due to the high sulfur and metal contents in heavy crude oils (Shah et al., 2010).

2.3 Heavy, Extra-Heavy Oil and Bitumen Upgrading Processes:

Due to their high viscosity and density, heavy, extra-heavy oils and bitumens have to be improved prior to being transported. In this context, upgrading can be defined as activities to convert unconventional petroleum into transportable crude oil. Consequently, upgrading operations add value to these non-traditional crude oils because they are transformed into suitable feedstocks for the refining market. Nowadays, there are two ways of upgrading unconventional oils. The first method is to upgrade the oil in the oil field (surface) leaving behind some by-products such as coke, asphaltenes or vacuum residue, and then pipelining the upgraded material as synthetic crude. The second method consists in carrying out upgrading *in situ* (inside the reservoir); in this case the oil coming from the reservoir will have acceptable properties in terms of transportability.

A final option that is already a common practice is to use conventional crudes located in the area to dilute the unconventional crude oil to produce acceptable pipeline material. This option is workable but does not represent any form of upgrading for the heavy oil; the operative term is dilution (Speight, 2013). In a context of shortage of diluents this activity would be limited compromising the sustainability of operations.

2.3.1 Surface Upgrading:

A general scheme for surface upgrading produced by Gray (2010) for the upgrading facilities built in northern Alberta, is shown in Figure 2.4; it can be noted that in very broad terms upgraders are divided into six major sections:

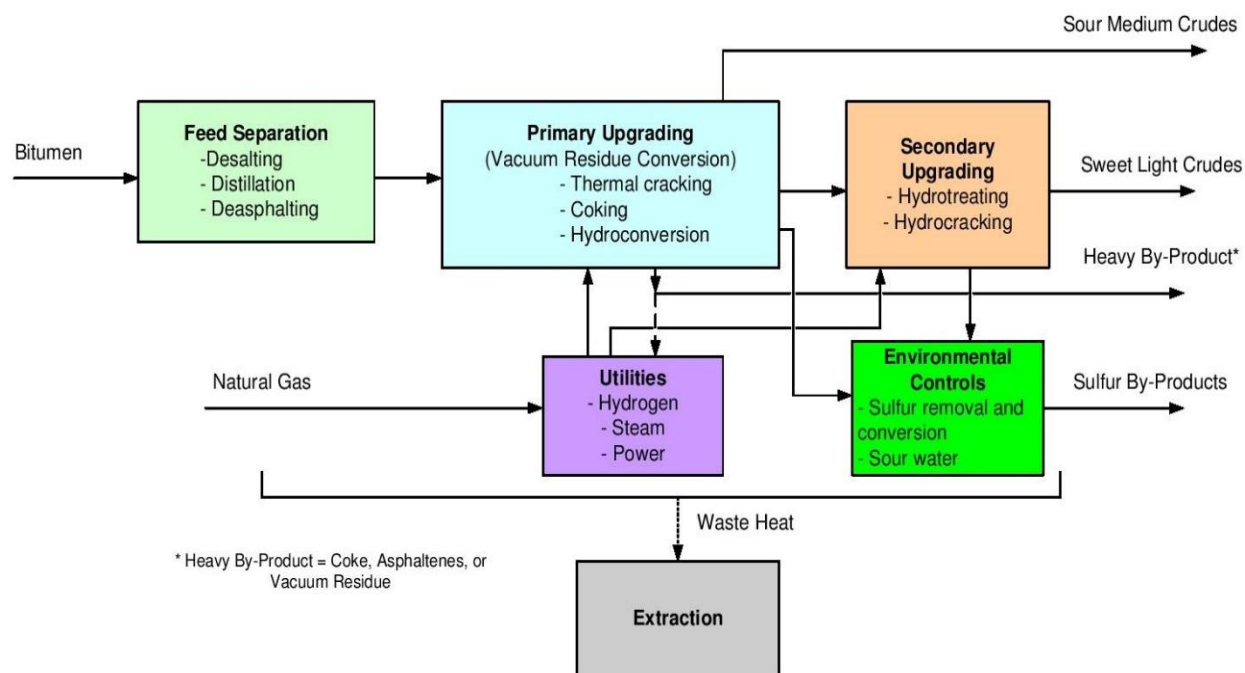


Figure 2.4: General Scheme for Surface Upgrading (Gray, 2010)

2.3.1.1.1 Feed Separation:

The goal of this step is to separate the heavier undesirable materials, i.e. asphaltenes or vacuum residue, which will undergo primary upgrading throughout a conversion process. This separation processes target the splitting of the feedstock into different products or “cuts” with certain specifications of physical properties such as boiling point, density or solubility.

2.3.1.1.1.1 Desalting:

Salt deposition on heat transfer surfaces and acids formed by decomposition of the chloride salts present in crude oils cause fouling and corrosion in process equipment resulting in significant costs. In addition, some metallic inorganic compounds dissolved in water emulsified with the crude oil can cause catalyst deactivation. The salt, inorganic compounds and solids (such as fine sand, clay and soil particles) are rejected by a process known as desalting. The

basic principle is to wash the salt from the crude oil with water. The pH, density, and viscosity of the crude oil, as well as the volume of wash water, affect the separation ease and efficiency. The salts are dissolved in the wash water and the oil and water phases are separated in settling vessels either by adding chemicals to assist in breaking the emulsion or by developing a high-potential electrical field across the settling vessel to accelerate coalescence of the droplets of salty water more rapidly (Gary and Handwerk, 2001).

2.3.1.1.2 Atmospheric and Vacuum Distillation:

This step consists in the separation of the crude oil into various fractions by the process of distillation. These fractions may be products in their own or may be feedstocks for other processing units. In the atmospheric tower, the oil is first heated to a maximum temperature allowable for the crude oil being processed to avoid excessive thermal cracking, and then fed to a fractionating tower which operates slightly above atmospheric pressure. It yields several distillate products and a bottom product which could not be vaporized under the conditions of temperature and pressure existing in the tower (Watkins, 1973).

Temperatures required for atmospheric pressure distillation of heavier fractions of crude oil are so high that thermal cracking would occur, with the resultant loss of product and equipment fouling. These materials are therefore distilled in a fractionation column known as the Vacuum Tower, operated under sub-atmospheric (vacuum) pressure because the boiling temperature decreases with lowering of the pressure (Gary, 2001).

2.3.1.1.3 Solvent De-Asphalting:

The purpose of a Solvent De-Asphalting unit (SDA) is to separate out the asphaltenes and some resins from the oily fractions contained in the feed. In this process a paraffinic solvent is injected into the feedstock to disrupt the colloidal suspension of components, causing the heavy

polar constituents to precipitate. A SDA unit often processes the residuum from the vacuum distillation unit and produces De-Asphalted Oil (DAO), used as a feedstock for the following applications (Wauquier, 1998):

- production of bright stock and waxes (lubricant production processes);
- preparation of catalytic cracking and hydrocracking feeds (extra conversion units);

The asphaltic residue (pitch), a residual fraction, can be used for:

- production of road quality asphalt;
- as component in industrial fuel oil or solid fuels;
- as feed for conversion units such as visbreakers, oxyvapogasifiers and cokers;

2.3.1.2 Primary Upgrading:

Heavy fractions separated in distillation or SDA units are fed into primary upgrading processes which involve the conversion of residue or De-Asphalted Oil (DAO) into lighter products by means of chemical reactions based on carbon rejection pathways, such as thermal cracking and coking, or hydrogen addition routes like hydroconversion.

2.3.1.2.1 Thermal Cracking:

The term cracking applies to the decomposition of the petroleum constituents that is induced by elevated temperatures (higher than 350 °C), whereby the higher molecular weight constituents of petroleum are converted to lower molecular weight products. Cracking reactions involve carbon-carbon bond rupture and are thermodynamically favored at high temperature. However certain products may interact with one another to yield products with higher molecular weights than the constituents of the original feedstock. Some of the products are gases, naphtha-range material, middle distillates, various intermediates, and other products such as coke (Speight, 2007). Visbreaking is a mild process alternative that relies on the thermal cracking of

high boiling point range hydrocarbons to reduce their viscosity and hence decrease the amount of required diluent to reach the fuel oil viscosity specifications (Pereira-Almao, 2013).

2.3.1.2.2 Coking:

Coking is the process to convert heavy feedstock into a solid carbonaceous material, called “coke”, and lower boiling point hydrocarbon products which are suitable as feedstock to other units for conversion into higher value transportation fuels. From the chemical point of view, coking can be considered as a severe thermal cracking process in which one of the end products is carbon, i.e. coke. Delayed Coking is the most widely used coking process at industrial scale. Fluid coking and Flexicoking are also available alternatives developed by Exxon (Gary and Handwerk, 2001).

2.3.1.2.3 Hydroconversion:

Hydroconversion, also called hydroprocessing, is a hydrogen addition process whose objective is the reduction of boiling point range of residual oils, e. g. vacuum residue and pitch, as well as the removal of substantial amounts of impurities such as metals, sulfur, nitrogen and reducing carbon forming compounds. There are numerous technologies which differ in catalyst, operating conditions, and process configuration. Among all the reactor technologies, fixed/mobile-bed reactors are still the most widely used in hydroconversion operations due to their flexibility and relative simplicity. Other type of reactors such as moving-bed and ebullated-bed reactors are also available, specifically for upgrading the heaviest fractions. The selection between each type of technology is dictated by catalyst deactivation, which depends on the nature of the feedstock (Ancheyta, 2013).

2.3.1.3 Secondary Upgrading:

Secondary upgrading processes address post-treatment of products and by-products to meet specifications such as sulfur content, or to increase the yield in naphtha and middle distillates boiling point range hydrocarbons. In the case of upgraders, these processes may be used to adjust the synthetic crude oil specifications. The most important technologies applied are:

2.3.1.3.1 Hydrotreating:

Hydrotreating is a hydrogen addition process to catalytically stabilize petroleum products and/or remove sulfur, nitrogen, oxygen, halides and trace metals from products or feedstocks. Stabilization usually involves converting unsaturated hydrocarbons such as olefins and gum-forming unstable diolefins to paraffins. Hydrotreating is applied to a wide range of feedstocks varying from naphthas to residua. Reaction temperature is carried out below 425 °C to minimize cracking (Gary and Handwerk, 2001).

2.3.1.3.2 Hydrocracking:

Hydrocracking is another hydrogen addition process used in the oil industry. In this case the goal is to convert heavy distillates into naphtha-range products by the use of bifunctional catalysts. From the chemical point of view, the mechanism of hydrocracking is a catalytic cracking with hydrogenation superimposed. Catalytic cracking is the scission of carbon-carbon single bonds, and hydrogenation is the addition of hydrogen to carbon-carbon double bonds. The cracking reaction is endothermic and the hydrogenation reaction is exothermic. The overall reaction provides an excess of heat because the amount of heat released by the hydrogenation is much greater than the amount consumed by cracking reactions. To increase hydrocracking catalyst life frequently the feedstock is hydrotreated to remove sulfur and nitrogen compounds as well as metals before it is sent to the hydrocracking unit (Gary and Handwerk, 2001).

2.3.1.4 Utilities:

These comprise auxiliary units to support main processes and facilities operation. Include: power, steam and hydrogen generation units, air for plant instrumentation and general use, water employed to produce steam or as cooling water circuit makeup, among others.

2.3.1.5 Environmental Controls:

These are applied for remediation and disposition of contaminants and by-products, e. g. acid gas removal, sour water treatment, sulfur recovery unit, etc.

2.3.1.6 Extraction:

This involves the use of unconventional (thermal) recovery methods to bring the petroleum to the surface, SADG and CSS are good examples of them.

2.3.1.7 Surface Upgrading Disadvantages:

There are two different points of view related to the extent of upgrading in the oil industry. The most common approach practiced in northern Alberta is the full upgrading approach, which consists in the production of a synthetic crude oil with at least 30 °API and significantly reduced sulfur content, such as the case of: CNRL Light Sweet Synthetic, CNS (36.3 °API, 0.04 wt.% of sulfur), Husky Synthetic Blend, HSB (31.7 °API, 0.10 wt.% of sulfur), Shell Synthetic Light, SSX (32.9 °API, 0.11 wt% of sulfur), or Suncor Synthetic A, OSA (31.8 °API, 0.16 wt% of sulfur). However, this scheme requires high complexity upgraders including high technology processes such as: hydroprocessing, gasification, hydrogen production via steam reforming, etc. Figure 2.5 clearly shows that Nelson complexity index, which provides a relative measure of the construction costs of a particular refinery based on its crude and upgrading

capacity (Johnston, 1998), increases with the extend of oil upgrading, meaning that these operations demand higher investment and operating costs.

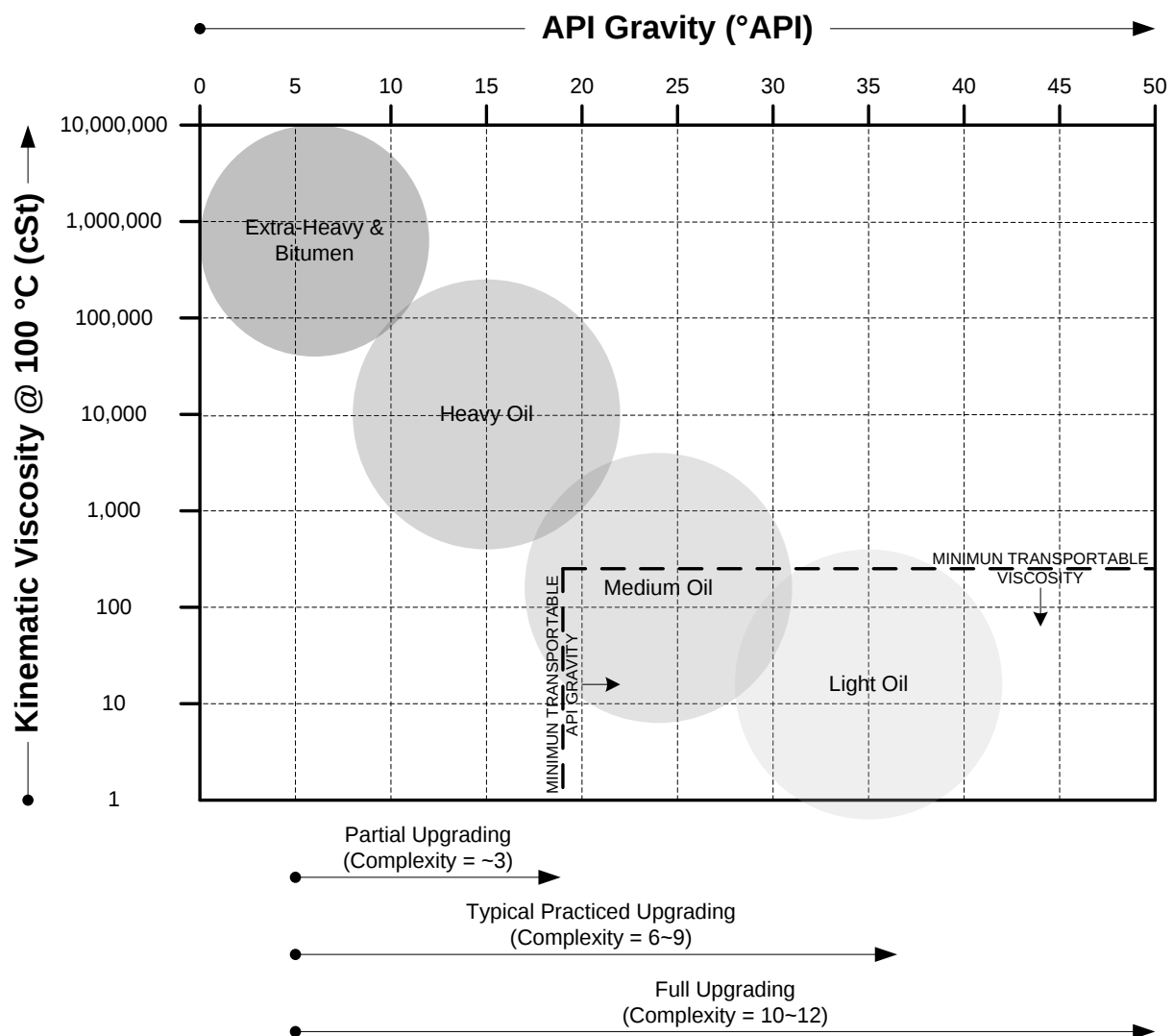


Figure 2.5: Heavy Oil, Extra-Heavy Oil and Bitumen Upgrading specification and facilities complexity (Nelson index)

Profitability of these facilities is compromised by the relative high cost of supplies (fuel gas, power, steam, hydrogen) due to their remote location. In addition, these upgrading schemes produce by-products such as coke or pitch (asphaltenes), which in most cases imply additional

costs for disposition and remediation. They also lack of efficiency from the thermal point of view, since heat has to be added to the reservoir (in order to decrease the oil viscosity by means of any steam-based EOR method), and also at the surface when the crude goes throughout the upgrading process. Dilution, even though it does not represent any oil improvement per se, is commonly used by some operators. However, the cost of diluents, their scarcity in remote zones and transportation-related costs, along with operating pipelines problems (plugging) due to asphaltenes precipitation, make this technique inconvenient in some cases.

If oils were only upgraded up to transportability specifications, i. e. 350 cSt at pumping conditions and 19 °API; significant lower complexity facilities would be required with lower capital and operating costs; this approach is known as partial upgrading. This implies the production of heavy-medium oil which would be transformed into valuable products in the already existing deep conversion refineries around the world.

2.3.2 *In Situ Upgrading:*

In Situ Upgrading consists in the combination of oil recovery and upgrading at the same time within the reservoir. This is possible due to the research and knowledge generated in several areas such as fluid flow in porous media, development of new catalysts, reaction pathways, etc. Recently, several methods of in situ upgrading have been conceived, even though most of them showed promising results at laboratory scale, they have faced technical difficulties for pilot tests which has ended up in a non-feasibility pathway or in failure due to field non idealities that may be overcome with further research.

A method based on solvent extraction was proposed by Butler and Mokrys (1993), called Vapor Extraction (VAPEX), which utilizes two horizontal wells and is closely related to SAGD process but with the steam chamber replaced by a chamber containing hydrocarbon vapor near

its dew point. They demonstrated that the quality of the bitumen or heavy oil can be improved substantially by in situ deasphalting with propane vapor. The removal of asphaltenes reduces the viscosity of the produced oil, which additionally can be more easily refined. However, experimental runs showed a massive asphaltenes precipitation, severe formation damage and consequently a large reduction in the oil rate production (Haghighat and Maini, 2008).

Oil constituents can be cracked into lighter hydrocarbons molecules at high-enough temperatures and pressures. Steam and thermal cracking reactions are carried out at high temperatures in refineries and upgraders, but such high temperatures are difficult to achieve in the reservoir, however cracking reactions can still occur at lower temperatures but lower reaction rates (Speight, 1013). Steam-based methods, even though were not conceptualized as *in situ* upgrading methods per se, with the combination of moderate temperature and long residence time, induce some degrees of thermal cracking, but this is not enough for reaching transportable properties. This also occurs by using methods based on in situ combustion (i. e. forward ISC, reverse ISC, High Pressure Air Injection and THAITM) whose numerous field observations have shown upgrading of 2-6 °API for heavy oils (Speight, 2013). In general, thermal methods have as major intrinsic disadvantage the generation of more and denser asphaltenes and producing olefins, which makes the need for further hydrotreating of produced crude oil on surface (before pipelining), posing an economic impractical burden (Pereira-Almao, 2012).

The use of a downhole catalyst bed in ISC processes at laboratory scale has shown to improve oil properties at least by 6 to 8 °API on top of the THAI process (Speight, 2013). However, these conventional catalyst would eventually plug, increasing the risk of well plugging and loss of stability and quality of the crude oil being produced (Pereira-Almao, 2012).

Ultra-Dispersed (UD) catalysts or nanocatalysts have been proposed due to their advantages over conventional catalysts, especially when processing feedstocks characterized by large molecules like those present in high boiling point cuts. High surface area, reduction in deactivation and diffusion problems, high density of particles per unit volume of feed and lower inter-particle distances are some of the benefits of these novel materials (Pereira-Almao, 2014). Based on these mentioned advantages of nanocatalysts, plus the predominance of heavy, extra-heavy oils and bitumen reservoirs over light reserves, and the need of developing new recovery/upgrading processes with less energy demand and emissions, Pereira-Almao and coworkers (2013) from the Catalyst for Bitumen Upgrading Group (GBUG) at the University of Calgary, have patented a novel process for in situ upgrading of bitumen and heavy oils via nanocatalyst.

The use of submicronic catalytic particles produced by decomposition of water-in-bitumen transient catalytic emulsions was patented by Pereira-Almao and coworkers (2007). This preparation was later tested by Galarraga and Pereira-Almao (2010). In their work, they performed hydrocracking reactions of Athabasca Bitumen with trimetallic (Ni/Mo/W) nanocatalyst in a batch reactor with 3.45 MPa hydrogen pressure, within a range of 320 °C to 380 °C of temperature and residence times between 3-69 h. Figure 2.6 shows the residue (+545 °C) conversion as function of residence time at different temperatures and the bitumen viscosity at 40° C as a function of residue (+545 °C) conversion. It is evident that at achievable reservoir conditions, as high as 60 % residue conversion can be reached, which represent 99% viscosity reduction.

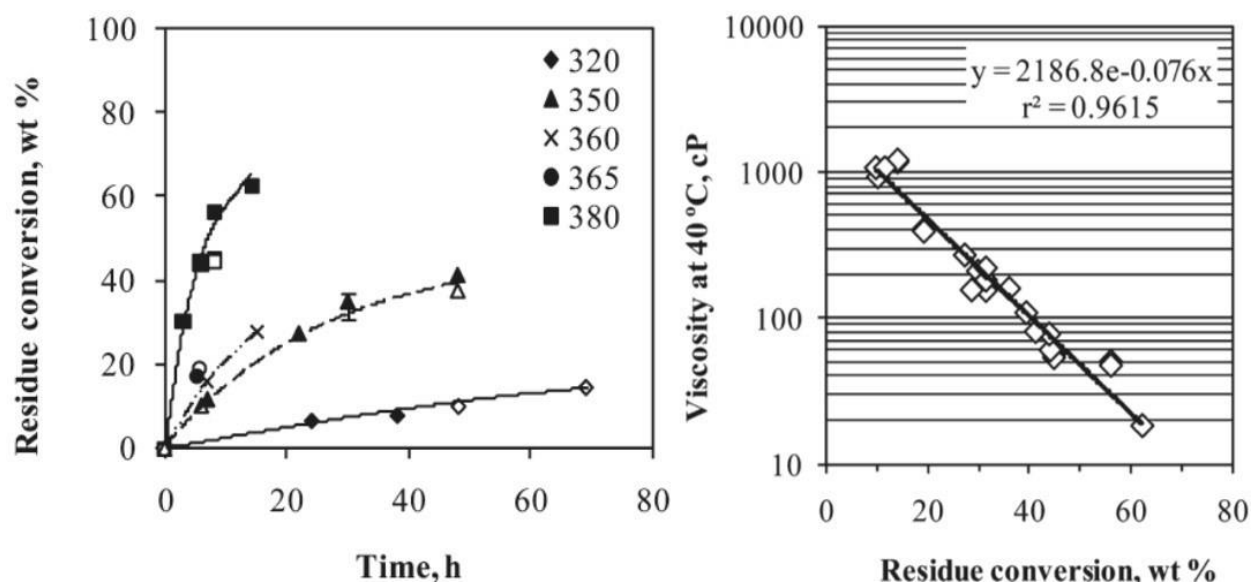


Figure 2.6: Hydroprocessing of Athabasca bitumen using nanocatalysts at In-reservoir conditions (Galarraga and Pereira-Almao, 2010)

These results proved that the trimetallic formulation enhanced hydrocracking reactivity of Athabasca Bitumen, inhibiting coke production when operating at relatively low temperatures, low pressures and long residence times. With the achieved conversion levels, significant reduction in coke production, viscosity reduction, sulfur removal, and reduction of MCR were reported.

Due to the need to study the transport of ultradispersed catalyst in porous media, Zamani, et al. (2010) carried out experiments to systematically examine the propagation of ultradispersed catalysts in sands packs. These experiments involved the injection of submicrometer-sized catalyst particles suspended in oil into a sandpack and the analysis of ultradispersed catalyst suspensions through the sand bed. In these experiments, two types of sandpacks were evaluated; one initially saturated with fresh water in order to experimentally model the presence of connate water in water-wet reservoirs, and one without connate water to model oil-wet reservoirs

(Zamani et al., 2010). The results showed that the use of commercial surfactant during the catalyst preparation produced the emulsification of the connate water causing a pressure drop increase, which further disappeared once the emulsion was displaced out of the sand pack. In addition, nanodispersed catalysts were determined as able to propagate through the sand, but larger (micrometer sized) agglomerated particles were filtered out causing permeability damage, however, the retention of truly nanosized particles (at low concentration) had a negligible effect on the pressure drop and caused no permeability damage. Finally, Zamani reported that 10% to 20% of the total catalyst injected in the sand pack was retained within the porous medium, which was determined to be irreversible and was attributed to adsorption.

Rendon (2011) conducted a thermodynamic study using model molecules representative of Athabasca Bitumen fractions. Thermal cracking (hydrogen production and hydrogen transfer), hydrocracking and hydrotreating reactions were evaluated by using the change in Gibbs free energy using group contribution methods for resins and asphaltenes model molecules. Results showed, that within the range 150-350 °C, spontaneity of cracking reactions was favored in the presence rather than in the absence of hydrogen. Rendon (2011) also showed that hydrogenation followed by cracking was more spontaneous than cracking followed by hydrogen saturation. Finally, since hydrocracking and hydrotreating reactions are exothermic, once they are triggered they can propagate the produced heat inside the reservoir.

In this research, Rendon also evaluated the flow of nanoparticles through porous media, however additional features were taken into account in these experiments in order to simulate similar environments as those achieved under in situ upgrading process, i. e. hydrogen injection and oil reactivity. In these experiments, Athabasca Bitumen with a trimetallic (Ni/Mo/W) nanocatalyst formulation and hydrogen (90 std. cm³/cm³ of oil) were continuously injected into

sand packs. Similarly to the results obtained by Zamani and coworkers (2010), the use of catalytic emulsions, composed by oil medium, surfactant and salt precursors, impaired the permeability of the porous medium, reporting a permeability reduction of 94%.

In order to overcome this issue, Rendon (2011) suggested carrying out the thermal decomposition of the precursor in a separate environment which is translated into a catalyst preparation unit thus, the injection of Athabasca Bitumen with trimetallic nanocatalyst and hydrogen in sand packs was tested. The operating conditions were chosen to be similar to achievable reservoir conditions, moderate temperatures within the range of 230 °C to 340 °C, long residence times within the range of 17-75 hours and two catalyst concentration levels: low (221 ppm) and high (699 ppm). In this set of experiments was proved that metal particles are able to navigate through the sand pack without affecting the permeability of the porous media. As the temperature and residence time increases, particle retention tended to increase, phenomenon that seems to be irreversible. Significant upgrading was achieved using temperatures in the 320-340 °C range with long residence times up to 74 hours. The viscosity of the bitumen was reduced by 97% with an increase in API gravity of 4.5 °API. Even though oil transportability properties were not achieved, it is thought that by further increasing the residence time and/or temperature, this goal can be reached.

Using the experimental data obtained in their work, Galarraga and coworkers (2011) proposed two kinetic models for Athabasca Bitumen hydroprocessing using nanocatalysts at low severity (in-reservoir) conditions. The first model, called model A, considers the conversion of residue (+545 °C) into lighter products as an irreversible first-order reaction. They found that a first-order reaction describes quite well the conversion of the residue fraction of Athabasca bitumen hydroprocessed in the presence of nanocatalyst. The reported average absolute error was lower

than 3%. By means of Arrhenius plot (natural logarithm of reaction rate vs. inverse of absolute temperature) they calculated an apparent activation energy of 204 kJ/mol, reporting a correlation coefficient, r^2 , of 0.98. Their second proposed model, called model B, consists of an adaptation of the model proposed by Sanchez and coworkers (2005) for moderate hydrocracking of heavy oils. This model includes 5 lumps: unconverted residue (+545 °C), Vacuum Gas Oil (343-545 °C), distillates (216-343 °C), naphtha (IBP-216) and gases; 10 first-order reactions are considered as shown in Figure 2.7:

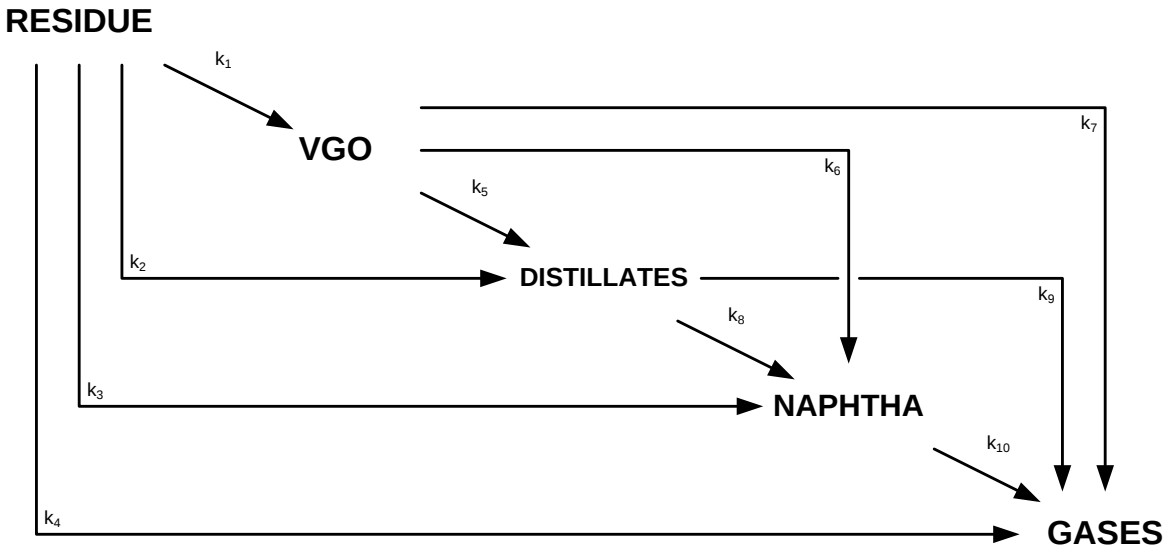


Figure 2.7: 5-Lumps Kinetic Model for Hydroprocessing

For each component, a kinetic expression was formulated as a function of component mass fractions, determined by distillation curves, and kinetic constants as shown from Equation 2 to Equation 6:

$$r_R = -(k_1 + k_2 + k_3 + k_4) \cdot y_R \quad \text{Equation 2}$$

$$r_{VGO} = k_1 \cdot y_R - (k_5 + k_6 + k_7) \cdot y_{VGO} \quad \text{Equation 3}$$

$$r_D = k_2 \cdot y_R + k_5 \cdot y_{VGO} - (k_8 + k_9) \cdot y_D \quad \text{Equation 4}$$

$$r_N = k_3 \cdot y_R + k_6 \cdot y_{VGO} + k_8 \cdot y_D - k_{10} \cdot y_N \quad \text{Equation 5}$$

$$r_G = k_4 \cdot y_R + k_7 \cdot y_{VGO} + k_9 \cdot y_D + k_{10} \cdot y_N \quad \text{Equation 6}$$

Where:

k : Reaction Constant [h^{-1}]

r : Reaction Rate [h^{-1}]

y : Component Mass Fraction [wt%]

Table 2.2 shows reaction constants, regression coefficients and activation energies for each reaction. The authors found that all the reactions producing gases were negligible in most cases except for the reaction of unconverted residue into gases, i. e. reactions 7, 9 and 10; fact that supports the reduction of the number of reactions taking into consideration to 7 in the proposed model.

Table 2.2: Kinetic Parameters for Hydrocracking of Athabasca Bitumen Using Submicronic NiWMo Catalyst as Described by Model B (Galarraga et al., 2011)

kinetic constant (h^{-1})	temperature			r^2	activation energy E_a (kcal/mol)
	320 °C	350 °C	380 °C		
k_1	1.18×10^{-3}	6.81×10^{-3}	4.48×10^{-2}	0.983	172.1
k_2	1.51×10^{-4}	4.49×10^{-3}	2.68×10^{-2}	0.978	276.7
k_3	1.79×10^{-4}	2.49×10^{-3}	2.87×10^{-2}	1.000	271.7
k_4	3.62×10^{-5}	5.09×10^{-4}	1.06×10^{-2}	0.995	303.1
k_5	9.78×10^{-4}	2.10×10^{-3}	1.78×10^{-2}	0.916	157.0
k_6	3.81×10^{-6}	3.13×10^{-4}	2.26×10^{-3}	0.965	342.9
k_7	3.62×10^{-8}	5.19×10^{-4}	0		
k_8	3.19×10^{-6}	5.86×10^{-4}	2.86×10^{-3}	0.928	242.0
k_9	1.54×10^{-4}	0	0		
k_{10}	1.24×10^{-4}	2.02×10^{-3}	0		

Calculated activation energies ranged from 157 to 342 kJ/mol, being the least energy-demanding reaction the conversion of VGO into distillates, followed by the conversion of residue into VGO, reactions 5 and 1 respectively, as shown in Figure 2.7. This indicates that these reactions are feasible at the lowest temperature evaluated. It was also confirmed that

naphtha and middle distillates are essentially nonreactive at the evaluated conditions. In general terms, all regression coefficients for each reaction were found to be higher than 0.9, residual analysis showed that the discrepancy between the experimental values and the ones predicted by the model may be of experimental nature. The reported average absolute error of the model was lower than 5%.

Loria et al. (2011) also presented a kinetic model for Hydroprocessing of Athabasca Bitumen at reservoir conditions by using trimetallic formulation of nanocatalyst; however in this case the experimental data was obtained from a tubular reactor in a pilot plant. Their model also consisted in an adaptation of the model proposed by Sanchez and coworkers (2005), for moderate hydrocracking of heavy oils (5 lump and 10 first-order reactions).

Similarly to the work by Galarraga and coworkers (2011), only traces of coke were observed which lead to consider coke production insignificant and be neglected in the kinetic modeling. Their results showed that kinetic rate constants corresponding to reaction producing gases (reaction 7, 9 and 10) were negligible except for reaction 4 (unconverted residue producing gases). They concluded that the gas production exclusively comes from the unconverted residue and that the naphtha hydroprocessing is negligible at temperatures in the range of 320 – 380 °C; this behavior has been also observed at higher temperatures (380-420 °C) by Sanchez et al. (2005). Table 2.3 shows reaction constants, regression coefficients and activation energies for each reaction of the kinetic model of Loria et al. (2011). Calculated activation energies ranged from 145 to 261 kJ/mol, being the least energy-demanding reaction the conversion of residue to VGO, followed by the conversion of VGO into middle distillates, reactions 1 and 5 respectively, as shown in Figure 2.7.

Table 2.3: Kinetic Parameters for Ultradispersed Catalytic Hydrocracking of Athabasca Bitumen (Loria et al., 2011)

$T, ^\circ\text{C}$	kinetic rate constants, h^{-1}							AAE%
	k_1	k_2	k_3	k_4	k_5	k_6	k_8	
320	0.00214	0.00131	0.00030	0.00006	0.00670	0.00491	0.00105	0.02
350	0.00845	0.00610	0.00113	0.00073	0.00282	0.00141	0.00046	4.58
360	0.01324	0.00951	0.00251	0.00085	0.00181	0.00073	0.00032	6.61
380	0.02650	0.03093	0.01130	0.00902	0.00045	0.00014	0.00007	0.69
E_A , kJ/mol	136	167	192	261	145	190	146	
$\ln A$ (A , h^{-1})	21.47	27.24	30.63	43.01	21.59	29.60	20.15	
r_L^2	0.9983	0.9949	0.9660	0.9683	0.9998	0.9952	0.9979	

This indicates that these reactions are feasible at the lowest temperature evaluated. It was also confirmed that naphtha is essentially nonreactive under the evaluated conditions, in contrast to Galarraga and coworkers (2011) who found that middle distillates conversion into naphtha seem to be feasible at these conditions. In general terms, all regression coefficients for each reaction were found to be higher than 0.95, being the average absolute error of the model lower than 7%.

This work also included the development of a computational program which besides the estimation of kinetic rate constants and estimation of product composition, can also provide the liquid product viscosity at 40 °C for a given reaction temperature and residence time. Figure 2.8 shows the product viscosity regression as a function of the residue conversion and as a function of reaction temperature and residence time for Athabasca Bitumen ultradispersed catalytic hydroprocessing. This information is valuable when planning future experiments, estimating the extent of bitumen upgrading or studying upgrading schemes (Loria et al., 2011).

All kinetics models have been generated using upflow empty-tube reactors in order to avoid variable concentration of catalyst when in the presence of sand. The catalyst nanoparticles

stick to the rock irreversible (Zamani et al., 2010) making a kinetic study with growing concentration of catalyst in the sand-bed an impossible task.

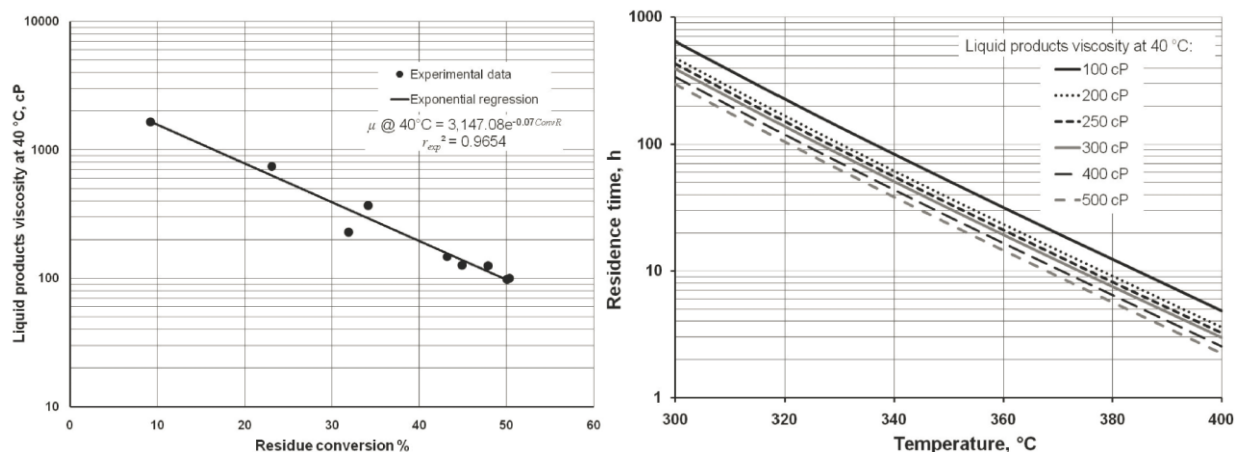


Figure 2.8: Product Viscosity as a function of conversion and as a function of reaction temperature and residence time of Athabasca Bitumen Ultradispersed Catalytic Hydroprocessing (Loria et al., 2011)

Coy (2013) tested the in-reservoir upgrading concept by using Athabasca Vacuum Residue with trimetallic ultradispersed catalysts and hydrogen into a sand pack. The effect of catalyst was proven by comparing thermal and catalytic runs at a temperature of 300 °C and 24h of residence time. The use of nanocatalyst increased the residue conversion from 4.4 wt% to 23.0 wt%, increase the API gravity from 2.3 °API to 4.2 °API, and a viscosity reduction from 49% to 99% with a permeability reduction of 20% with respect to the initial value.

Once the sand pack was decorated with the ultradispersed nanocatalyst, fresh Athabasca vacuum residue (without catalyst) was injected into the porous media under SAGD reservoir conditions (temperature within a range of 260 – 300 °C and 291 hours of residence time). Significant upgrading was found even though the feedstock did not contain catalyst; the conversion of the residue fraction was as high as 32%, API gravity was improved by 6.1 °API,

and there was a viscosity reduction of 98%, with a permeability reduction of 21% with respect to the initial value. Further, fresh Athabasca Bitumen (without catalyst) was injected to the same sandpacked reactor containing catalyst under the same conditions used for Athabasca vacuum residue, reaching conversion of the residue fraction of 16%, an increment of 4.1 °API and viscosity reduction of 80%, with a permeability reduction of 30% of the original value. Finally, Coy and coworkers (2012), analyzed sand grains after processing from several sections of the sand pack by Scanning Electron Microscopy (SEM), confirming the presence of catalyst particles through the entire media and suggesting that the initially formed catalyst particles sizes remained at the nanometer range during the entire experiment (no aggregation observed).

CHAPTER 3: EXPERIMENTAL SECTION

This chapter includes the detailed description of the activities carried out as part of the experimental plan of the present thesis. This part has been divided into five sections; the first one contains general information about the processes employed in this research, the following shows a description of the feedstock used in the experiments. The analytic methods section, describes all the characterization tools used for feedstock and products analysis; the fourth section shows a detailed description of the pilot plants involved, and finally, details about the experimental plan are presented.

3.1 Processing Scheme:

In order to conduct the kinetic study of ultradispersed catalytic hydroprocessing of vacuum residue and pitch from Athabasca bitumen, several processing steps have to be carried out. Figure 3.1 shows the processing scheme followed to accomplish the objective of this research. Athabasca bitumen is first submitted to a solvent deasphalting process to produce one of the products of interest which is the asphaltene-rich phase called pitch. Then the UD catalyst was incorporated into this sample prior the kinetic study.

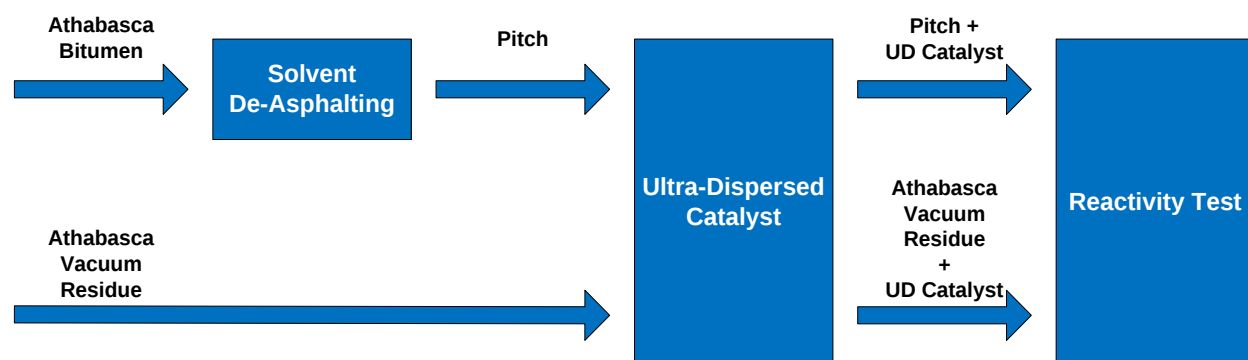


Figure 3.1: Processing scheme for this research

In the case of Athabasca vacuum residue, this sample was provided by Suncor Energy Inc. so there was no need to any additional steps before the nanocatalyst incorporation and the subsequent kinetic study.

3.2 Materials:

During the development of this research, the following materials were used as feedstocks:

3.2.1 Athabasca Bitumen:

A bitumen sample from Athabasca reservoirs obtained by means of Steam-Assisted Gravity Drainage (SAGD) was used as a feedstock for the pitch production. This sample was supplied by Japan Canada Oil Sand Limited, and some of its properties are shown in Table 3.1.

Table 3.1: Athabasca Bitumen Properties

Property	Value
API Gravity, °API	9.5
Viscosity, cP 40 °C	9,545
Distillation Cuts, wt%	
Naphtha (IBP-216 °C)	2.84
Distillates (216-343 °C)	15.37
VGO (343-550 °C)	34.02
Residue (>550°C)	47.77
Metal Content, ppm wt	
Nickel	78.7
Molybdenum	12.2
Vanadium	191.1

3.2.2 Athabasca Vacuum Residue:

Vacuum residue from Athabasca Bitumen obtained industrially by Suncor Energy Inc. at their upgrader facilities was used for the kinetic study; its properties are shown in Table 3.2:

Table 3.2: Athabasca Vacuum Residue properties

Property	Value
API Gravity, °API	2.4
Viscosity, cP 125 °C	10,600
Distillation Cuts, wt%	
Naphtha (IBP-216 °C)	0.0
Distillates (216-343 °C)	0.8
VGO (343-550 °C)	25.1
Residue (>550°C)	74.2
Metal Content, ppm wt	
Nickel	123.9
Molybdenum	16.5
Vanadium	297.9

3.3 Analytical Methods:

This section describes the analytical methods for the characterization of feedstocks and products involved in this thesis:

3.3.1 High Temperature Simulated Distillation (HTSD):

Simulated Distillation (SimDis) is a Gas Chromatographic technique (GC) that separates individual components in the order of their boiling point, and is used to simulate time-consuming

laboratory-scale physical distillation procedures. The separation is accomplished with a chromatography column coated with a nonpolar stationary phase, and uses a gas chromatograph equipped with an oven and injector which can be temperature programmed. A Flame Ionization Detector (FID) is used for detection and measurement of the hydrocarbon analytes. The chromatographic elution times of the hydrocarbon components are calibrated to the Atmospheric Equivalent Boiling Point (AEBP) of the n-alkane as described in a method from ASTM by using n-alkane reference material. In HTSD method, the calibration reference covers the boiling range 36-750 °C, which makes it appropriate for residue-containing samples (Villalanti, Raia and Maynard, 2000).

In this research, the methodology used consisted in the dilution of around 0.15 grams of sample with 20 ml of carbon disulfide (CS₂). Sample and solvent were weighted inside of a 20 milliliter vial, once homogenized it was transferred to a 2 milliliter vial. The vials were placed in an Agilent Gas Chromatograph model 6890N coupled with an automatic injector (series 7683B) calibrated for 1 microliter injection volume. The sample was eluted with helium as a carrier gas into a FID detector. The GC is controlled via *ChemStation* software (by Agilent), and the chromatographic data were analyzed and converted into a True Boiling Point with the *SimDis Expert* software provided by Separation Systems.

3.3.2 API Gravity:

This parameter was calculated indirectly by measuring the sample density and applying Equation 1. The measurement of the density was performed using a technique developed by Carbognani and coworkers (2011) based on solution pycnometry. For each sample, between 0.7 to 1.0 grams were weighted in 20 milliliters vials, then mixed with about 5 milliliter of toluene and shaken until the sample dissolved completely in the solvent. The mixture was quantitatively

transferred into a pycnometer rinsing the vial with toluene, being the pycnometer previously calibrated with pure water and solvents, and introduced in a thermal bath set at 15.6 °C. While reaching thermal equilibrium conditions, toluene was added as needed until the capillary tube was totally filled. Once stabilized, the pycnometer was capped, dried and weighted. Finally, the sample density was calculated by using:

$$\rho_s = \frac{m_s}{V_P - \frac{m - m_s}{\rho_T}} \quad \text{Equation 7}$$

Where:

ρ_s : Sample density [g/cm^3]

m_s : Sample mass [g]

V_P : Pycnometer volume [cm^3]

m : Total mass [g]

ρ_T : Toluene density [g/cm^3]

3.3.3 Viscosity:

Two procedures were used in this work for viscosity measurements depending on the viscosity of the sample. They will be described as follow:

3.3.3.1 Low Temperature Viscometer:

This procedure was used when viscosity measurements were possible at temperatures lower than 100 °C, specifically for Athabasca vacuum residue samples and its hydroprocessed products. The viscometer employed was a Brookfield DV-II+Pro coupled with a thermal bath (TC-502). The principal operation of the DV-II+Pro is to drive a spindle, contacting a film of test fluid, measuring the torque of a calibrated spring. The measurement range of a DV-II+Pro (in centipoise) is determined by the rotational speed of the spindle, the size and shape of the spindle,

the sample thickness in contact with the rotating spindle, and the full scale torque of the calibrated spring (Brookfield Engineering Laboratories, 2014).

3.3.3.2 High Temperature Viscometer:

High Temperature Viscometer, for temperatures greater than 100 °C, was used for heavier samples such as pitch and its hydroprocessed products. The equipment used was a Thermosel System supplied by Brookfield which included a viscometer DV-II+Pro, a heating chamber and a temperature programmable controller. This device is located inside of an enclosure to ensure inert environment (nitrogen) under sub-atmospheric pressures; the purpose of this setup is to prevent sample oxidation and degradation during viscosity measurements, especially at high temperatures. Even though the geometry of the body immersed in the fluid is different, the viscosity measurement principle is the same as the low temperature viscometer.

3.3.4 *Micro-Deasphalting:*

Micro-Deasphalting technique was used in the present research in order to determine the asphaltene content of feedstock and products. It consists in mixing 0.4 grams of sample with 20 milliliter of n-pentane or n-heptane in a beaker placed over a heating plate at 100 °C, for 30 minutes. Ultrasonication is used to help the formation and growth of solid particles, solvent evaporation was minimized by covering the beaker with a Petri dish. The mixture is then cooled down to ambient temperature and filtered using a tared Teflon membrane (0.45 micrometer pores, GH Polypro 47 mm Hydrophilic Polypropylene from Pall corporation). The membrane is dried in an oven at 100 °C for 10 minutes. Asphaltene content is calculated as the ratio of the recovered solids (asphaltenes) weight to the initial sample weight. In this work the solvent used in the Micro-Deasphalting method was n-pentane, so asphaltene content is expressed as n-pentane insoluble unless otherwise specified.

3.3.5 SARA Analysis:

SARA analysis (Saturates, Aromatics, Resins and Asphaltenes), separates any crude oil components according to their polarizability and polarity. Saturates family comprises linear, branched and cyclic paraffins, which are non-polar. Aromatics, as shown previously, comprise hydrocarbons with one or more aromatic rings which are slightly polarizable. The remaining two fractions, resins and asphaltenes, have polar substituents (Fan, Wang et al., 2002). SARA analysis method conducted at the CBUG is a two-step procedure, the first of which consists in the application of the above described Micro-Deasphalting method (see 3.3.4), and the second step consist in Thin Layer Chromatography with Flame Ionization Detector (TLC-FID) analysis of the malthenes phase gotten in the previous stage (Larter, 2007).

Malthene sample is diluted with toluene to reach a concentration of 10 mg of malthenes per milliliter of solution. Then one microliter aliquots are spotted over quartz rods covered by a thin film of sintered silica gel microparticles. Saturates are eluted with n-heptane up to 10 centimeters; aromatics are eluted with toluene up to 6 centimeters, while resins remain near the spotting zone of the rod. The rods are quantified for carbonaceous material by passing them through the FID flame with a motorized device incorporated into the chromatograph Model MK-6 Iatroscan supplied by IATRON Laboratories. Signals are acquired and processed by PeakSimple v3.21 software by SRI Instruments.

3.3.6 Metal Analysis:

Since the catalysts used in this work were a trimetallic formulation (Ni\Mo\W), metal analysis was used to determine the amount of these metals in the feedstock before and after catalyst preparation and then quantify the effective catalyst concentration. Metal analysis comprises two steps: sample digestion and Inductively Couple Plasma (ICP) analysis. The

method used for the digestion (mineralization) was developed by Berezinski et al. (2010), which consist in mixing 0.3 grams of sample with 10.5 milliliters of nitric acid, 1.0 milliliter of phosphoric acid and 25 microliter of cobalt standard solution (1000 ppmwt). The mixtures were then digested into the Microwave Accelerated Reaction System (MARS 6) provided by CEM Corporation. The equipment was programmed to heat at 10 °C per minute up to 210 °C and remained in that temperature for 20 minutes. After a cooling down period, digested samples were diluted to a known volume with water and analyzed with ICP-AES (IRIS Intrepid II XDL by Thermo Scientific), where metals in solution are atomized with a pressurized argon plasma. Previous calibration of each characteristic emission wavelengths allows the quantification of particular elements. An in-house prepared standard solution containing external calibration standards was used to calibrate the equipment. This methodology allows for the determination of Ni, Mo, W, Fe, V, and Co for the studied samples.

3.3.7 Gas Chromatography:

Compositional determination of gas samples was carried out by means of Gas Chromatography (GC), which was performed online by analyzing the gas taken directly from the source (pilot plant). A GC model 8610C supplied by SRI Instruments was employed; this apparatus is provided with four detectors: two Thermal Conductivity Detectors (TCD), one Flame Ionization Detector (FID) and one Flame Photometric Detector (FPD). TCD measures the difference in thermal conductivity in the carrier gas flow caused by analyte peaks. Due to its high thermal conductivity and safety, helium carrier is mostly used with TCD's. However, other carrier gases may be used such as nitrogen, argon or hydrogen (SRI Instruments, 2014). TCD1 used helium as a carrier gas allowing the detection of multiple hydrocarbon compounds, carbon

monoxide, carbon dioxide, and hydrogen at high concentrations. TDC2 used argon to detect hydrogen at low concentrations.

In the FID the gas sample is sent through a flame, which ionizes the eluted compounds and produces positive and negative ions, producing current signals collected by electrodes. This detector is suitable to detect any compound with hydrogen and carbon bonds (SRI Instruments, 2014). However, in this thesis the FID detector was not calibrated since optimum conditions setup for peaks separation were compatible for TCD's and FPD detectors. When compounds are burned in the FPD flame, they emit photons of distinct wavelengths. The FPD uses a photomultiplier tube (PMT) to selectively detect compounds containing sulfur or phosphorus as they combust in the hydrogen flame (SRI instruments, 2014). In this work FPD the detector was calibrated for hydrogen sulfide (H_2S) and Sulfur Dioxide (SO_2). Praxair gas mixture certified standards were used to calibrate all the detectors of the GC. PeakSimple v3.72 by SRI Instruments was used for GC control, data acquisition, processing and analysis.

3.4 Process Units:

This section refers to the description of all the process units used in each stage of this research. In general terms, the research processes can be classified in three major groups: de-asphalting, catalyst preparation, and kinetics study. Each stage or group is represented by a pilot plant, described as follows:

3.4.1 Solvent De-Asphalting Unit (SDA):

De-Asphalting operations were carried out at the Catalyst for Bitumen Upgrading Group (CBUG) facilities at the University of Calgary. The SDA unit was built by CBUG personnel with the sponsorship of CNOOC-Nexen Inc. After initial exploratory runs with the unit, several modifications were proposed and applied in the context of this research in order to improve

experiment accuracy, repeatability and safety of the experiments. All design details of the Solvent De-Asphalting (SDA) Unit shown in this section refers to its final design.

3.4.1.1 Process Description:

Solvent De-Asphalting consists in a separation process based on liquid-liquid extraction. The key property which promotes the separation is solubility, since asphaltenes have a low or no solubility in paraffinic solvents in comparison with paraffins, aromatics and resins. In this research, the solvent used was n-pentane because this is one of the most used solvents at industrial scale, and due to the higher yield in DAO when compared with lighter paraffinic solvents such as propane (Wauquier, 1998). Figure 3.2, the process flow diagram of the Solvent De-Asphalting pilot plant, shows all the pieces of equipment, pressure regulators, main process lines and controllers. For the SDA unit, the process was conceptualized in batch mode being a stirred tank the heart of the plant. The plant has been designed to process different type of feedstocks including whole crude oil, bitumens and residue fractions.

The process start with an inertization procedure, which consists in repeated pressurization (with nitrogen) and purge of the entire plant until a non-explosive environment is reached, typically repeating this procedure three times is deemed sufficient to warranty these conditions. The required amount of solvent, calculated based on the plant throughput and the solvent to oil ratio, is transferred from the Solvent Tank (TK-2) by using the Solvent Pump (P-2). Then the Extractor (R-1) is pressurized up to 300 psig, and heated up to extraction temperature. The extractor consists in a 5 gallons stirred tank (PARR Instrument Company, model 4550) provided with a heating jacket through which circulates heating oil in a close-loop, heated by a thermal bath (Extractor Heater, E-1).

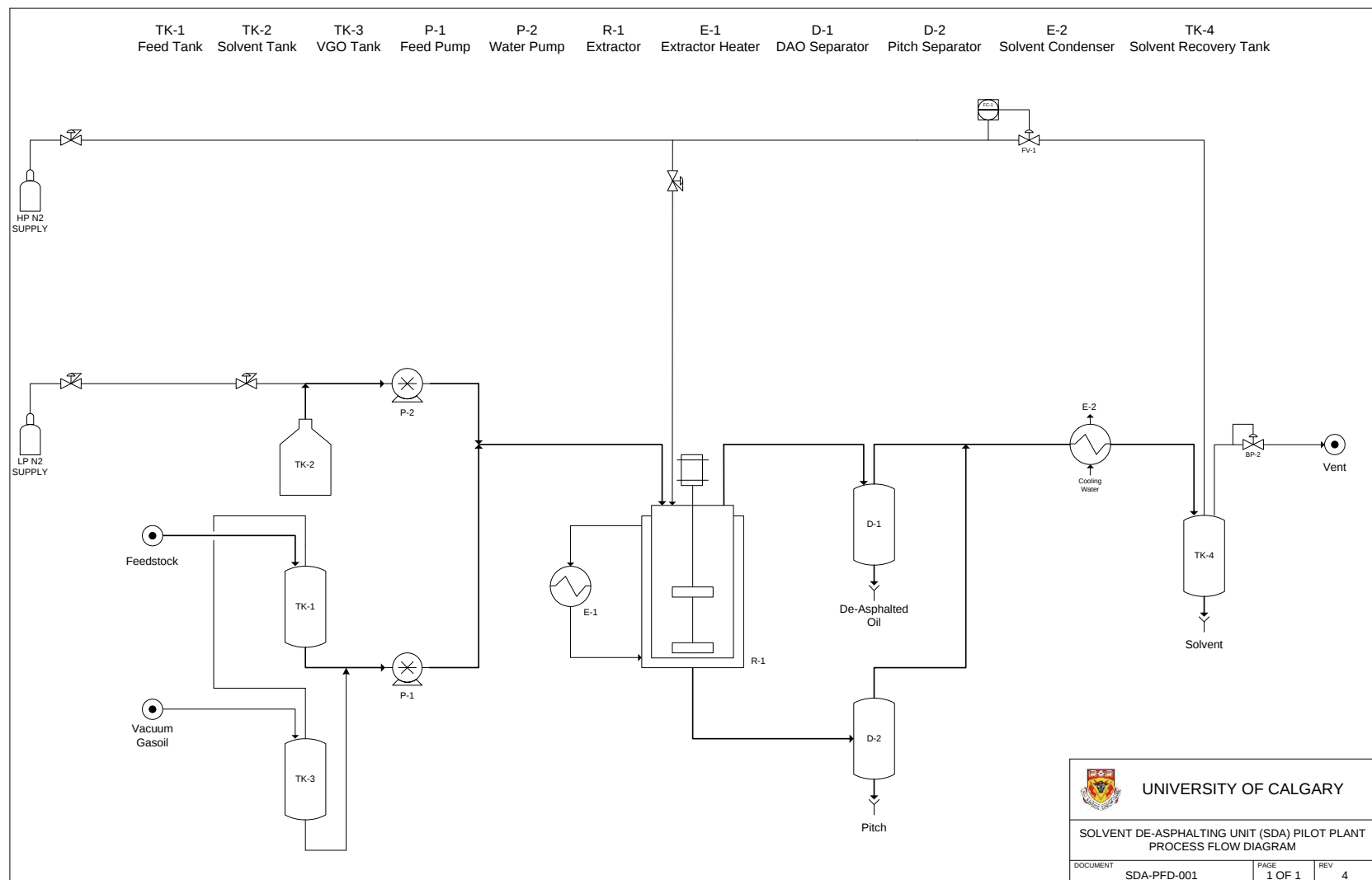


Figure 3.2: Solvent De-Asphalting Unit Process Flow Diagram

Agitation is started to increase the internal heat transfer of the solvent, which helps to speed up the heating process. The next step is to heat up the rest of the plant up to a temperature high enough to easily pump the fluid to be deasphalted; when working with bitumen temperatures within the range of 75-100 °C are required; if the feedstock is vacuum residue temperatures within the range of 125-150 °C are necessary for this purpose. Once the extractor temperature has reached the desired value and is stable, the feedstock (bitumen or vacuum residue) is transferred from the Feed Tank (TK-1) to the extractor by using the Feed Pump (P-1). Oil amount is controlled by allowing it to flow into the extractor for a specific period of time calculated with the calibration of the Feed Pump (P-1) previously performed.

When the required amount of oil has been fed into the extractor, its pressure is adjusted up to 500 psig to make sure that solvent is kept in liquid phase. Then continuous agitation for a period of 60 minutes at 500 rpm is allowed in order to promote a good mixing between the oil and the solvent. Subsequently, agitation is stopped and 60 minutes of settling time are allowed to promote phase separation, i. e. an upper phase enriched in solvent and de-asphalted oil, and a denser phase (pitch) with a high concentration of asphaltenes, plus a small fraction of resins and solvents. Agitation and settling times were chosen based on previous published results in de-asphalting carried out in batch mode (Sattarin et al., 2006; Sámano et al., 2009; Al-Sabawi et al., 2011).

Once the settling time has elapsed, the upper phase is slowly transferred from the extractor to the DAO Separator (D-1) where n-pentane is vaporized, condensed in the Solvent Condenser (E-2) and stored in the Solvent Recovery Tank (TK-4). The lower phase is transferred to the Pitch Separator (D-2), and similarly to the previous step the remaining solvent in the pitch is vaporized, condensed and recovered. Finally, recovered solvent, de-asphalted oil and pitch

products are drained from their tank, weighted, and samples are taken for analytical methods. For more details about configuration and operation of the Solvent De-Asphalting Unit go to Appendix A: Standard Operating Procedure for Solvent De-Asphalting Unit, and Appendix B: Piping & Instrumentation Diagram for Solvent de-asphalting unit.

3.4.1.2 Experimental Runs:

Experimental runs with the SDA unit were carried out in two stages: the goal of the first step was to evaluate the performance of the unit which led to propose changes in design to optimize the operating procedures and improve experimental accuracy. All changes to the Solvent De-Asphalting unit were applied taking into consideration the following factors:

- Process Safety: focused on preventing fires, explosions, spills of chemicals and/or hazardous materials.
- Process Control: dealing with mechanisms for maintaining process variables within a specific range for safety or processes considerations.
- Experimental Accuracy: targets the minimization of sources of error, increasing confidence, repeatability and quality of the obtained results.

The second phase was focused on the final testing on the unit, and processing experiments for producing pitch from Athabasca bitumen to continue with the processing scheme as illustrated in Figure 3.1. Table 3.3 shows a summary of the experimental runs carried out with the SDA unit, feedstocks used, process conditions, and goals for each experiment.

Table 3.3: Description of experimental Runs for the Solvent De-Asphalting Unit

Stage	Name	Process Characteristics						Goal
		Feed	Solvent	Temperature (°C)	Pressure (psig)	Solvent-to-Oil Ratio	Number of Runs	
Testing	Cold	N/A	Water	Ambient	150	N/A	1	Test solvent circuit, extractor agitation
	Hot	VGO	Water	100	300	10	2	Test temperature controllers, extractor heater
	AVR	Athabasca	n-Pentane	150	500	10	1	Exploratory Run
		Vacuum Residue						
Validation & Processing	AVR	Athabasca	n-Pentane	150	500	4	1	Plant Design Validation
		Vacuum Residue						
	AB	Athabasca Bitumen	n-Pentane	150	500	4	10	Verify experiment repeatability Pitch production for kinetic study

3.4.2 *Ultra-Dispersed Catalyst Preparation Unit:*

The Ultra-Dispersed Catalyst Preparation unit (UDCP) unit is a proprietary design equipment by CBUG researchers at the University of Calgary, used in this project to incorporate nanocatalyst particles into the feedstock before conducting the kinetic study. Due to the pitch and vacuum residue high viscosity, a previous dilution was required to decrease their viscosity sufficiently to pump them at room temperature into the UDCP unit. A dilution of 50 wt% toluene and 50 wt% pitch was required to reach a viscosity of 500 centipoises, and a dilution of 25wt% gasoline and 75 wt% was prepared in the case of vacuum residue to reach the same value of viscosity which was a suitable target for the pumping devices installed in the unit. The dilution procedure consisted in mixing the sample and the diluent in a stirred tank pressurized at 300 psig and heated up to 150 °C, the mixture was agitated for 60 minutes at 500 rpm.

The method for catalyst preparation is based on short-lived emulsion as it has been extensively used at the CBUG (Galarraga et al., 2010; Rendon, 2011; Loria et al., 2011; Coy, 2013; among others). The diluted pitch is mixed with 1 wt% of an in-house formulated surfactant (SPAN 80 from Sigma and TWEEN-80 from Sigma Aldrich at a ratio of 65:35 in weight) for 30 minutes. Then the mixture is fed into the UDCP unit where is mixed with aqueous solutions of metal salts (ammonium heptamolybdate, ammonium metatungstate and Nickel Acetate) and the sulfiding agent (Ammonium Sulfide) to activate the formation of metal sulfides known as active species in hydroprocessing reactions (Galarraga et al., 2010). The flow of each solution and the sulfiding agent are controlled to reach the desired catalyst concentration in the resulting product. This mixture is sent to the decomposition reactor which operates at temperatures higher than 360 °C, to efficiently decompose the salts and produces the metal nanoparticles, and lower than 400 °C to avoid excessive thermal cracking of the oil. Residence time in the decomposition reactor is

about 2 minutes. Then the reactor product is sent to a hot separator whose objective it to distill the diluent and the water from the metal dispersions. The bottom product from the hot separator comprises the pitch with the incorporated ultradispersed nanocatalyst. Vapors coming from the hot separator (water and diluent) are condensed and recovered in the cold separator. Figure 3.3, an ultra-dispersed catalyst preparation procedure diagram, shows all the involved steps (including the UDCP unit) for the incorporation of catalyst nanoparticles into the feedstock.

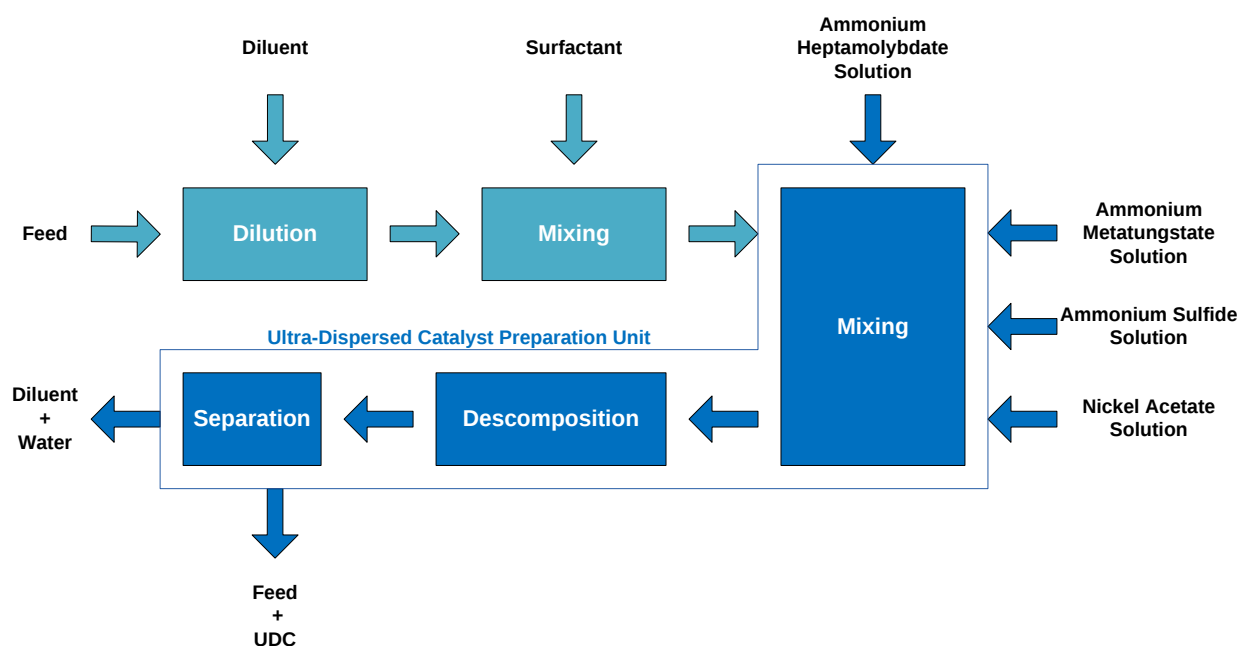


Figure 3.3: Ultra-Dispersed Catalyst Preparation Procedure

Targeted values for catalyst concentrations were based on previous investigations, Galarraga et al. (2010) used 1,000 ppmwt of trimetallic Ni/Mo/W (Ni/metals = 0.30 and Mo/Ni=3.0) for Athabasca bitumen, Loria et al. (2011) used 1,200 ppmwt with the same formulation and feedstock. In the work presented by Rendon (2011), two concentration levels with Athabasca Bitumen using sandpacks were studied; low catalyst concentration was 220

ppmwt (Ni/metals = 0.21 and Mo/Ni=1.27) and high catalyst concentration which was 700 ppmwt (Ni/metals = 0.17 and Mo/Ni=2.76). Finally, Coy (2013) used a catalyst concentration of 650 ppmwt (Ni/metals = 0.15 and Mo/Ni=3.1) using Athabasca vacuum residue in a sandpack. Table 3.4 shows targeted and actual (nominal) values for each feedstock processed in the UDCP unit for the present work.

Table 3.4: Catalyst concentration for this research

Feedstock	Targeted Values		Nominal Values	
Athabasca	1,200 ppmwt		1,107 ppmwt	
Vacuum Residue	Ni/Metals = 0.30	W/Mo = 3.0	Ni/Metals = 0.21	W/Mo = 2.9
Pitch	720 ppmwt		773ppmwt	
	Ni/Metals = 0.30	W/Mo = 3.0	Ni/Metals = 0.29	W/Mo = 2.5

3.4.3 Reactivity Test Unit 2:

Reactivity Test Unit 2 is a pilot plant located at Catalyst for Bitumen Upgrading Group (CBUG) facilities at the University of Calgary. The unit was initially built for the research conducted by Rendon (2011) and subsequently expanded by Coy (2013). The initial design and later modifications were conceived to have the capability of performing kinetic studies of a variety of feedstocks, especially heavy fractions such as vacuum residue, bitumen or pitch, with or without hydrogen, with or without UD catalyst, and under different condition of pressure and temperature. In this research, it was used targeting the study of Ultradispersed Catalytic Hydroprocessing of Athabasca vacuum residue and pitch at in-reservoir conditions.

3.4.3.1 Process Description:

The Reactivity Test Unit 2 (RTU-2) has been conceived to carry out kinetic studies of different feedstocks under a variety of process conditions. It consists in a multiple reactor unit with the capability of working under long residence times. This pilot plant has been provided with safety and process control features which allow the user to run experiments remotely without compromising safety operation or results quality. Figure 3.4, a RTU-2 process flow diagram, show the major pieces of equipment and features of the unit. Major details of the unit in terms of design basis, specifications, operation procedures, and troubleshooting is presented in the work presented by Coy (2013) from the CBUG.

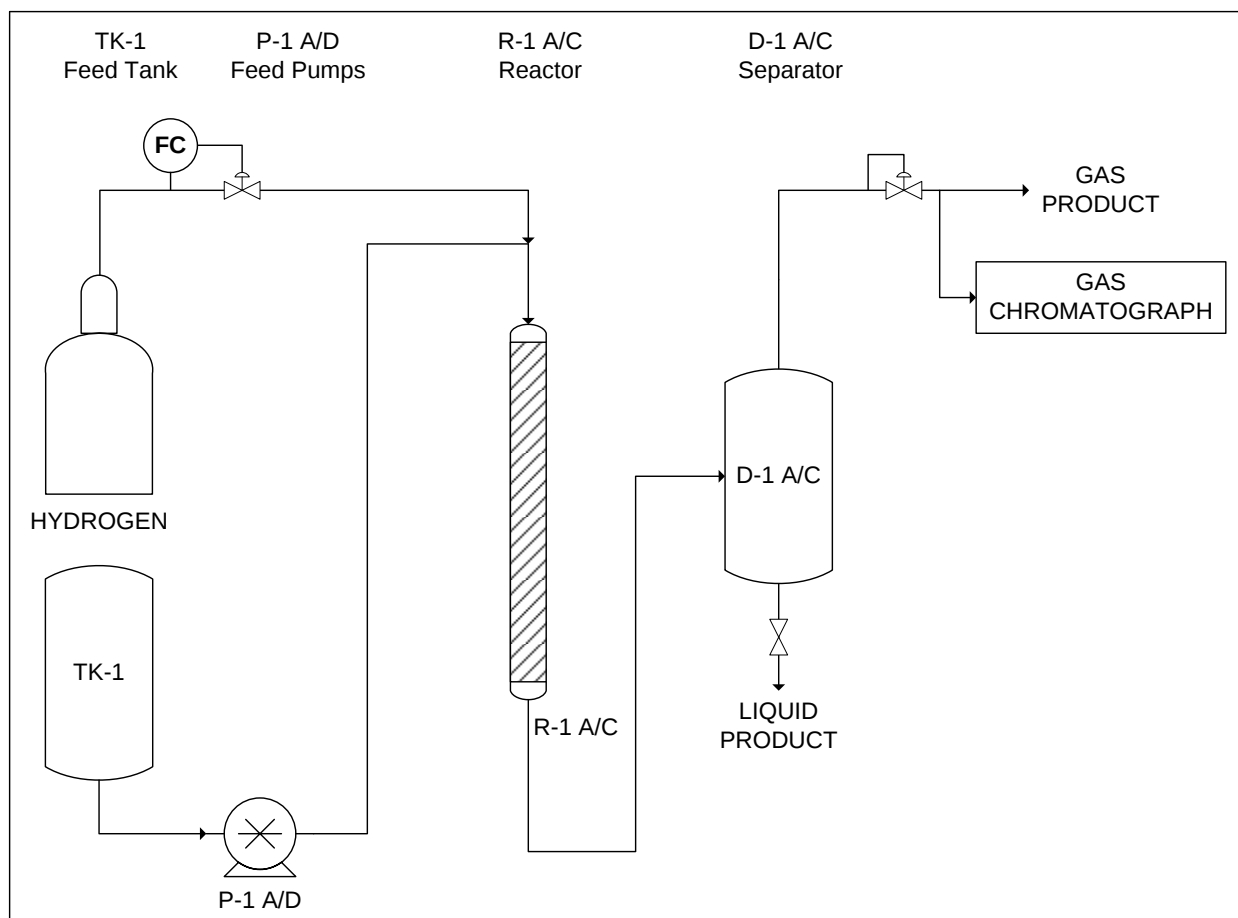


Figure 3.4: Reactivity Test Unit 2 Process Flow Diagram

The feedstock is stored and heated by means of temperature-controlled heating tapes in order to decrease the viscosity up to a point that can be pumped efficiently through the system. When working with vacuum residue, temperatures around 150 °C are required; in case of pitch, higher temperatures are necessary to reach transportability (approximately 180 °C). The feedstock is transported from Feed Tank (TK-1) by Feed Pumps (P-1 A/D), pumps 1 to 3 are used to deliver the feedstock to each reactor system while pump 4 is used as a backup. The feedstock is then heated up to 20 °C lower than the targeted reaction temperature, mixed with a controlled hydrogen flow and sent to the respective reactor. Reactors (R-1 A/C) are configured with a downflow pattern, provided by two temperature-controlled heating tapes to ensure that thermal energy is uniformly distributed across the reactor length. Additionally, a 7 point thermocouple is placed in the center of the reactor to monitor a detailed reactor temperature profile, which is used to determine its average temperature.

The product of the reactor is then cooled down to approximately 80 °C and sent to the Separators (D-1 A/C), where gases comprised by unreacted hydrogen, product gases (Hydrogen Sulfide, Carbon Dioxide, Carbon Monoxide, pentane and lighter hydrocarbons) and nitrogen used for pressurization purposes are separated from the liquid product. Reactor pressures are controlled by using back-pressure regulators placed at the gas outlet of the Separators. Gas flowrate is measured online using a volumetric gas flowmeter provided by Ritter (model MGC MilliGas Counter); samples from this stream are taken for compositional analysis using a GC. Finally, product gases are neutralized in a Potassium Hydroxide trap before being disposed in the extraction system. Liquid products drained during mass balances procedures are stored for subsequent analysis.

3.4.3.2 Experimental Runs:

Reactivity study runs were conducted with the objective of generating the minimum experimental data required to develop a kinetic model by means of numerical regression. Table 3.5 shows all the runs conducted in this stage. For all conditions 500 psig of pressure were fixed as well as the hydrogen-to-oil ratio with a value of 90 standard cubic centimeter of hydrogen per cubic centimeter of oil.

Table 3.5: Experimental Runs for the Reactivity Study

Name of the Run	Feed	Reactor Temperature (°C)	Residence Time (h)
AVR-320-30	Athabasca Vacuum Residue	320	30
AVR-380-20*		380	20
AVR-380-40*		380	40
AVR-380-50*		380	50
AVR-395-24	Athabasca Pitch	395	24
AP-320-96		320	96
AP-320-120		320	120
AP-350-48		350	48
AP-350-96		350	96
AP-380-24		380	24
AP-380-48		380	48

* Meneses (2013).

CHAPTER 4: SOLVENT DE-ASPHALTING UNIT

In this chapter all results related to the Solvent De-Asphalting pilot plan redesign, optimization and operation are presented. Redesign of the unit was essential to improve experiments accuracy and repeatability. Modifications were carried out in two stages, in the first one they were based on investigations of similar systems published by other researchers, and on process simulation of the unit carried out with an commercial software available at the University of Calgary for academic purposes. Changes on the second stage were proposed as a result of the analysis based on an exploratory run using Athabasca vacuum residue; once they were implemented, a validation run was performed to corroborate the behavior of the unit. Finally repeated runs (at the same process conditions) were executed to produce pitch from Athabasca Bitumen with the purpose of producing enough amount of sample to complete the tests proposed in the experimental plan. These results were also used for a statistical validation of the experiments.

4.1 Solvent De-Asphalting preliminary modifications:

Original design of the unit considered the use of filtering devices with the purpose of avoiding asphaltenes particles been withdraw from the extractor within the De-Asphalted Oil stream. However, there was a concern related to the possibility of filter plugging which led to the revision of previous works related to Solvent De-Asphalting setups working in batch mode using stirred tanks (autoclaves) as an extraction device. Earlier investigations (Sattarin et al., 2006; Sámano et al., 2009; Al-Sabawi et al., 2011) showed that if a sufficiently long settling time is provided, DAO and asphaltene phases can be easily separated by slowly suctioning the upper phase though a pipe dipped into it.

Based on this information, extractor internals were removed and two levels of sampling were used for DAO withdrawing. Figure 4.1, an extractor internals configuration scheme, shows the final layout of the system. The interfase between upper and lower phases was estimated using the feedstock's asphaltene content, the amount of sample to be deasphalted, and the solvent-to-oil ratio for the experiment. One inch of safety margin was added to this estimation. This procedure is described in Appendix A: Standard Operating Procedure for Solvent De-Asphalting Unit.

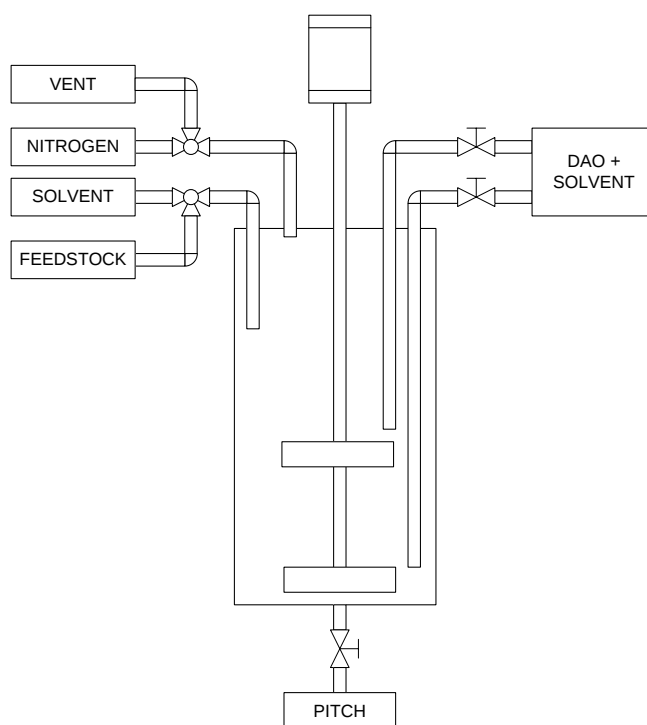


Figure 4.1: Extractor configuration scheme

Another modification that was necessary, not only in terms of accuracy but also for safety reasons, was the incorporation of a solvent condenser. The original design of the unit did not consider a solvent condenser; however, a study based on the use of a commercial process simulation package was carried out to determine whether or not it was required. A simulation

model was built in UniSim® Design provided by Honeywell, using Peng Robinson equation of state as a thermodynamic model for working with hydrocarbon mixtures. A distillation curve of a sample of DAO from Athabasca vacuum residue obtained in a laboratory scale deasphalting unit was introduced to model the DAO, and n-pentane was chosen from the component databank to model the solvent. Laboratory procedure uses high solvent-to-oil ratios (as high as 20), pitch is collected by means of filtration, similar to the Micro-Deasphalting technique described in section 3.3.4 of this thesis. Bubble point temperature calculations were implemented at different pressures and solvent-to-oil ratios. Results are shown in Figure 4.2, which contain bubble point curves at two different solvent-to-oil ratios.

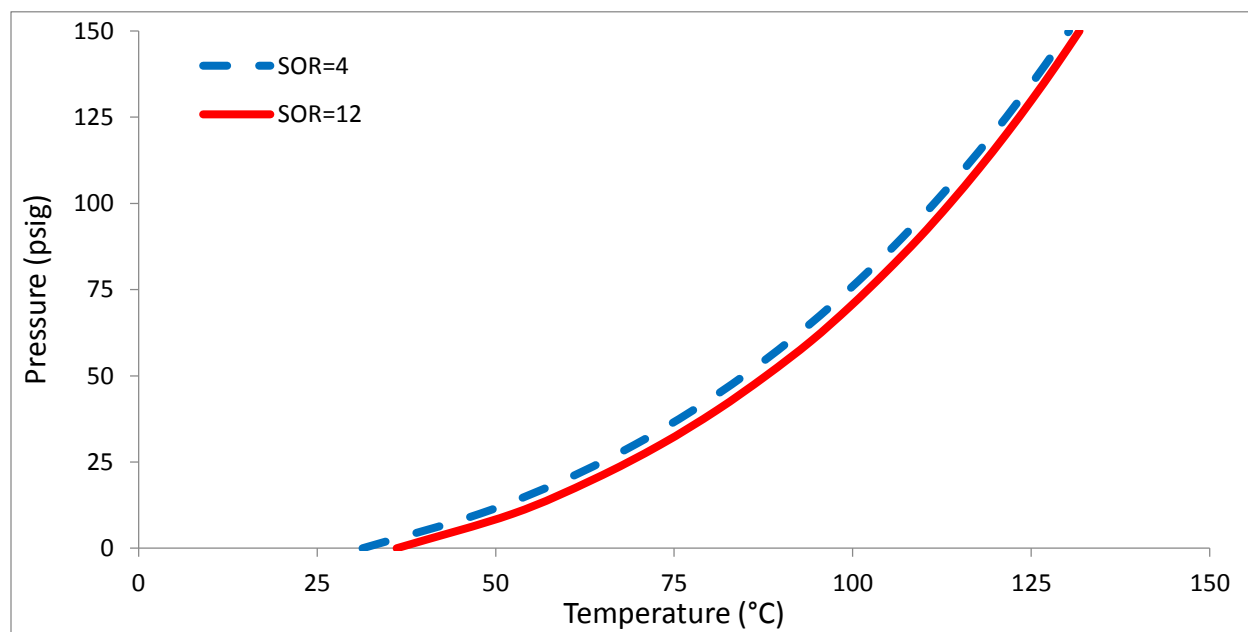


Figure 4.2: Bubble point curve for DAO and n-pentane mixtures.

This information confirms the need of a solvent condenser, because if the solvent and DAO mixture (upper phase) were transferred from the extractor to a lower pressure system, e.g. 50 psi, the bubble point temperature at that pressure would be about 87 °C, so any temperature

higher than this value, such as 150 °C as targeted in this research, would represent significant losses of solvent affecting mass balance calculations and causing an unsafe operating condition.

4.2 Exploratory run:

This run targeted an evaluation of the SDA unit behavior after the implementation of the preliminary modifications. Athabasca vacuum residue was deasphalted with n-pentane at 140 °C and 500 psig, using a solvent-to-oil ratio of 10. In this experiment previous changes were proven to be successful since DAO and pitch separation were carried out without entrainment, i. e. pitch particles in the DAO and solvent phase; in addition, solvent losses were kept lower than 10%. Table 4.1 shows the mass balance summary of the experiment.

Table 4.1: Mass Balance Summary of Exploratory Run in the SDA unit

Parameter	Component	Value
Mass In (g)	Vacuum Residue	440
	Solvent	2,500
	Total	2,940
Mass Out (g)	Solvent	2,271
	DAO	177
	Pitch	120
	Total	2,569
Mass Balance (%)	Solvent	90.9
	Oils	67.7
	Total	87.4

From this information it can be concluded that oil mass balance was not closing at acceptable values ($\pm 5\%$ for the oil phase). This was confirmed with a visual examination of the plant, since significant amount of oil components, especially pitch, remained inside of the unit.

For solving this issue a dead volume reduction was required, specifically in the sections containing the pitch product. Solvent mass balance can be considered as acceptable taking into consideration the high volatility of the n-pentane. Even though some efforts were made to minimize this factor, about 10 wt% of the solvent were systematically lost in each experiment.

4.3 Post Exploratory run modifications:

After the exploratory run, changes in the unit were addressed to improve oil mass balance to acceptable values, thus improving the overall mass balance of experiments. Dead volume reduction was done to the entire unit focused on the pitch section. In addition, the concept of the plant was changed by incorporating DAO and pitch separators, based on similar industrial deasphalting process such as: UOP/FW Solvent Deasphalting Process (see Figure 4.3) and or the KBR ROSE® process (Figure 4.4).

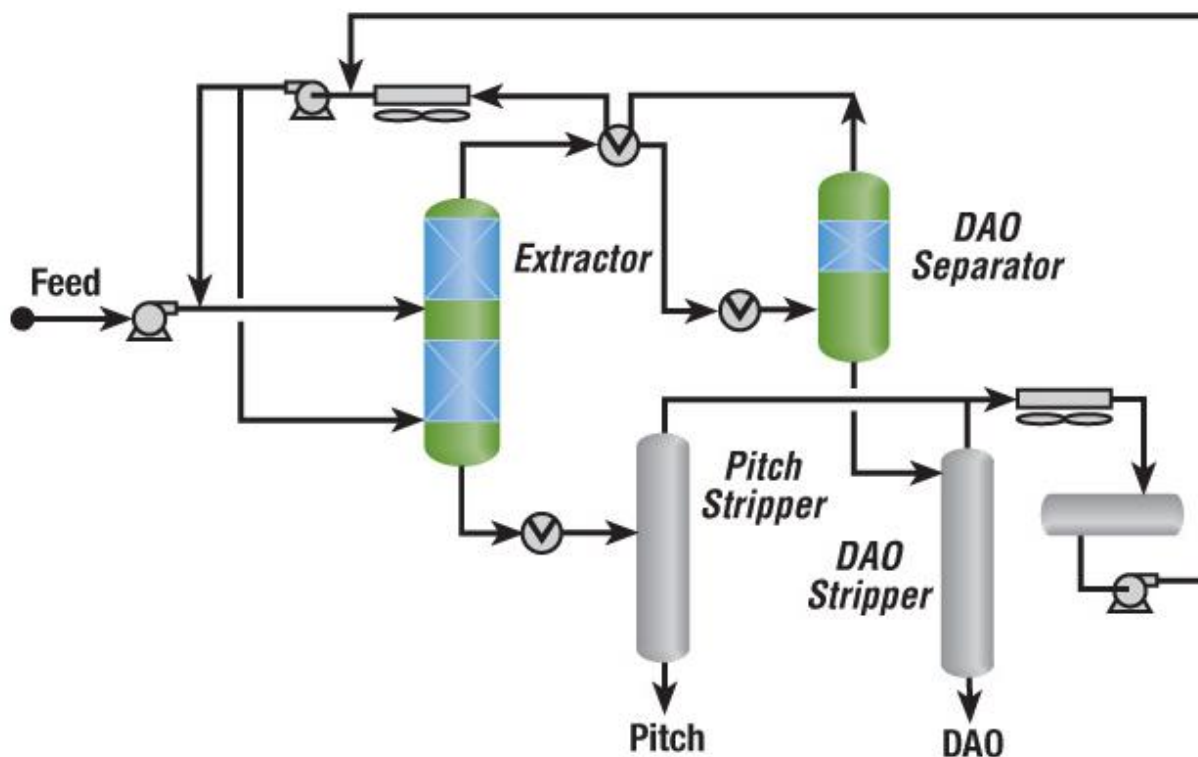


Figure 4.3: Process flow diagram for UOP/FW Solvent Deasphalting process

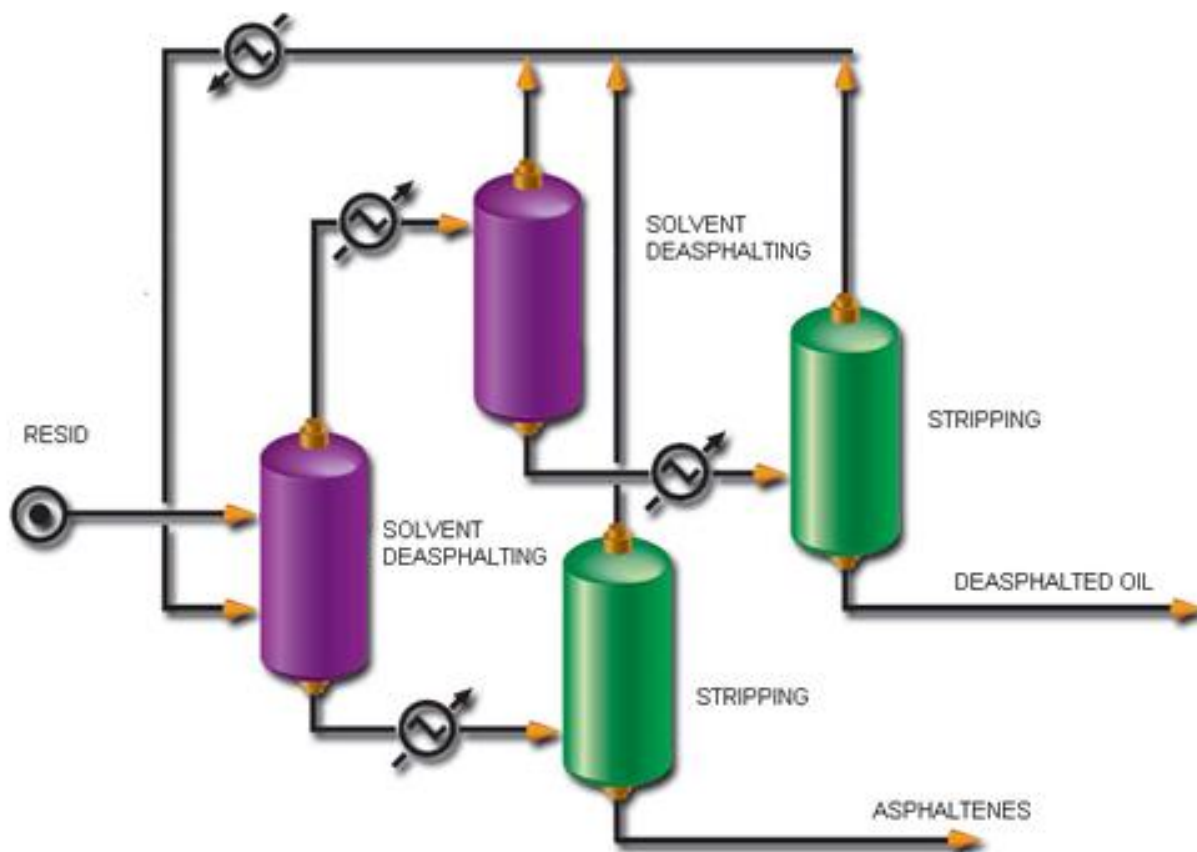


Figure 4.4: Process flow diagram for KBR ROSE® process

The DAO separator carries out the solvent separation in the plant by means of distillation. The initial design of the unit considered this process to be performed into an external rotary evaporator. However, by doing this, additional losses may be presented due to fluid transfer between pieces of equipment. Proper selection of conditions in the DAO separator have to be determined in order to achieve good separation between the solvent and the DAO, without incurring in undesirable losses. A sensitivity analysis was performed in a commercial process simulator (UniSim® Design by Honeywell) calculating the recovery of each product as a

function of the DAO separator temperature. Figure 4.5 shows simulated solvent and DAO recoveries as a function of the DAO separator at 50 psig.

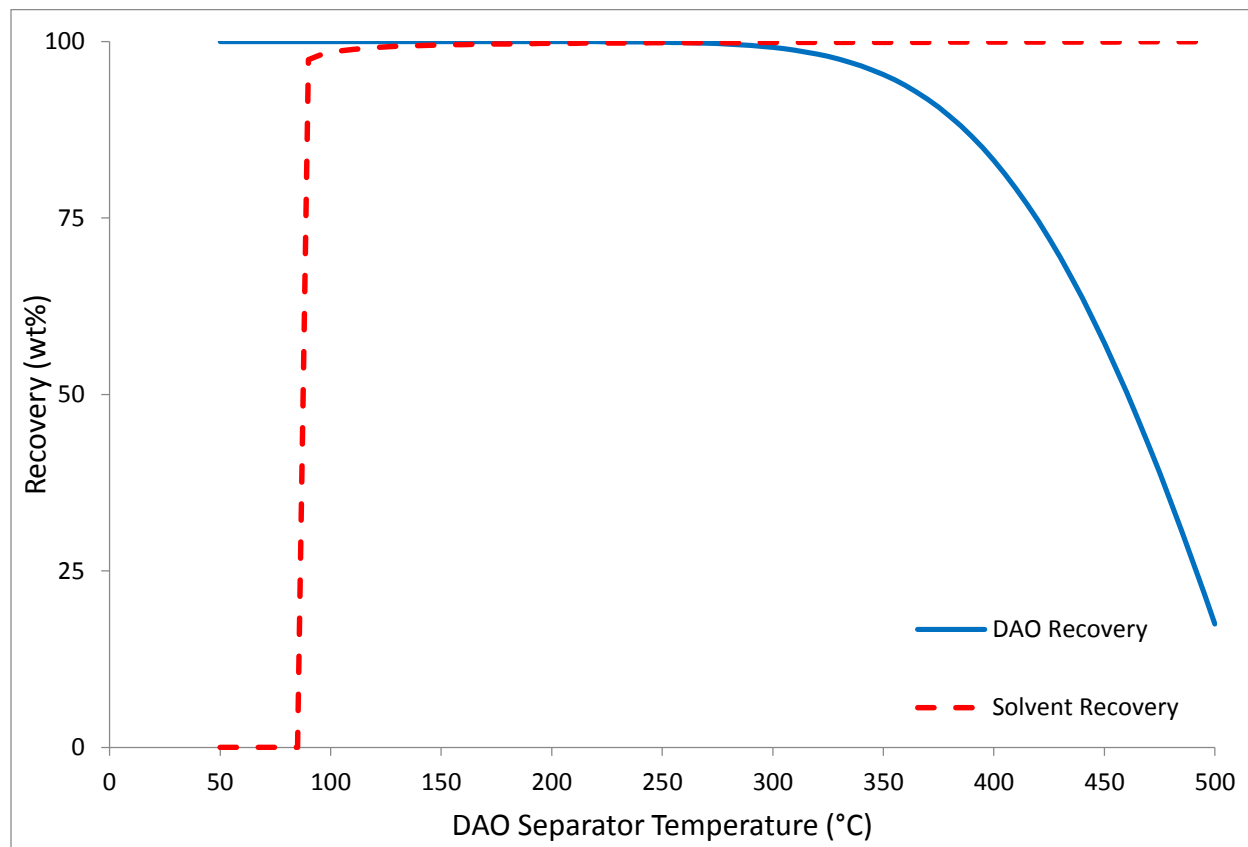


Figure 4.5: Simulated solvent and DAO recoveries as a function of DAO separator temperature at 50 psig

Solvent recovery was defined as the ratio of the mass of solvent in the top product to the mass of solvent in the feed to the DAO separation; similarly DAO recovery was defined as the mass of DAO in the bottom product to the mass of DAO in the feed. At temperatures lower than 87 °C (bubble point), there is no vapor product, yielding 0% and 100% of recovery for solvent and DAO respectively.

As the temperature increases, solvent is vaporized from the mixture and its recovery increases sharply. At certain temperature (high for practical purposes), DAO recovery decreases

since its vapor pressure is high enough to vaporize a fraction of it. From the preceding, it is clear that there is a compromise between solvent and DAO recoveries with respect to separation temperature. The optimum point would be the one yielding the maximum recovery for each product, in practical terms any temperature within the range of 205-270 °C would give recoveries higher than 99.75%.

The Pitch separator helps to recover the remaining amount of solvent present in the pitch product. Because of the significant difference of solvent and pitch boiling points, the pitch separator temperature is not as critical as in the DAO separator case. In consequence, any temperature within the range of 250-350 °C would produce an acceptable separation between the solvent and the pitch. The use of high temperatures, equal or higher than 300 °C, produce a substantial decrease in pitch viscosity making easier to drain it from the separator.

4.4 Validation experiment:

This run targeted the verification of the implemented changes of the unit as well as the validation of the SDA unit as an acceptable setup to perform the subsequent set of experiments to produce representative samples of pitch. Athabasca vacuum residue was deasphalted with n-pentane at 150 °C and 500 psig, setting a solvent-to-oil ratio of 4. The solvent-to-oil ratio was reduced to the minimum industrially practiced with the objective to maximize the production of pitch per run, reducing the amount of runs required for producing the targeted amount of pitch required for the following processing steps.

Table 4.2 shows a mass balance summary for the validation run. Results show that the implemented changes in the plant were successful, since oil mass balance improved from 67.7%

to 99.7%. However, solvent mass balance stayed pretty much at the same value; at present it is believed that missing solvent is due to its high volatility.

Table 4.2: Mass Balance Summary of Validation Run in the SDA unit

Parameter	Component	Value
Mass In (g)	Vacuum Residue	970
	Solvent	2,520
	Total	3,490
Mass Out (g)	Solvent	2,283
	DAO	568
	Pitch	399
	Total	3,250
Mass Balance (%)	Solvent	90.6
	Oils	99.7
	Total	93.1

A summary of the Athabasca vacuum residue and its solvent deasphalting product properties is shown in Table 4.3. DAO obtained from Athabasca vacuum residue showed better quality compared to the feedstock: API gravity was 4.6 °API higher, viscosity reduced by 95.4% and C5-asphatenes content decreased by 95.0%. The reported yield in DAO of this experiment was 58.5 wt%. The increase in API gravity and viscosity reduction basically respond to the

reduction of the asphaltene content, which is the major cause of the high viscosity in heavy oil fractions. DAO yield was lower than expected; this is because the separation between the two phases is controlled by the height of the pipe dipped into the upper phase, which was estimated by the asphaltene content on the feedstock plus a safety margin of 1 inch. This safety margin is translated into a DAO yield reduction (or a pitch yield increment) which systematically will be observed in the rest of the experiments. Pitch (asphaltene-rich phase) showed lower API gravity and higher viscosity with respect to the initial feedstock, as expected.

Table 4.3: Athabasca vacuum residue deasphalting property summary

Property	Athabasca Vacuum Residue	De-Asphalted Oil	Pitch
API Gravity (°API)	-2.9	1.7	-4.8
Viscosity @ 125 °C (cP)	960	44 ¹	45,000 ¹
C5-Asphaltenes (wt%)	23.9	1.2	56.0 ²

¹Extrapolated by exponential equation fitting, ²Calculated by mass balance

In order to evaluate products quality from the boiling point of view, distillation curves using HTSD method were employed. Figure 4.6 shows distillation curves for Athabasca vacuum residue, its solvent deasphalting products (DAO and pitch), and a simulated blend calculated based on the products distillation curves and their yields.

The results showed expected tendencies: the DAO product was the lightest since contains the major fraction of paraffins, aromatics and resins present in the feedstock; on the contrary, the pitch showed the highest boiling point due to its high asphaltene content. Also, the DAO and vacuum residue showed similar initial boiling points because the low boiling point components tend to be extracted with the solvent phase, thus partitioning into the DAO product. Simulated

blend distillation curve perfectly matches the feedstock with an average relative difference of 1.3% that can be attributed to typical HSTD experimental errors. This also confirms the validity of the mass balance performed in this experiment. Figure 4.7 shows the component distribution by boiling point for Athabasca vacuum residue, its solvent deasphalting products, and for the simulated blend.

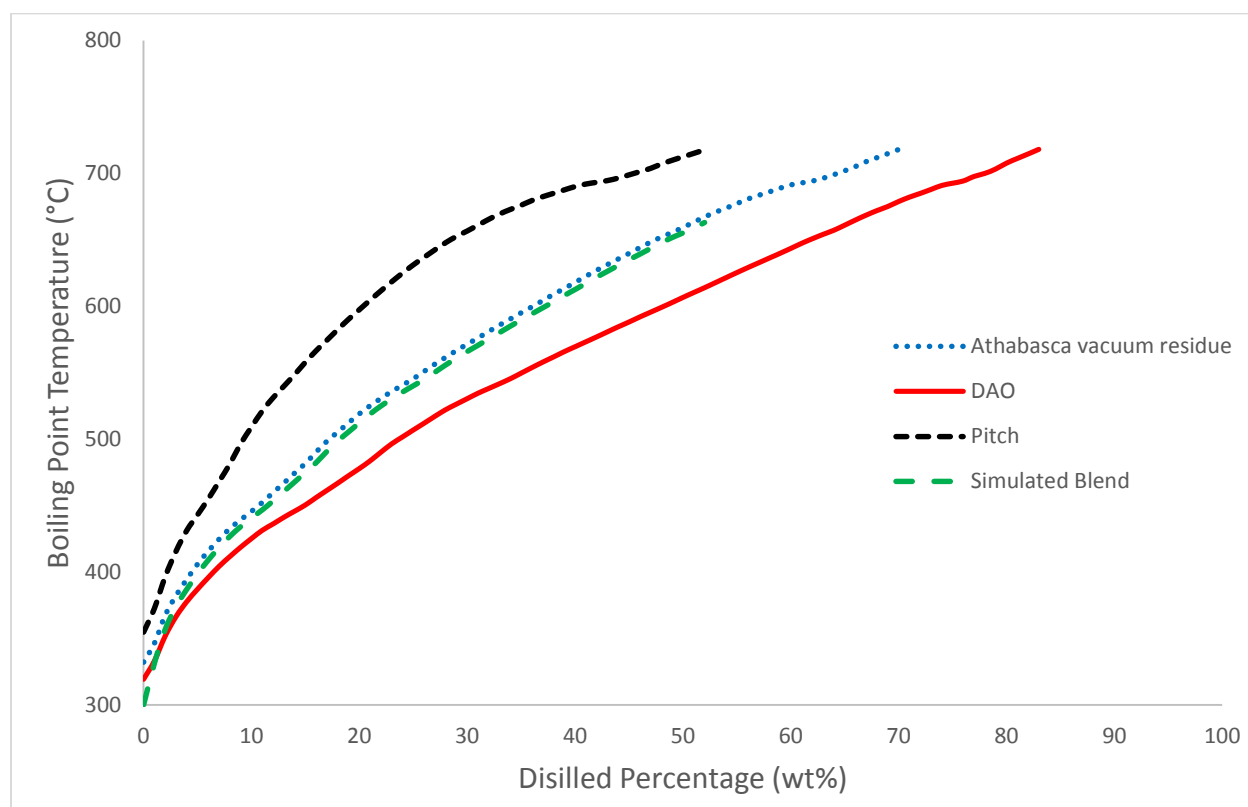


Figure 4.6: Distillation curve for Athabasca vacuum residue, deasphalting feedstocks and products (validation run)

The components were defined as: naphtha (IBP-216 °C), distillates (216 – 343 °C), VGO (343-550 °C) and residue (+550 °C). This nomenclature will be used along the present thesis otherwise noted. Athabasca vacuum residue and the simulated blend practically showed the same

composition. DAO had a higher proportion in distillates and VGO boiling point range components while pitch contained a major amount of residue.

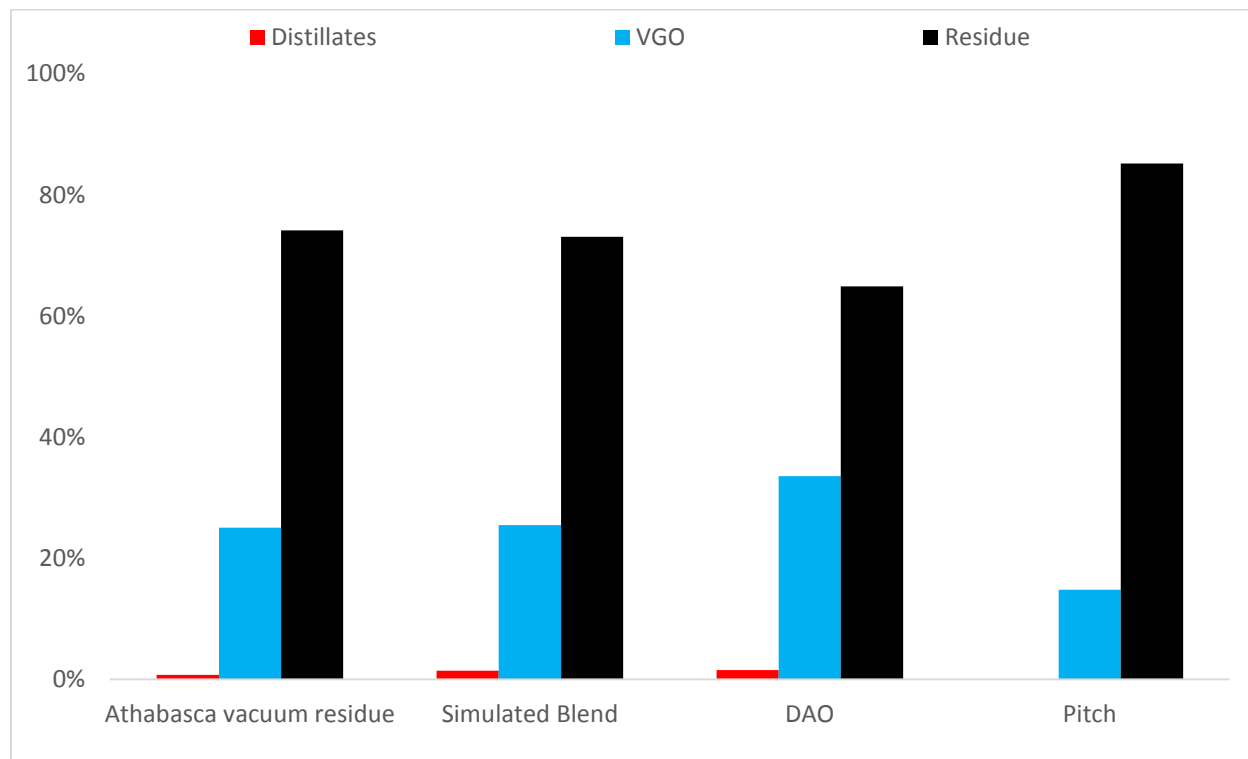


Figure 4.7: Component distribution by boiling point for Athabasca vacuum residue, and its solvent deasphalting products (validation run)

4.5 Athabasca pitch production runs:

The goal of these runs was to corroborate experiment repeatability and also the production of enough amount of Athabasca pitch to perform the following reactivity tests. Athabasca bitumen was deasphalted with n-pentane at 150 °C and 500 psig, setting a solvent-to-oil ratio of 4. In order to produce a sufficient amount of pitch for the subsequent ultradispersed hydroprocessing tests, 11 identical runs were carried out in the unit. Table 4.4 shows the average mass balance summary for the pitch production runs. Results showed the same tendency as the previous run

providing an acceptable oil mass balance ($100.4 \pm 3.6 \%$), and about 10% of solvent losses, presumably due to the n-pentane volatility.

Table 4.4: Mass Balance Summary of Athabasca pitch production runs in the SDA unit

Parameter	Component	Value (ave $\pm$ std)
Mass In (g)	Vacuum Residue	$1,050 \pm 28$
	Solvent	$2,600 \pm 0$
	Total	$3,650 \pm 28$
Mass Out (g)	Solvent	$2,398 \pm 41$
	DAO	727 ± 41
	Pitch	268 ± 23
	Total	$3,3993 \pm 236$
Mass Balance (%)	Solvent	89.9 ± 1.6
	Oils	100.4 ± 3.6
	Total	92.9 ± 1.6

From the table it can be seen that solvent addition was really precise, since the reported standard deviation was lower than 1 gram. Feedstock delivery, even though it showed standard deviation in the range of 28 grams, this only account for 0.8% of the total mass balance. In regards to the DAO and pitch products, they showed a relative percent standard deviation equivalent to 21.7% and 17.3 %, respectively. This is because the nature of the experimental procedure related to the phase separation, and the lack of a measurement method for the liquid

level inside of the extractor. However, despite the variability in the amount of products, mass balances are still considered within acceptable ranges.

A summary of the Athabasca bitumen and its solvent deasphalting products is shown in Table 4.5. DAO obtained from Athabasca bitumen also showed a better quality than the feedstock: API gravity was higher by 3.5 °API, viscosity and C5-asphaltenes content corresponded to 71.1 wt% and 97.1 wt% of the feedstock values, respectively. The pitch showed lower API gravity and higher viscosity with respect to the bitumen, as expected. The average yield in DAO for these experiments was 73.1 wt% which was lower than expected (87 wt% based on analytical C5 laboratory deasphalting), due to the uncertainties in phase separation commented in the previous case.

Table 4.5: Athabasca bitumen deasphalting property summary

Property	Athabasca Bitumen	De-Asphalted Oil	Pitch
API Gravity (°API)	8.3	11.8	-4.8
Viscosity @ 120 °C (cP)	45	13 ¹	140,000 ¹
C5-Asphaltenes (wt%)	17.0	2.2	57.2 ²

¹Extrapolated by exponential equation fitting, ²Calculated by mass balance

Figure 4.8 presents distillation curves for Athabasca bitumen, its solvent deasphalting products (DAO and pitch), and a simulated blend calculated based on the products distillation curves and yields. The DAO product was the lightest sample containing the major fraction of paraffins, aromatics and resins present in the feedstock; contrary, the pitch showed the highest boiling point due to its higher asphaltene content. In this case, the simulated blend distillation

curve differs from the feedstock with an average relative difference of 10.0%, being heavier, i. e. it showed higher boiling point at the same distilled percentage. This discrepancy can be mainly attributed to the loss of light components, especially in the range of naphtha components (IBP-216 °C), that were distilled in the DAO separator along with the solvent. Indeed, a semi-quantitative analysis performed over the recovered solvent (using HSTD method), suggested that about 2.5 wt% of the recovered solvent were light components originally present in the deasphalted bitumen.

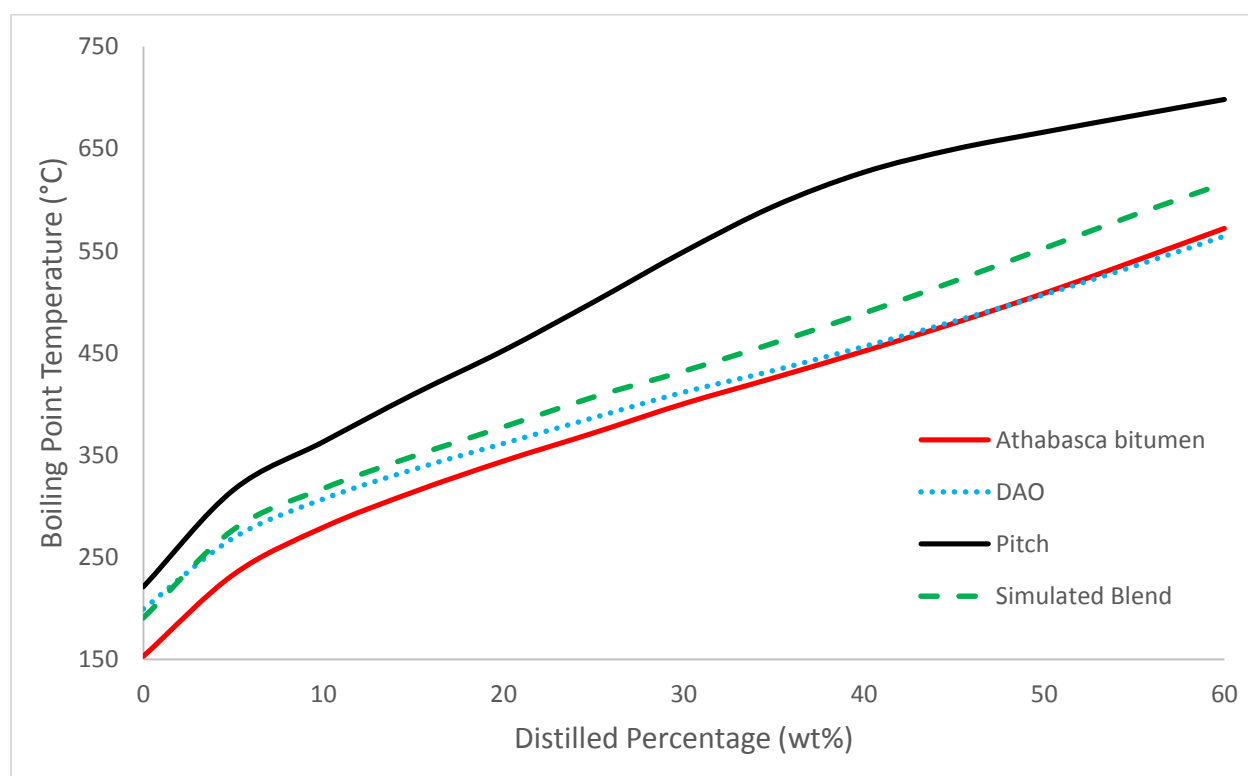


Figure 4.8: Distillation curves for Athabasca bitumen, and its deasphalting products (pitch production runs)

Figure 4.9 shows the component distribution by boiling point for Athabasca bitumen, its deasphalting products (DAO and pitch), and the simulated blend based on product yields of the experiment. In this case, the simulated blend showed a similar composition to the DAO with a

2.7 wt% reduction of products in the naphtha-range, which agreed the estimated valued obtained through the HTSD method applied to the solvent sample. The DAO showed a higher proportion of VGO while the pitch contained a noticeable increased fraction of residue. Figure 4.10 shows a comparison of the distillation curves of Athabasca bitumen solvent deasphalting products (DAO and pitch) produced from the SDA unit and those gathered at laboratory scale. The laboratory procedure uses high solvent-to-oil ratios (as high as 20); the pitch is collected by means of filtration.

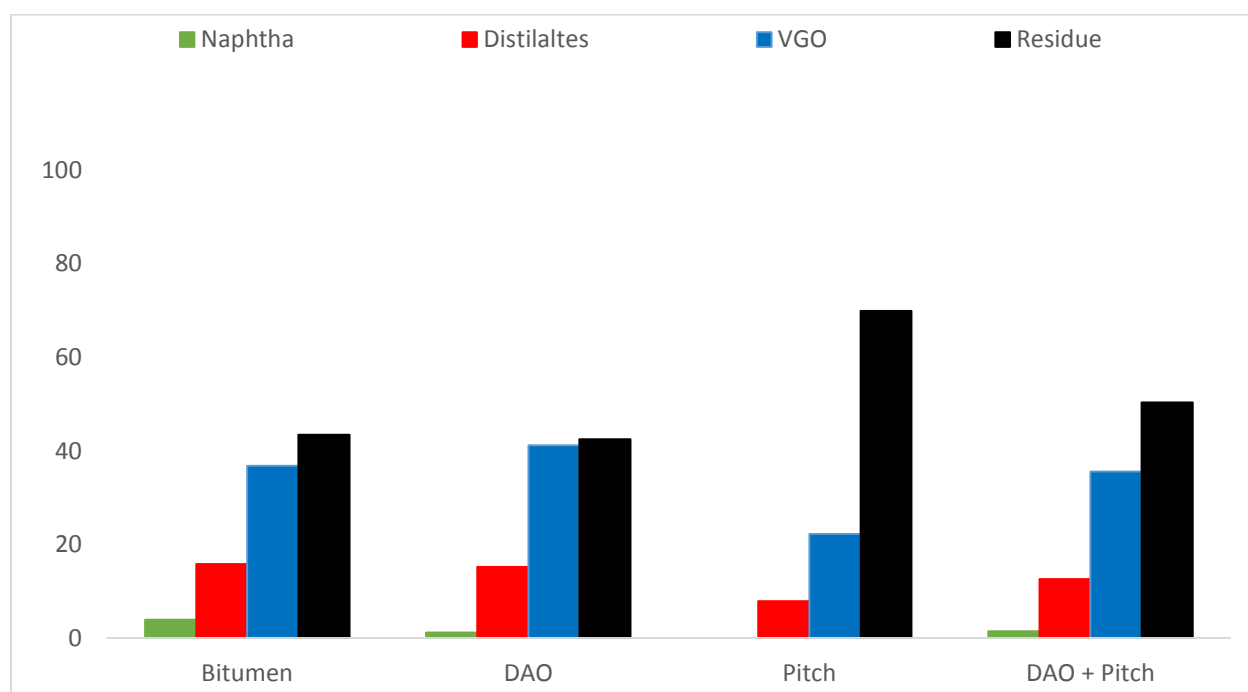


Figure 4.9: Component distribution by boiling point for Athabasca bitumen, and its solvent deasphalting products (validation run)

The DAO product from the SDA unit showed a similar distillation curve than the sample obtained from the laboratory, reporting higher boiling points (up to 22 °C) which can be caused by the distillation of light components and the slightly higher asphaltene content of the SDA unit sample in comparison with the laboratory one. In the case of the pitch, the laboratory sample was

more abundant in heavy compounds. This is because at the higher solvent-to-oil ratio used at laboratory scale, there is a higher resins extraction level, leaving behind a more concentrated pitch (in asphaltene) sample; nonetheless, initial boiling point for both samples reported a difference in the range of 3.9%.

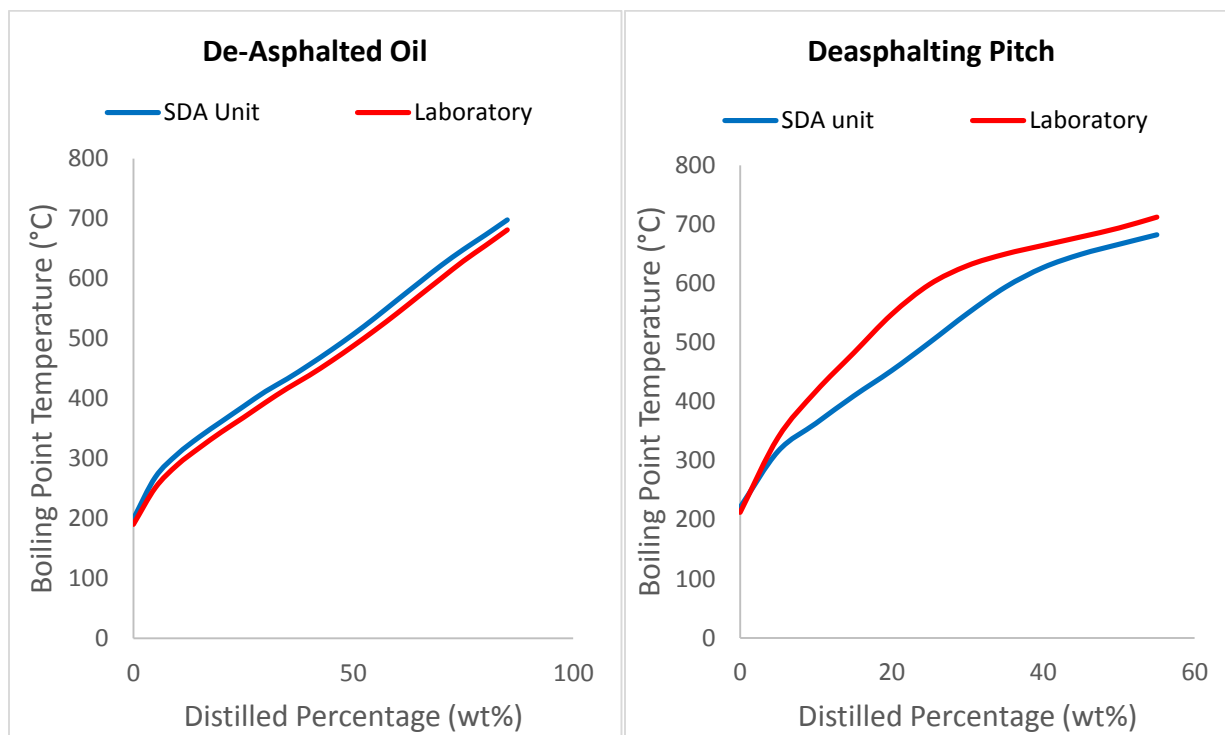


Figure 4.10: Comparison of Athabasca bitumen deasphalting products distillation curves obtained from SDA unit and laboratory

4.6 Solvent De-Asphalting Unit final remarks:

Experiments in the SDA unit designed and built in-house proved that the use of filtering devices is not required to separate DAO and pitch phases. One hour of settling time was enough for separating both phases, as published by other researchers, and the use of pipes strategically located into the upper phase provides a solution for phase separation. However, the uncertainty about the location of the interphase led to separation of products based on a fixed volume, which made impossible to determine the real DAO yield, nonetheless, this was not a critical factor for

the objectives of this research. As a recommendation for future investigations in solvent deasphalting using the built pilot plant, a method to locate the interphase between the upper and lower phase inside the extractor is required to improve the separation of DAO and pitch, allowing determining their yields more accurately.

Based on process simulation, the incorporation of a condenser was required since at typical operating temperatures and at DAO separator pressures, most of the solvent will vaporize, which besides being an unsafe condition (gases vented in the plant), it may affect the mass balance performance in the unit. Even though some efforts were made to minimize solvent losses, systematically 10 wt% of it was lost in the experiments. At present it is believed that this situation is due to the high volatility of the solvent (n-pentane). The application of measures to mitigate solvent losses such as the use of refrigerant instead of cooling water as a refrigeration fluid to decrease the condenser outlet temperature is recommended. Also, heavier solvents, like n-heptane, might be used to demonstrate it.

The implementations of the DAO and pitch separators, in order to mimic the industrial process, as well as the reduction of dead volume in the SDA unit were successfully carried out. These modifications improved the mass balance performance: oil mass balances were improved at least in 32.7 wt%, reporting 100.4 ± 3.6 wt%; solvent mass balances achieved similar values around 89.9 ± 1.4 wt%; overall mass balances improved by 5.6 wt% yielding 92.9 ± 1.4 % in 12 runs.

CHAPTER 5: REACTIVITY TESTS

This chapter presents all the results and analysis about reactivity test of the ultradispersed catalytic hydroprocessing of pitch and vacuum residue streams obtained from Athabasca bitumen. It is divided into two sections; the first one shows the outcomes for the pitch experiments while the second one aims to present the finding for vacuum residue tests. Properties of interest, such as distillation curves, viscosity and API gravity among others; are shown in order to evaluate the performance of the Catalytic In-Situ Upgrading technology.

5.1 Athabasca pitch reactivity test:

Athabasca pitch was hydroprocessed in a downflow reactor with a hydrogen-to-oil ratio of 90 cubic centimeters of hydrogen at standard conditions per cubic centimeter of oil. Ultradispersed catalyst was previously incorporated into the feedstock, with the following formulation: 773 ppmwt (Ni\Mo\W), Ni/Metals=0.29, and W/Mo=2.5. Six experiments were carried out within the range of achievable reservoir conditions, i. e. from 320 to 380 °C of temperature, and from 24 to 120 hours of residence time. HTSD curves provide distillation cuts distribution for oil samples of different nature. HTSD analysis is key in determining the degree of upgrading of oil samples processed under varying severity. Figure 5.1 shows the HTSD for the Athabasca pitch and its catalytic hydroprocessing products.

From this figure, it is evident that there are important effects of temperature and residence time on products' quality. In general terms, if the reaction temperature and/or the residence time increase, the product shows lower boiling point temperatures, which means that it contains a higher proportion of lower molecular weight hydrocarbons as a consequence of hydroprocessing reactions. The set of conditions which showed a higher degree of upgrading was 380 °C at 48 hours of residence time.

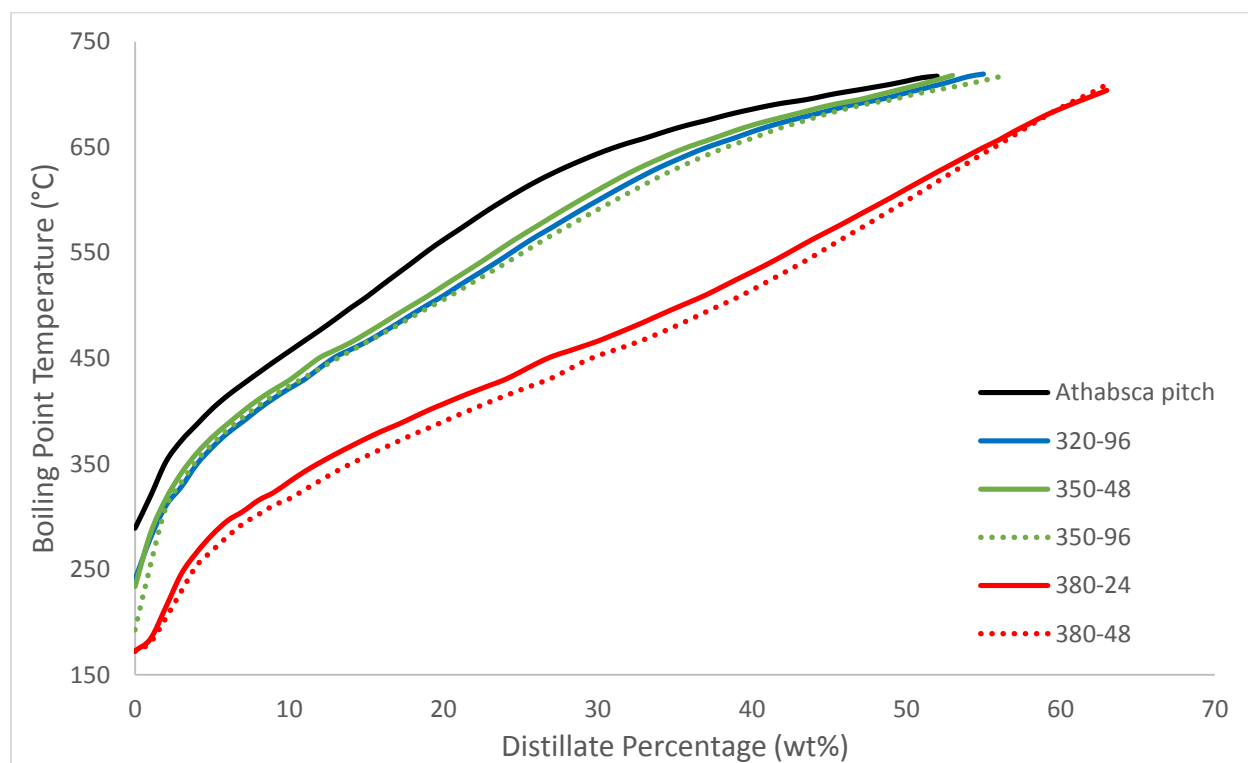


Figure 5.1: Distillation curves for Athabasca pitch and its ultradispersed catalytic hydroprocessing products

From the figure, it can be seen that changes in residence time produced a minor impact than the increase in temperature. For example, when residence time is doubled from 48 hours to 96 hours at 350 °C, boiling point temperature decreased about 2% (in average), whereas when temperature is increased from 350 °C to 380 °C at 48 hour of residence time, boiling point temperatures decreased about 25%. Based on the distillation curves, it is possible to conduct a compositional analysis defining pseudocomponents, or lumps, depending on the boiling points. For this reactivity study, and for kinetic modeling purposes, the following components were defined: gases, naphtha (IBP-216 °C), distillates (216-343 °C), VGO (343-550 °C) and residue (+550 °C). Figure 5.2 shows the components distribution for Athabasca pitch and its ultradispersed catalytic hydroprocessing products.

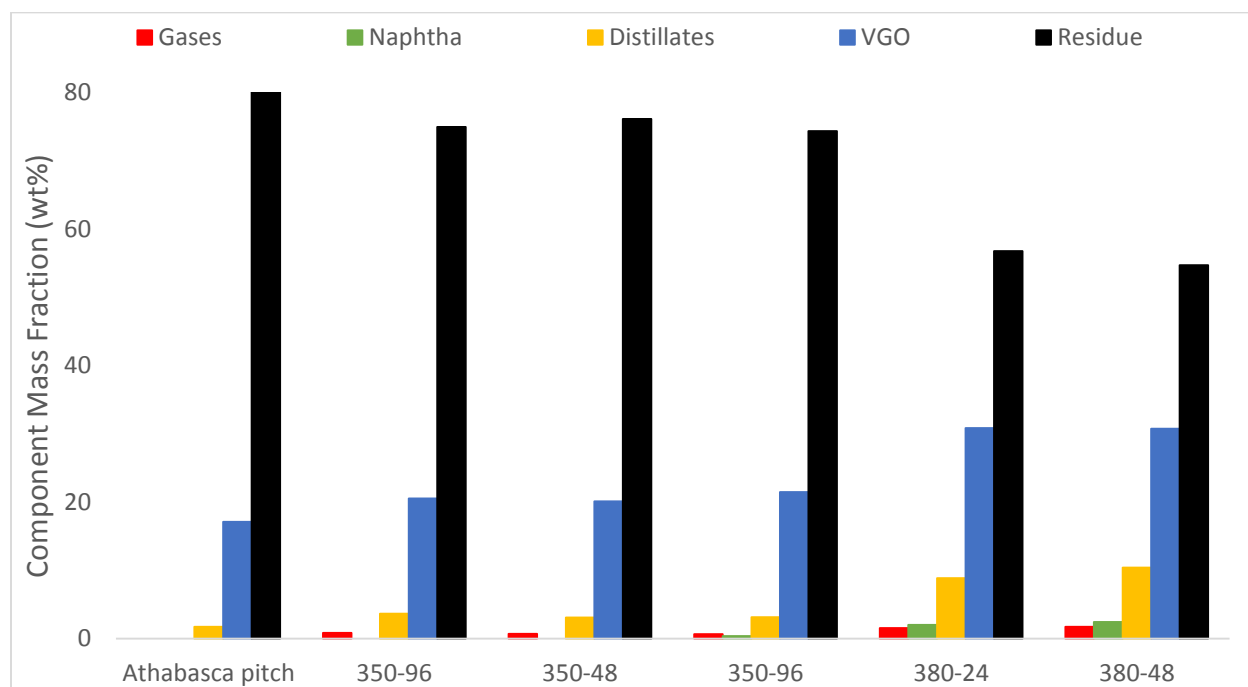


Figure 5.2: Composition distribution for Athabasca pitch and its ultradispersed catalytic hydroprocessing products

Results show that if reaction temperature and/or residence time increase, there is a reduction in the residue and an increase in VGO, distillates, naphtha and gases fraction. It can be also noted that the production of the VGO fraction is greater than the increase in distillate, naphtha and gases, suggesting reactions are more selective towards VGO at least within the range of the evaluated conditions. However, as the reaction progresses, the rate of VGO production decreases while naphtha and gases rate of production increases, implying that a fraction of the VGO is being consumed to produce lighter compounds.

For this section two conversion definitions have been employed, residue conversion and asphaltene conversion. Residue conversion is defined as the mass of residue (+550 °C) consumed respect to the mass of residue fed into the reactor calculated using the distillation curve obtained by HTSD. In mathematical terms, the residue conversion is calculated using Equation 8 :

$$\text{Residue Conversion} = \left(1 - \frac{y_R^{PRODUCT}}{y_R^{FEED}}\right) \times 100 \quad \text{Equation 8}$$

Where:

y : Component Mass Fraction [wt%]

R : Residue

Asphaltene conversion is defined as the mass of C5-asphaltene consumed respect to the mass of C5-asphaltene fed into the reactor calculated by asphaltene contend using Micro-Deasphalting. In mathematical terms, the asphaltene conversion is calculated using Equation 9:

$$\text{Asphaltene Conversion} = \left(1 - \frac{Asph^{PRODCUT}}{Asph^{FEED}}\right) \times 100 \quad \text{Equation 9}$$

Where:

$Asph$: C5-asphaltene content [wt%]

Table 5.1 shows the most important properties for Athabasca pitch and its ultradispersed catalytic hydroprocessing products. Results match with the distillation curves and composition analysis previously shown, i. e. higher residue and asphaltene conversions are reached working at high temperature; however, increasing residence time seems to have a minor effect on both conversions. In addition, as conversion increases, there is an improvement in API gravity, due to hydroprocessing reactions. Regarding C5-asphaltene content, in general the higher the temperature and/or the residence time, the lower the asphaltene content of the liquid product. Asphaltene conversion resulted to be higher than residue conversion, this can be explained taking into consideration that asphaltene molecules could have been upgraded, reducing its molecular weight, heteroatoms content (sulfur, nitrogen, oxygen, etc.), and aromaticity; however, the produced material would still be within the boiling point range of the residue fraction. Due to the

asphaltene content reduction significant improvement in terms of API gravity and viscosity is reached.

Table 5.1: Properties for Athabasca pitch and its ultradispersed catalytic hydroprocessing products

	Feedstock	320 °C 120 hours	350 °C 48 hours	350 °C 96 hours	380 °C 24 hours	380 °C 48 hours
Residue						
Conversion (wt%)	-	6.9	5.6	7.8	29.0	31.5
C5-Asphaltenes						
Conversion (wt%)	-	19.3	18.1	21.8	30.3	38.3
API Gravity (°API)	-4.4	-1.4	-2.5	-1.9	0.7	1.0
C5-Asphaltenes						
(wt%)	67.9	53.9	54.7	52.2	46.6	41.2

Figure 5.3 shows the component mass fraction as a function of residue conversion (+550 °C) for Athabasca pitch ultradispersed catalytic hydroprocessing. Residue mass fraction decreases according to the extent of the reaction; this is because it is only consumed during the process. Even though the rest of the components (VGO, distillates, and naphtha) might be produced and consumed during the process, they showed a positive net production at the evaluated extend of the reaction. In the case of VGO, the linear relationship between mass fractions and the residue conversion suggest that it is mainly produced by residue hydroprocessing rather than consumed to produce lighter components at least at the evaluated conditions. For the distillates cut a similar conclusion can be achieved: the slope of the distillate fraction curve is positive, which means a positive net production, i. e. the rate of production is

greater than the rate of consumption; also it can be said that as the curve shows a linear tendency ($r^2=0.987$), distillates come primarily from residue hydroprocessing. For the naphtha cut and gases, this type of analysis cannot be performed due to the uncertainties inherent to the analytical methods.

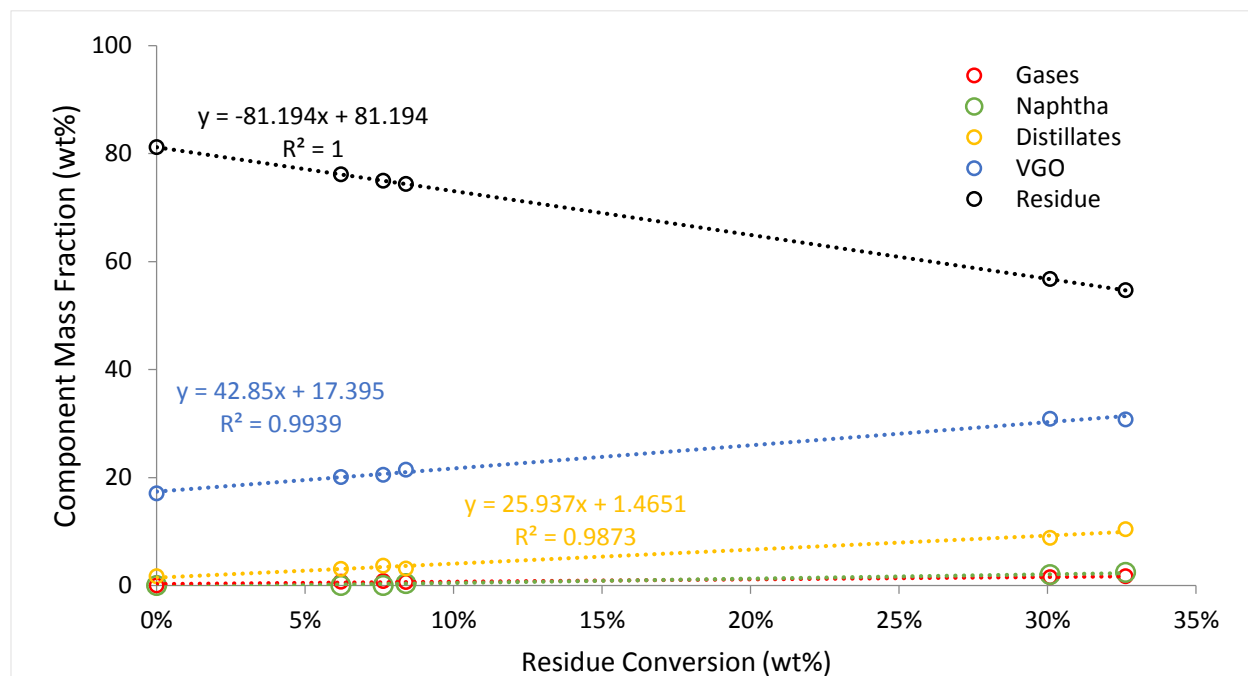


Figure 5.3: Component mass fraction as a function of residue conversion for Athabasca pitch ultradispersed catalytic hydroprocessing

5.2 Athabasca vacuum residue reactivity test:

Athabasca vacuum residue was hydroprocessed in a downflow reactor with at hydrogen-to-oil ratio of 90 cubic centimeters of hydrogen at standard conditions per cubic centimeter of oil. Ultradispersed catalyst was previously incorporated into the feedstock, with the following formulation: 1,107 ppmwt (Ni\Mo\W), Ni/Metals=0.21, and W/Mo=2.9. Five experiments were carried out within the range of achievable reservoir conditions, i. e. from 320 to 395 °C of temperature, and from 24 to 75 hours of residence time. Figure 5.4 shows the distillation curves determined by HTSD for the Athabasca vacuum residue and its catalytic hydroprocessing products.

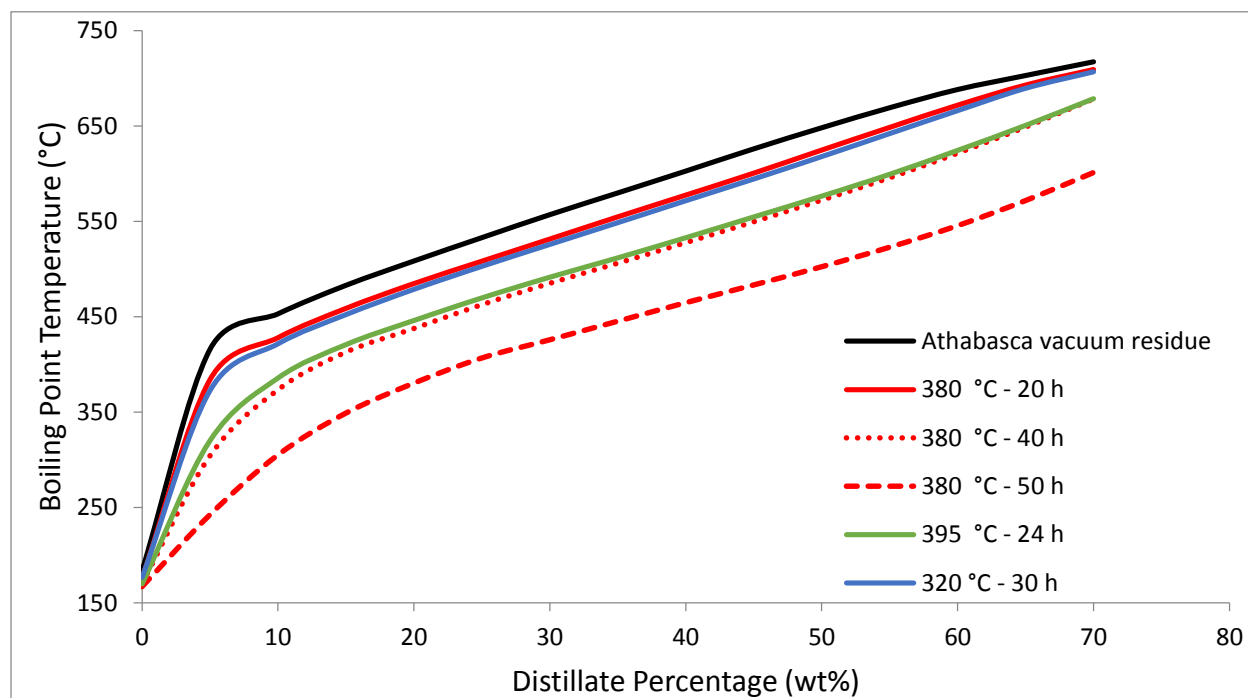


Figure 5.4: Distillation curves for Athabasca vacuum residue and its ultradispersed catalytic hydroprocessing products

From this figure, it is evident that there are important effects of temperature and residence time on products' quality. In general terms, if the reaction temperature and/or the residence time

increase, the product shows lower boiling point temperatures, which means that it contains a higher proportion of lower molecular weight hydrocarbons as a consequence of hydroprocessing reactions. The set of conditions which showed the highest degree of upgrading was 380 °C at 50 hours of residence time. The experiment carried out at 380 °C at 40 hours presented a similar upgrading than the one at 395 °C at 24 hours. This means the shorter residence time was compensated by the increase of temperature in the second condition. Unintentionally, the rest of conditions (380 °C at 20 hours, and 320 °C at 30 hours) exhibited a similar trend. Figure 5.5 shows the components distribution for Athabasca vacuum residue and its ultradispersed catalytic hydroprocessing products.

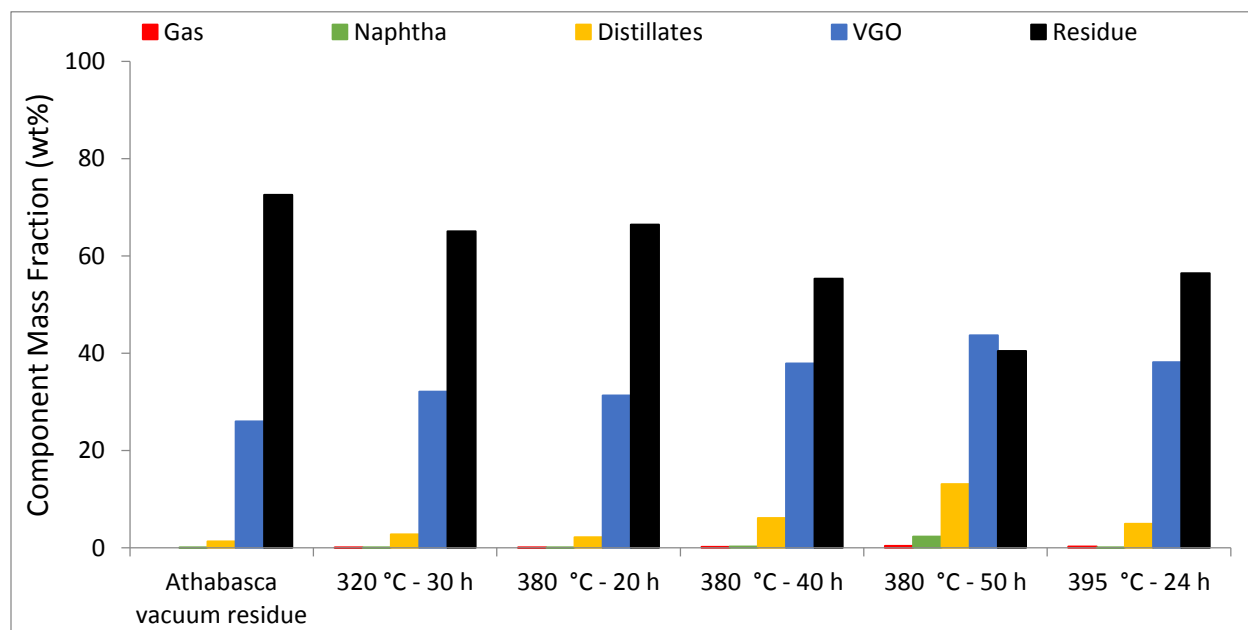


Figure 5.5: Composition distribution for Athabasca vacuum residue and its ultradispersed catalytic hydroprocessing products

Results show that if reaction temperature and/or residence time increase, there is a reduction in the residue and an increase in VGO, distillates, naphtha and gases fractions. It can be also noted that the production of VGO and distillates fractions is greater than the increase in naphtha and

gases, suggesting reactions are more selective towards VGO and distillates within the range of the evaluated conditions. However, as the reaction progresses, the rate of production of VGO decreases, implying that a fraction of the VGO is being consumed to produce lighter compounds. Table 5.2 shows the most important properties for Athabasca vacuum residue and its ultradispersed catalytic hydroprocessing products. The results match with the distillation curves and the compositions previously shown: the run at 380 °C and 50 hours reached the highest conversion, followed by 380 °C at 40 hours and 395 °C at 24 hours, which reported similar conversion values.

Table 5.2: Properties for Athabasca vacuum residue and its ultradispersed catalytic hydroprocessing products

	Feedstock	320 °C 30 hours	380 °C 20 hours	380 °C 40 hours	380 °C 50 hours	395 °C 24 hours
Residue						
Conversion (wt%)	-	10.3	8.5	23.6	44.0	22.0
C5-Asphaltenes						
Conversion (wt%)	-	20.7	24.6	32.8	41.6	49.0
API Gravity						
(°API)	2.4	4.1	3.5	5.9	8.9	5.4
Viscosity						
(cP) @ 80 °C	78,400 ¹	2,760	3,557	641	75	949
Sulfur content						
(wt%)	4.8	4.3	4.2	3.7	3.6	3.9
C5-Asphaltenes						
(wt%)	26.5	21.0	20.0	17.8	15.5	13.5

¹Extrapolated by exponential equation fitting

Figure 5.6 shows the component mass fraction as a function of residue conversion (+550 °C) for Athabasca vacuum residue ultradispersed catalytic hydroprocessing. Residue mass fraction decreases according to the extent of the reaction; this is because it is only being consumed during the process. Even though the rest of the components (VGO, distillates, and naphtha) might be produced and consumed during the process, they showed a positive net production at the evaluated extent of the reaction. In the case of VGO, the linear relationships between mass fractions and the residue conversion suggest that it is mainly produced by residue hydroprocessing rather than consumed to produce lighter components at least at the evaluated conditions. At high conversion values, a light decrease in the slope indicates that its rate of consumption is becoming significant in comparison to its rate of production.

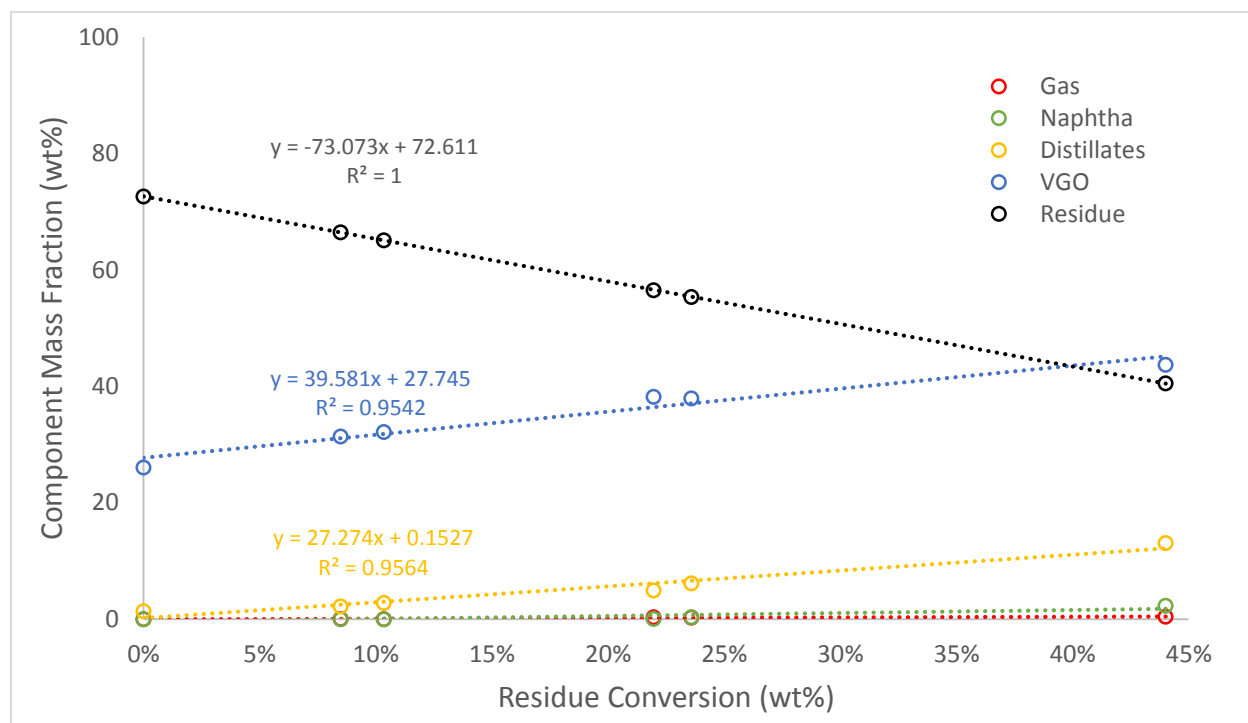


Figure 5.6: Component mass fraction as a function of residue conversion for Athabasca vacuum residue ultradispersed catalytic hydroprocessing

For the distillates cut a similar conclusion can be achieved: the slope of the distillate fraction curve is positive, which means a positive net production, i. e. the rate of production is greater than the rate of consumption; also it can be said that as the curve shows a linear tendency ($r^2=0.956$), distillates comes primarily from residue hydroprocessing. An increase in the distillate curve at high severity implies that significant fraction of its production may come from VGO hydroprocessing, which matches what was discussed previously.

For the naphtha cut and gases, this type of analysis cannot be performed due to the uncertainties inherent to the analytical methods in the range of low values found. Figure 5.7 and Figure 5.8 respectively show API gravity and viscosity of the liquid product obtained by ultradispersed catalytic hydroprocessing of Athabasca vacuum residue. Acceptable correlations were obtained from the experimental data, which can be used for estimating these properties given a reaction temperature and a residence time within the range of evaluated conditions.

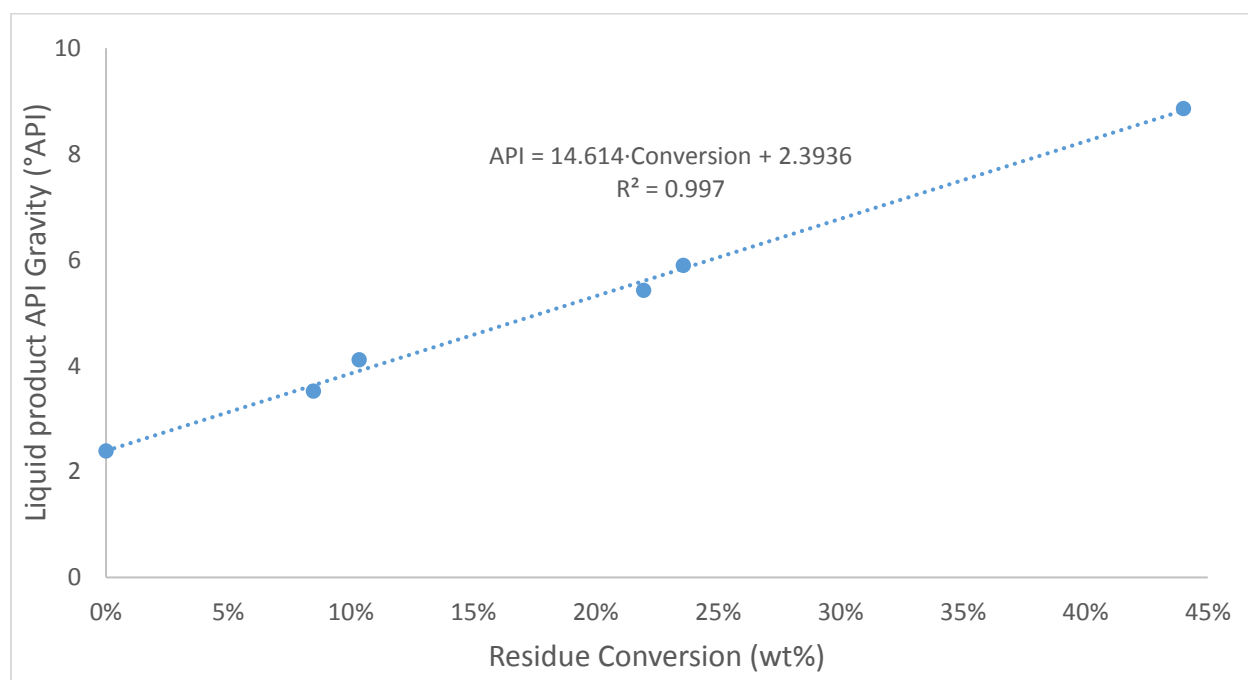


Figure 5.7: Liquid product API gravity as a function of residue conversion of Athabasca vacuum residue ultradispersed catalytic hydroprocessing

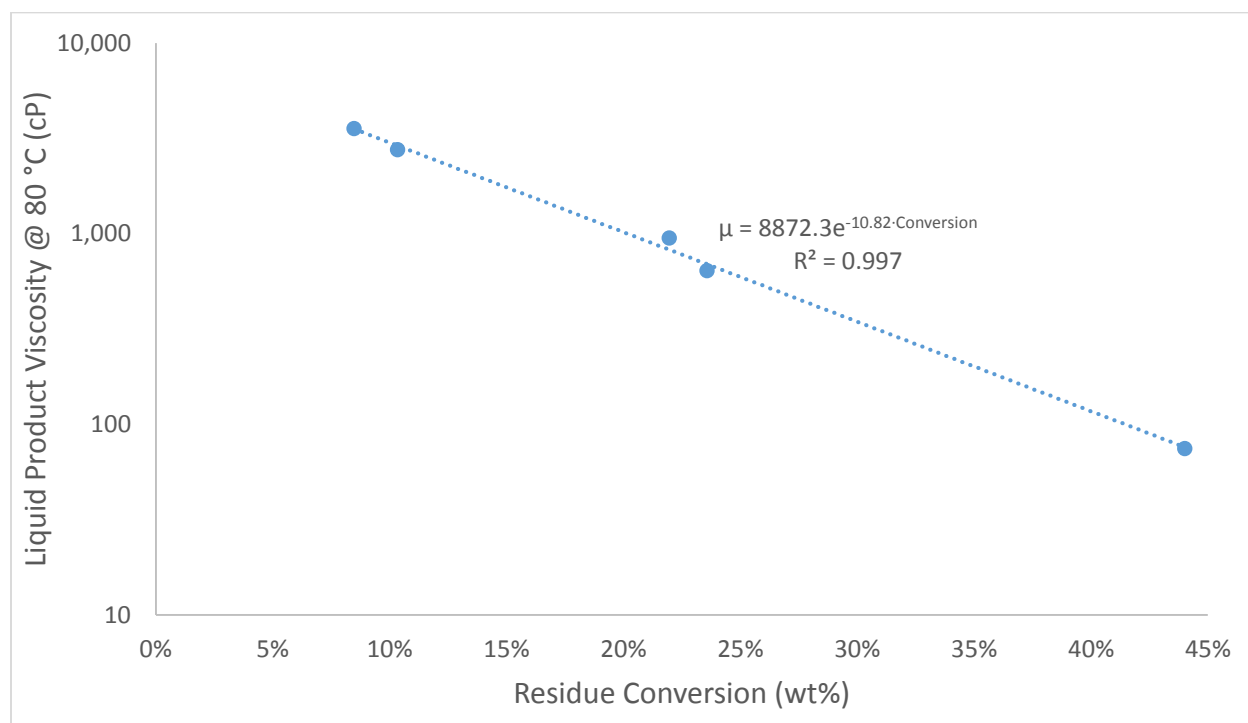


Figure 5.8: Liquid product viscosity as a function of residue conversion of Athabasca vacuum residue ultradispersed catalytic hydroprocessing

CHAPTER 6: IN SITU UPGRADING KINETIC MODELING

This chapter represents the core of the present thesis, which is the development of kinetic models for ultradispersed catalytic hydroprocessing of Athabasca bitumen, vacuum residue, and pitch at achievable reservoir conditions. Results are shown in four sections; the first one contains the description of the method used to carry out the numerical regression of the experimental results in order to determine the parameters of proposed kinetic models. The second section shows the results obtained with the developed method when applied to the experimental data gathered by Loria and coworkers (2011) in their model describing ultradispersed catalytic hydroprocessing of Athabasca bitumen. Finally, the third and fourth sections present the kinetic models for ultradispersed catalytic hydroprocessing of Athabasca vacuum residue and pitch developed in this research.

6.1 Kinetic model regression method:

Modeling petroleum reactions is a challenging task due to the complexity of the oil composition, comprising up to several hundreds of thousands compounds, and the number of reactions that may be taking place within the reactive system. In order to overcome these difficulties, the definition of pseudocomponents and pseudoreactions is used to simplify the modeling problem, not only from the mathematical point of view but also by the demand of oil characterization analytical methods.

Developing kinetic models for refining processes is an iterative process: a reaction scheme is proposed, including the number of pseudocomponents and the reaction network; then the kinetic parameters have to be determined based on experimental data, and finally the model proven in terms of deviation and consistency. If the model is rejected, the process starts over by

proposing a new component breakdown and/or a reaction scheme. This procedure ends up when a proposed model fits the experimental data with acceptable consistency.

The component breakdown and reaction scheme of the kinetic model proposed in this work is based on the model suggested by Sanchez et al. (2005) for Maya heavy oil hydrocracking, which was later applied by Galarraga and coworkers (2011) for ultradispersed catalytic hydroprocessing of Athabasca bitumen in a batch reactor, and subsequently used by Loria and others (2011) for ultradispersed catalytic hydroprocessing of Athabasca bitumen in a continuous tubular reactor. The model includes 5 lumps: residue (+550 °C), VGO (343-545 °C), distillates (216-343 °C), naphtha (IBP-216) and gases, and 10 first-order reactions as shown in Figure 6.1:

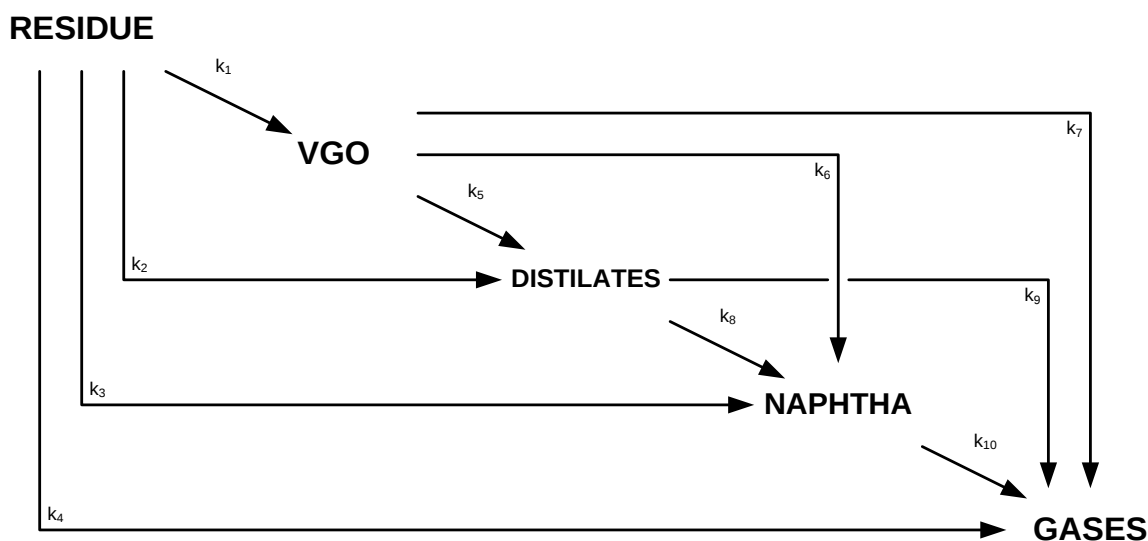


Figure 6.1: 5-Lumps kinetic model for hydrocracking and hydroprocessing

For each component, a kinetic expression was formulated as a function of component mass fractions, determined by distillation curves and kinetic constants as shown from Equation 10 to Equation 14:

$$r_R = -(k_1 + k_2 + k_3 + k_4) \cdot y_R \quad \text{Equation 10}$$

$$r_{VGO} = k_1 \cdot y_R - (k_5 + k_6 + k_7) \cdot y_{VGO} \quad \text{Equation 11}$$

$$r_D = k_2 \cdot y_R + k_5 \cdot y_{VGO} - (k_8 + k_9) \cdot y_D \quad \text{Equation 12}$$

$$r_N = k_3 \cdot y_R + k_6 \cdot y_{VGO} + k_8 \cdot y_D - k_{10} \cdot y_N \quad \text{Equation 13}$$

$$r_G = k_4 \cdot y_R + k_7 \cdot y_{VGO} + k_9 \cdot y_D + k_{10} \cdot y_N \quad \text{Equation 14}$$

Where:

k : Reaction Constant [h^{-1}]

r : Reaction Rate [h^{-1}]

y : Component Mass Fraction [wt%]

Each reaction constant, i. e. from 1 to 10, can be expressed as a function of the temperature by the Arrhenius Equation 15:

$$k_i = k_0^i \cdot \exp\left(-\frac{E_A^i}{RT}\right) \quad \text{Equation 15}$$

Where:

k_i : Reaction constant [h^{-1}]

E_A : Activation Energy [kJ/mol]

k_0^i : Frequency or pre-exponential factor [h^{-1}]

T : Reaction Temperature [K]

R : Universal Gas Constant [$kJ/mol \cdot K$]

Determination of kinetic parameters, i. e. frequency or pre-exponential factors and activation energies for each reaction, is in fact an optimization problem, since a certain number of unknowns are adjusted with the goal of minimizing the model deviation with respect to the experimental data, taking into consideration some constraints. Typical objective functions are

defined only taking into consideration the deviation of model prediction to the experimental data. One commonly used objective function is the performance index, shown in Equation 16 (Loria et al., 2011):

$$PI = \sum_{j=1}^m \sum_{i=1}^n (y_{i,j}^{EXP} - y_{i,j}^{MOD})^2 \quad \text{Equation 16}$$

Where:

PI : Performance index [*dimensionless*]

n : Number of components [*dimensionless*]

m : Number of evaluated conditions [*dimensionless*]

Alternatively, the average percentage error (Equation 17) may be used as objective function (Loria et al., 2011):

$$APE = \frac{\sum_{j=1}^m \sum_{i=1}^n \frac{|y_{i,j}^{EXP} - y_{i,j}^{MOD}|}{y_{i,j}^{EXP}}}{n \cdot m} \times 100 \quad \text{Equation 17}$$

Where:

APE : Average percentage error [%]

However, the use of this type of objective function divides the problem into two stages, as shown in Figure 6.2. The first stage consist in the determination of the reaction constants at different temperatures, which implies the application of a number of optimization steps equal to the number of evaluated temperatures. Once all experimental data have been regressed at different temperatures reaching the minimum deviation, the reaction constants are plotted in an Arrhenius plot (reaction constant against inversed temperature), and by least squares method, pre-exponential factor and activation energies are calculated.

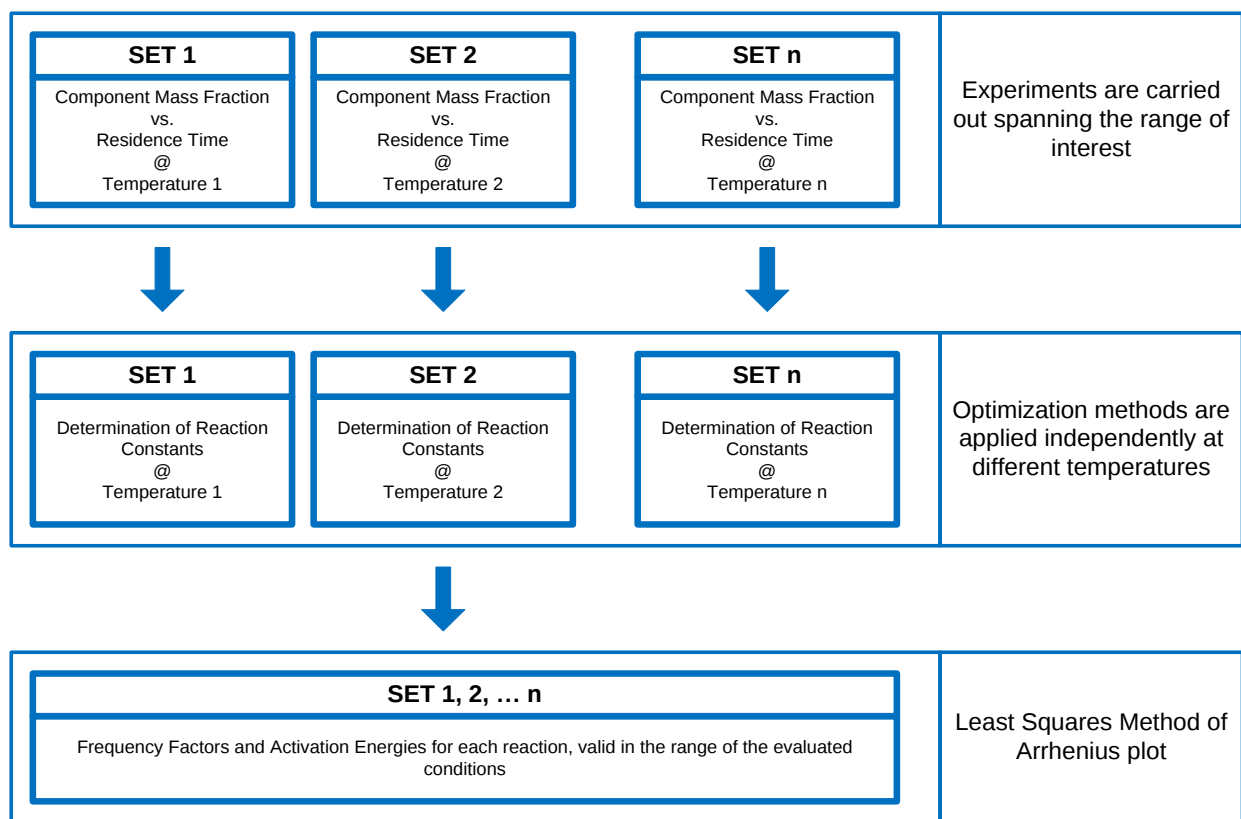


Figure 6.2: Typical kinetic regression method

During the linear regression step, three cases may be observed as shown in Figure 6.3. The first case corresponds to the “best” situation in which the regressed data perfectly fits a linear trend. It is a common practice to consider a model as acceptable when its correlation coefficients is higher than 0.95. Another possible outcome may be the existence of an apparent linear trend with high data dispersion due to different sources of error (experimental); despite the acceptance of this type of cases, low correlation coefficients affect the accuracy of the model, increasing its deviation error. The third case consists in an apparent linear tendency but in fact it has a non-linear trend, which can be tested by conducting a residual analysis. When determining kinetic parameters, several solutions may be considered acceptable from a mathematical point of

view, which is especially common when using a limited number of experiments, however, inclusion of a measure of a fitting factor for the Arrhenius equation, will reduce the number of possible solutions, increasing its consistency.

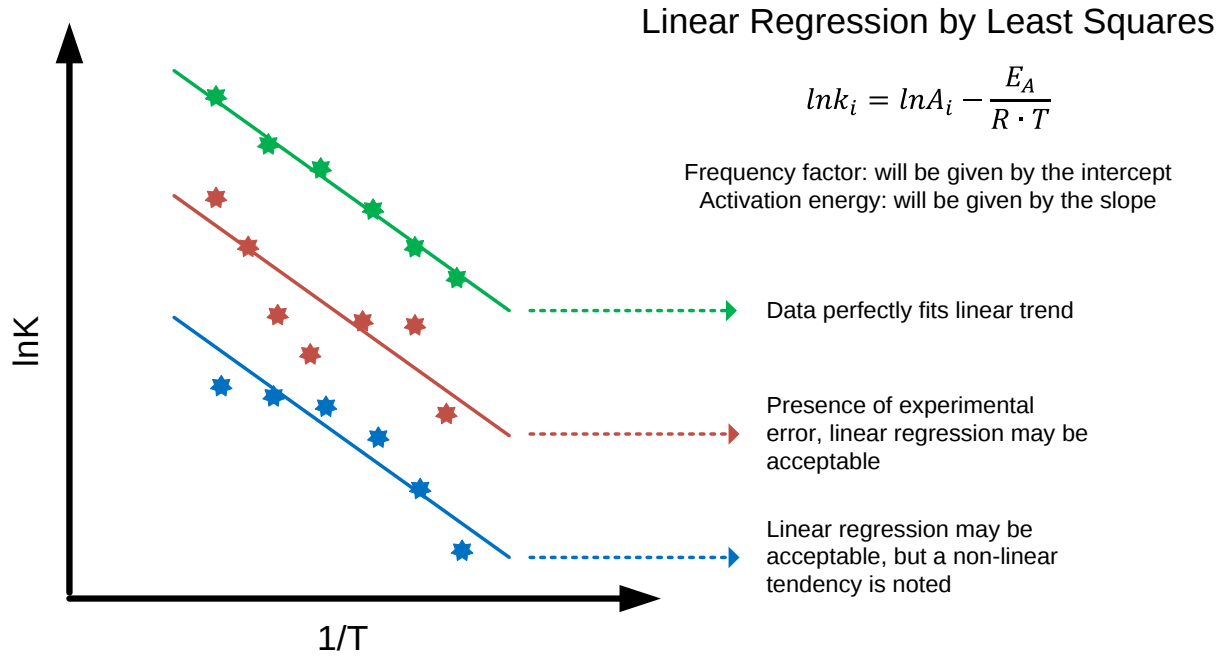


Figure 6.3: Possible outcomes of the linear regression of Arrhenius plot

Equation 18 is the objective function defined in this research for the kinetic regression. The first term of the right-hand side includes the performance index which evaluates the model deviation, and the second term measures the fitting of the reaction constant data to the Arrhenius equation. Weight factors are included to adjust the sensibility of the optimization algorithm respect to these two criteria.

$$OF = W_{PI} \cdot PI + W_R \cdot \left(nr - \sum_{k=1}^{nr} r_k^2 \right) \quad \text{Equation 18}$$

Where:

OF : Objective function [*dimensionless*]

W_{PI} : Performance Index Weight Factor [*dimensionless*]

W_R : Arrhenius Fitting Index Weight Factor [*dimensionless*]

nr : Number of reactions [*dimensionless*]

r^2 : Correlation coefficient [*dimensionless*]

Once this objective function is implemented, the regression method strategy matches what is depicted in Figure 6.4. The same data used in the classical approach is required in this method. The main difference lies on the optimization step, since just one global optimization is applied by guessing all the reactions constants that produces the minimum value for the objective function.

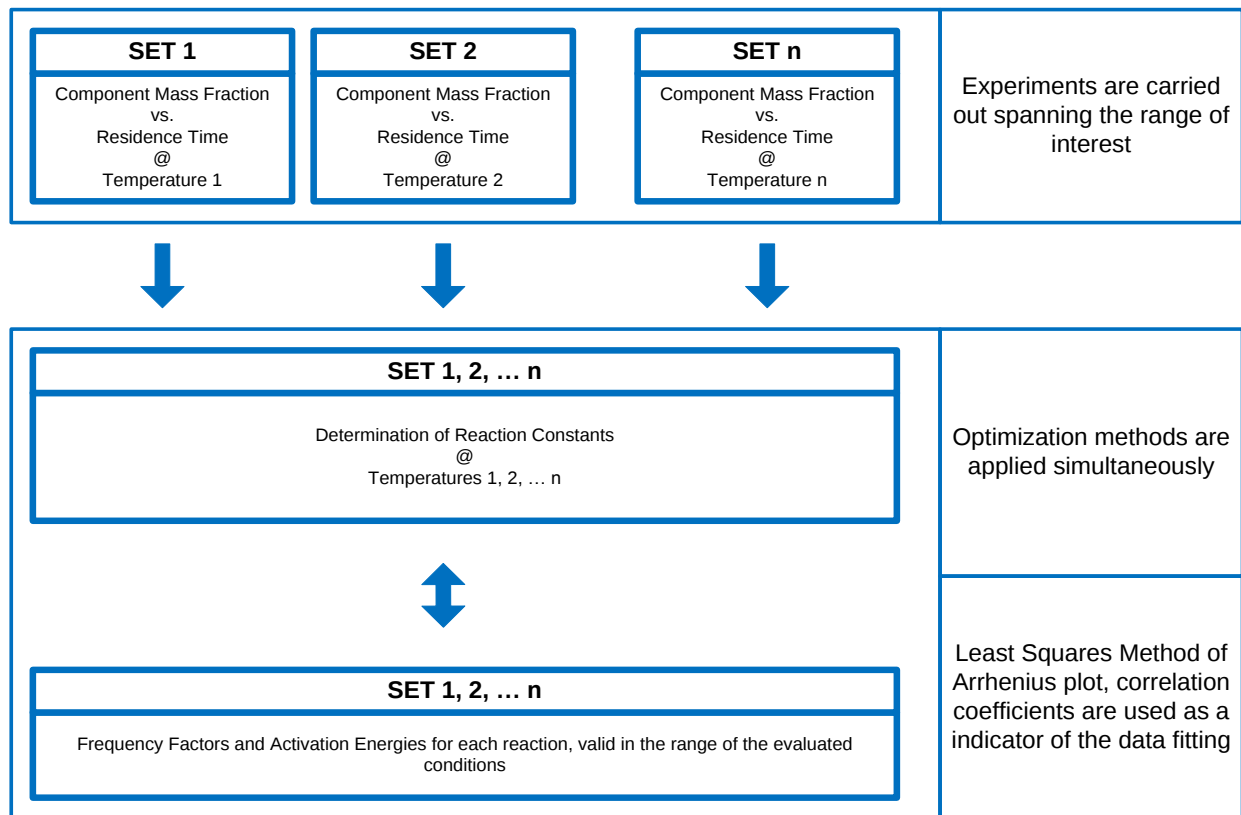


Figure 6.4: Proposed kinetic regression method

One disadvantage on this method was the demand of calculation requirements; however, nowadays overcome with the advances in the computing science. A program in Visual Basic for Applications coupled with Microsoft Excel was developed due to the convenience of data management, ease programing and the solver complement available in the software. Figure 6.5 shows the configuration panel of the kinetic regression program developed, it allows the selection of different types of constraints, solver configuration, algorithm selection, and the possibility to solve the problem based on the classical approach or the one proposed in this thesis.

Kinetic Constants

Constraints:

☐ $k_1 = 0$ ☐ $k_6 = 0$ ☐ $k_1 + k_2 + k_3 + k_4 = k_{global}$

☐ $k_2 = 0$ ☐ $k_7 = 0$ ☐ Minimum Kis: 0.000001

☐ $k_3 = 0$ ☐ $k_8 = 0$ ☐ Maximum Kis: 0.1

☐ $k_4 = 0$ ☐ $k_9 = 0$ ☐ $AE > 0$

☐ $k_5 = 0$ ☐ $k_{10} = 0$ ☐ $A_0 > 0$

Calculation Method:

☒ Integrated

☐ Independet AB320

Solver Configuration:

Constrain Precision: 0.00000001

Convergence: 0.00000001

Solving Method: GRG Nonlinear

Cancel Reset Values Load Run Load and Run

Figure 6.5: Kinetic regression program configuration panel

6.2 Athabasca bitumen kinetic model:

Kinetic models for Athabasca bitumen ultradispersed catalytic hydroprocessing were proposed first by Galarraga and coworkers (2011), who used experimental data obtained from runs in a batch reactor. Later Loria et al. (2011) proposed a model using data obtained from a continuous setup provided with a tubular reactor similar to the one used in the present work. For the kinetic regression of the Athabasca bitumen the experimental data published by Loria et al. (2011) was used with the idea of proving the proposed regression method and to verify if the model accuracy can be improved. In the Appendix C: Experimental data for Athabasca bitumen ultradispersed catalytic hydroprocessing obtained by Loria et al. (2011), all the information employed for the kinetic regression is shown. Table 6.1 presents the kinetic parameters for Athabasca bitumen ultradispersed catalytic hydroprocessing obtained by using the proposed kinetic regression method. Negligible reactions were not included within the table.

Table 6.1: Kinetic parameters for Athabasca bitumen ultradispersed catalytic hydroprocessing

Reaction Constant (h ⁻¹)	Temperature (°C)				Pre-Exponential	Activation	R ²	
	320	350	360	380	Factor (h ⁻¹)	Energy (kJ/mol)		
	1	0.00220	0.00899	0.01344	0.02945	4.273·10 ⁹	139.5	1.000
	2	0.00114	0.00496	0.00761	0.02796	6.914·10 ¹¹	168.3	0.987
	3	0.00041	0.00177	0.00326	0.01098	8.334·10 ¹¹	174.3	0.990
	4	0.00006	0.00071	0.00180	0.00937	5.881·10 ¹⁹	272.9	0.999
	5	0.00067	0.00315	0.00493	0.01614	4.214·10 ¹¹	168.3	0.995
	6	0.00000	0.00002	0.00006	0.00038	3.151·10 ²²	324.0	1.000
8	0.00000	0.00004	0.00023	0.01015	4.441·10 ⁴⁸	633.3	1.000	

Reactions 1 to 4, which are respectively related to the conversion of residue into VGO, distillates, naphtha and gases, showed activation energies within the range of 139.5-272.9 kJ/mol matching similar reactive systems published by other researchers including Sanchez et al. (2005), Hassanzadeh et al. (2010), and Galarraaga et al. (2011). Reactions 7, 9, and 10, producing gases from VGO, Distillates, and naphtha, respectively, resulted in negligible reaction constants at the evaluated conditions, suggesting that gas production comes exclusively from hydroprocessing of the residue fraction, which also implies that naphtha hydrocracking is insignificant in this system. Figure 6.6 shows the kinetic model indicating the relative differences between reaction constants for Athabasca bitumen ultradispersed catalytic hydroprocessing, the darker the color, the higher the calculated reaction constant and vice versa.

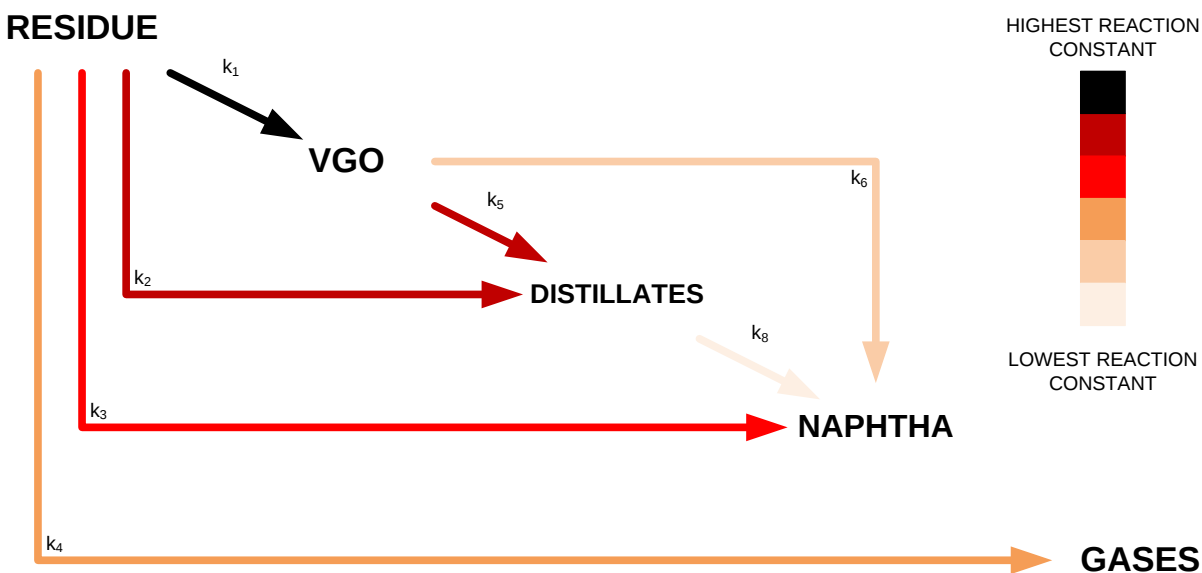


Figure 6.6: Comparison of reaction constants for Athabasca bitumen ultradispersed catalytic hydroprocessing

From Figure 6.6 and Table 6.1, it can be seen that residue reactions are dominant, being the production of VGO the more selective of this set of reactions. Distillates production is the second lump being favored, showing that the hydroprocessing of residue and VGO possess a similar level of reactivity. Naphtha production comes mainly from residue conversion, since VGO and distillates hydrocracking evolving towards naphtha showed reaction constants much lower than residue hydrocracking towards naphtha, this being more accentuated at the lower temperatures evaluated. Figure 6.7 shows the Arrhenius plot (natural logarithm of reaction rate vs. inverse of absolute temperature) for the evaluated system. All the linear regressions were acceptable, reporting the lowest correlation coefficient of 0.987 for reaction 2, showing no significant deviation within the range of evaluated conditions. This confirms that the proposed model is representative of the system, and also that reactions are kinetically controlled.

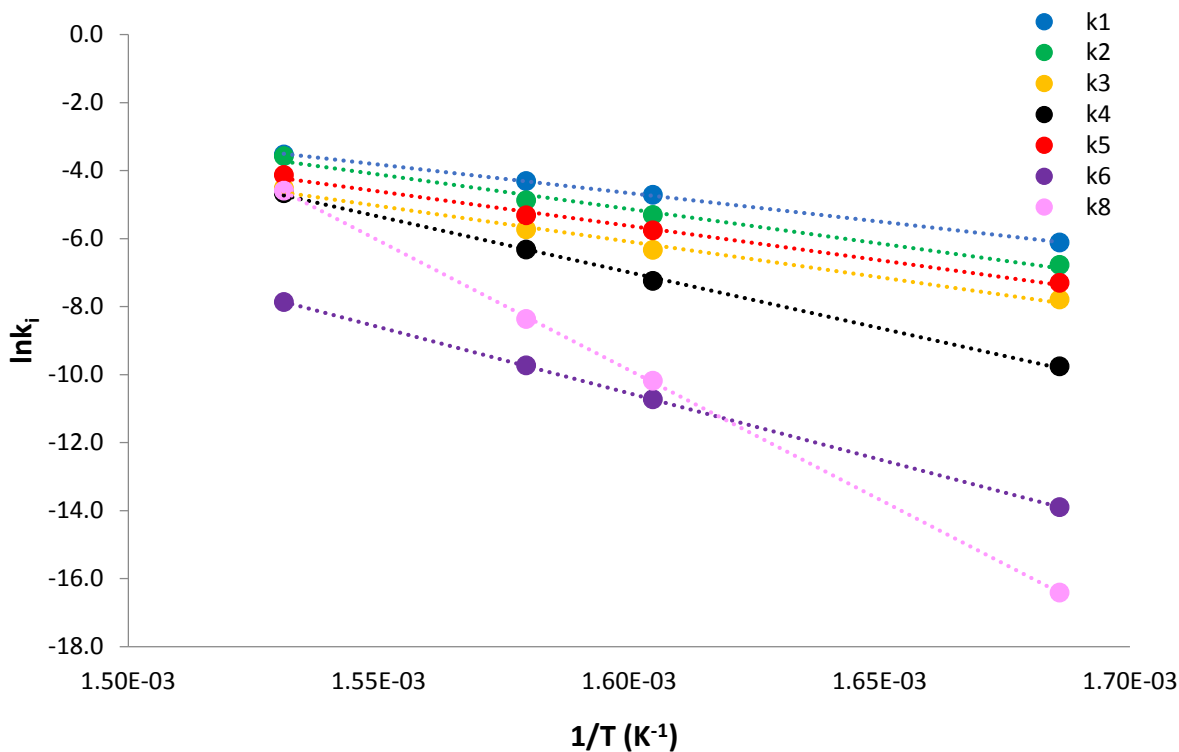


Figure 6.7: Arrhenius Plot for Athabasca bitumen ultradispersed catalytic hydroprocessing

Figure 6.8, a comparison between predicted and experimental component mass fraction for Athabasca bitumen ultradispersed catalytic hydroprocessing, shows good prediction for the proposed model, reporting a correlation coefficient of the entire data of 0.978 and an average percentage error of 3.11%. Deviation of the model can be attributed to the inherent experimental error of the runs, error of the analytical techniques, e. g. HSTD may produce error within the range of 2 wt%, and errors due to the interpolation of boiling point curves.

The model proposed in this research showed better component mass fraction estimations than the one proposed by Loria et al. (2011), which presented a correlation coefficient of 0.972 and an average percentage error of 6.25%. In addition, in the opinion of the author, this model is more comprehensive since the residue fraction showed a higher level of reactivity than lighter oil cuts, i. e. VGO and distillates.

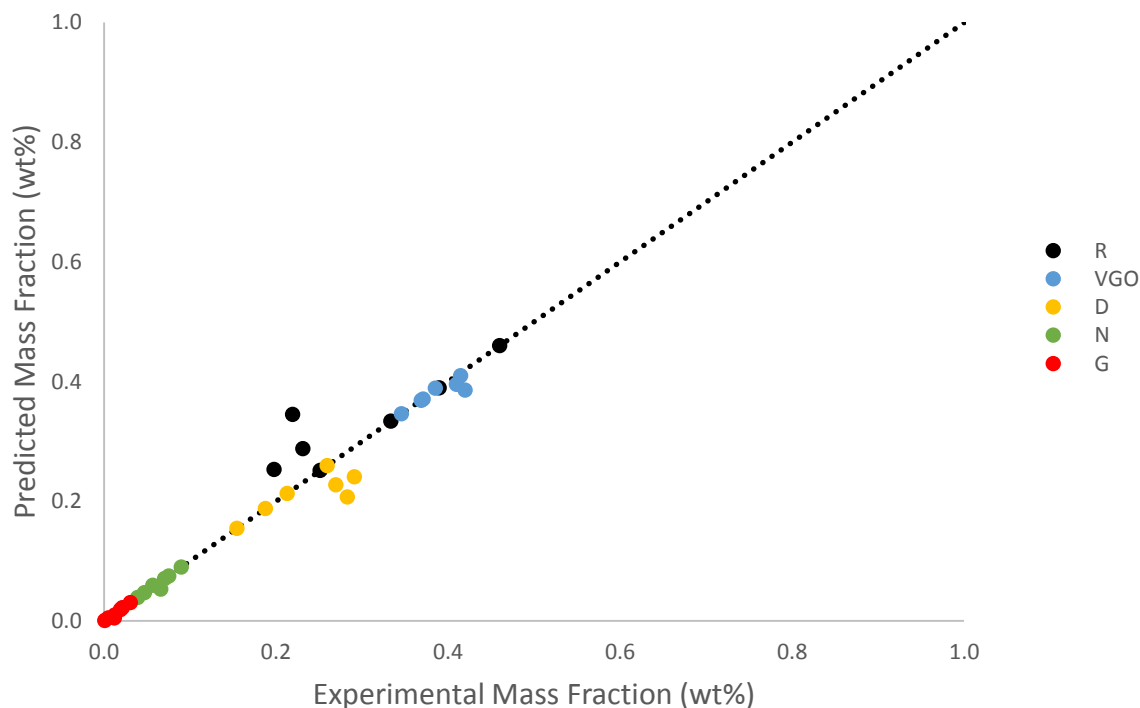


Figure 6.8: Comparison between predicted and experimental component mass fraction for Athabasca bitumen ultradispersed hydroprocessing

6.3 Athabasca pitch kinetic model:

Experimental runs were carried out to obtain enough data to develop a kinetic model for Athabasca pitch ultradispersed catalytic hydroprocessing. Appendix D: Experimental data for Athabasca pitch ultradispersed catalytic hydroprocessing, shows a table containing all the experimental data obtained from these runs. The same reaction scheme and component breakdown used in the previous case was implemented, however, during the calculation process and based on evident experimental trends, several reactions were neglected until the best fit was obtained with the most comprehensive results.

Similarly to the previous case, applying the simplest kinetic model (feed is converted into products), the apparent activation energy of the reactive system was determined by using the Arrhenius plot. Figure 6.9 shows the Arrhenius plot for Athabasca pitch ultradispersed catalytic hydroprocessing. The correlation coefficient of the natural logarithm of the global reaction constant and the inversed temperature was 0.851, leading to an activation energy value of 153.5 kJ/mol. Even though the correlation coefficient was relatively low, the apparent activation energy resulted to be in the range of typical bitumen ultradispersed catalytic hydroprocessing.

Table 6.2 presents the kinetic parameters for Athabasca pitch ultradispersed catalytic hydroprocessing obtained by using the proposed kinetic regression method. Negligible reactions were not included within the table. Based on these results, it can be said that reactions 7, 9, and 10, producing gases from VGO, Distillates, and naphtha, respectively, showed negligible reaction constants at the evaluated conditions, suggesting that gas production comes exclusively from hydroprocessing of the residue fraction, which also implies that naphtha hydrocracking is insignificant in this system. Also, the conversion of VGO into naphtha resulted in an

insignificant value for this reaction constant which supported the assumption of neglecting this reaction, thus decreasing the number of reactions to six.

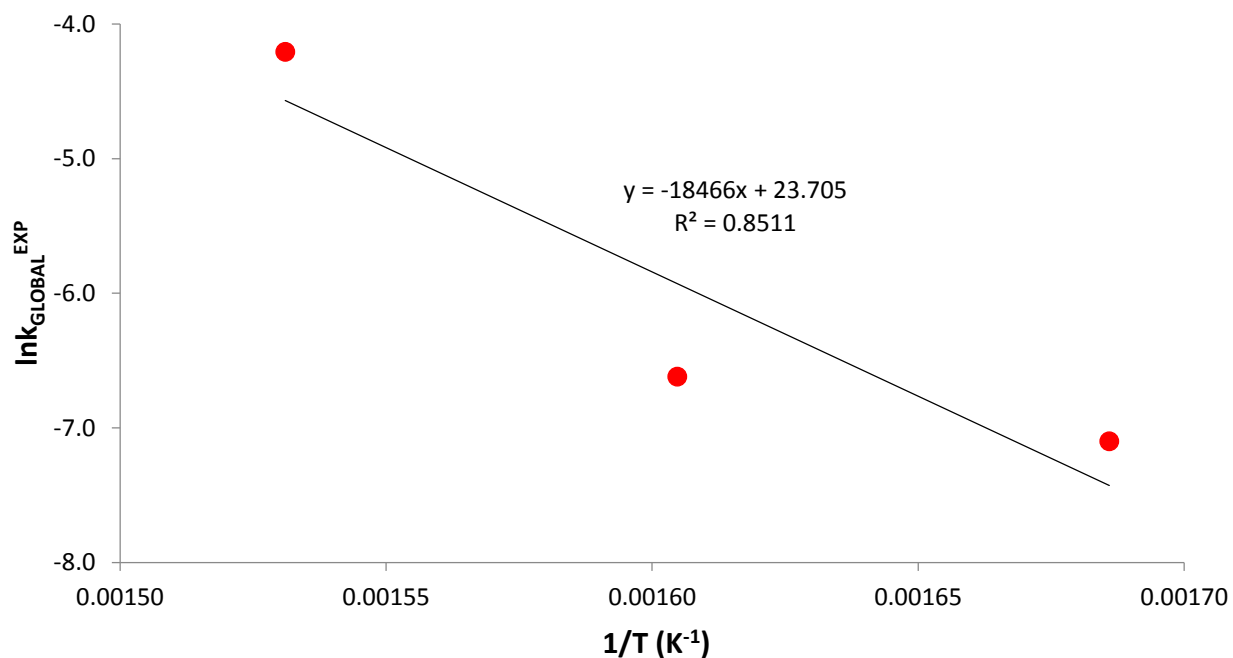


Figure 6.9: Arrhenius plot for Athabasca pitch ultradispersed catalytic hydroprocessing

Table 6.2: Kinetic parameters for Athabasca pitch ultradispersed catalytic hydroprocessing

Temperature (°C)					Pre-Exponential	Activation	R²
					Factor (h⁻¹)	Energy (kJ/mol)	
Reaction Constant (h⁻¹)	1	0.00061	0.00170	0.00915	2.840·10⁹	144.4	0.972
	2	0.00016	0.00059	0.00400	2.557·10¹¹	173.3	0.982
	3	0.00006	0.00029	0.00158	3.665·10¹¹	179.8	0.999
	4	0.00000	0.00001	0.00017	1.779·10¹⁸	276.0	0.992
	5	0.00003	0.00014	0.00063	1.807·10¹⁰	168.3	1.000
	8	0.00000	0.00018	0.01365	1.434·10³⁷	487.9	1.000

From Table 6.2 and Figure 6.10 it can be noticed that similarly to the case of Athabasca bitumen, residue reactions are also dominant, being the production of VGO the more selective of this set of reactions. Distillates production is the second cut being favored. Naphtha production comes mainly from residue conversion, and a smaller fraction comes from distillates hydrocracking. Among the differences with the previous case (bitumen) it can be noted that VGO fraction showed lower reactivity, which is expected due to the lower paraffin content of the pitch sample. Also the distillates hydrocracking showed higher reaction constant at high temperatures than gas production reaction. This can be related to the experimental error associated to the estimation of distillates, naphtha and gas cuts which may affect the estimation of their parameters.

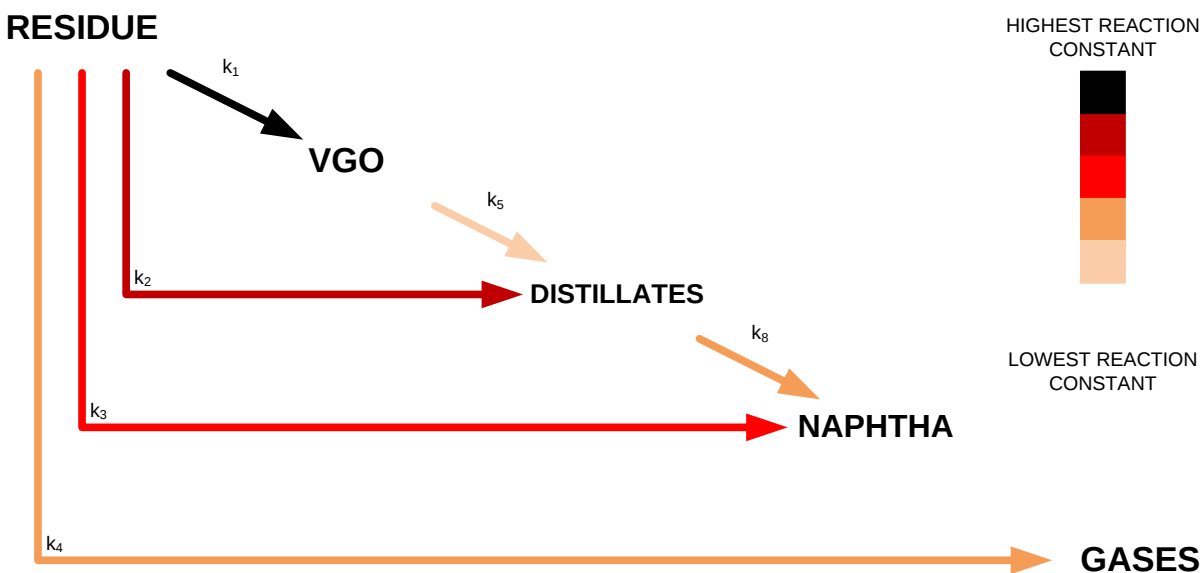


Figure 6.10: Comparison of reaction constants for Athabasca pitch ultradispersed catalytic hydroprocessing

Figure 6.11 shows the Arrhenius plot (natural logarithm of reaction rate vs. inverse of absolute temperature) for the evaluated system. All the linear regressions were acceptable, reporting the lowest correlation coefficient of 0.972 for reaction 1, showing no significant deviation within the range of evaluated conditions. This confirms that the proposed model is representative of the system, and also that reactions are kinetically controlled.

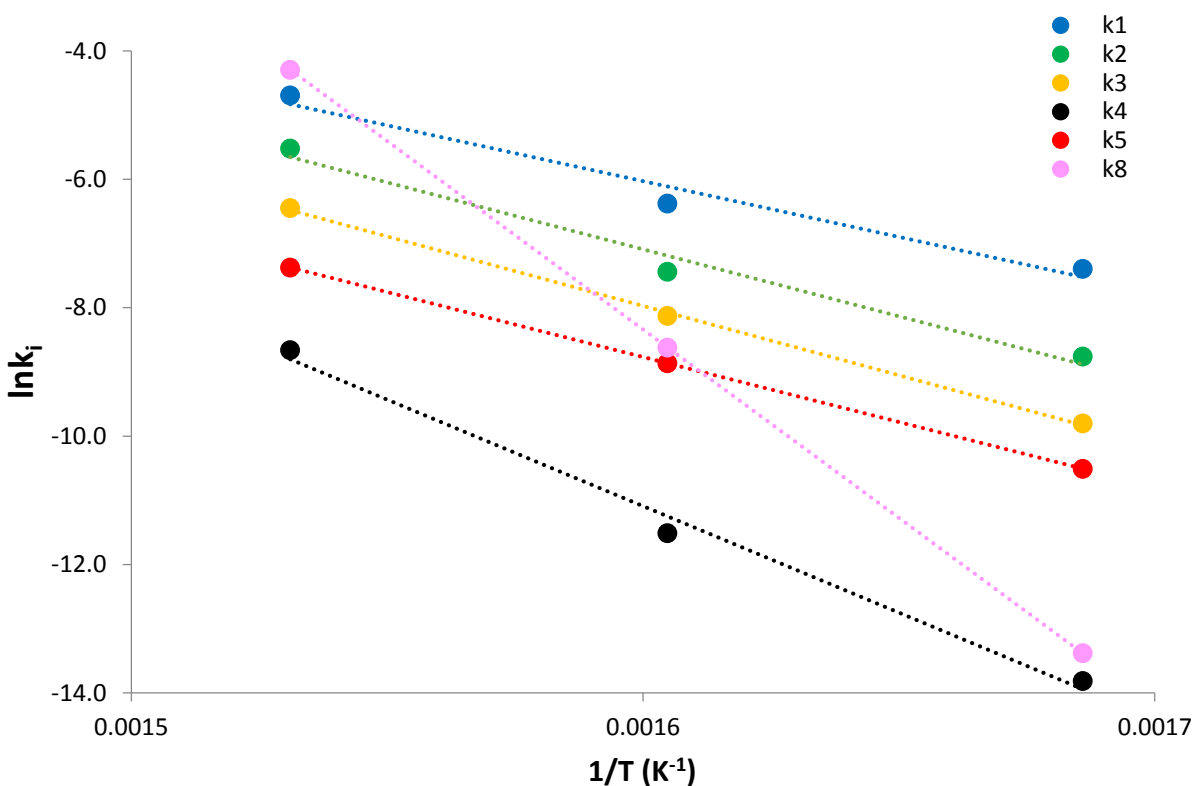


Figure 6.11: Arrhenius Plot for Athabasca pitch ultradispersed catalytic hydroprocessing

Figure 6.12, a comparison between predicted and experimental component mass fraction for Athabasca vacuum residue ultradispersed catalytic hydroprocessing, shows good prediction for the proposed model, reporting a correlation coefficient of the entire data of 0.993 and an average percentage error of 7.13%. Deviation of the model can be attributed to the inherent

experimental error of the runs, error of the analytical techniques, and errors due to the interpolation of boiling point curves.

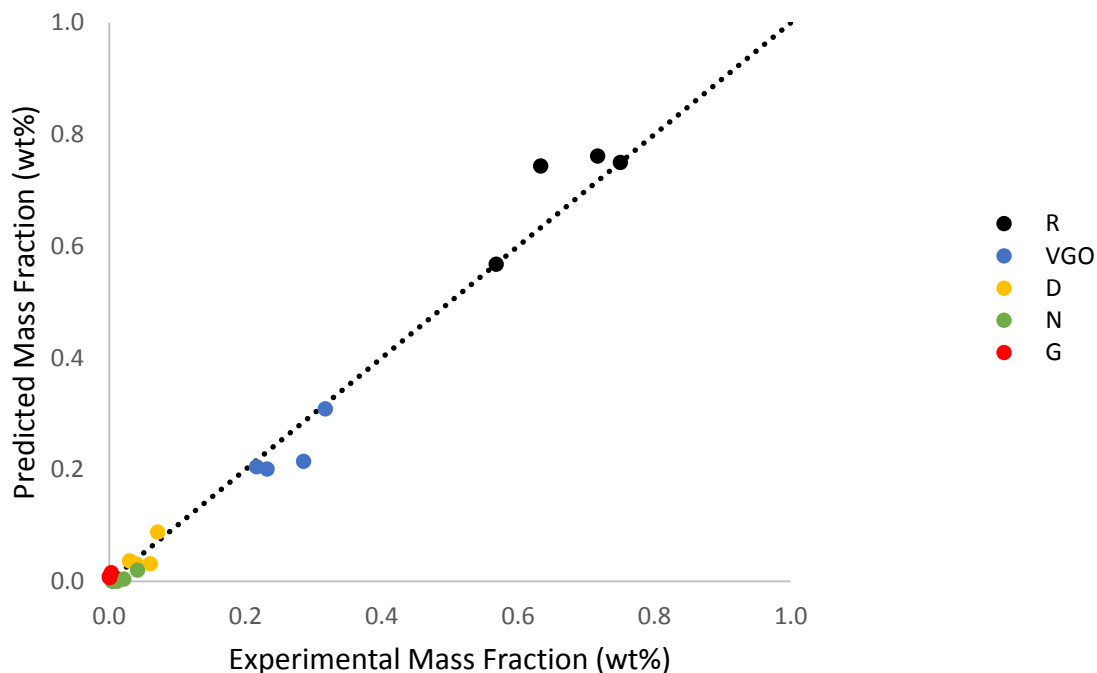


Figure 6.12: Comparison between predicted and experimental component mass fraction for Athabasca pitch ultradispersed hydroprocessing

6.4 Athabasca vacuum residue kinetic model:

Experimental runs were carried out to obtain enough data to develop a kinetic model for Athabasca vacuum residue ultradispersed catalytic hydroprocessing. Appendix E: Experimental data for Athabasca vacuum residue ultradispersed catalytic hydroprocessing, shows a table containing all the experimental data obtained from these runs. The same reaction scheme and components breakdown used in the previous case was implemented, however, during the

calculation process and based on evident experimental trends, several reactions were neglected until the best fit was obtained with the most comprehensive results.

Assuming the simplest kinetic model, i. e. feed is converted into products, it was possible to determine the apparent activation energy of the reactive system by using the Arrhenius plot. Figure 6.13 shows the Arrhenius plot for Athabasca vacuum residue ultradispersed catalytic hydroprocessing. An acceptable correlation between the global reaction constant and the inversed temperature was found reporting a correlation coefficient of 0.912, leading to an activation energy of 44.8 kJ/mol.

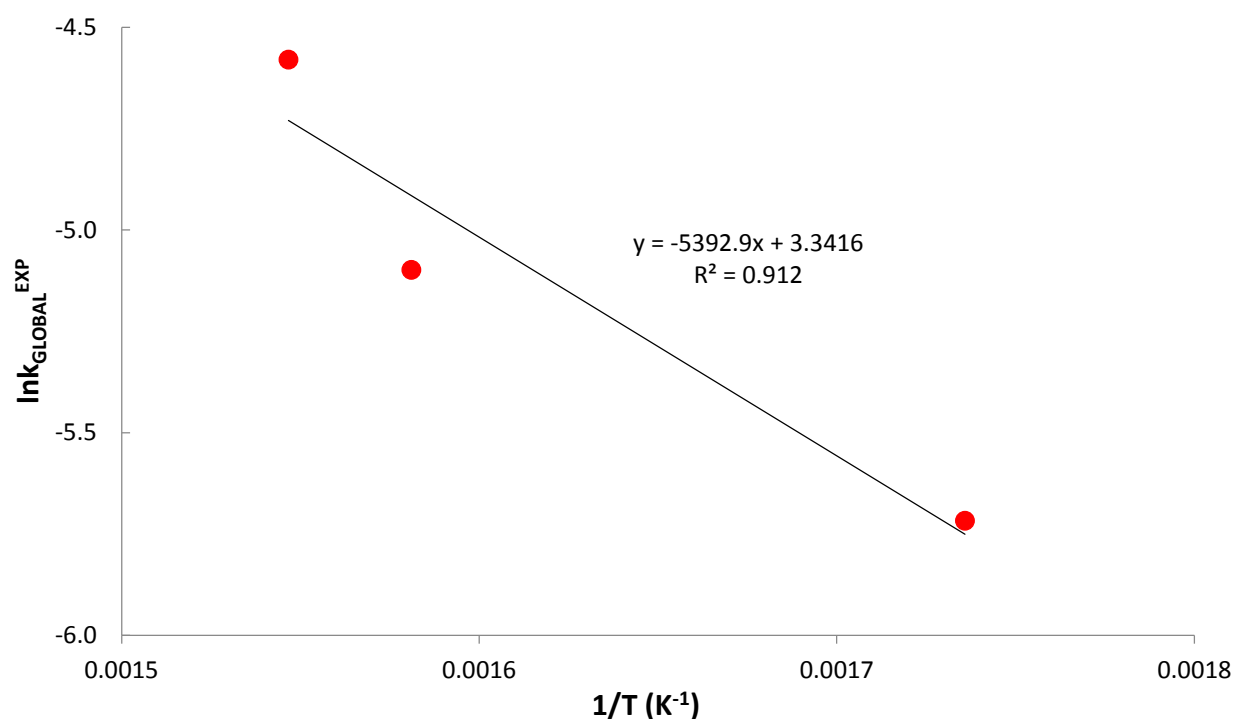


Figure 6.13: Arrhenius plot for Athabasca vacuum residue ultradispersed catalytic hydroprocessing

Table 6.3 presents the kinetic parameters for Athabasca vacuum residue ultradispersed catalytic hydroprocessing obtained by using the proposed kinetic regression method. Negligible

reactions were no included within this table. Based on these results, it can be said that reactions 7, 9, and 10, producing gases from VGO, Distillates, and naphtha, respectively, showed negligible reaction constants at the evaluated conditions, suggesting that gas production comes exclusively from hydroprocessing of the residue fraction, which also implies that naphtha hydrocracking is insignificant in this system. Also, the conversion of VGO into naphtha resulted in an insignificant value for the reaction constant, which supported the assumption of neglecting this reaction, decreasing the number of reactions to six.

Table 6.3: Kinetic parameters for Athabasca vacuum residue ultradispersed catalytic hydroprocessing

		Temperature (°C)			Pre-Exponential	Activation	R ²
		320	380	395	Factor (h ⁻¹)	Energy (kJ/mol)	
Reaction Constant (h ⁻¹)	1	0.00126	0.00441	0.00792	6.831·10 ³	76.6	0.979
	2	0.00060	0.00124	0.00166	3.745	43.2	0.988
	3	0.00012	0.00037	0.00046	16.145	58.1	1.000
	4	0.00001	0.00009	0.00021	5.486·10 ⁷	146.6	0.995
	5	0.00042	0.00145	0.00217	7.045·10 ²	70.8	0.996
	8	0.00000	0.00092	0.00392	9.15·10 ²⁵	362.7	1.000

Figure 6.14 shows the kinetic model indicating the relative differences between reaction constants for Athabasca vacuum residue ultradispersed catalytic hydroprocessing, the darker the color, the higher the calculated reaction constant and vice versa. From Figure 6.14 and Table 6.3, it can be seen that similarly to the cases of Athabasca bitumen and pitch, residue reactions are also dominant, being the production of VGO the more selective of this set of reactions. Distillates production is the second lump being favored, showing that the conversion of residue

and VGO into distillates cut possesses a similar level of reactivity. At lower temperatures, naphtha production comes mainly from residue conversion, but as the temperature increases, this reaction becomes more significant. The only difference with the bitumen is that in this case the distillate hydrocracking showed a higher reaction constant than gas production, however, this can be related to the experimental error associated to the gas measurement which may affect the estimation of its parameters.

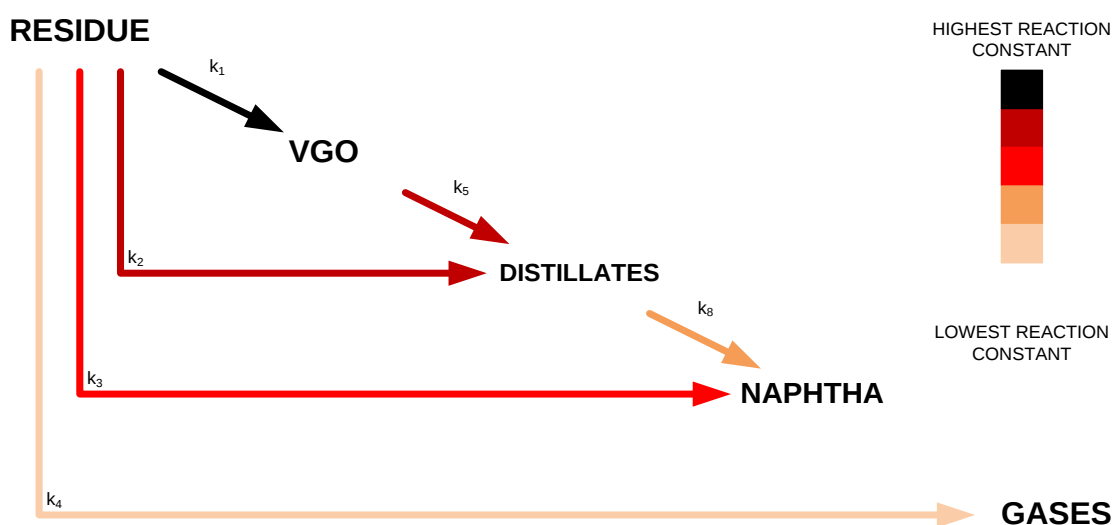


Figure 6.14: Comparison of reaction constants for Athabasca vacuum residue ultradispersed catalytic hydroprocessing

Figure 6.15 shows the Arrhenius plot (natural logarithm of reaction rate vs. inverse of absolute temperature) for the evaluated system. All the linear regressions were acceptable, reporting the lowest correlation coefficient of 0.979 for reaction 1, showing no significant deviation within the range of evaluated conditions. This confirms that the proposed model is representative of the system, and also that reactions are kinetically controlled. Finally Figure 6.16, a comparison between predicted and experimental component mass fraction for Athabasca

vacuum residue ultradispersed catalytic hydroprocessing, shows a quite well prediction of the proposed model, reporting a correlation coefficient of the entire data of 0.997 and an average percentage error of 3.97%. Deviation of the model can be attributed to the inherent experimental error of the runs, error of the analytical techniques, and errors due to the interpolation of boiling point curves.

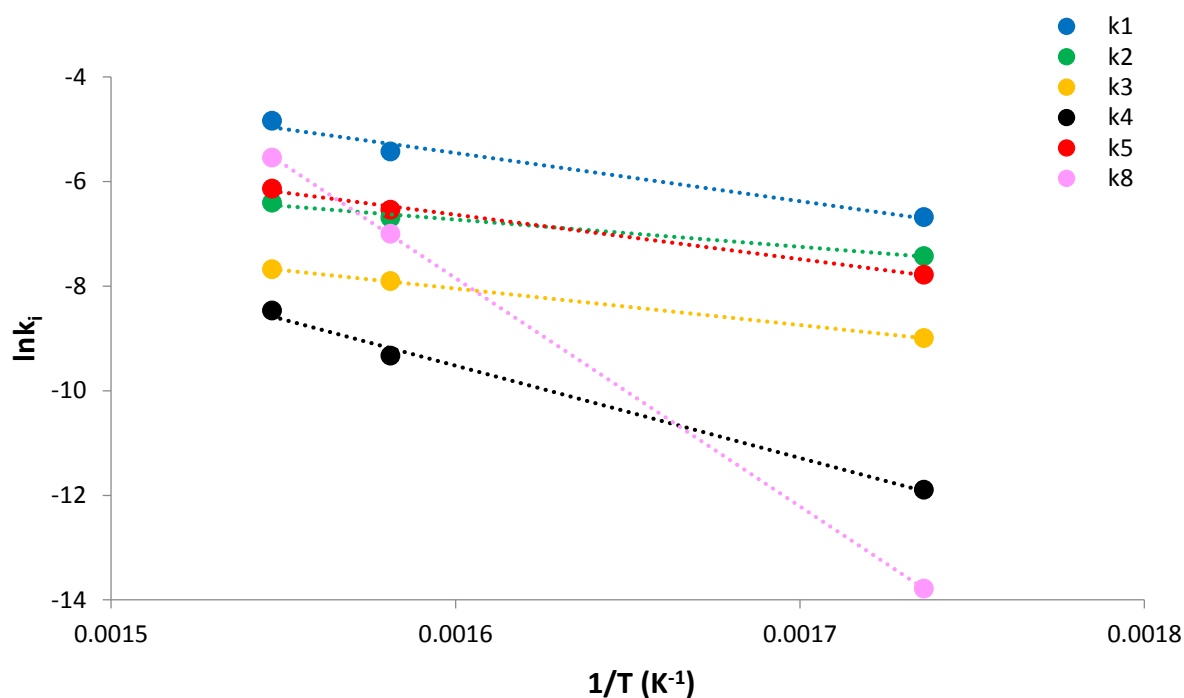


Figure 6.15: Arrhenius Plot for Athabasca vacuum residue ultradispersed catalytic hydroprocessing

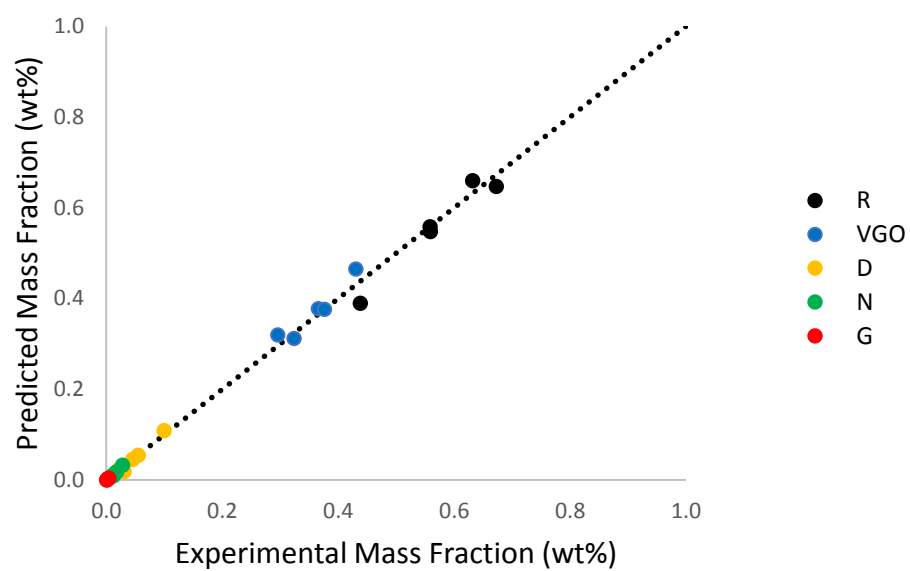


Figure 6.16: Comparison between predicted and experimental component mass fraction for Athabasca vacuum residue ultradispersed catalytic hydroprocessing

CONCLUSIONS AND RECOMMENDATIONS

In this chapter major findings reached from this study as well as recommendations for future research in this topic are presented. They are grouped by chapter of result:

Solvent De-Asphalting Experiments:

- The in-house designed and built SDA unit at CBUG produced the expected results: DAO showed a significant lower asphaltene content, boiling point and viscosity and high API gravity when compared with the feedstock; on the other hand, pitch (asphaltene-rich product), reported high viscosity, boiling point and density consistent with its high asphaltene content. It was found that about 2.6 wt% of the light components present in the feedstock are recovered with the solvent when Athabasca bitumen is solvent deasphalted. The separated DAO and pitch showed similar properties to products obtained at laboratory scale, confirming that they can be used as representative samples for further studies.

Athabasca pitch and vacuum residue reactivity test:

- Ultradispersed catalytic hydroprocessing of Athabasca pitch and vacuum residue clearly showed the effect of process variables on product quality. In the pitch case, residue conversion values about 30.0 wt% were reached at the most severe conditions (highest temperature) with an asphaltene conversion around 40.0 wt% and improvement of API gravity up to 5.4 °API. For vacuum residue the maximum residue conversion reported was 44 wt% with a noticeable decrease in viscosity (99.9%) and, improvement in API gravity (6.5 °API). In both cases, increase in all distillable cuts, i.e. VGO and lights, was evidenced, with the highest proportion in the VGO range.
- Pitch ultradispersed catalytic hydroprocessing showed that liquid product boiling point is more sensible to changes in temperature than changes in residence time under the evaluated

conditions. Increase in distillates, naphtha and gases yields are only noticeable at high reaction severity. Asphaltene conversion was higher than the residue conversion suggesting that asphaltene molecules could have been upgraded, reducing its molecular weight, heteroatoms content (sulfur, nitrogen, oxygen, etc.), and aromaticity; however, the produced material would still be within the boiling point range of the residue fraction.

- Vacuum ultradispersed catalytic hydroprocessing also showed a noticeable increase in distillates, naphtha and gases yields at high reaction severity. Models for predicting liquid products API gravity and viscosity as a function of the residue conversion were developed, reporting correlation coefficient of 0.997 for both cases.

Athabasca bitumen, pitch and vacuum residue kinetic modeling:

- A kinetic regression method was proposed to calculate the kinetic parameters of a reactive system using a 5 lump/10 reactions scheme. The use of an objective function which accounts for model deviation and Arrhenius plot linearity, yield comprehensive results for the proposed kinetic models. An application developed in Microsoft Excel coupled with Visual Basic for Applications showed reasonable results. As a recommendation, a more robust software can be developed using the concept proposed in this research, employing a more powerful programming language, such as MATLAB or C, and the incorporation of a wider variety of optimization algorithms, possibly leading to improve even more model accuracy.
- A kinetic model was proposed in this research for Athabasca bitumen ultradispersed catalytic hydroprocessing at achievable reservoir conditions. The reported average percentage error was 3.11%, with an overall correlation coefficient of 0.978. It was proven that gases are mostly produced from residue hydroprocessing, naphtha is essentially non-reactive, and the dominant reaction under the evaluated conditions was residue conversion. VGO

hydrocracking is also important but mainly produces distillates-range hydrocarbons (216-343 °C). Linear regressions of the Arrhenius plot data showed correlation coefficients higher than 0.987. Activation energies for residue conversion spanned within the range of 139.5-272.9 kJ/mol, which is in agreement with the literature for similar systems. Naphtha production from VGO and distillates resulted in the most energy demanding reactions.

- Likewise, a kinetic model was proposed in this research for Athabasca vacuum residue ultradispersed catalytic hydroprocessing at achievable reservoir conditions. The reported average percentage error was 3.97%, with an overall correlation coefficient of 0.997. Similarly to the bitumen case, it was also proven that gases are mostly produced from residue hydroprocessing, that naphtha is non-reactive, and the dominant reaction under the evaluated condition was residue conversion. VGO hydrocracking is also important, only producing distillates-range hydrocarbons (216-343 °C). Linear regressions of the Arrhenius plot data showed correlation coefficients higher than 0.979. In this case, activation energies of residue conversion reactions were significantly lower than the ones obtained for the bitumen, spanning within the range of 43.2-146.6 kJ/mol. Naphtha production from distillates resulted in the most energy demanding reactions, and naphtha production from VGO is practically negligible.
- A kinetic model was proposed in this research for Athabasca pitch ultradispersed catalytic hydroprocessing at achievable reservoir conditions. The reported average percentage error was 7.13%, with an overall correlation coefficient of 0.993. Once again, it was also proven that gases are mostly produced from residue hydroprocessing, that naphtha is non-reactive, and that the dominant reactions under evaluated conditions were VGO hydrocracking and residue conversion. Linear regressions of the Arrhenius plot data showed correlation

coefficients higher than 0.972. Activation energies for residue conversion spanned within the range of 144.4-276.0 kJ/mol, which is in the same range than the ones calculated for the bitumen case. Naphtha production from distillates resulted in the most energy demanding reactions, and naphtha production from VGO is practically negligible.

- Results in this thesis showed a lower reactivity of the residue sample suggesting three possible causes: the sample supplied by Suncor Energy Inc. is not from the Athabasca reservoir, the sample was submitted to a thermal treatment (cracking) prior the reactivity test performed in this research, or hydrogen diffusion limitation were present during the reactivity test. To solve this unknown, it is recommended to perform a kinetic study of catalytic ultradispersed hydroprocessing of a vacuum residue sample directly obtained from Athabasca bitumen sample.
- As a next step for studying catalytic in situ upgrading technology, it is suggested to perform the injection of Athabasca deasphalting pitch with nanocatalysts in sandpacks. This will allow the confirmation of the effect of nanoparticles over the porous media, the determination of residue and asphaltene conversion levels, and the quantification of oil viscosity and density reduction, among other important parameters that support to define the feasibility of this method.

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**APPENDIX A: STANDARD OPERATING PROCEDURE FOR SOLVENT DE-
ASPHALTING UNIT**

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1. Purpose / Background:

In the context of the Nexen technology project it was requested to research on the Solvent De-Asphalting process. To accomplish this objective the construction and operation of the SDA unit was necessary.

2. Scope:

This document covers the procedures for the operation, samples collection and emergency shutdown of the Solvent De-Asphalting (SDA) unit.

3. Prerequisites:

Before starting the operation of the unit, the operator must be familiar with the procedure for the operation and emergency shutdown of this setup. Also the operator must be aware of the risk involved for using some chemical compounds such as: pentane, hexane, condensate, bitumen, vacuum residue and toluene. A separate document provides all the Safety Material Data Sheet for these compounds.

Safety equipment required for the operation of this set-up is:

- Lab coat,
- Safety glasses, and
- Rubber or neoprene gloves.

4. Unit Description:

The Solvent De-Asphalting (SDA) unit was design to operate under batch mode. The unit can be divided into three major sections which are:

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- Feed section,
- Extractor section, and
- Separation and Solvent recovery section.

Details of each section are presented below:

4.1. Feed Section:

This section comprises all the tanks and pumps needed to transfer the feedstock (i. e. bitumen/vacuum residue, solvent, and vacuum gasoil) into the Extractor (R-1). Feed Tank (TK-1) is pressurized with nitrogen to ensure a positive pressure on Feed Pump (P-1) suction and is heated by using Feed Tank Temperature Controller (TIC-1), which is connected to a heating tape. A relief valve (PSV-1) was installed to prevent any tank's overpressure (> 135 psig). Thermocouple (TI-1) is used to record the temperature inside of this tank.

A reciprocating controlled-volume pump (P-1) is used to transport the feed, either bitumen or vacuum residue, from the Feed Tank TK-1 to the Extractor (R-1). Several valves, thermocouples and pressure gauges are used to ensure both precision and safety during this process. The temperature of these valves and lines can be increased by a heating tape connected to a temperature controller (TIC-2), while temperature is recorded by thermocouples TI-2 and TI-3 (both at the inlet of the pump).

The three-way valve V-5 is used:

- To verify that the line at the inlet of the Feed Pump (P-1) is filled up (**position A**), and
- To allow the line-up of the tank Feed Tank (TK-1) to the Feed Pump (P-1) (**position B**).

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The pressure gauges PI-2 and PI-3 are used to monitor the pressure at the inlet and outlet of the Feed Pump (P-1), respectively. The line at the pump outlet and the three-way valve V-8 can be heated using the heating tape connected to the loop temperature-controller (TIC-3), and the temperature is recorded by thermocouple TI-4. At the outlet of pump P-1, a relief valve (PSV-2) was installed to prevent any overpressure at the outlet of the pump (> 800 psig). The three-way valve V-8 is used:

- To ensure that the pump outlet line is filled up (**position A**), and
- To line-up of the Feed Pump (P-1) with the Extractor (R-1).

The line between valves V-8 and V-10 can be heated by using temperature controllers TIC-4 and TIC-5, which are connected to heating tapes. Temperature is recorded by thermocouples TI-5 and TI-9. The three-way valve V-10 is used:

- To calibrate and/or confirm the flowrate set by pump P-1 (**position A**). This procedure is accomplished by using the back-pressure regulator valve V-12. This valve is set at the same operating pressure to be used during the experiment in the extractor (500 psig). This line can be heated by using the heating tape connected to the loop temperature-controller (TIC-6), and the temperature is recorded by thermocouple TI-10, and
- To line-up the discharge of the pump P-1 is to Extractor (R-1) (**position B**).

The Solvent Tank (TK-2) has an approximate capacity of 5 liters. The tank rests on a balance, so the operator can estimate the mass of solvent pumped into the extractor as a function of time. This tank can be pressurized with nitrogen up to 10 psig to ensure a positive pressure on the

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suction of the Solvent Pump (P-2). The relief valve (PSV-6) was installed to prevent any tank's overpressure (>10 psig). A centrifugal pump (P-2) is used to transfer the solvent from the tank TK-2 to the Extractor (R-1). Several valves, thermocouples and pressure gauges are used to ensure both precision and safety during this process. The relief valve PSV-8 was installed to prevent any damage in the Solvent Pump by overpressure (100 psig).

The three-way valve V-25 is used:

- To check if the line at the inlet of the Extractor (R-1) is filled with solvent (**position A**), and
- To line-up of the Solvent Pump (P-2) to the Extractor (R-1) (**position B**).

Valve V-11 allows the entry of the feedstock into the Extractor (R-1). This valve works in combination with three-way valves V-10 and V-25 allowing the admission of bitumen/vacuum residue, or solvent.

A Vacuum Gas Oil (VGO) Tank (TK-3) with a similar configuration to the Feed Tank (TK-1) was included during the design of the unit. VGO is used to clean lines after all the bitumen or vacuum residue required for the experiments has been delivered from the Feed Tank (TK-1) into the Extractor (R-1).

4.2. Extractor Section:

A stirred jacket-heated vessel with a nominal capacity of 2 gallons was selected as extractor to carry out the de-asphalting process. Several modifications were incorporated into the design of

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the extractor system to ensure a safe operation and an optimum experiment. Some of the features of this system are:

- Thermal Bath to heat up the Extractor (R-1) by circulating a heat transfer fluid (Duratherm 450) through a heating jacketed cylinder welded around the extractor.
- An explosion proof variable speed motor was selected to drive the agitation in the reactor.
- To Hot Oil Cooler (E-3) to speed up the cooling process of the Extractor (R-1).

The operating conditions within the extractor are monitored and controlled in the control box, which are:

- Internal temperature (TI-21),
- Pressure (PI-5B), and
- Agitation speed (SC-1).

Also, the pressure inside the vessel can be also monitored by PI-5A, while the temperature of the heat transfer fluid at the inlet and the outlet of the jacket-welded cylinder can be monitored by thermocouples TI-7 and TI-8, respectively.

The de-asphalting process is carried out at specific operation conditions and, as consequence two phases are separated inside the extractor, the first one is a low density liquid comprising the De-Asphalted Oil (DAO) and the solvent, and the second phase (asphaltenes) is a high density liquid phase (semi-solid).

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4.3. Separation and Solvent Recovery Section:

This section comprises the separation of the extractor product in three fractions: solvent recovered, de-asphalted Oil (DAO) and Pitch. This separation is achieved in two steps: the first takes place into the Extractor. Once the bitumen/vacuum residue and the solvent have been mixed for 60 minutes, 60 additional minutes are given to allow the formation of two phases into the Extractor (R-1). The upper phase will mainly have the DAO and the solvent while the lower phase will consists in a mixture of asphaltenes and a small fraction of DAO and solvent (Pitch).

Based on the literature review, the separation in the extractor can be done by using tubes strategically located and dipped into the upper phase. This will be done by using two tubes at different levels, which have to be located previous to the experiment based in the estimation of the interphase height. Valve V-28, V-29 and V-30 are used to transfer the upper phase to the DAO Separator (D-1). These lines can be heated by using the Temperature Controller TIC-7 and the temperature is recorder by the thermocouple TI-17. Valve V-37 is used to transfer the lower phase into the Pitch Separator (D-2). This line can be heated by using the Temperature Controller TIC-10.

In the DAO Separator (D-1) solvent and DAO are separated by distillation at the specific conditions. The temperatures in the vessel D-1 and in the top product line are set by the Temperature Controllers TIC-8 and TIC-9, and they are recorded by thermocouple TI-18 and TI-14, respectively. Solvent is vaporized and condensed in the Solvent Condenser (E-2) and collected in the Solvent Recovery Tanks (TK-4). A constant nitrogen flow is fed to the Solvent

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Recovery Tank (TK-4) to provide blanketing reducing the partial pressure of the solvent. The DAO is collected from the bottom by using valve V-31. Solvent is recovered from the bottom of the Solvent Recovery Tank (TK-4) by opening valves V-34 and V-61.

Pitch Separator (D-2) is used to separate any remaining solvent present in this stream in this stream. This separator can be heated by using the temperature controller TIC-11, and the temperature is recorded by thermocouple TI-15. The Pitch can be collected from the bottom by using valve V-38. The line connecting the Pitch Separator (D-2) and the Solvent Condenser (E-2) can be heated by heating tapes controller by TIC-12. Solvent Condenser (E-2) inlet and outlet temperatures can be monitored by thermocouples TI-14 and TI-13, respectively.

5. Operating procedure:

The operating procedure includes several steps which have to be performed as indicated in order to warranty safety and optimum process conditions. The procedure described below has been developed for producing one DAO batch. If more than one batch is required, a modification of the present procedure has to be done considering process safety.

The process is divided into 9 steps: Extractor Preliminary Configuration, Unit Preparation, Solvent Feeding, Extractor Condition Setup, Bitumen/Vacuum Residue Feeding, Extractor Mixing and Settling, Products Separation, Cool Down and System Cleaning.

5.1. Extractor Preliminary Configuration:

5.1.1. This step consists in the estimation of the interphase level which can be done performing a mass balance assuming recovery factors for each phase. A minimum

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distance between the interphase and the lower system of 0.5 inch is recommended to avoid pitch entrainment in the upper phase.

5.1.2. If the Extractor (R-1) has been previously opened, a Leak Test must be performed.

5.1.3. Feed Tank (TK-1), Solvent Tank (TK-2), and VGO Tank (TK-3) must be filled.

5.1.4. Connect cooling water lines to Solvent Condenser (E-2) and Hot Oil Cooler (E-3).

5.2. Unit Preparation:

5.2.1. Check the extraction system in the Feed Preparation Room.

5.2.2. Make sure the entire unit is depressurized.

5.2.3. Make sure all the valves are closed in the unit.

5.2.4. Open LP Nitrogen valve V-41 and check the pressure in the LP Nitrogen cylinder (P-12A). The pressure should be higher than 200 psig.

5.2.5. Set the pressure for the LP Nitrogen supply at 30 psig by adjusting pressure regulator V-42 (PI-12B). Open valve V-43.

5.2.6. Open HP Nitrogen valve V-53 and check the pressure in the HP Nitrogen cylinder (P-16A). The pressure should be higher than 700 psig.

5.2.7. Set the pressure for the NP Nitrogen supply at 600 psig by adjusting pressure regulator V-54 (PI-16B). Open valve V-55.

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5.2.8. Ensure that the tank TK-1 is filled up with feedstock. Fully open valve V-44 to pressurize it with nitrogen at 30 psig (PI-1). Make sure that valve V-1 is completely closed.

5.2.9. Ensure that the tank TK-3 is filled up with VGO (use level glass by fully opening valves V-51 and V-52, once the level is read close V-51 and V-52). Fully open valve V-46 to pressurize it with nitrogen at 30 psig (PI-2). Make sure that valve V-48 is completely closed.

5.2.10. Power up the plant. Check the following devices: Temperature Controller, Extractor Control Box, Nitrogen Flow Controller, Thermocouples Displays, Feed Pump (P-1), Solvent Pump (P-2), and Solvent Tank (TK-2) scale.

5.2.11. Start cooling water circulation in Solvent Condenser (E-2) by fully opening valve V-40.

5.2.12. Start heating up feed line (controllers TIC-01, TIC-02, TIC-03, TIC-4, TIC-5, TIC-7, TIC-8, TIC-9, TIC-10, TIC-11, and TIC-12) up to 150 °C. The increase of temperature must be done step-wisely using a rate of 20 °C each 5 minutes.

5.3. Solvent Feeding:

5.3.1. Set the Solvent Tank (TK-2) pressure at 10 psig by adjusting the pressure regulator V-14. Fully open valves V-16, V-17. Make sure valve V-15 is completely close.

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5.3.2. Fully open valve V-18, V-19, and V-23. Switch V-25 to position A, and open V-26. Once solvent is collected at the outlet of V-26 close it completely and switch V-25 to position B. Make sure V-21 is completely closed.

5.3.3. Record the initial weight of the Solvent Tank TK-2.

5.3.4. Turn on Solvent Pump (P-2). Fully open valve V-11 to allow the solvent to be fed into the Extractor (R-1).

5.3.5. Monitor the weight of Solvent Tank (TK-2), when the required amount of solvent has been transferred into the Extractor (R-1), valve V-11 is completely closed and the pump P-2 is stopped.

5.4. Extractor Condition Setup:

5.4.1. Start Extractor hot oil circulation by fully opening valve V-27, turning on the Thermal Bath (E-3). Set the temperature at experiment conditions. Monitor internal Extractor temperature TI-21.

5.4.2. Start heating up the extractor feed and calibration lines (TIC-06) up to 150 °C. The increment of temperature must be done step-wisely using a rate of 20 °C each 5 minutes.

5.4.3. Increase the pressure in the Extractor (R-1) with nitrogen by fully opening valve V-56. Set the regulator V-57 up to 500 psig (PI-16B), fully open valve V-58 and switch V-59 to position A.

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5.4.4. Start the agitation in the extractor accordingly with operating conditions selected (SC-1).

5.4.5. Adjust the Thermal Bath (E-3) temperature until the target temperature inside the extractor is reached (TI-21). After the target temperature value is reached allow a period of 60 minutes for temperature stabilization.

5.4.6. If necessary adjust the pressure in the extractor by using valve V-59.

5.5. Bitumen/Vacuum Residue Feeding:

5.5.1. Check that temperatures in the Feed Tank (TK-1) and feed line are between 130-150 °C (TI-1, TI-2, TI-3, TI-4, TI-5, TI-9, and TI-10).

5.5.2. Fully open valve V-2 and V-5 is switched to position A to check if the lines are filled with feedstock. Once the feedstock is collected V-5 is switched to position B.

5.5.3. Valve V-8 is switch to position B, valve V-10 is switched to position A and valve V-12 and V-13 are fully opened.

5.5.4. Start pump P-1 (HS-1), pressures on the gauge PI-3 and PI-4 must be monitored constantly.

5.5.5. Once the feedstock is collected at the outlet of valve V-13, set the discharge pressure of the P-1 at 500 psig by adjusting the back pressure regulator valve V-12.

5.5.6. Determine the mass flowrate using a stopwatch and a scale. Once the flowrate is properly calculated determine the amount of time required to feed the extractor with the targeted amount of feedstock.

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5.5.7. V-10 is switch to position B and V-11 is completely opened to allow the extractor to be fed. Record the initial time.

5.5.8. After all the feedstock required is transferred into the extractor the valve V-11 is completely closed and valve V-10 is switched to position A.

5.5.9. Valve V-50 is fully opened and V-3 is completely closed to start the cleaning process with VGO.

5.5.10. When VGO is collected at the outlet of the valve V-13 switch V-8 to position A, fully open valve V-9 and close valve V-12 and V-13.

5.5.11. When VGO is collected at the outlet of valve V-9, stop pump P-1 and completely close valve V-9.

5.5.12. Switch V-5 to position A, when VGO is collected, switch V-5 to position B.

5.5.13. Set the temperature of the controllers TIC-01, TIC-02, TIC-03, TIC-04, TIC-5, and TIC-06 to 0 °C.

5.6. Extractor Mixing and Settling:

5.6.1. A period of 60 minutes of agitation is allowed to warranty a good mixing between the solvent and the bitumen/vacuum residue. After this amount of time stop extractor agitation (SC-1).

5.6.2. A period of time of 60 minutes for sedimentation is allowed in the Extractor (R-1) for asphaltene settling.

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5.7. Products Separation:

5.7.1. Make sure V-30, V-37, V-31, V-38, V-34, V-61, and V-35 are completely close.

Open valves V-32, V-39, V-33, and V-62. Pressurize the system up to 50 psig by slowly opening valve V-63 (PI-6, PI-7, PI-8, PI-9, and PI-10). Fully close valve V-63.

5.7.2. Set a nitrogen flow of 100 SCCM in flow controller FC-1, and set a pressure of 50 psig by using the back-pressure regulator V-36 (PI-9).

5.7.3. Set a temperature of 200 °C in TIC-7, 250 °C in TIC-8 and 250 °C in TIC-9 (DAO Separator).

5.7.4. Set a temperature of 300 °C in TIC-10, TIC-11 and TIC-12 (Pitch Separator).

5.7.5. Slowly open valves V-28 and V-30 to transfer the upper phase liquid from the Extractor (R-1) to the DAO Separator (D-1). Monitor the pressure registered by PI-6 and P-7.

5.7.6. When no more liquid is transferred from the upper system, slowly open valves V-29 and V-30 to transfer an additional fraction of the upper phase liquid from the Extractor (R-1) to the DAO Separator (D-1). Monitor the pressure registered by PI-6 and P-7. Once finished fully close valves V-28, V-29 and V-30.

5.7.7. Slowly open V-37 to transfer the lower phase (pitch) from the Extractor (R-1) to the Pitch Separator (D-2). Monitor PI-10. On is finished close V-37.

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5.7.8. Allow 60 minute to distill and recover the solvent from DAO Separator (D-1) and Pitch Separator (D-2) into the Solvent Recovery Tank (TK-4).

5.7.9. Recover solvent from Solvent Recovery Tank (TK-4) by fully opening V-34 and slowly opening V-61.

5.7.10. Recover DAO from the DAO Separator (D-1) by slowly opening V-31.

5.7.11. Recover pitch from the Pitch Separator (D-2) by opening V-38.

5.8. Cool Down:

5.8.1. Set the temperature of the controllers TIC-07, TIC-08, TIC-09, TIC-10, TIC-11, and TIC-12 to 0 °C.

5.8.2. Set the temperature of the Extractor Heater (E-1) to 0 °C. Keep Hot Oil circulation.

5.8.3. Open valve V-20 to circulate cooling water the Hot Oil Cooler (E-3).

5.8.4. Close valve V-58. Switch V-59 to position B to depressurize the Extractor (R-1). Fully open valve V-36. Set a flow of 0 SCCM in FC-1. Close valve V-55 and fully open valve V-63.

5.8.5. Close valve V-43. Fully open valve V-15.

5.8.6. For safety reasons the solvent tank must be removed and all the solvent remained in the lines must be drained by switching V-25 to position A and opening

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valve V-26. Once the solvent has been drained, valves V-16, V-17, V-18, V-19, V-23, and V-26 are closed and valve V-25 is switched to closed position.

5.8.7. Solvent tank TK-6 must put into a fire proof cabinet.

5.9. System Cleaning:

5.9.1. Once the unit is depressurized and cold, the Extractor (R-1) is opened it. Open valve V-37 and make sure valves V-38 and V-39 are fully closed.

5.9.2. Add at least 2 liters of Toluene in the Extractor (R-1) and let it in the system for about 4 hours.

5.9.3. Drain the solvent by opening valve V-38. Repeat step 5.9.2 until the system is clean.

5.9.4. Add at least 4 liters of Toluene in the Extractor (R-1) and close it.

5.9.5. Close Valves V-28, V-29, and V-37. Open valve V-55, set a pressure of 100 psig by using pressure regulator valve V-57 (PI-18B), fully open valve V-58 and switch valve V-59 to position A.

5.9.6. Close valves V-31 and V-32. Open valves V-28 and V-30 for 10 minutes, then close valve V-28 and open V-29 for 10 minutes.

5.9.7. Drain the solvent by opening valve V-31. Repeat step 5.9.6 until the system is clean.

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6. Emergency shutdown procedure:

The emergency shutdown procedure is described below:

- In the event of a spill of solvent follow these steps:
 - Stop the solvent pump immediately (if this operation is in progress).
 - Push the RED button (located in the wall at one side of the door at the exit of this room). This action will increase the extraction of the ventilation system in the feedstock preparation room. Leave this room immediately. DO NOT return to the feedstock preparation room until it is safe (alarm goes OFF).
- In the event of uncontrolled temperature and/or over pressure on the Extractor (R-1) during the mixing and settling operation:
 - Stop the heating of the heat transfer fluid from the Hot Oil Heater (E-3), open valve V-20 immediately.
 - Push the RED button (located in the wall at one side of the door at the exit of this room). This action will increase the extraction of the ventilation system in the feedstock preparation room. Leave this room immediately. DO NOT return to the feedstock preparation until the problem is solved (temperature below 100 °C and pressure below 500 psig inside the extractor).
- In the event of a spill and/or leak of DAO + solvent during the transfer process from the Extractor (R-1) to the DAO Separator (D-1):

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- Stop the transfer process by closing the valves V-28, V-29, V-30 and V-31 immediately.
 - Push the RED button (located in the wall at one side of the door at the exit of this room). This action will increase the extraction of the ventilation system in the feedstock preparation room. Leave this room immediately. DO NOT return to the feedstock preparation until the problem is solved (alarm goes OFF).
- In the event of a spill and/or leak of solvent during the transfer process from the DAO Separator (D-1) to Solvent Recovery Tank (TK-4):
 - Stop the transfer process by closing the valve V-32, V-34, V-61 immediately.
 - Push the RED button (located in the wall at one side of the door at the exit of this room). This action will increase the extraction of the ventilation system in the feedstock preparation room. Leave this room immediately. DO NOT return to the feedstock preparation until the problem is solved (alarm goes OFF).
- In the event of a spill and/or leak of solvent during draining of Solvent Recovery Tank (TK-4):
 - Stop the transfer process by closing the valve V-34, V-61 immediately.
 - Push the RED button (located in the wall at one side of the door at the exit of this room). This action will increase the extraction of the ventilation system in the feedstock preparation room. Leave this room immediately. DO NOT return to the feedstock preparation until the problem is solved (alarm goes OFF).

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7. Training:

The training of this unit is based on the understanding of the procedure for the operation of the unit. Two weeks are required to train a new operator for this unit.

8. Monitoring Requirements:

The operators will monitor the alarm system and the extraction system of the feedstock preparation room continuously. During the operation of the unit; two operators MUST be present all the time. The rest of the people working in the Pilot Plant facilities MUST be informed during the operation of this unit.

9. Record Management:

Date of issuance: May 6th, 2013.

10. References:

<http://hazard.com/msds/mf/baker/baker/files/p0737.htm>

11. Definitions:

Do not apply.

12. Emergency Contacts:

University Emergency: 403- 220-5333

Emergency Telephone Number: 911

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13. University Notification:

There is not any concern that EH&S should be made aware of prior to the start of a particularly hazardous protocol, such as a disruption to a water source, loss of power, loss of gas detection systems etc.

Signed: _____ Date: _____

14. Document of Reference:

Solvent DE-Asphalting (SDA) – Process Flow Diagram: SDA-PFD-001 Rev 4.

Solvent DE-Asphalting (SDA) – Piping & Instrumentation Diagram: SDA-PID-001 Rev 10.

Material Safety Data Sheet for SDA (MSDS).

Mass Balance for the SDA Unit.

**APPENDIX B: PIPING & INSTRUMENTATION DIAGRAM FOR SOLVENT DE-
ASPHALTING UNIT**

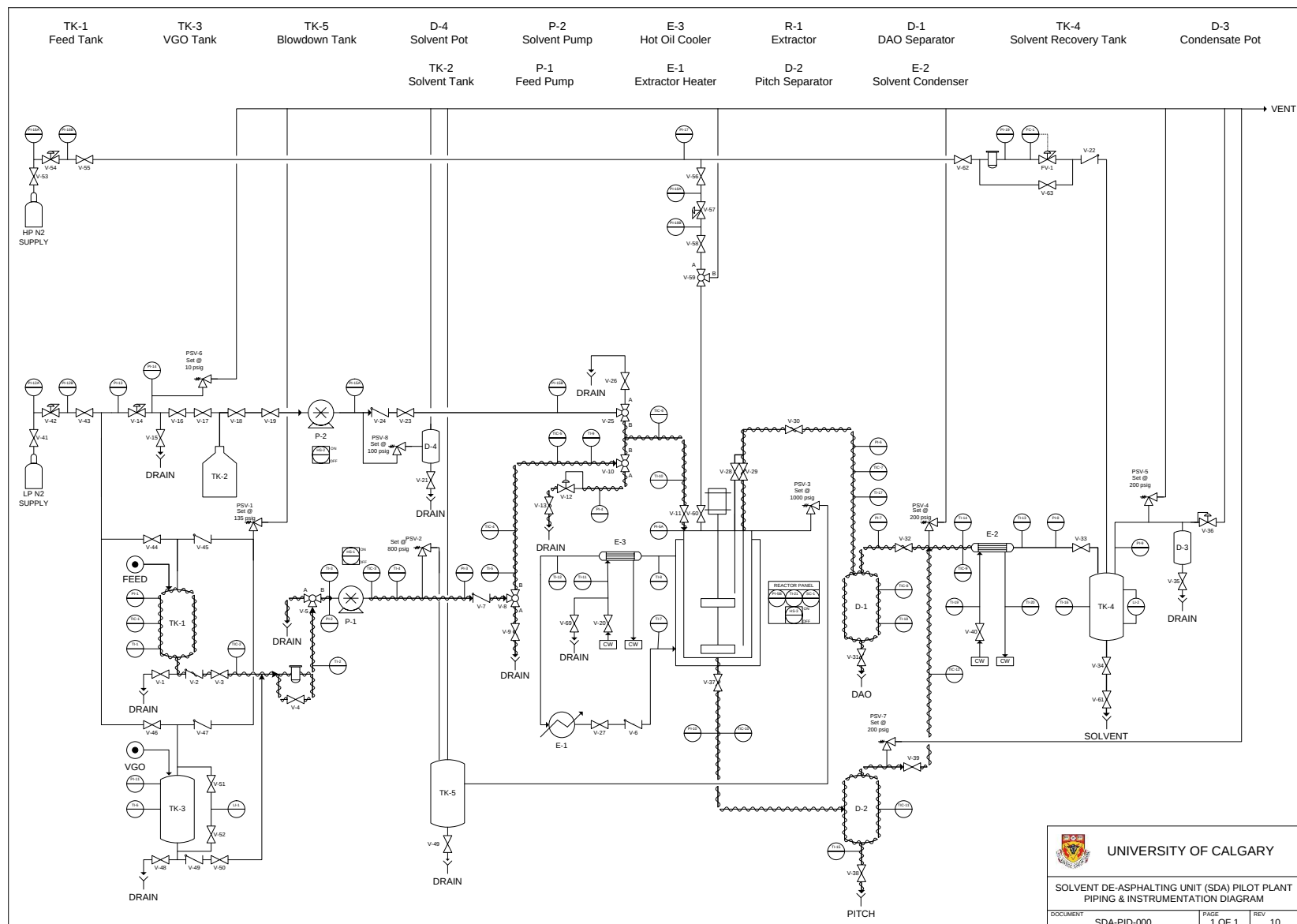


Figure B.1: Piping & Instrumentation Diagram for the SDA unit

APPENDIX C: EXPERIMENTAL DATA FOR ATHABASCA BITUMEN
ULTRADISPERSED CATALYTIC HYDROPROCESSING OBTAINED BY LORIA ET
AL. (2011)

Table C.1: Experimental data for Athabasca bitumen ultradispersed catalytic hydroprocessing (Loria et al., 2011)

Temperature (°C)	Residence Time (h)	Component Mass Fractions (wt%)					Residue Conversion (wt%)
		Residue	VGO	Distillate	Naphtha	Gas	
-	-	50.7	32.5	13.5	3.4	0.0	0.0
320	25.4	46.0	34.6	15.4	3.9	0.1	9.2
350	16.0	39.0	37.1	18.8	4.7	0.5	23.1
350	51.0	34.5	38.6	20.7	5.3	1.0	31.9
360	16.0	33.4	38.9	21.3	6.0	0.5	34.2
360	30.0	28.8	39.5	22.7	7.0	1.9	43.2
360	36.0	25.3	41.0	24.1	7.5	2.2	50.1
380	9.0	25.2	36.9	25.9	9.0	3.1	50.3

APPENDIX D: EXPERIMENTAL DATA FOR ATHABASCA PITCH
ULTRADISPERSED CATALYTIC HYDROPROCESSING

Table D.1: Experimental data for Athabasca pitch ultradispersed catalytic hydroprocessing

Temperature (°C)	Residence Time (h)	Component Mass Fractions (wt%)					Residue Conversion (wt%)
		Residue	VGO	Distillate	Naphtha	Gas	
-	-	81.19	17.08	1.72	0.00	0.00	0.00
320	96	75.00	20.51	3.66	0.00	0.83	7.62
350	48	76.16	20.09	3.07	0.00	0.68	6.20
350	96	74.38	21.47	3.11	0.38	0.66	8.39
380	24	56.77	30.85	8.84	2.02	1.52	30.08
380	48	54.71	30.75	10.41	2.44	1.70	32.62

APPENDIX E: EXPERIMENTAL DATA FOR ATHABASCA VACUUM RESIDUE
ULTRADISPERSED CATALYTIC HYDROPROCESSING

Table E.1: Experimental data for Athabasca vacuum residue ultradispersed catalytic hydroprocessing

Temperature (°C)	Residence Time (h)	Component Mass Fractions (wt%)					Residue Conversion (wt%)
		Residue	VGO	Distillate	Naphtha	Gas	
-	-	71.4	27.1	0.6	0.7	0.0	0.0
320	30.0	64.7	32.0	2.4	1.0	0.0	9.4
380	20.0	65.9	31.2	1.8	1.0	0.0	7.6
380	40.0	54.7	37.8	5.5	1.8	0.2	23.3
380	50.0	39.0	46.5	10.9	3.2	0.4	45.4
395	24.0	55.8	37.6	4.6	1.7	0.3	21.8