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University of Alberta

Fundamental Study of the Role of Fines in Upgrading

by

Janeth Liendo ©

A thesis submitted to the Faculty of Graduate Studies and Research in partial
fulfillment of the requirements for the degree of Master of Science

in

Chemical Engineering

Department of Chemical and Materials Engineering

Edmonton, Alberta
Fall, 2005

ABSTRACT

Conventional naphthenic-based extraction processes are not efficient at removing fine solids from bitumen. These solids are alumino-silicate clays partially coated with a toluene insoluble organic phase, and can cause operational problems such as fouling and plugging of equipment and catalysts. Bitumen solids are known to participate in thermal upgrading reactions when no hydrogen is present, reducing the rate of coke formation compared to solids-free feeds. The goal of this research is to identify the mineralogy of bitumen solids and to determine if there is an optimum concentration of solids in the feed to a coking unit. Several analyses were used in the characterization of bitumen solids, followed by a systematic study of the effects of solids in coking reactions under fluid-coking-type conditions. Solids composition was found to be primarily illite and kaolinite. Bitumen solids affect the yield of distillates during coking reactions with no effect on the yield of coke.

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CHAPTER 1
INTRODUCTION

1.1. Background

Bitumen and heavy oil reserves in northern Alberta are promising in terms of their great magnitude. However, due to their physical and chemical properties, processability represents a significant challenge for the petroleum industry in terms of recovering and upgrading these reserves to obtain commercially useful products. As the amount of conventional crude worldwide decreases and the demand for oil-derived fuels and petrochemicals increases, the use of bitumen and heavy oil becomes more important. With the increased interest in heavy feeds, the study of the upgrading process becomes ever more relevant.

The Athabasca oil sands bitumen is being extracted using mainly open pit mining technology, with a smaller amount of bitumen produced from in-situ operations. For the surface-mined oil sands, the hot water extraction process is the main approach for the separation of the bitumen from its associated mineral matrix. Following extraction, a synthetic crude oil is produced from the oil sands through a process called upgrading. Upgrading produces a synthetic crude oil with a lower sulfur, nitrogen and metal content compared to the parent bitumen, as well as a higher H/C ratio, and is therefore suitable for refining and pipelining.

The upgrading of bitumen and petroleum residues to distilled products is achieved by two main processes involving either hydrogen addition to the native bitumen or thermal cracking to produce distillates from the high boiling point fractions (Liu, 2002). In the case of thermal cracking processes, coking (which includes delayed and fluid

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coking ®) is the most extensively used technology to crack the bigger molecules contained within the bitumen and to separate the lighter products from the heavy residue. At present, the majority of the bitumen produced from the Alberta oil sands is processed using coking as the primary upgrading process (Liu, 2002).

Bitumen produced from surface mining of the oil sands and conventional froth treatment contains a relatively large concentration of filterable solids, ranging from 0.9 wt % up to 1.8 wt%. These solids, which are mainly composed of organic-coated aluminosilicate clay crystallites, are known to cause operational problems such as fouling and plugging of transfer lines, process units, and catalysts. They are also known to participate in the thermal upgrading reactions of vacuum distillation residues.

The important role played by fine solids in the upgrading of Athabasca bitumen has been recognized. Several studies have revealed the effects of solids in the overall performance of the upgrading units. The elucidation of the structure of the bitumen solids has also been the main focus of a significant amount of research. Of particular interest is the effect of bitumen solids in coking reactions. Previous studies (Liu, 2002; Sanaie et. al. 2001; Tanabe & Gray, 1997) have found that fine solids reduce the amount of coke formed compared to solids-free bitumen, with no effect on volatiles formation. On the other hand, bitumen solids have been repeatedly associated with operational problems such as fouling and plugging of process units and catalysts (Bensebaa et. al, 2000; Kotlyar et. al., 1998; Sparks et.al., 2003). As consequence, an optimum concentration of solids seems to be needed to enhance the operability of the coking units. Field experience also indicates that delayed cokers processing Athabasca bitumen have fewer problems

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compared to units processing solids-free feeds in terms of the formation of shot coke, which suggests an effect of bitumen solids on the type of coke formed.

At this point, the effect of bitumen solids on thermal cracking reactions is speculative. However, there is still a significant incentive to gain further understanding of the role that bitumen solids play in coking processes.

1.2. Research Objectives

Athabasca bitumen, from the naphthenic extraction process, contains a relatively large amount of bitumen solids. The main focus of this research is to study the effect that these fine solids have on the upgrading processes.

Bitumen solids are the finest mineral fraction associated with the bitumen from the oil sands. With a particle size distribution ranging from less than 1 μm up to 100 μm, they can be divided into two major fractions: filterable and nonfilterable ultrafines. The filterable fraction of the fine solids (particles greater than 0.22 μm) is significantly larger than the nonfilterable fraction and is the object of this study. Bitumen solids are known to contain a large amount of strongly associated organic matter. Due to their nature, they are potentially important in affecting the operability of the process units as well as the reactions that take place during upgrading.

The first objective of this research is to gain more insights into the structure and composition of the filterable fraction of the fine solids that reach coking units. It is also useful to understand how these bitumen solids change from the extraction stage to the upgrading stage of the synthetic crude oil production process.

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As mentioned earlier, there are two main technologies using thermal cracking reactions to approach the complex process of upgrading heavy oil and bitumen. Both delayed coking® and fluid coking® technologies are of particular importance to Canada, as the centerpiece for the upgrading of Athabasca bitumen in Alberta. Very little data are available on the role of fine clays on bitumen upgrading using fluid coking technologies. Experimental evidence indicates that when solids are removed from the bitumen, coke forms more rapidly. However, these data correspond to coking conditions similar to those of a delayed coking unit in which relatively large residence times and feed volumes are dominant.

Given the great relevance of the use of fluid coking technology, a second objective focuses on the study of coking reactions under fluid-coking-type conditions, specifically the study of the effect of bitumen solids on the yield of coke and distillate products at shorter reaction/residence times, with a very thin film of reacting bitumen and higher temperatures than for delayed coking. The objectives will finally allow for the evaluation of the optimum concentration of solids that is desirable for the upgrading operation of Athabasca bitumen through the use of fluidized coke.

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CHAPTER 2
LITERATURE REVIEW

2.1. Oil Sands

Canadian oil sands represent the largest heavy oil reserves in the world. Within the province of Alberta there are over 1 trillion barrels of extra heavy oil and bitumen present at relatively shallow depth and distributed in several deposits, the largest of which is in the Athabasca region in the north of the province.

Oil sands, tar sands and bituminous sands are all commonly used terms to refer to the complex mixture of bitumen, sand, clay, and water that form the deposit. Most of this reserve is covered by too much overburden to be recovered by surface mining. About 10% of the formation, however, is close enough to the surface to be extracted using open-pit mining methods. Of the remaining 90% of the bitumen, a fraction is being extracted by in-situ methods of production. There is an intermediate amount of bitumen that cannot be surface-mined or recovered by in-situ processes.

Two major companies, Syncrude Canada Ltd. and Suncor Energy, operate commercial surface mining plants for bitumen recovery. From the total amount of bitumen produced from the oil sand deposits, roughly 75% comes from mining techniques and 25% from in-situ techniques (Gray & Masliyah, 1998).

2.1.1 Characteristics of Athabasca Oil Sands

As mentioned previously, typical oil sands are a mixture of sand grains of various particle sizes, water, bitumen and clays. As represented in Figure 2.1, each sand grain is wetted or enveloped within a film of water of a thickness raging between 10nm up to 15

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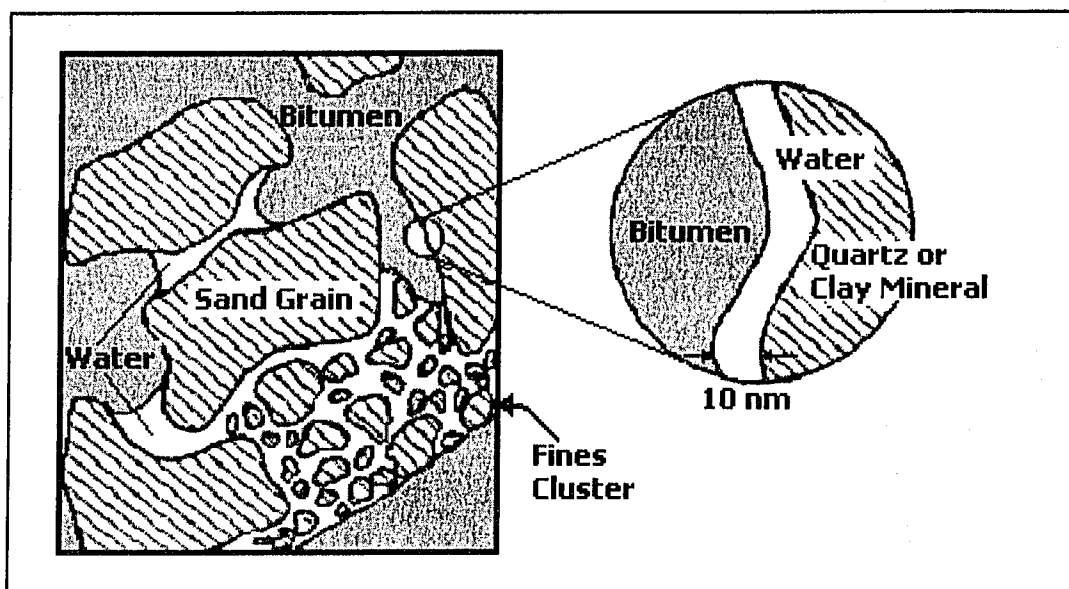
Figure 2.1. Schematic model structure of oil sands (Reprinted from *Minerals Engineering*, 17, Madge, D.N. et. al., "Hydrocarbon cyclones in hydrophilic oil sand environments", 625-636, Copyright (2004), with permission from Elsevier)

6

μm, which becomes greater at the grain-to-grain contact points (Madge et. al., 2004). Bitumen surrounds the wetted sand grains and somewhat fills the voids, in combination with a small volume of gas (air or methane) that might also be present. Clay minerals are suspended in the liquid phase. The sand grains are packed to a void volume of about 35% which corresponds to a mixture of approximately 83 wt% of sand for a moderate grade. The remaining percentage is balanced with bitumen, water and clays (Hendrickson, 1975).

Although the magnitude of the in-place reserves is very impressive, the quality of the oil is very poor. It commonly contains high concentration of sulfur, nitrogen, oxygen and trace metals such as vanadium, nickel and iron. Oil sands can be classified by grades (Table 2.1) according to the percentage of bitumen (oil saturation) (Takamura, 1982). Typically mined oil sand falls in the range of 10-11 wt% bitumen (Gray & Masliyah, 1998).

Table 2.1. Classification of oil sands according to oil saturation levels

Grade	Bitumen Content (wt%)
Highest	18
Rich	10-18
Moderate	6-10
Lean	< 6

Several relationships among the various components of the oil sand have been previously established. According to Hendrickson (Hendrickson, 1975), the fine content is directly proportional to the water content of the oil sand; an inverse correlation

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between bitumen and fine contents has also been proven. For example, the total amount of fines (mineral particles smaller that 44 μm) in a high grade sample is below 3 wt%. In contrast, a lower grade sample has a larger percentage of fines that could reach as much as 15 wt%. It is also known that the particle size distribution of the mineral solids is a function of the bitumen content of the oil sand ore; in consequence the lower the grade, the finer is the mineral portion of the sample (Takamura, 1982). The water associated with the sand grains has a composition similar to that of sea water, containing ions such as Na^+, K^+, Ca^{++} and Mg^{++}. The amount of these ions is inversely proportional to the grade of the oil sand, in other words, rich grade oil sands contain a lower salt content while lean grade oil sands have a higher salt content. In consequence, physical properties of the individual components of oil sand greatly affect its processability, regarding the additives used, the amount of water and the levels of energy consumption.

2.2. Bitumen Recovery Processes

Different methods combined with some further processing have been used for recovering bitumen from oil sand deposits. Surface mining techniques and in-situ recovery are the main methods of bitumen extraction, however, bitumen recovered by open-pit mining accounts for the majority of the production from the deposits located in northern Alberta.

2.2.1. Bitumen Recovery by Surface Mining Techniques

Due to the geological characteristics of the Athabasca region, surface mining techniques are currently used for the recovery of the oil sands from the deposits. The ore

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body varies between 20 to 90 m thick, laying below a layer of approximately 30 m of overburden material. These characteristics have allowed for the use of truck and shovel in the mining operations performed by Syncrude and Suncor. The grade of the oil sand ranges between rich and moderate, according to the classification presented in Table 2.1, giving an average yield of 1 barrel of bitumen per 1700 Kg of mined oil sand (Gray & Masliyah, 1998).

2.2.2. Bitumen recovery by in-situ production

Besides bitumen production via open pit mining, in-situ production methods are also used on bitumen deposits placed at depths greater than 30-60 m, which make the deposit too deep for mining to be economical (Gray, 2003). These techniques include steam injection, solvent injection, and firefloods in which oxygen is injected and part of the resource burned to provide heat. Steam injection has been that of most popular use since it has given the most favorable field results (Gray, 2003). Key variables for this method account for viscosity of the oil at formation temperature and permeability of the formation. Bitumen production by in-situ methods is constantly challenged by characteristics of the Athabasca deposit, such as high viscosity of the bitumen and the geological heterogeneity of the reservoir (Carrigy, 1986).

Bitumen produced by in-situ methods contains practically no bitumen solids (Zhao et.al., 2001) and therefore subsequent processing of this feed will not carry the problems associated with the fine solids. The absence of bitumen solids in in-situ produced bitumen has been attributed to the greater depth of the deposit and consequently less contaminated with mineral compounds. In addition, the conditions of temperature

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and velocity of the bitumen when drained from the reservoir may be such that waste layers are left behind and therefore a cleaner bitumen is obtained (Zhao, 2001).

2.3. Bitumen Extraction and Upgrading Processes

The sequence of processes described in this section corresponds to that used for oil sands extracted by open-pit mining techniques. The processes mentioned in this section correspond to those currently used by both Syncrude and Suncor.

2.3.1 Extraction Process Via Clark Hot Water Extraction (CHWE)

A schematic of the main steps of the mining/extraction process is presented in Figure 2.2. The CHWE process operates at temperatures between 70-80 °C. The mined oil sand is mixed with hot water and caustic soda (NaOH), creating a slurry that is transported to the extraction plant using hydrotransport pipelines. During transportation, the separation of the bitumen from the mineral matrix starts taking place. pH levels and temperature are key variables in the process. The mixture is fed into large gravity separation vessels in which the bitumen froth, water and sand are separated based on density differences. Froth is recovered from the top, and most of the water and coarse sand settle and are fed into tailing ponds. A mid stream (middlings) from this separation vessels is processed in flotation cells for recovering of the remaining oil content.

The floated bitumen or primary froth from separation vessels and flotation cells, undergoes de-aeration with steam, dilution with naphtha to reduce density and viscosity, centrifugation to remove remaining water and minerals, and distillation for naphtha recovery. The composition of the de-aerated bitumen froth is roughly 60% bitumen, 30%

10
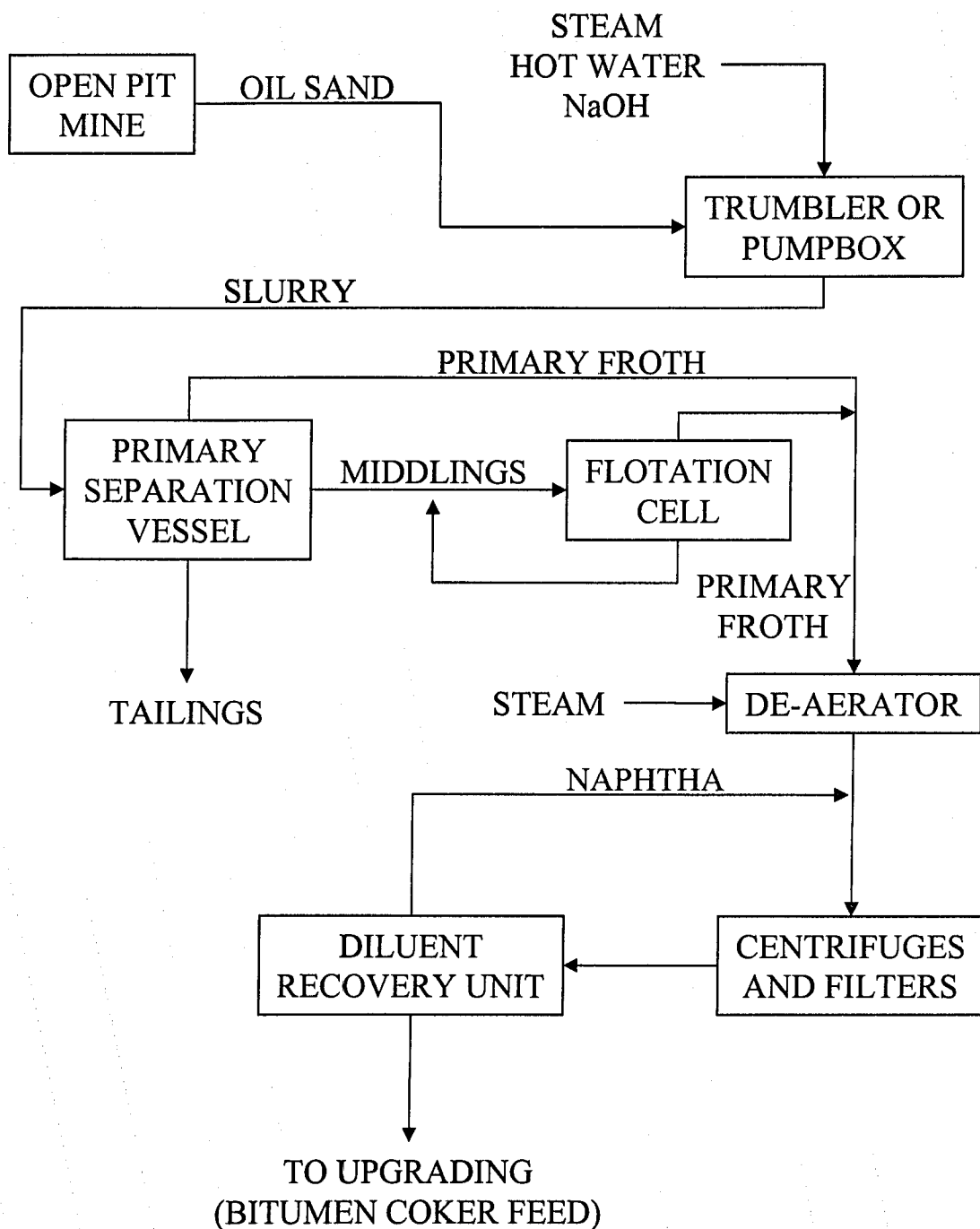
Figure 2.2. Generalized scheme of a commercial oil sand mining and extraction process

water and 10% solids (Kotlyar et.al., 1998; Shaw et.al., 1996). After the distillation step, diluent-free bitumen is sent to the upgrading plant; this stream is commonly seen as coker feed bitumen. The trend in the industrial extraction process is heading towards a reduction in the temperature as well as a caustic-free process due to environmental regulations.

2.3.2. Upgrading Process

Upgrading is the most complex area of operation in an oil sands recovery plant. The bitumen obtained from the extraction stage is not suitable for pipelining and refining due to its viscosity and impurities, such as nitrogen, sulfur, minerals and metals. The purpose of upgrading is to purify the bitumen into synthetic crude oil which is then suitable for pipeline transport to a refinery.

Depending on the approach used by the operators within the Alberta province, different schemes of upgrading can be seen, such as thermal cracking and hydrogen addition processes. The ultimate goal is to produce a high-quality crude oil substitute, able to supplement the demand for conventional light sweet crudes (Gray, 2003).

A generalized schematic of upgrading operations is presented in Figure 2.3. In general, following the recovery of the naphtha at the Diluent Recovery Unit (DRU), the bitumen undergoes separation steps in which the lighter components of the feed are collected and some undesirable components, such as salts, are removed. Vacuum distillation is one of the processes that take place in the feed separation stage. These distillation units operate at pressures of 3-5 kPa and temperatures between 380-450 °C (Gray, 2003), and allow recovering of light and heavy gas oils of boiling point up to

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Feed Separation processes
- Desalting
- Atmospheric/vacuum distillation
- Deasphalting

Primary Upgrading
- Delayed/fluid Coking
- L-C Finer

Product Separation
- Distillation

Utilities
- Hydrogen
- Steam

Secondary Upgrading
- Removal of sulfur compounds, nitrogen compounds and metals
- Products stabilization
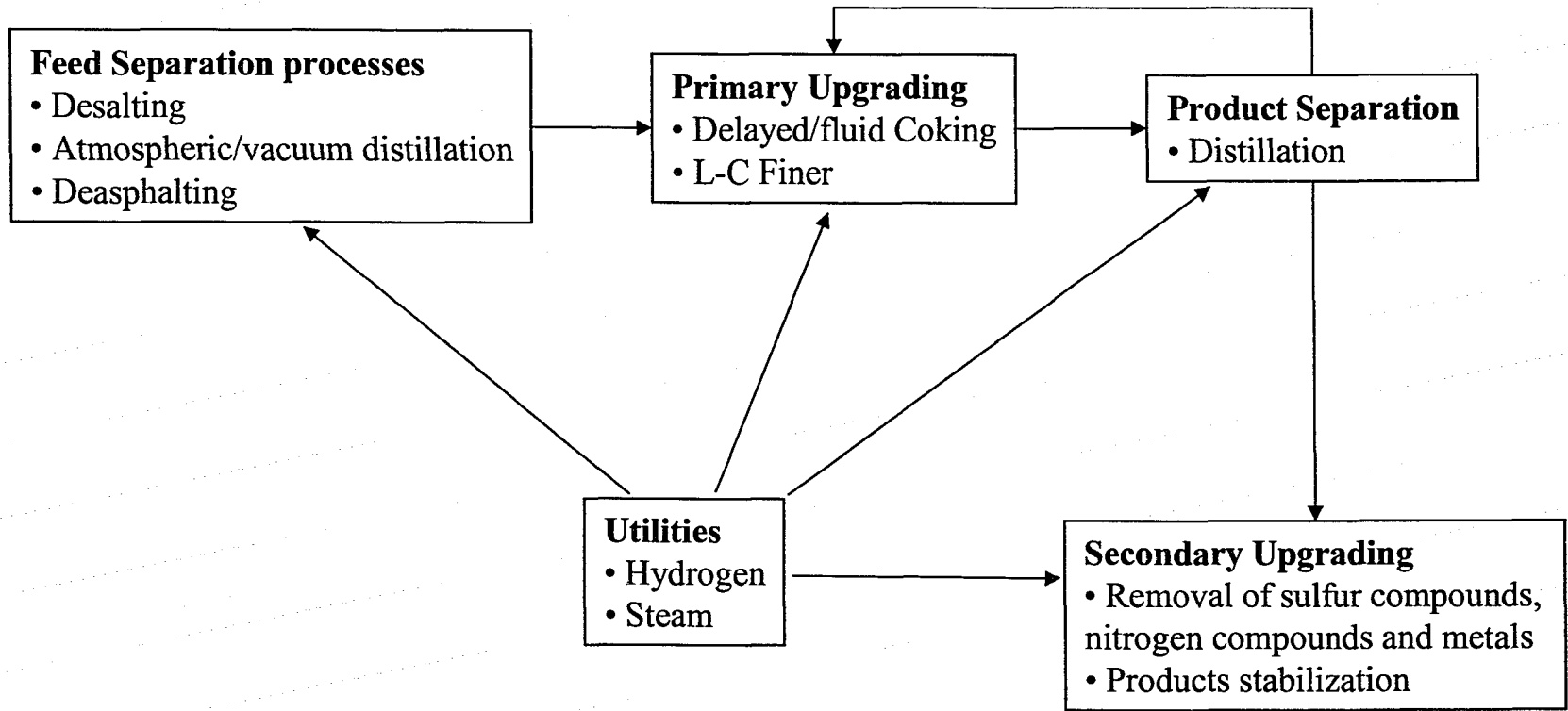
Figure 2.3. Generalized schematic of upgrading operations (Modified from Gray, 2003)

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524°C. The top products are sent to secondary upgrading while the bottoms undergo primary upgrading. The bottom product of the vacuum distillation column at Syncrude upgrader, also called Athabasca Vacum Residue (AVR), represents the majority of the feed of the cokers and the object of study of this research. Properties of AVR are presented in Table 2.2.

During primary upgrading, reaction steps allow for the feed to be cracked to lighter molecules that are later separated by distillation. Sulfur, nitrogen and metals are removed at the latest purification steps or secondary upgrading.

Table 2.2. Properties of Athabasca Vacuum Residue (AVR) (Gray et. al., 2004)

Toluene insoluble (wt%)	1.8
MCR (wt%)	27.8
Sulfur (wt%)	5.7
Nitrogen (wppm)	7206
Density @ 20 °C (Kg/m^3)	1086.8
Boiling fractions (wt%)	
524 °C-	10
524-650 °C	40
650 °C+	50

Primary upgrading includes coking and LC-fining units. The LC-Finer hydroprocessor present at Syncrude upgrader breaks down bitumen feed through a reaction with hydrogen over an ebulated catalyst bed and produces a light gas oil. Unconverted feed or residuum from the LC-Finer is sent to the cokers for further cracking. The cost of catalyst is a major limiting factor to the wider application of hydroprocessing to upgrade whole Athabasca vacuum residues.

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The most common processing option utilized with vacuum residues is thermal cracking or coking. During coking processes the larger molecules present in the feed are broken down, producing light ends (gases), liquid products (naphtha and gas oils) and a solid product (coke). Coke is defined as a carbonaceous solid that results from high temperature calcining of a carbon rich starting material (Gray, 2003). This product has a sulfur, metal, and clay content greater than that of the feed and is insoluble in toluene. There are different types of coke depending on the technologies used for carrying out coking reaction (fluid and delayed coking). Coking processes are known to be efficient at rejecting minerals and metals, as well as to be responsible for some rejection of nitrogen and sulfur.

Two major technologies are being used for the coking of bitumen from the northern Alberta oil sands; delayed and fluid coking. The delayed coking process uses long reaction times in the liquid phase to transform the feed into gas, liquid and solid products. It consists in a semi-batch process in which the feed is heated at 500 °C and placed into large drums in which the vapor produced during the reaction (gases and distillate) are removed off the top of the drum and the coke is accumulated until reaching the capacity of the drum. At this point the feed is switched into another drum while the previous one is emptied; completing a cycle typically takes about 48 hours. The fluid coking process or fluidized-bed coking is a continuous process in which the feed enters the reactor containing a bed of fluidized coke particles that are about 100 μm in diameter. The unit operates in the range of approximately 510 to 550 °C and the residence time in the fluidized bed is shorter compared with delayed coking process. The vapors exit the top of the fluidized coker with the fluidization steam, and cyclones remove the coke

particles entrained in the products stream. Part of the coke produced in the coker (cold coke) is stripped with steam and conducted towards a burner in which a portion of it is burned to meet the energy requirements and the rest is heated up to reaction temperatures and returned to the coker (hot coke). Factors such as shorter resident times, enhanced heat transfer in the fluidized bed, as well as higher reaction temperatures, have a favorable effect in the products yield compared to delayed cokers. These factors give more cracking of volatiles from coke, reduce the yield of coke, and consequently increase the yields of gas oils and olefins. On the other hand, problems such as overcracking of molecules in the vapor phase may arise in this type of units. Variables such as temperature of reaction, behavior of the fluidized bed, and composition of the feed are critical for the successful operation of the whole unit.

There have been several studies on the fundamental of delayed-coking-type reactions involving bitumen solids (Liu, 2002; Parviz et. al., 1999; Sanaie et. al., 2001; Tanabe & Gray, 1997). Findings from these research imply that the removal of solids from the feed tends to increase the amount of coke produced. On the basis of these results, this research focuses on the effect of bitumen solids in the thin film regime under fluid-coking-type condition.

As a closing remark, it is important to highlight that the process of upgrading bitumen to synthetic crude oil faces a number of challenges in the near future. These challenges include maintaining costs, improving the quality of synthetic crude, and developing of catalysts that can improve conversion and reduce emissions, among others. In this entire picture, bitumen solids play an important role as a component to be taken into consideration, from both operational and kinetics points of view.

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2.4. Clay Mineralogy

Before investigating in more detail the solids associated with bitumen and their role in the upgrading process, it is important to understand some of the key concepts related with clay mineralogy. Since the composition of bitumen solids has been associated with that of mineral clays, a better understanding of clay formation, characteristics and properties will set the basis for a more successful study of the role of bitumen solids in chemical reactions of heavy oil.

Clays occur widely in nature and their use has been greatly extended over the last decades. Their study has become very important in many fields of scientific disciplines and a large amount of data is now available in the literature (Deer et. al., 1966; Gillott, 1987; Grim, 1962; Moore, 1989; van Olphen, 1963; Weaver, 1989)

2.4.1. Definition and Characteristics of Clays and Clay Minerals

The term clay has been frequently used along with terms such as shales and soils, to refer to different characteristics or properties of rocks among different fields of study. The most convenient definition to the extend of this research is that clays are a "natural, earthy, fine-grained material, largely composed of hydrous aluminum and magnesium silicates, which develops plastic properties when mixed with a limited amount of water" (Gillott, 1987). Some definitions make emphasis in the preservation of shapes upon drying and the increase of strength with shape retention upon firing (Grim, 1953). On the other hand, clay minerals receive a definition that, encompassing the definition of clays, refers more specifically to the particle size of the grain (Gillott, 1987; Grim, 1953). In this regard the general tendency is the use of 2 μm as the maximum particle size for a

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grain to be considered a clay mineral. Clays therefore are composed of clay-sized mineral particles in which clay minerals generally represent a significant portion and non-clay minerals, organic material, and water soluble salts account for the rest. Among the non-clay mineral it could be found various amounts of quartz, calcite, feldspar, and pyrite. The composition of clays is believed to be a consequence of chemical processes involving crystallization of gels, hydrothermal action, and decomposition reactions, and physical processes like erosion of sedimentary rocks (parent material) or precipitation of new material.

The characteristics and properties of clays are defined by far by the following factors (Grim, 1953):

- Clay mineral composition: this is referred to the amount of the clay minerals, its crystallinity, and whether there are discrete particles or an interlayer mixture.

- Non-clay mineral composition: this refers to the nature, abundance, and particle size of species like pyrite, feldspars, gibbsite and other minerals that usually exist within clay deposits.

- Organic material: Their presence can be as organic particles mixed with clays or organic molecules adsorbed on the surface of the clays. In any case, organic materials may contribute to specific properties like catalytic among others.

- Exchangeable ions and soluble salts: Salts and cations may be found entrained in the clay or adsorbed on its surface, allowing for an ion exchange when the clay is in solution. The degree of cation substitution is

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called Cation Exchange Capacity (CEC) and it is known to be directly related with the plastic properties of the clay.

The clay composition is usually the most important in defining the chemical and physical properties of clays.

Another factor to take into account when studying properties of clays is the types of binding forces that can occur on the surface of the particles. Forces of attraction between particles, intermolecular forces, electrostatic forces and bonding action of adsorbed polar molecules are just a few that can be enumerated within clay materials, having a significant impact on their properties and behavior.

Clays are multicomponent systems in which solid, liquid and gas phases are commonly present. Chemical analysis of clays shows that the composition is frequently silica, alumina, and water, with considerable quantities of iron, alkalies and alkaline earths (Grim, 1953). The atomic structure of most clay minerals has been defined based on two main units (Grim, 1962). One is formed by two sheets of packed oxygen atoms or hydroxyls, in which aluminum, iron, or magnesium atoms are entrained in an octahedral array. The second unit is built of silica tetrahedrons. The two-dimensional combination of these two units is the principle of the group *phyllosilicates* under which clays are classified. The tetrahedral and octahedral sheets may have different arrangements forming layers that at the same time may combine to give place to the different groups, sub-groups, and species. Table 2.3 shows part of the classification of the *phyllosilicates* related to clays. A 1:1 layer refers to a combination of one tetrahedral sheet and one octahedral sheet, while a 2:1 layer consists on an octahedral sheet placed between two tetrahedral sheets.

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Table 2.3. Classification of *phyllosilicates* related with clays

and clay minerals (Weaver, 1989)

Layer type	Group	Sub-group	Species
1:1	Serpentine-kaolin	Serpentines	Chrysolite, antigorite, lizardite, amesite, berthierine
		Kaolins	Kaolinite, dickite, nacrite
2:1	Talc-pyrophyllite	Talcs	Talc, willemseite
		Pyrophyllites	Pyrophyllite
	Smectite	Saponites	Saponite, hectorite, stevensite
		Montmorillonites	Montmorillonite, beidellite, nontronite
	Mica	Trioctahedral micas	Trioctahedral mica
		Dioctahedral micas	Muscovite, paragonite, illite, phengite, celadonite, glauconite

Understanding how the structure of clay changes when undergoing heating is also important. When clays are exposed to temperature up to 120 °C, they loose most of their adsorbed water. At higher temperatures, dehydroxilation takes place. The temperatures at which this phenomenon occurs depends on the type of clay, the presence of impurities, the heating rate, the water vapor pressure, among other experimental conditions. Table 2.4. shows the temperature range at which kaolinite, illite, and montmorillonite loose water due to this phenomenon. It is also known that the lost of water is reversible up to some point, as part of the plastic properties of clays. Irreversibility usually occurs when the modification of the crystalline structure due to high temperatures takes place followed by the recrystallization to a high-temperature-stable phase.

Table 2.4. Range of temperature causing lost of water in clays by dehydroxilation

Clay	Temperature range (°C)
Kaolinite	500-600
Montmorillonite	500-750
Illite	350-600

Among the many species of clays defined up to date, there are three specific types in which more emphasis will be made in following sections, because of their reported occurrence in bitumen solids. They are: kaolinite, montmorillonite, and illite.

2.4.2. Kaolinite

The clay minerals of the kaolinite group have an almost perfect 1:1 layer structure and the difference among the various species is basically the layer stacking geometry. Kaolinite is a nonexpandable type of clay when combined with water, although it has been proven some expandable effect when combined with some salts and strong hydrogen bonding compounds (van Olphen, 1963). The cohesive types of energy accountable for are electrostatic augmented by van der Waals attraction, and some hydrogen bonding forces established between the hydroxyl groups of one layer and the oxygen atoms of the neighboring layer. The CEC of this clay (3.6-18 meq/100g of dry clay) is relatively low when compared to illite and montmorillonite (Weaver, 1989).

In Figure 2.4, a representation of the structure of kaolinite is sketched as well as an electron micrograph of this clay. The structure of kaolinite is composed of a single silica tetrahedral sheet and a single aluminum octahedral sheet (Grim, 1953). The arrangement of the layers is such that a common layer is formed between the tip of the silica tetrahedrons and one of the layers of the octahedral sheet (Grim, 1963). Analyses of

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(a)

○ Oxygen

Ⓞ Hydroxil

● Aluminum

● ○ Silicon

(b)

20kV   2kx   5.0µm 8603   '05   2000
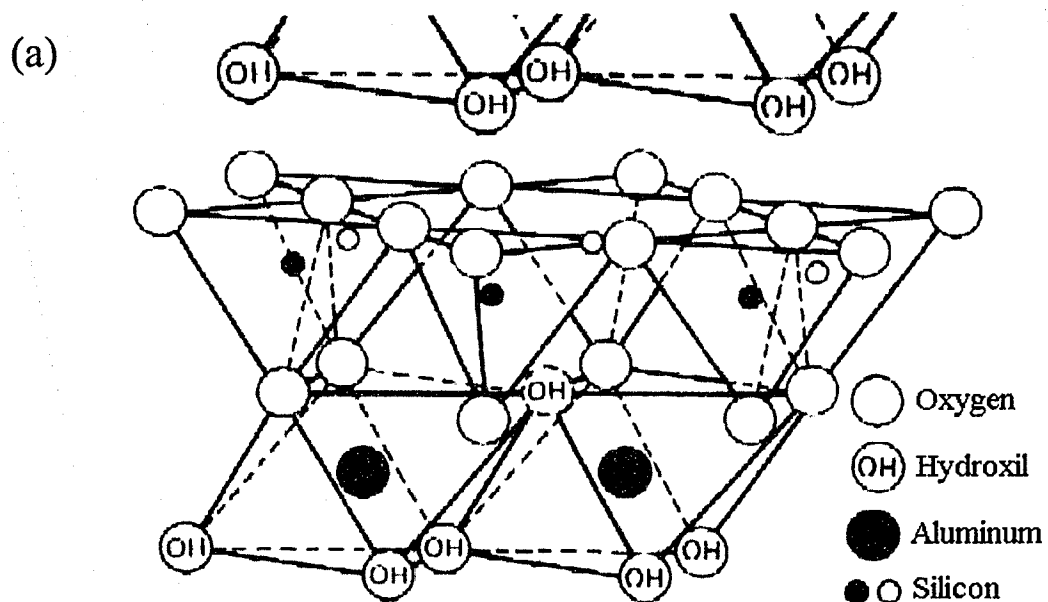
Figure 2.4. (a) Sketch of the lattice structure of kaolinite (Grim, 1953). (b) Electron micrograph of kaolinite material (Mineralogy Database. http://webmineral.com/data/Kaolinite.shtml. Accessed August 2005)

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many samples of kaolinite have shown that there is very little substitution of ions within the lattice structure, with few cases of iron and/or titanium for aluminum (Grim, 1963).

The structural formula for kaolinite is $Si_4Al_4O_{10}(OH)_8$ and the theoretical composition expressed in oxides is presented in Table 2.5. Pure kaolinite is rarely found in nature. Some other compounds such as iron, magnesium, titanium, calcium, potassium, and sodium oxides are usually present. Mineral impurities like quartz, anatase, rutile, pyrite, feldspar, montmorillonite, and mica are also found along with kaolinite.

Table 2.5. Chemical composition of kaolinite samples

from various U.S.A. locations (Weaver, 1989)

Compound	Composition (%)
SiO_2	43.26
Al_2O_3	38.67
H_2O	13.69
Fe_2O_3	0.53
TiO_2	1.16
MgO	0.25
Others	2.44

2.4.3. Montmorillonite

The structure of the minerals of the montmorillonite sub-group is similar to that of pyrophyllite $[Al_4Si_8O_{20}(OH)_4.nH_2O]$ and talc. Differences are based on the substitutions of certain atoms as well as the presence of excess water. The montmorillonite minerals occurred in very small particles, reason for which the data available comes only from powder/bulk properties rather than single crystals (Grim, 1953). Furthermore, the small particle size makes this clay susceptible to mineral impurities (quartz and other clays) that may affect to some extent its physical and chemical properties as well as its identification. In general, the composition of the montmorillonite clays is as shown in

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Table 2.6; the percentages are susceptible to variation depending on the exchangeable cation, substitutions and impurities.

Table 2.6. Chemical composition of montmorillonite samples from various U.S.A. locations (Weaver, 1989)

Compound	Composition (%)
SiO_2	55.50
Al_2O_3	21.00
Fe_2O_3	2.66
FeO	0.07
MgO	3.41
CaO	1.83
Na_2O	0.19
K_2O	0.37
TiO_2	0.20
H_2O	14.04
Others	0.73

As noted earlier in Table 2.3, one member of the montmorillonite sub-group is itself called montmorillonite which has the following general formula: $(Na,Ca)_{0.3}(Al,Mg)_2Si_4O_{10}(OH)_2 \cdot nH_2O$, with aluminum partially substituted for sodium or magnesium. One layer of montmorillonite clay is composed of two sheets of silica tetrahedral surrounding a central alumina octahedral sheet, as sketched in Figure 2.5.a. In the tetrahedral sheet, silicon may be replaced by aluminum while in the octahedral sheet there may be replacement of aluminum by magnesium and in some cases sodium, iron, chromium, zinc, or lithium. When the atom substitution results in a deficit of positive charges, the adsorption of cations takes place on the surface of the crystal. In the presence of water, the cations on the surface may be easily exchanged by others in solution resulting in a higher value of CEC compared to kaolinite (80-150 meq / 100g of dry clay) (Gillott, 1987).

(a)

Exchangeable Cations
n·H₂O

◯ Oxygen (OH) Hydroxyl ● Aluminum or Magnesium
◯ ● Silicon - Ocassionally aluminum

(b)
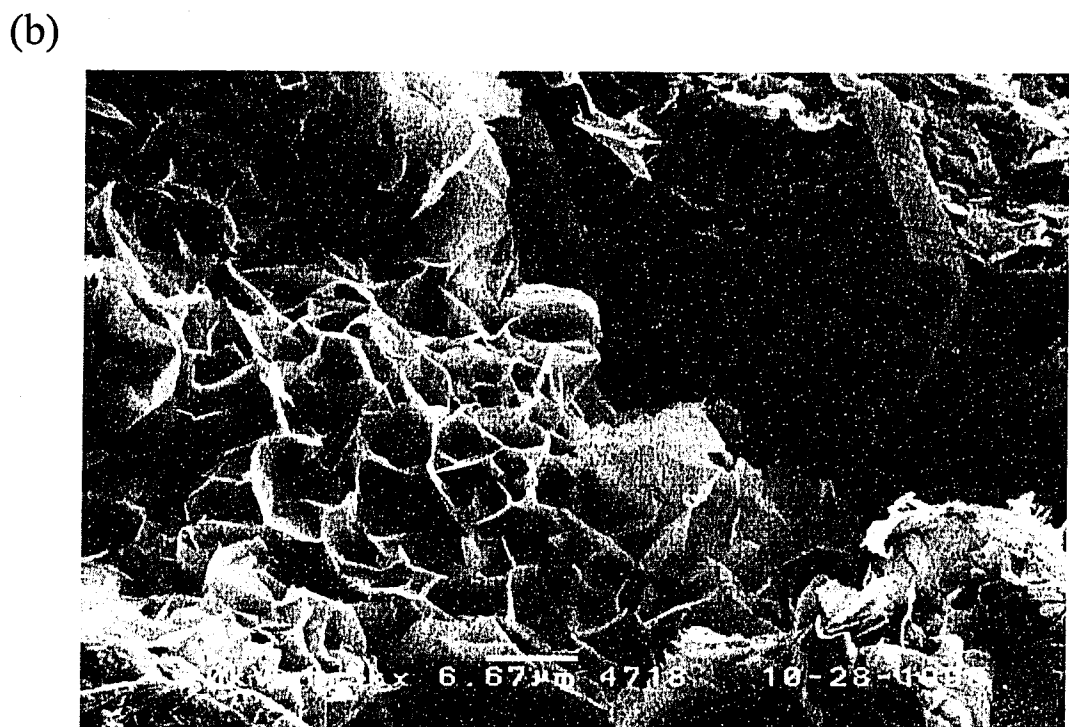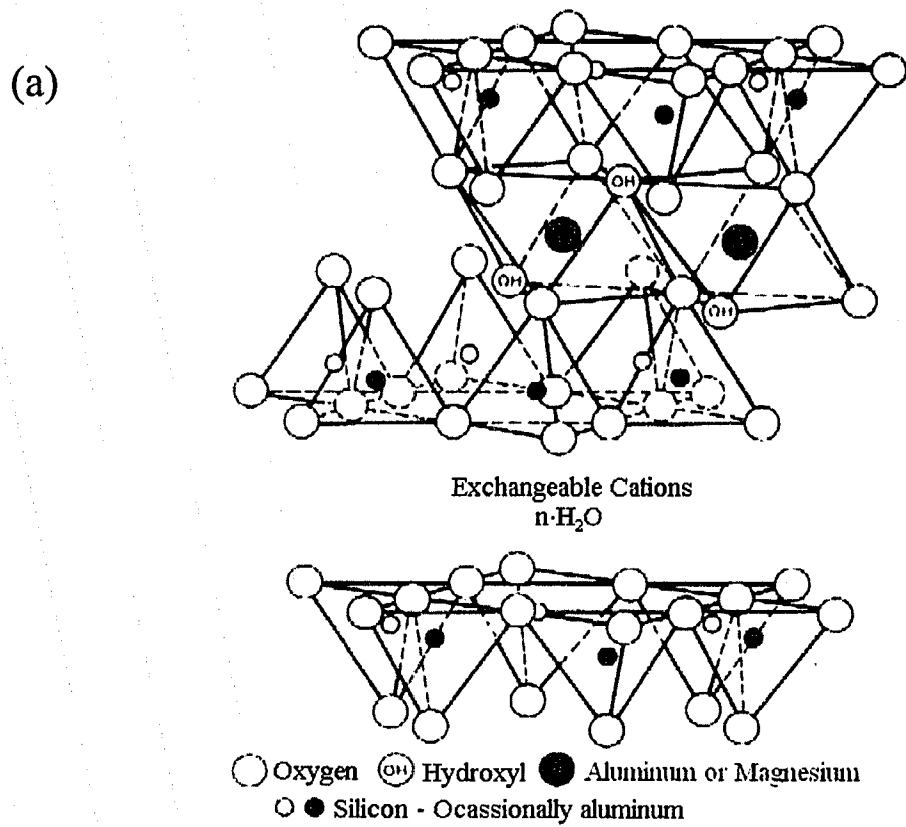
Figure 2.5. (a) Sketch of the lattice structure of montmorillonite (Grim, 1953)
(b) Electron micrograph of montmorillonite material (Mineralogy Database.
http://webmineral.com/data/Montmorillonite.shtml. Accessed August 2005).

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A montmorillonite particle is formed by a stack of layers with the exchangeable atoms located on both faces of each layer. When the clay is contacted with water (either liquid or vapor), the water molecules penetrate the layers causing the effect called interlayer swelling, which is a very important characteristic of the clays of the montmorillonite group. Interlayer swelling leads to an increase of volume up to twice the original volume of dry clay, when as many as four layers of molecular water fill the interlayer space. A much larger degree of swelling can also be observed in montmorillonite, caused by another mechanism called osmotic swelling, where repulsion between the surfaces of individual particles pushes them apart creating room for more water molecules. The expansion properties due to swelling are reversible up to some extent. Not only water but also molecules from organic compounds of polar or ionic character can enter between the layer units of this clay. The degree of swelling will depend on the nature on the exchangeable cation and the vapor pressure of the liquid.

2.4.4. Illite

The basic structural unit of the illite minerals (two external silica tetrahedral sheets and one central octahedral sheet) is the same as that for montmorillonite (See Figure 2.6). What differentiates these clays is that in illite frequently one sixth of the silicon atoms are replaced by aluminum and the resultant charge deficiency is balanced with potassium ions located in the interlayer region. This location affects the illite structure in two ways: first it makes the ions not available for exchange, and second makes the unit layers of the structure relatively fixed in position. As a consequence, the

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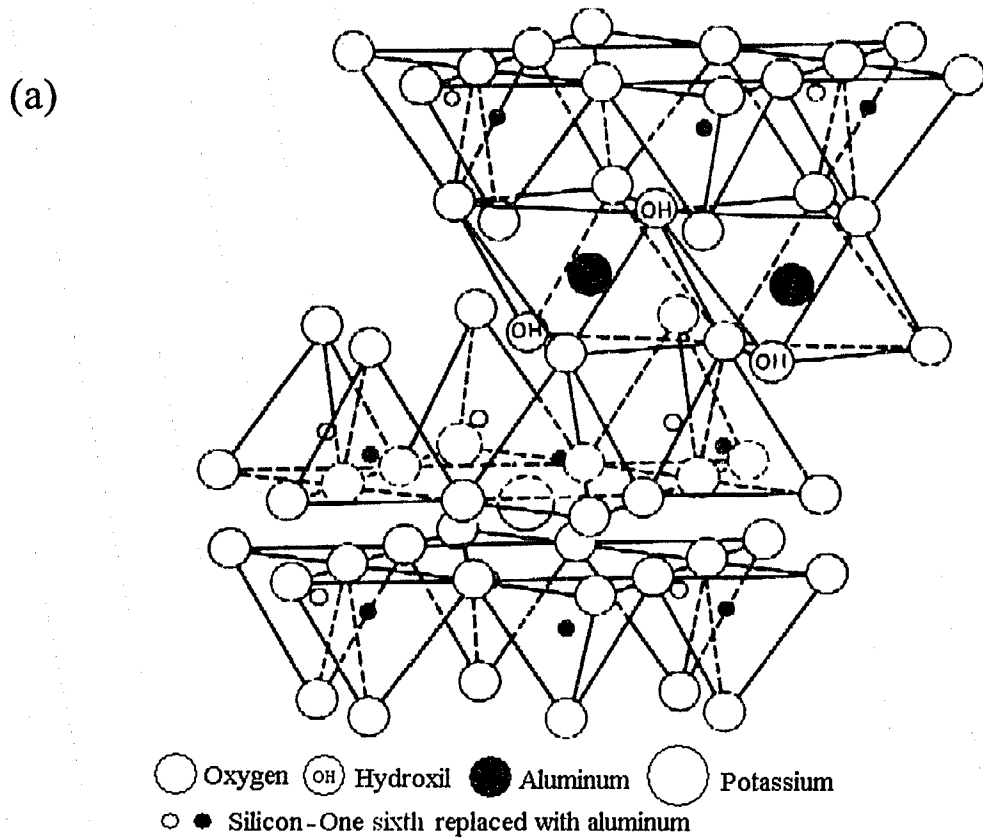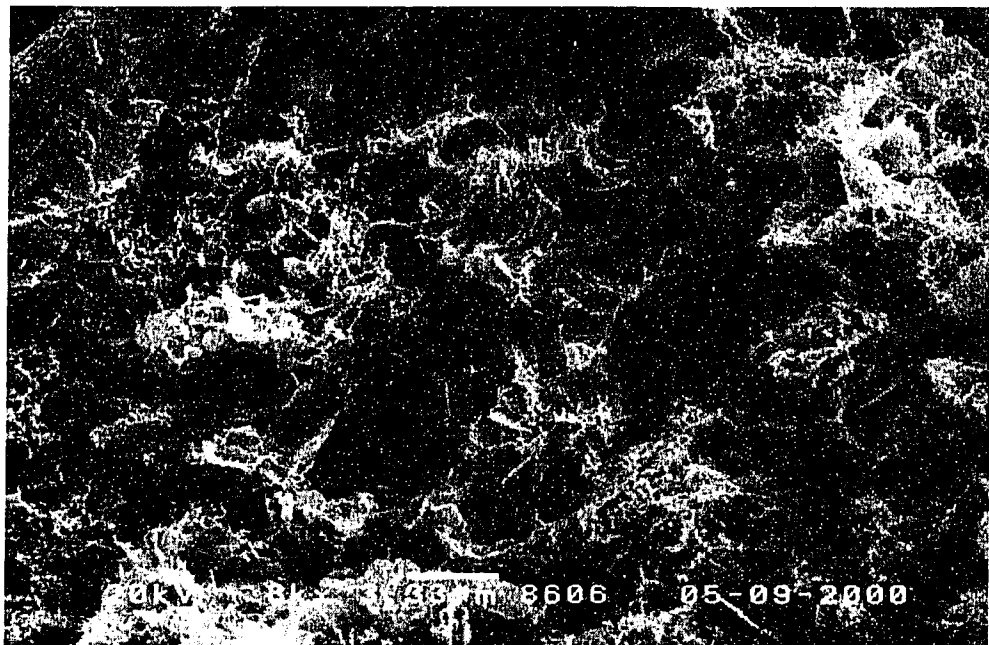
Figure 2.6. (a) Sketch of the lattice structure of illite (Grim, 1953) (b) Electron micrograph of illite material (Mineralogy Database. http://webmineral.com/data/Illite.shtml. Accessed August 2005)

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illite clays are characterized by the absence of interlayer swelling with water or organic compounds.

The general formula of illite is $(K,H)(Al,Mg,Fe)_2(Si,Al)_4O_{10}(OH)_2 \cdot nH_2O$ and the theoretical composition is shown in Table 2.7. As montmorillonites, they also occur in very small particle size mixed with other clay minerals. The CEC values for illites are lower than montmorillonite but greater than kaolinite, ranging between 10-40 meq / 100g of dry clay (Gillott, 1987).

Table 2.7. Chemical composition of illite samples

from various U.S.A. locations (Weaver, 1989)

Compound	Composition (%)
SiO_2	50.39
Al_2O_3	23.99
Fe_2O_3	4.82
FeO	1.00
MgO	2.72
CaO	0.42
Na_2O	0.19
K_2O	8.00
TiO_2	0.83
H_2O	7.63
Others	0.01

2.5. Fine Solids and Their Role in Bitumen Processability

In order to understand the role of fine solids in bitumen processability, it is important to know the amount, characteristics and nature of both the mineral and the organic components of fine solids.

As mentioned earlier, a fraction of the total amount of sand grains and mineral particles forming the oil sands is able to remain with the bitumen froth after the Hot

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Water Extraction Process. It has been shown (Kotlyar, 1988) that part of these particles are covered with an organic layer which allows them to associate with the bitumen phase; the organic free solids can be isolated with the aqueous fraction. The organic coated particles are frequently referred to as organic rich solids (Sparks et. al., 2003) and comprises biwettable, ultra fine clays (particle size less than 3μm) and mineral aggregates.

Bitumen solids associated with the bitumen phase are characterized by a large content of organic matter, insoluble in toluene, and strongly bounded to the mineral matrix, which represents from 15 wt% of the solids of larger size up to 40 wt% of the smaller particles (Bensebaa et. al., 2000; Chung et. al., 1998; Kotlyar et. al., 1998; Li et. al., 2004; Sparks et. al., 2003). This organic coating is believed to have its origins in humic matter, plants, and polar compounds from the hydrocarbons that have been in contact with sedimentary solids and interacted with the clays (Chung et. al., 1998; Sparks et. al., 2003). The nature of the organic coating allows bitumen solids to act as water/bitumen emulsion stabilizers, a characteristic that greatly affects the extraction process. As a reason for the biwettable characteristics of the solids, it has been proposed that the organic material is not evenly distributed all along their surface (Bensebaa et. al., 2000; Li et. al., 2004; Sparks et. al., 2003). Experimental results have shown that a portion of the solids stayed at the water phase while the rest remained in the oil phase or the interface, probably due to the formation of emulsions stabilized by the ultra-fine particles (Li et. al., 2004; Sparks et. al., 2003).

The clay fraction of the bitumen solids has been analyzed and the main components have been found to be alumino-silicates, with kaolinite and illite as the most

frequent clay minerals, and montmorillonite present in smaller amounts (Li et. al., 2004; Sparks et. al., 2003; Tu et. al., 2004). Particle size ranges from a maximum of 100μm down to less than 1μm, with a major occurrence of the smallest size.

Elemental analysis has found considerable amounts of heavy metals, attributed to minerals in the form of pyrites, titanium oxide, iron oxide, etc. (Bensebaa et. al., 2000; Chung et. al., 1998; Kotlyar et. al., 1998). It is possible that mineral aggregates form when compounds such as calcium carbonates, iron oxides or organic material bond together the mineral particles, originating agglomerates that can reach up to 50μm in size (Sparks et. al., 1998; Sparks et. al., 2003).

Fossils have also been found as part of the oil sands. They are primarily the skeletal remains of algae and diatoms (Sparks et. al., 2003). Their composition is high in sulfur and their size range (10-100μm) allows for removal during settling and centrifugation stages. Since many of the fossils are hollow particles, broken pieces may make their way to downstream units.

It is known that the solids associated with oil sands can be classified as inert or active solids depending on their role during the separation of the bitumen from the mineral matrix (Sparks et. al., 2003). Inert solids, which represent the bulk solids, are those for which the separation process occurs through physical means due to the lack of adsorbed organic matter. Active solids, which represent about 5 wt% of the total mineral component of the oil sands, usually affect negatively the separation and quality of the bitumen due to complex interactions between them (their organic coating) and the oil phase components. The general performance of the oil sands during the extraction and upgrading processes seems to be determined by the concentration and properties of the

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fraction of active solids. Separation of the inert and active mineral components of the oil sands starts at early stages of the extraction process, as noted in section 2.2.

The presence of intractable water and associated salts in bitumen froth has been identified as one of the causes of corrosion of downstream sections. The salts are known to have a high chloride content, which favors corrosion reactions, and the biwettable character of the solids allows them to carry out these salts further down to the upgrading units (Kotlyar, 1998; Liu, 2002).

The combination of a small particle size and the organic coating has enabled previous research to relate the solid content in bitumen with operational problems during the extraction and upgrading of Athabasca bitumen, such as fouling of process equipment and packed-bed hydrotreaters, a problem that leads to an increase of the pressure and consequently the unscheduled shut down of the units (Bensebaa, 2000; Sparks, 2003).

Bitumen solids have also been described as potential contributor of coke formation in process vessels and catalysts surface due to the nature of the organic coating and the large and active surface exposed by the solids (Bensebaa, 2000; Kotlyar, 1998; Li, 2004; Liu, 2002). Previous investigations found similarities between the bitumen solids organic material and the n-pentane insoluble fraction of the bitumen (asphaltenes) which is known for favoring the formation of coke (Kotlyar, 1998). Mineral solids could also participate in nucleation mechanisms during the formation of coke, or flocculate with the recently formed coke phase. In contrast, previous studies carried out under delayed coking type reactions (moderated severity), has shown an increase of the yield of coke formed when solids are removed from the feed (Liu, 2002; Tanabe & Gray, 1997).

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CHAPTER 3
MATERIALS AND METHODS

3.1 Feeds, Chemicals and Clays Minerals

Two hydrocarbon feeds produced by Syncrude Canada Ltd., Diluent Recovery Unit (DRU) feed and Athabasca vacuum residue (AVR), were evaluated in this project. The feeds were collected in 2003 and 1995 respectively. DRU feed is a mixture of naphtha and froth from the hot water extraction process to liberate the oil from the sand and has a concentration of approximately 60 vol% of bitumen. AVR is a 524°C + boiling fraction used as the Fluidized Coker feed at Syncrude and is a product from the vacuum distillation unit (VDU) (Kotlyar et. al., 1998). Properties of AVR can be seen in Table 2.2.

Toluene (certified ACS), methylene chloride (HPLC grade), heptane (reagent grade), and 1,2,3,4 tetrahydronaphtalene (teralin) were supplied by Fisher Scientific Co. and used as delivered. Hydrogen peroxide, 35 wt% solution, was supplied by Sigma-Aldrich Canada Ltd. and used as delivered.

Commercial clays were provided by three different suppliers: illite (green shale) and montmorillonite (bentonite) came from Ward's Natural Science Establishment, Inc. from Rochester, NY and Panther Creek, CO respectively. Illite was grinded to a powder form prior to use and montmorillonite was used as delivered. Rutile was obtained from Sigma-Aldrich Canada Ltd and kaolinite was supplied from Georgia Hydrate. Both were used as delivered.

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3.2 Solid Content and Recovery of Fine Solids and Asphaltenes from Feeds

Heavy oil produced from surface mining operations has a significant content of fine clays. For the feeds used in this study, DRU feed had 0.4 wt% solids content and AVR had up to 1.8 wt% solids (Kotlyar et. al., 1998; Tanabe & Gray, 1997)

For the determination of the solid content of the DRU feed, 300 ml of a solution 10 wt% feed in toluene was prepared. The solution was placed in the sonic bath for 30 min and then divided into three equal aliquots of 100 ml each. Each aliquot was separately vacuum filtered using 0.22 μm Millipore ® filter membranes. The solid content of each aliquot was determined gravimetrically with the weights of the filter membranes before and after the filtration. For the determination of the solid content of the AVR, approximately 300 ml of a 2.5 wt% solution of feed in toluene was prepared and mixed in the ultrasonic bath for 45 min to ensure complete dilution. The solution was equally divided into three aliquots and each one was vacuum filtered using 0.22 μm Millipore ® filter membranes. Similarly to DRU feed, the solid content was gravimetrically determined. Table 3.1 summarizes the results of solid content determination, comparing these results with values previously reported.

Table 3.1. Solid content of DRU feed and AVR

Feed	Solid Content – Experimental (wt%)	Solid Content – Previously Reported (wt%)
DRU feed	(0.32 ± 0.04)	0.40[*]
AVR	(1.40 ± 0.22)	1.80[**]

* Kotlyar et.al., 1998.
**Tanabe & Gray, 1997

Two types of solids were recovered from DRU feed, coarse and suspended solids. Coarse solids are the particles within the DRU feed that settled by gravity during a 24 h period and were recovered from the bottom of the sample container. Suspended solids comprised the rest of the particles that remained in suspension in the liquid after 24 h settling. The parent DRU feed sample was left to settle and the supernatant liquid was then carefully decanted to separate it from the bottom fraction. Solutions were prepared separately using liquid and bottom fractions and toluene in a 1:1 mass ratio; each one was mixed in the ultrasonic bath for 15 min to ensure complete mixing. The solutions were then centrifuged at 40,000 relative centrifugal force (RCF) for 45 min. The centrifugation speed and time was chosen in order to remove over 90% of the total solids content (Sparks et. al., 2003). The supernatants were decanted and the solids were repeatedly washed with toluene until the washing solution was clear. Coarse and suspended solids were finally dried under vacuum until constant mass. Similarly, AVR solids were recovered by centrifuging a 2.5 wt% solution of AVR in toluene under the same conditions.

AVR asphaltenes were recovered in order to use them for coating of mineral clays. First, the solids were removed from the feed. A solution of 40 parts of toluene and 1 part of AVR was prepared and mixed in an ultrasonic bath for 40 minutes. The solution was then vacuum filtered in order to remove solids with a 0.22 μm Millipore® filter membrane. The filtrate solution was recovered and the solvent removed by rotary evaporation; the solids-free feed was dried under vacuum at 80 °C for 8+ hours. To collect the asphaltenes, the feed was then diluted in a 40:1 ratio solids-free AVR–heptane and mixed in an ultrasonic bath for 40 min. The solution was vacuum filtered

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with a 0.22 μm Millipore® filter membrane in order to recover the solids-free-asphaltene filter cake.

3.3 Reactive Extraction of the Organic Coating

Solids associated with Athabasca bitumen are coated with a strongly adsorbed layer of asphaltenes-like material that cannot be removed by solvent washing. The initial procedure for removing the organic coating was mild thermal cracking in the presence of a hydrogen donating solvent. Since the reaction products were soluble in organic compounds, toluene was used as washing solvent after the reaction.

The reaction was carried out following a modified method that was originally described by Liu (Liu, 2002). The reactor used was a microbatch reactor made from stainless steel tubing and fitting provided by Swagelok® (see Figure 3.1). The temperature of the reaction was changed from the original method (430 °C) to a lower value (350 °C), based on the temperature at which the solids have been exposed to during the extraction and first stages of the upgrading processes (Gray, 2003). The reaction conditions were set as follow:

- Temperature: 350 °C
- Pressure: 1 MPa (N_2) at atmospheric temperature
- Reaction time: 40 min

Approximately 250 mg of bitumen solids were mixed in the reactor with 7 ml of tetralin. The reactor was sealed and pressure tested for leaks by filling it with N_2 at 10 MPa. The oxygen was purged from the reactor by repeatedly filling it up with 10 MPa of N_2 and releasing the gas. Finally the reactor was closed with 1MPa of N_2 to ensure an

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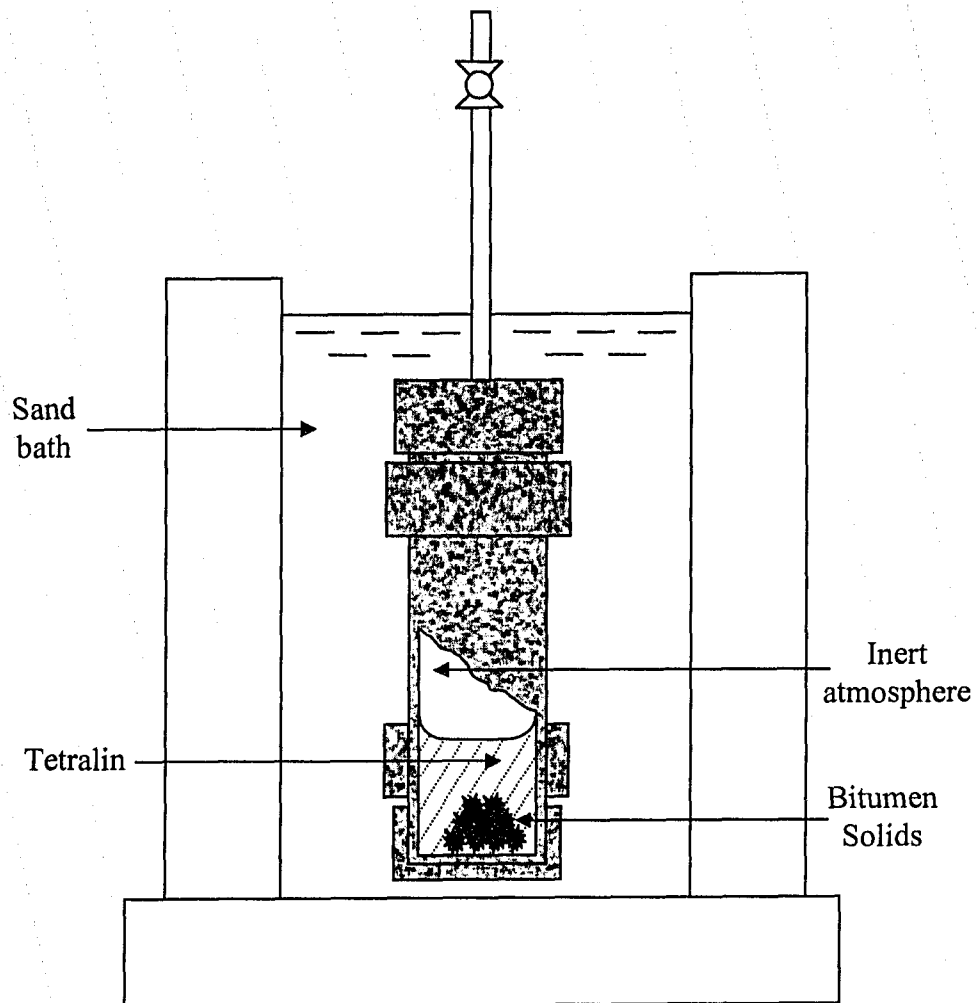
Figure 3.1. Schematic for the microbatch reactor used in thermal cracking reactions

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inert reaction atmosphere. The system was placed inside a 350 °C sand bath for 40 min. After the reaction, the gas product was vented and the solids were centrifuged and washed with toluene until the washing solution was clear. The solids were finally dried under vacuum at 90 °C.

The second step of the cleaning procedure was a bleaching reaction for removing the residual organic coating that still remained after the thermal cracking reaction. For this, H_2O_2 was used in an aqueous media. Approximately 1 g of the dry reacted solids and 50 ml of 30 wt% solution of H_2O_2 were mixed in an ultrasonic bath for 30 min. The mixture was then boiled at 100 °C for 2 hours. Distillated water was used to replace loses by evaporation. After the boiling time, the solids were centrifuged and washed with distillated water.

3.4 Bitumen Solids Analytical Techniques

Five analytical techniques were used to characterize bitumen solids from DRU feed and AVR. The combination of such techniques allowed the design of a model solid to be used for studying the effects of bitumen solids in the upgrading process.

3.4.1 Thermogravimetric Analysis

Thermogravimetric analysis was conducted using a Netzsch STA 409 PC located at the University of Alberta's Chemical and Materials Engineering Building. Prior to analysis, the solids samples were vacuum dried at 80 °C for over 8 hours and maintained in a desiccator to avoid moisture from altering the comparative results. A sample of approximately 7 mg of solids was placed into the ceramic sample holder and then inside

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the oven. Weight loss was measured as the sample was heated up to 1000 °C, at a heating rate of 5 K/min, under air at atmospheric pressure. The total mass loss was determined by the difference between the weight of the sample before and after being heated.

3.4.2 Scanning Electron Microscopy and Energy Dispersive X-ray Analysis

With the aim of gaining a better understanding of the morphology of the bitumen solids and its elemental composition, Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray (EDX) analyses were done. The equipment used was a Scanning Electron Microscope Hitachi S-2700, provided with a Princeton Gamma-Tech Imix (digital imaging and EDX), and located at the University of Alberta's Chemical and Materials Engineering Building. Prior to analysis, samples of bitumen solids were diluted in ethanol and mixed in an ultrasonic bath for about 5 min. A few drops of the solution were placed in the sample holder, the ethanol was evaporated and the solids were coated with carbon.

3.4.3 X-ray Diffraction Analysis

X-ray Diffraction analyses (XRD) were performed to identify the clays present in bitumen solids. Samples of commercial clays as well as bitumen solids from the two different feeds were analyzed for comparison purposes. The samples, which were in a powder form and cleaned from the organic coating, were placed in the sample holder which had a capacity of 0.6 ml. The system used was a Rigaku model Geigerflex 2173 equipped with a cobalt X-ray tube model AEGFK 61-10 and a graphite monochromator to filter K-beta wavelengths, located in the University of Alberta's Earth Sciences

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Building. The machine is provided with an ICDD database. This is a search/match program that searches for the closest match to the unknown sample for clay identification. The detection limit of the equipment is ~ 2 %.

3.4.4 Inductively Coupled Plasma Mass Spectroscopy Analysis

Samples of cleaned bitumen solids from both feeds and commercial clays were sent out for Inductively Coupled Plasma Mass Spectroscopy analysis (ICP-MS) to the Loring Laboratories Ltd. (Calgary, AB). This analysis was done to gain insights on the quantitative composition of metals in bitumen solids. Samples of clays were also submitted for comparison purposes.

3.5 Coating of Clays with AVR Asphaltenes

The clays used for the coking reactions were coated with AVR asphaltenes to ensure good distribution of the clay within the AVR matrix as well as resembling the structure of the bitumen solids.

For coating the clays, 1 g of solids-free AVR asphaltenes was dissolved in 250 ml of toluene. 250 ml of heptane were added and the solution mixed for 10 min. Finally 5 g of the clay were added into the solution and mixed for 24 h at room temperature. Once the solution was stirred it was then vacuum filtered through a 0.22 μm Millipore® filter membrane and the asphaltene-coated clay filter cake was recovered and vacuum dried at 50°C.

3.6 Coking Reactions

This section describes the operating procedures for coating the strips, setting up and running the coking reactions, and collecting the products.

Since the aim of this stage of the research was the study of the effect of solids in coking reactions, only the nature and concentration of solids was varied. Experimental parameters such as Curie point of the strips, frequency of the induction furnace, time of reaction and feed were kept constant for all the experiments.

With the objective of minimizing the experimental error and obtaining consistent results, all experiments were repeated at least three times and average results and standard deviations calculated for each concentration/type of solids.

3.6.1 Experimental Set-up

Figure 3.2 shows a process flow diagram of the experimental set-up following that presented in earlier studies (Gray et. al., 2004; Soundararajan, 2001). The Nitrogen (99.998%) and liquid carbon dioxide were both provided by Praxair and used as delivered. The nitrogen was used as sweep gas which allowed keeping the reaction atmosphere free of oxygen and cracked hydrocarbon products. The carbon dioxide used as coolant gas allowed the reaction to take place only during the time set (15 s) due to a rapid cooling of the feed below the coking temperature.

Nickel-iron strips with a Curie point of 510 °C were used for the coking reactions. Curie point, also called Curie temperature, is a transition temperature that marks a change in the magnetic or ferroelectric properties of a substance (in this case an alloy), especially the change from ferromagnetism to paramagnetism. The exact Curie point depends on the
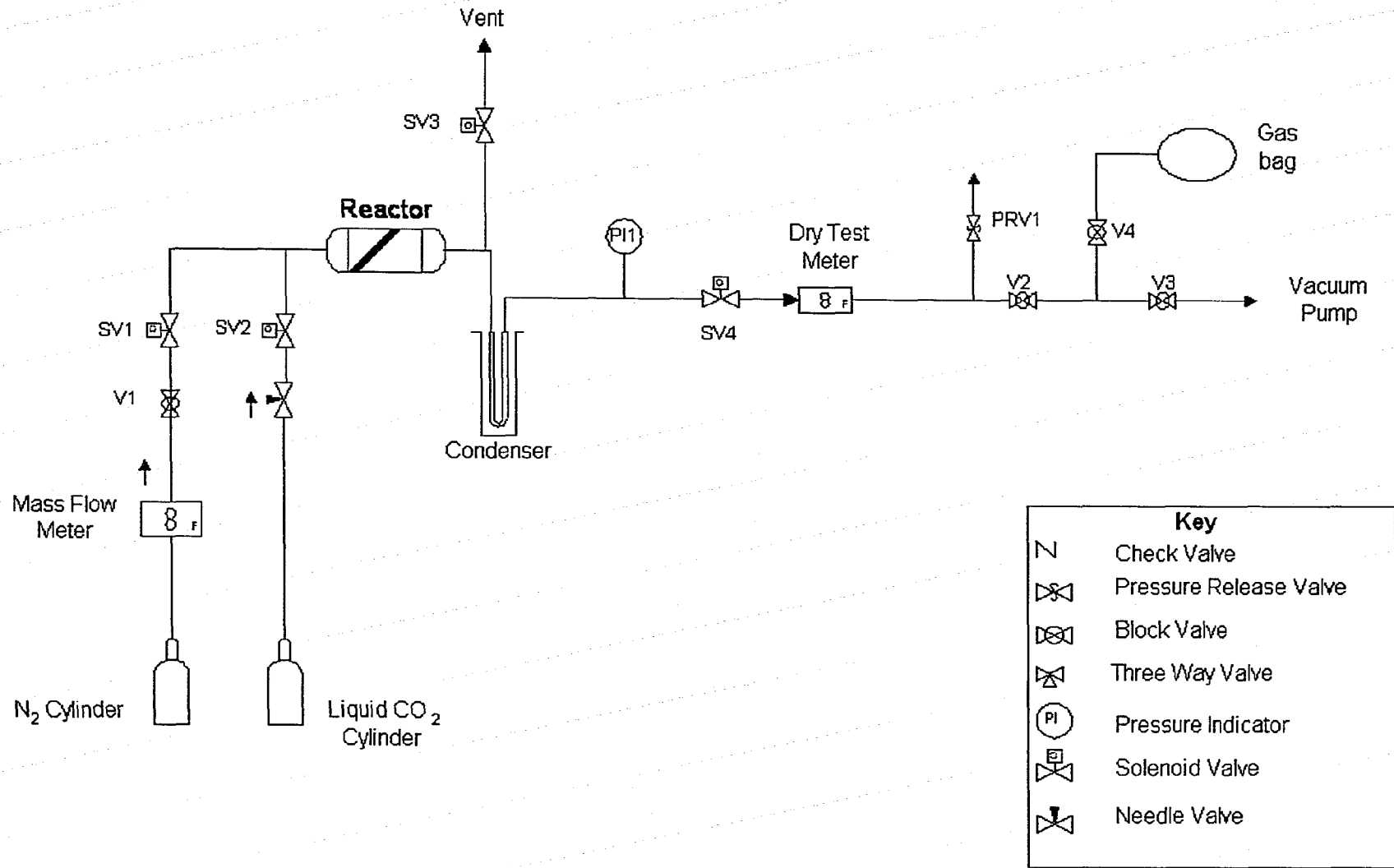
Figure 3.2. Process flow diagram of the experimental unit used for the coking reactions
(Reprinted with permission from Gray et.al., 2004. Copyright 2004. American Chemical Society)

nature of the material or the composition of the alloy and can be reached by an induction field. The use of an induction furnace allowed for a rapid and even heating of the strip. The Curie temperature of the strips was determined by attaching three thermocouples to equidistant points of the strip and monitoring the temperature reached when the induction furnace was turned on.

The reactor consisted of a Pyrex ® glass tube placed inside the coil of the induction furnace and containing a set of six strips coated with bitumen and supported by two ceramic holders. The coil receives an alternating current which creates an alternating magnetic field around the strips, allowing them to reach their Curie point. The condenser consisted of a "U" tube made from stainless steel Swagelok ® tubing and fitting, filled with glass wool and placed inside a container with liquid nitrogen. The induction furnace and the opening/shutting of the solenoid valves regulating the flow of nitrogen, carbon dioxide and gas products were automatically controlled by the acquisition program Advantech GeniDAQ®. The rest of the tubes and fitting upstream and downstream of the reactor were also Swagelok ® stainless steel.

3.6.2 Coating of Curie Point Alloy Strips

AVR was evenly sprayed on both faces of each strip using an air gun apparatus as represented in Figure 3.3. The set up used for the spraying was a modified version of the procedure previously used by Soundararajan (Soundararajan, 2001). The strips were 25 cm long and 2.1 cm wide with an area of 48.3 cm^2 available for coating. Six strips were used for each experiment for an adequate sample size. The container feeding the air gun was filled with a 7 wt% solution of AVR-methylene chloride to ensure a viscosity low

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Aluminum
Railing

Motor

Curie-point
Strip

Feed
Container

Magnetic stirrer

To power

b) Side View

Curie-point
Strip

Air Gun

Compressed
Air

Feed
(AVR)

Magnetic stirrer
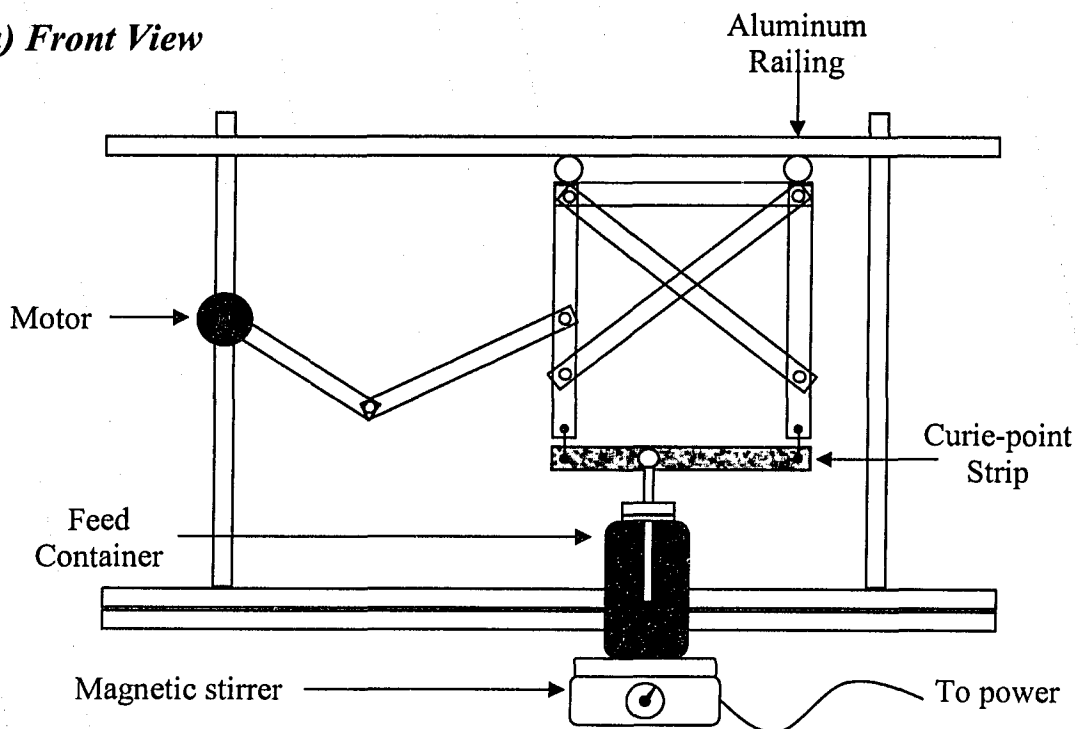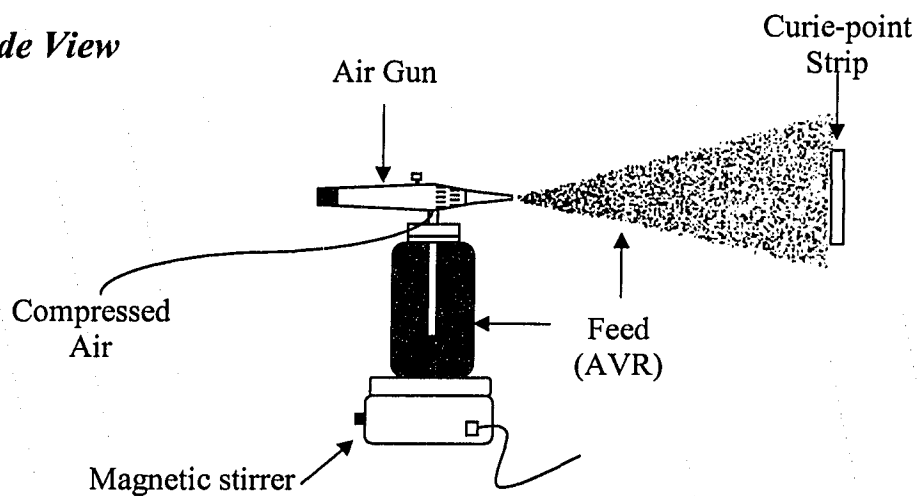
Figure 3.3. Schematic of the apparatus used for coating the Curie-point strips

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enough so that the bitumen solids or clay particles could be carried out by the fluid to the surface of the strip. A mixing system was designed and placed inside the feed container to allow the solution to be homogeneous (see Figure 3.4). After spraying, each strip was weighed and placed in a ventilated area for at least 8 hours to ensure total evaporation of the methylene chloride.

The thickness of the film coating the strips was chosen to be (20 ± 2) µm to minimize mass transfer effects (Soundararajan, 2001) and was calculated gravimetrically by weighing each strip before and after the spray and after the solvent was evaporated. The film thickness was obtained following equation 3.1:

$$\delta = \frac{m_{AVR}}{W_{strip} * L_{strip} * \rho_{AVR}} \qquad (3.1)$$

where,

δ -   Film thickness

m_{AVR} -   Mass of feed on the strip

W_{strip} -   Length of the strip

L_{strip} -   Width of the strip

ρ_{AVR} -   Density of AVR (as reported in Table 2.2)

3.6.3 Experimental Procedure

Six strips coated with AVR were held by two ceramic holders and tightened by two strings. Another set of six clean strips were identically assembled and used to regulate the frequency of the induction furnace to be less than 153 MHz, thus preventing the furnace to shut down for overheating.

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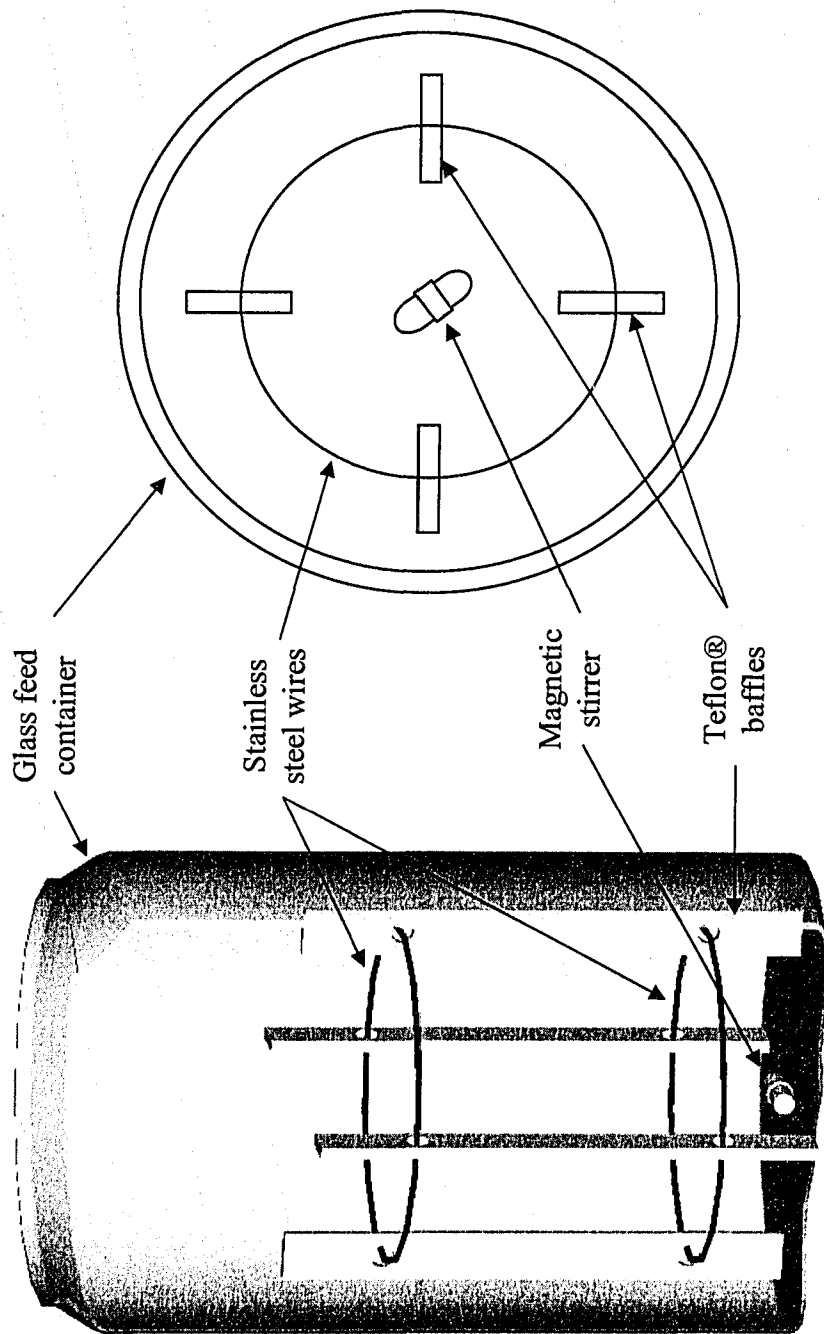
Figure 3.4. Schematic of the feed container and mixing system

Glass feed container

Stainless steel wires

Magnetic stirrer

Teflon® baffles

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Weights of the coated strips, strings and ceramic holders, as well as the components of the experimental set-up were recorded in a log sheet before and after the reaction (see Appendix I).

Once the frequency of the furnace was set to be less than 153 MHz, the coated-strips assembly was placed inside the induction furnace and the rest of the components tightened so that the whole system was sealed. The condenser ("U" tube) was submerged in liquid nitrogen. A flow of nitrogen was set between 11-13 l/min for a purging period of 15 min, time during which the joints were checked for leaking and retightened if necessary.

After the purging time, the system was controlled through the software. Initially valves SV1 and SV3 were opened for an extra 5 min of continuous flow of nitrogen. During this time SV2 was opened for 5 s to purge the line of carbon dioxide from any oxygen remaining. After the 5 min were over, the induction furnace was turned on, SV3 was closed and SV4 opened simultaneously to allow the reaction products to flow through the condenser. The furnace was turned off 15 s later and at the same time SV1 was closed and SV2 was opened to allow carbon dioxide to flow and cool down the reactor. The cooling period lasted 20 s, time after which SV2 was closed.

Once the reaction was carried out, the condenser was taken out of the liquid nitrogen and the system was dissembled so the components could be placed aside until room temperature was reached. Finally all the elements and removable components of the system were weighed for mass balance calculations.

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3.6.4 Products Recovery and Mass Balance Calculations

Distillate products, coke and unreacted material were recovered separately for yield and mass balance calculations.

The distillate product consisted of all the material trapped or condensed throughout the system, from the copper tube used for delivering the carbon dioxide (placed upstream from the reactor), including the Pyrex ® glass tube and the downstream components, to the condenser. All these elements, except for the Pyrex ® glass tube, were weighed before and after the reaction and the differences were added to the total amount of distillate product recovered. The glass tube was wiped out with Kimwipes ® sheets and methylene chloride. The sheets were weighed before cleaning the glass tube and after the solvent had vaporized, and the difference accounted for distillate product. The yield of distillate products was calculated using equation 3.2:

$$\%Distillate = \frac{m_{dsc} + m_{dgt} + m_{dc}}{m_{AVR} - m_{clay}} * 100 \qquad (3.2)$$

where,

$\%Distillate$ -   Yield of distillate products

m_{dsc} -   Mass of distillate products on the system components

m_{dgt} -   Mass of distillate products on the Pyrex ® glass tube

m_{dc} -   Mass of distillate products on the condenser

m_{AVR} -   Mass of feed on the strips

m_{clay} -   Mass of the clay portion of the solids added to feed

The term m_{clay} was obtained by the difference between the proportional mass of solids present in the reacted feed and the amount of organic coating of the solids.

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Coke yield was calculated from the coke recovered from the strips. After the reaction, the strips were weighed and washed with methylene chloride by placing each strip in an aluminum beaker 3.5 cm diameter and 30 cm height, with 250 ml of the solvent, in the ultrasonic bath for 30 min. The washing solution was vacuum filtered through a 0.22 μm Millipore® filter membrane. The filter membranes were weighed before and after the filtration of the solution and the difference accounted for insoluble material. After cleaning in the sonic bath, the strips were weighed again to account for the amount of residual coke still attached to the strip. The coke yield for each strip was finally calculated as indicated in equation 3.3. The overall coke yield for the reaction was calculated as the average of the coke yield of each strip.

$$\%Coke = \frac{(m_{cokestrip} + m_{ins.mat}) - m_{clay}}{m_{AVR} - m_{clay}} * 100 \qquad (3.3)$$

where,

$\%Coke$ -   Yield of coke of the strip

$m_{ins.mat}$ -   Mass of insoluble material recovered from filtration

$m_{cokestrip}$ -   Mass of coke remaining on the strip after the sonic bath

The extractables yield was defined as the mass of unreacted feed divided by the mass of initial feed on a solids-free basis. The total amount remaining on the strip after the reaction yielded to the sum of the amounts of extractables, solids and coke formed during the reaction. The mass of extractables was then calculated by subtracting the mass of solids present and the mass of coke recovered to the total remaining on the strip after reaction, as described in equation 3.4:

$$\%Extractables = \frac{(w_{afterRxn} + w_{beforeRxn}) - (m_{cokestrip} + m_{ins.mat})}{m_{AVR} - m_{clay}} * 100 \qquad (3.4)$$

where,

$\%Extractables$ -   Yield of extractables

$w_{afterRxn}$ -   Weight of strip after reaction

$w_{beforeRxn}$ -   Weight of strip before reaction

Finally, the yield of gas was calculated as the difference between a 100% mass balance and the yields of products and unreacted material, as shown in Equation 3.5:

$$\%Gas = 100\% - \%Distillate - \%Coke - \%Extractables \qquad (3.5)$$

where,

$\%Gas$ -   Yield of gas

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CHAPTER 4
RESULTS AND DISCUSSION

Bitumen separated from Athabasca oils sands contains a fraction of inorganic material or bitumen solids. It is known that the mayor constituent of these bitumen solids are alumino-silicate clay crystallites coated with an organic matter that is insoluble in toluene (Bensebaa et al., 2000). In this chapter, results of the analysis of bitumen solids from two different feeds are presented, diluent recovery unit (DRU) feed and Athabasca vacuum residue (AVR) or coker feed, followed by a study of the effect of bitumen solids and clay minerals on thermal cracking reactions in thin films.

4.1 Characterization of Bitumen Solids

4.1.1. Analysis of the Organic Content of Bitumen Solids

As mentioned in earlier chapters, bitumen solids are coated with an asphaltene-like material that is insoluble in toluene. This organic coating represents up to 40 wt% of the solids, and is responsible for much of the behavior of the solids during thermal upgrading of the bitumen. The organic content also represented an impediment for the proper characterization of the fines using the analytical techniques mentioned in section 3.4.

The cleaning procedure described in section 3.3 was done with the aim of eliminating the organic content from the mineral portion of the solids, in order to obtain cleaner mineral particles suitable for analysis. Thermogravimetric Analysis (TGA) was used to measure the success of the cleaning procedure. In Figures 4.1 and 4.2, TGA

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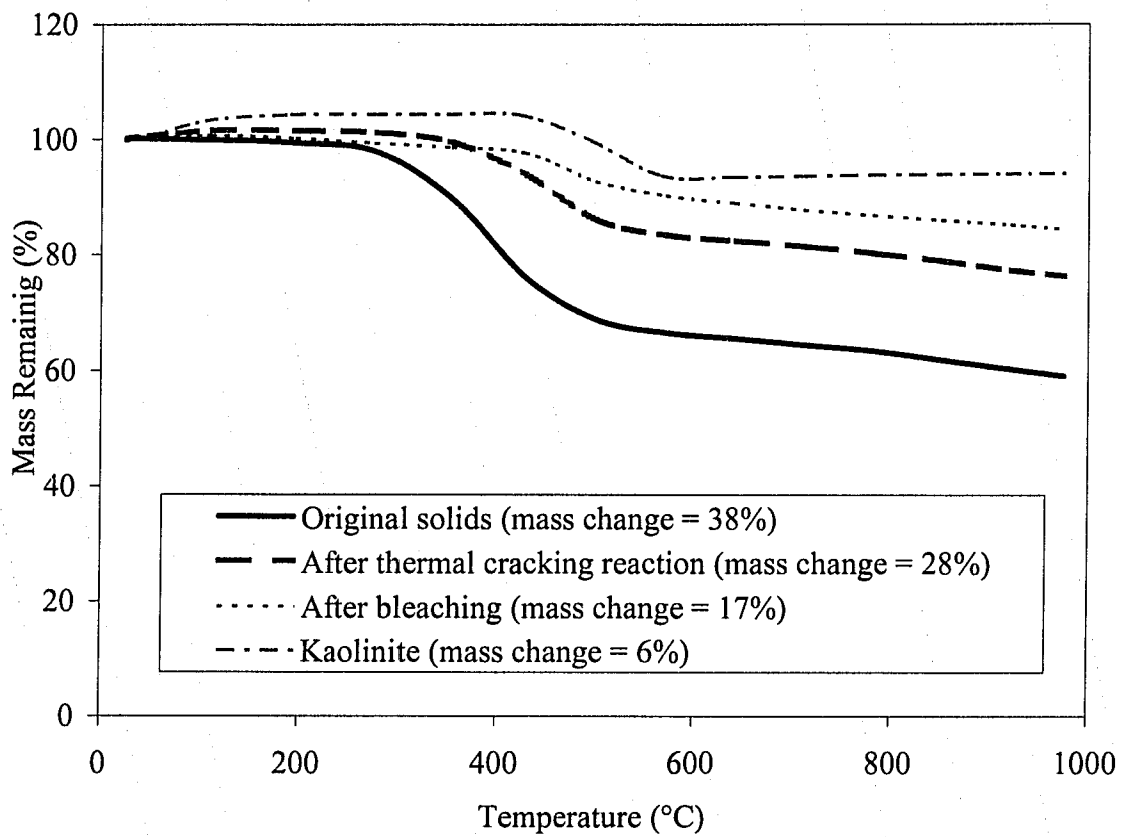
Figure 4.1. Thermogravimetric analysis of DRU feed bitumen solids

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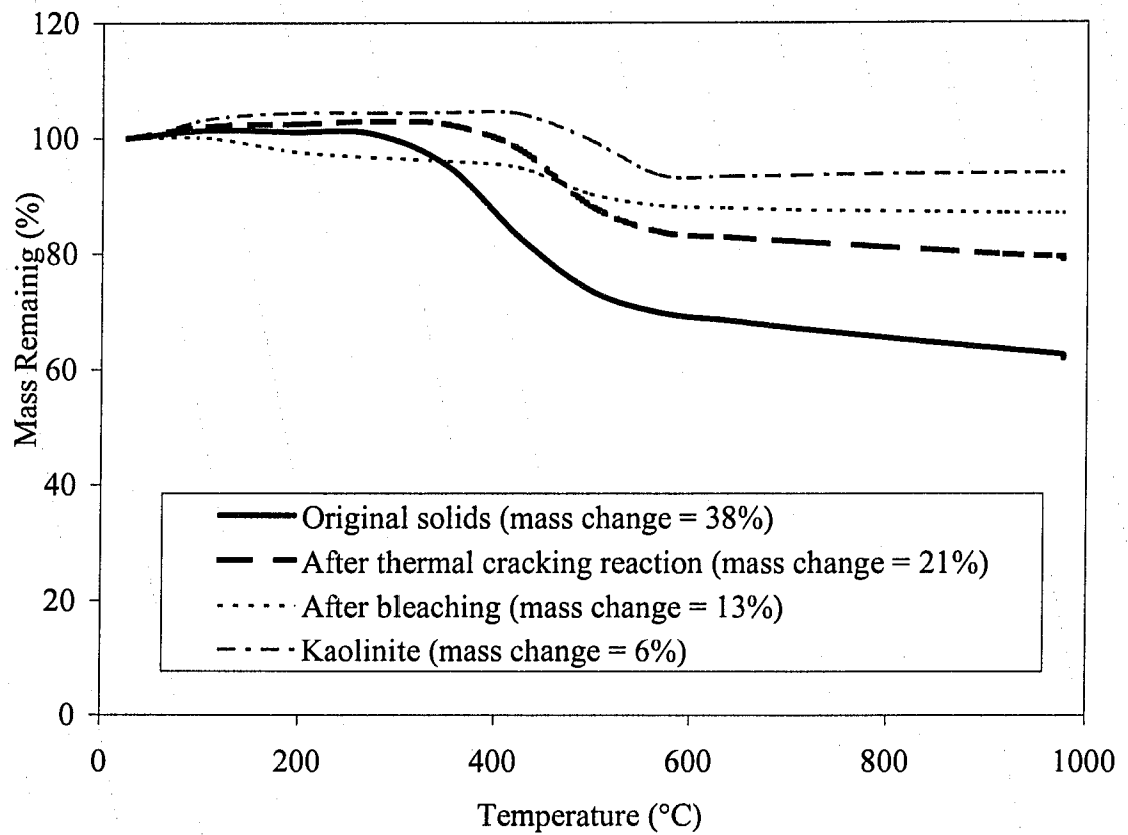
Figure 4.2. Thermogravimetric analysis of AVR bitumen solids

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results showing the weight loss of bitumen solids (DRU feed and AVR respectively) before and after each cleaning step are compared with commercial kaolinite. As indicated in figures 4.1 and 4.2, the majority of the organic content of the bitumen solids was removed by thermal cracking and bleaching reactions. The small amount of weight loss of the kaolinite is attributed to the water content of the sample. The total mass removal obtained for the DRU and AVR solids was 21% and 25% respectively. For both kinds of bitumen solids, the amount of organics lost was comparable.

As mentioned in Section 3.5., a procedure for coating samples of commercial clays with asphaltenes was used to facilitate the distribution of the clays within the bitumen, as well as resembling the organic coating of the bitumen solids. Previous research (Liu, 2001) shows that, as bitumen solids, silica particles coated with asphaltenes have an effect on the yield of coke obtained from coking reactions of AVR. On the contrary, uncoated silica showed no effect on the yield of coke under the same reaction conditions. Based on these results, commercial samples of kaolinite, illite, and rutile were treated with asphaltene obtained from AVR. Table 4.1 summarizes the TGA results for each of the commercial clays before and after being coated with AVR asphaltenes.

Table 4.1. TGA of commercial clays before and after coating with asphaltenes

Commercial Clay	Mass change Before coating (%)	Mass change after coating (%)
Kaolinite	5.8	25.89
Illite	9.04	15.43
Rutile	1.28	2.76

As shown in Table 4.1, the amount of organics adsorbed on the surface varies significantly from one clay to another. These results suggest that the affinity of the surface of each clay for the asphaltene molecules is different and so may be their behavior when they come in contact with the bitumen. Among the three clays, kaolinite showed a much higher affinity for the asphaltene material.

4.1.2 Change of Fine Solids from Extraction to Upgrading

Solids recovered from Diluent Recovery Unit (DRU) feed and Athabasca Vacuum Residue (AVR) were analyzed in order to determine the differences in form, particle size and composition.

Thermogravimetric analysis was employed to evaluate the amount of organic coating present on the bitumen solids obtained from DRU feed and AVR. The results were used to determine if the amount of the organic coating on the surface of the solids changed in the industrial process as the bitumen moved from the Diluent Recovery Unit through the vacuum tower. Figure 4.3 shows the amount of mass loss in the TGA experiments for DRU feed solids and AVR solids. Samples of coarse and suspended solids from DRU feed were compared. No significant difference was observed in the amount of organic coating in the smaller and larger particles within the DRU feed. There was also no significant change in the amount of organic coating of the particles as they moved through the diluent recovery unit (DRU solids) and the vacuum tower (AVR solids). It is possible that organics free solids are coated with asphaltenes during processing once the naphtha has been added to the froth. Experimental observations of DRU feed solids as well as the results of coating of standard clays (Table 4.1.) suggest

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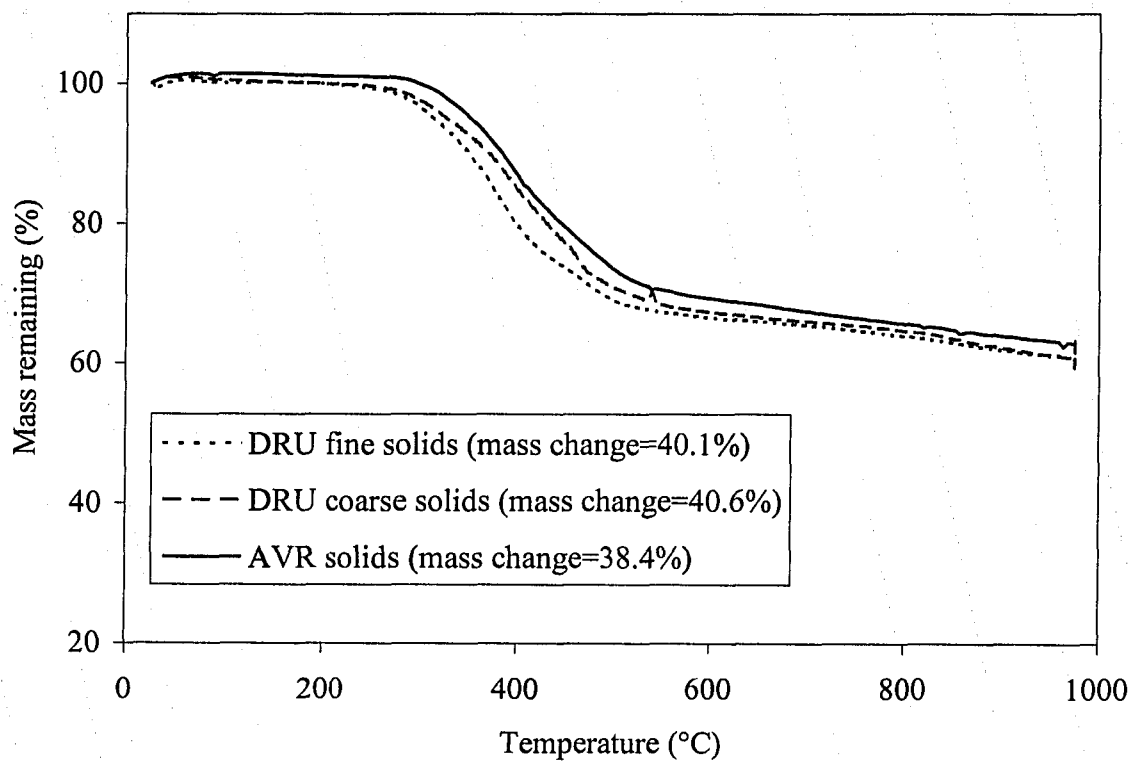
Figure 4.3. Thermogravimetric analysis of DRU feed and AVR solids

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that part of the coating could have been added while the solids were in contact with bitumen dissolved in a naphthenic solvent and when the solvent is removed in the DRU.

According to previous work (Sparks et al., 2003) the organic coating on the bitumen solids represents between 15 to 40 wt% (reported as toluene insoluble organic carbon) of the particles, depending on the geological location of the bitumen, the commercial process used for its extraction, and the stream they have been taken from. This organic content is comparable to the results obtained from elemental and thermogravimetric analysis of the bitumen solids (see Table 4.2). It has been found that the study of the amount and composition of the solids organic coating has relevant consequences to the extraction and upgrading processes (Bensebaa et al., 2000; Sparks et al., 2003). These previous studies agree with the participation of the organics compounds adsorbed in the fines surface in the separation of bitumen from the sand, the fouling of process units, or the formation of coke during bitumen upgrading.

Table 4.2. Elemental analysis of AVR bitumen solids

Nitrogen, wt%	0.3926
Carbon, wt%	16.9376
Hydrogen, wt%	1.5822
H/C atomic ratio	1.12

Scanning Electro Microscopy (SEM) and Energy Dispersive X-Ray (EDX) analysis were used to identify semi-quantitatively the elements present in the fine solids. Results for the DRU and AVR solids are presented in Figures 4.4 and 4.5, respectively.
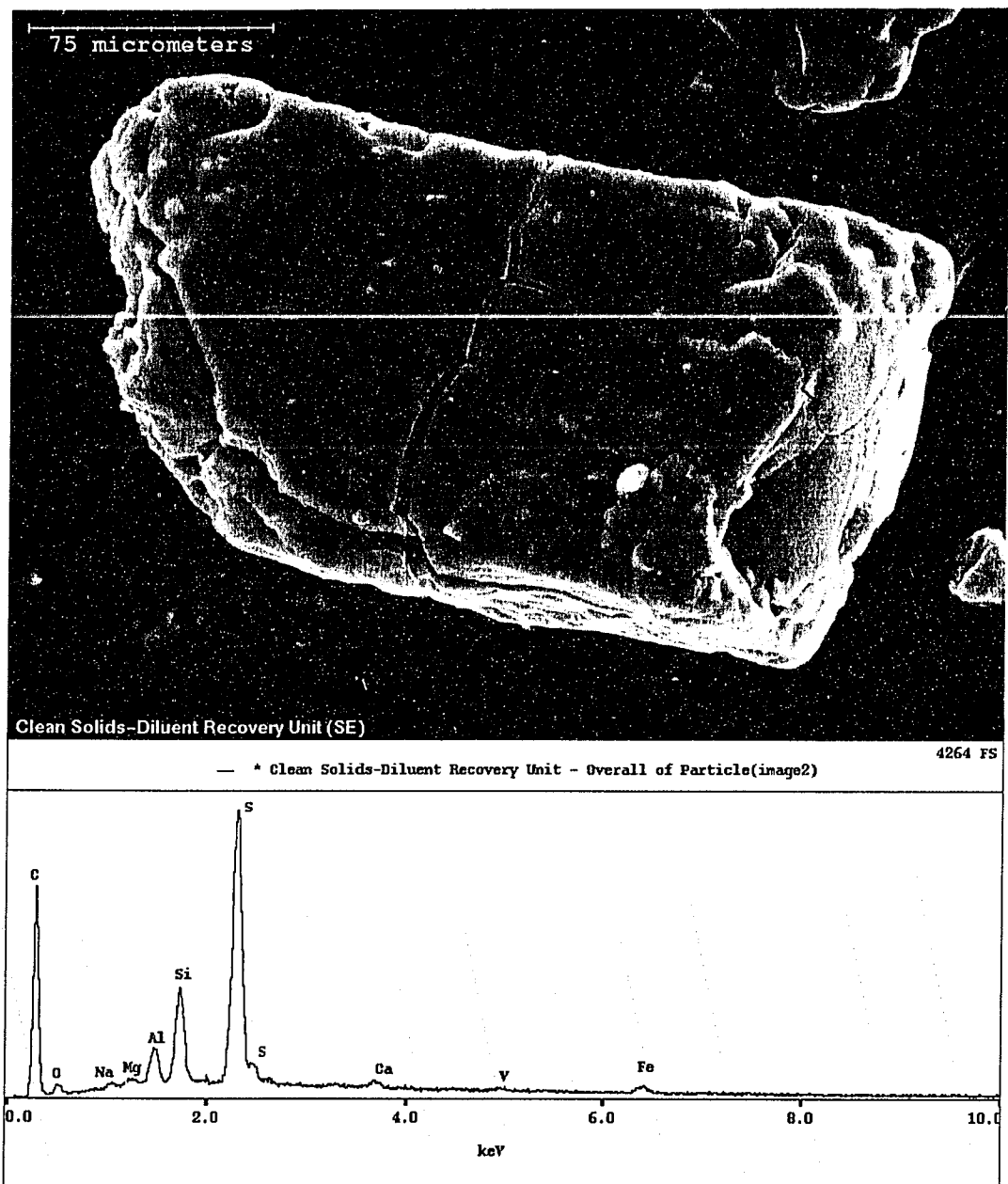
Figure 4.4. SEM micrograph and EDX spectrum of clean DRU feed solids

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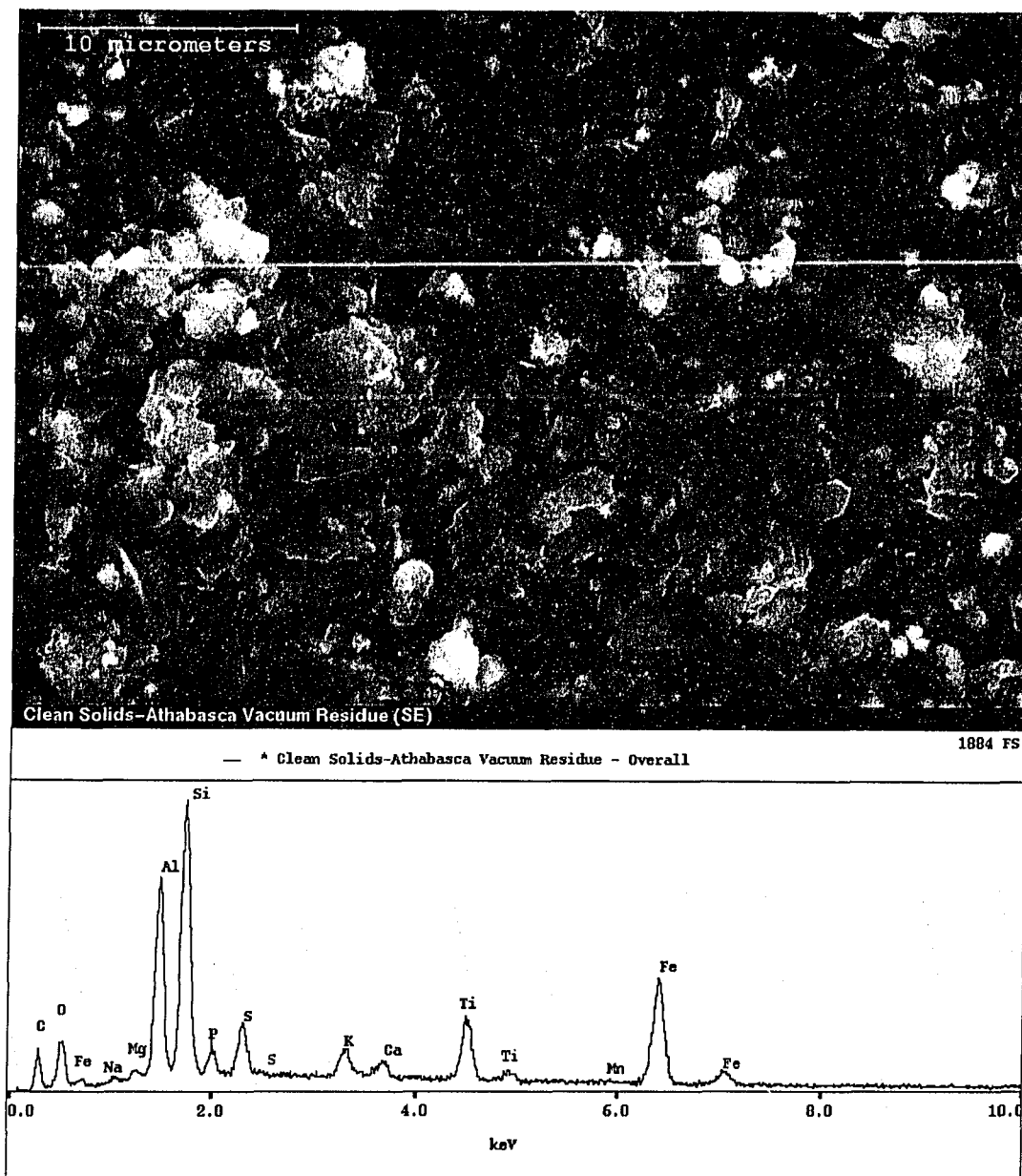
Figure 4.5. SEM micrograph and EDX spectrum of clean AVR solids

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The DRU feed solids appeared to be larger than the AVR solids. Results from the EDX analysis show that the composition of DRU feed solids is a combination of aluninosilicates and a carbonaceous material with high sulfur content. In contrast, the composition of AVR solids corresponds with that typically found for clays: high silicon and aluminum content. These differences may be attributable to the time difference between the sampling of both feeds and the variability in the quality and composition of the ore in the mine site.

4.1.3 Clays Identification

In order to gain a better understanding of the types of clays present in fine bitumen solids, X-Ray Diffraction (XRD) analysis was used on samples of DRU feed solids and AVR solids. Kaolinite, illite and montmorillonite have been previously associated with the composition of bitumen solids (Omotoso & Mikula, 2003; Tu et al., 2004). For comparison, XRD spectra of standard samples of these three clays and the bitumen solids are presented in Figure 4.6.

When comparing the standard clays with DRU feed solids and AVR fine solids, both similarities and differences were found. One of the most evident differences was found contrasting the montmorillonite spectrum with the bitumen solids spectra (both DRU and AVR solids). Peaks around 2-Theta values of 8.3° and 33.2° from the montmorillonite spectrum did not appear in the bitumen solids spectra. These data suggests that montmorillonite as discrete clay is not among the predominant clays present in bitumen solids. Previous work suggests the presence of montmorillonite in the mineral matrix of oil sands (Hendrickson, 1975) as either pure or in the mixed-layer form

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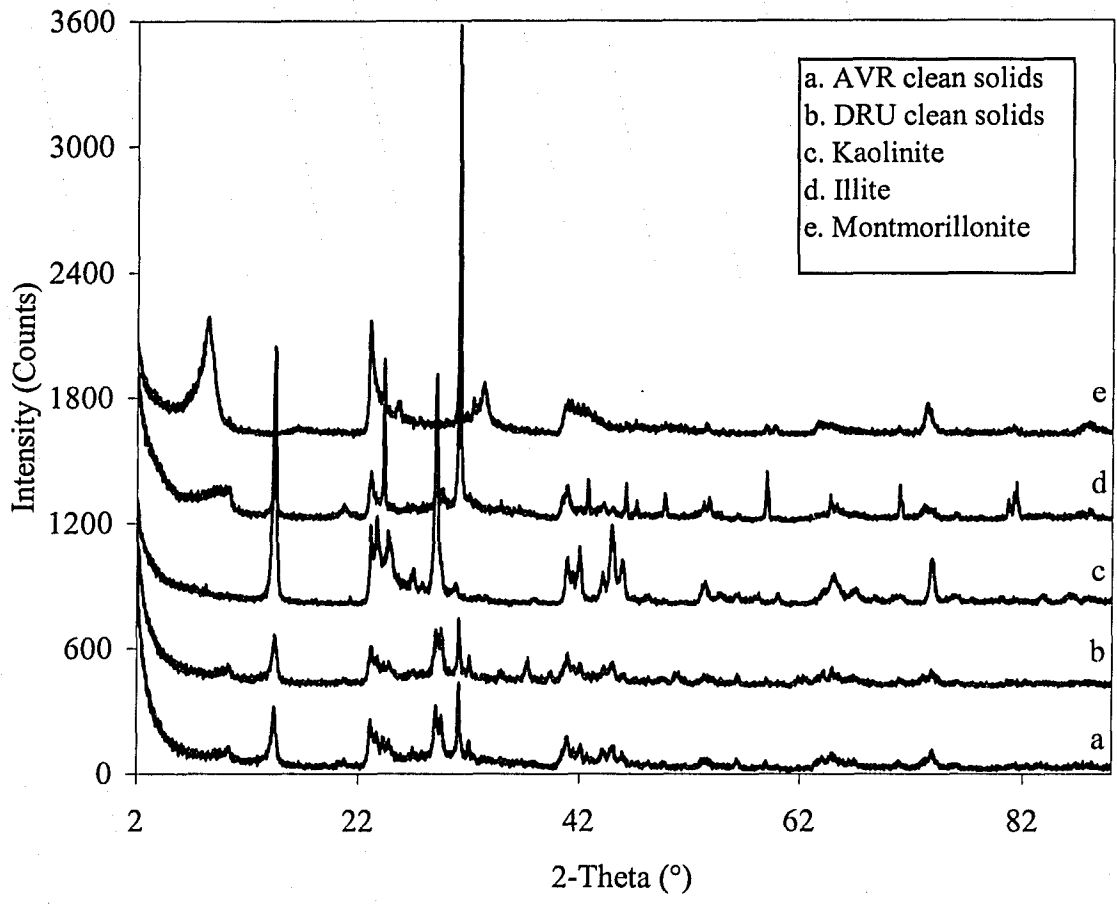
Figure 4.6. XRD spectra of DRU feed and AVR solids compared with standard clays

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associated with kaolinite and illite, in proportions that range between 9 to 11 wt% of the clay size fraction. Another study (Omotoso & Mikula, 2003) has reported that the montmorillonite content, usually around 1 wt% of the clay fraction for the discrete clay and 10 wt% for the mixed-layer form in core samples, is known to vary across the Athabasca deposit and be reduced in samples taken downstream of the extraction process. This last result agrees with the one found in samples from DRU feed and AVR solids, and suggests a significant reduction of the smectite form of clay during the extraction process. Furthermore, studies of the settling and rheological properties of mature fine tailings as well as the analysis of its mineralogy where smectite has been found (Omotoso & Mikula, 2003), supports the fact that the amount of montmorillonite originally existing in the oil sand is reduced through the first steps of the extraction process. The reason for such reduction may be attributed to the much stronger hydrophilic behavior of the montmorillonite when compare with kaolinite and illite, along with the rejection of most of the water content during the first stages of the extraction process.

The XRD spectra obtained from the DRU feed solids and the AVR solids were also compared with each other (Figure 4.7.). In general, the XRD analyses were similar for the bitumen solids.

XRD analyses included the identification of the clay and mineral components of the bitumen solids and commercial clay samples. Results were obtained by contrasting the bitumen solids XRD spectra with the equipment data base. The results are summarized in the Table 4.3.

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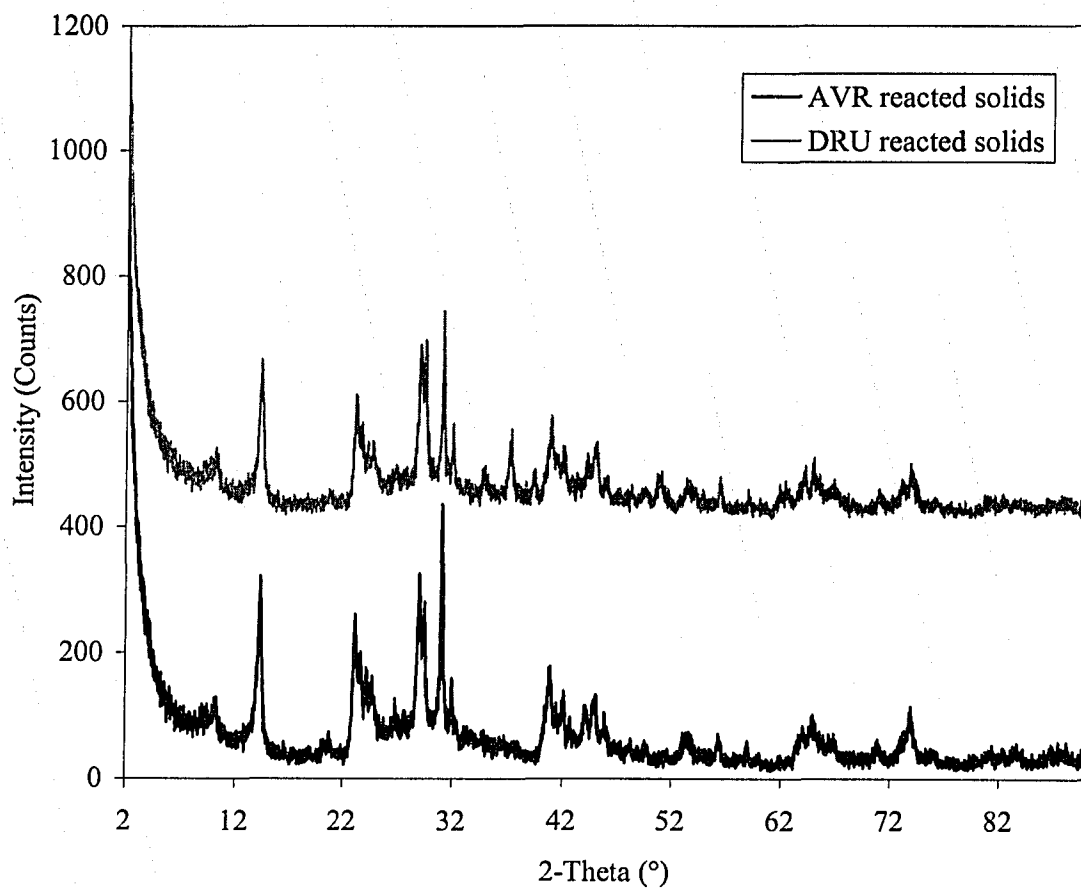
Figure 4.7. Comparison of XRD analysis of DRU feed solids and AVR solids

Table 4.3. Clays identified by X-Ray Diffraction analysis

Minerals and Clay Minerals Identified	Sample				
	Kaolinite	Illite	Montmorillonite	AVR solids	DRU feed solids
Albite			✓		
Anatase		✓		✓	✓
Anorthite			✓		
Beidellite			✓		
Gibbsite	✓				
Kaolinite	✓	✓		✓	✓
Muscovite / Illite		✓	✓	✓	✓
Norrishite				✓	
Phlogopite				✓	
Pyrite					✓
Quartz		✓	✓	✓	✓
Rutile				✓	✓
Siderite					✓
Titanite		✓	✓	✓	✓

The XRD analysis of clay standards (illite, kaolinite and montmorillonite) was used to verify the technique and to asses the purity of the standard clay samples. From these results, it is apparent that the sample of illite submitted for analysis was not pure illite but a mixture of this clay with kaolinite, quartz, anatase, and titanite, where the extra clays could be considered as associated impurities. Unfortunately, XRD could not be used to quantify the concentrations of these impurities. Interestingly, the sample of montmorillonite did not match with the information of this type of clay available in the

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XRD data base but was identified as beidellite. This is not surprising, since montmorillonite and beidellite are closely related minerals and both are members of the smectite group (Deer et al., 1966; Gillot, 1987; Grim, 1953). Specifically, montmorillonite and beidellite are chemical variations of the basic formula $Al_4Si_8O_{20}(OH)4 \cdot nH_2O$ and vary slightly in Na, Ca and Mg content (Deer et al., 1966). These similarities are reflected in their XRD spectra (Figure 4.8). Hence, it is still valid to use this sample for comparison with bitumen solids.

The clay-identification results in Table 4.3 show that not all of the clays present in DRU feed solids are present in AVR solids, likely due to the time difference between collection of these samples. It is also known that bitumen undergoes a heat treatment from the DRU to the vacuum tower in which the feed is exposed to temperatures up to 350 °C (Gray, 2003). This exposure of the feed to such temperatures can cause modification on the structure of some of the clays and consequently on the types of clays identified (Gillot, 1987; Grim, 1962). However, in order to obtain a full identification of the clay species, much more detailed work is required.

Since XRD results were qualitative, a quantitative analysis was necessary to estimate the amount of each clay mineral in the bitumen solids. Inductively Coupled Plasma-Mass Spectroscopy (ICP-MS) was used to measure the amount of each of the different components in the standard clays and in the DRU and AVR solids. The results, reported in terms of salts and oxides compounds, are presented in Figure 4.9. As expected for clays, the bitumen solids were predominantly silicon and aluminum oxides. The concentration of ferric oxide in the bitumen solids (DRU and AVR) suggests that they carry a significant amount of impurities that may be associated with wear of the mining

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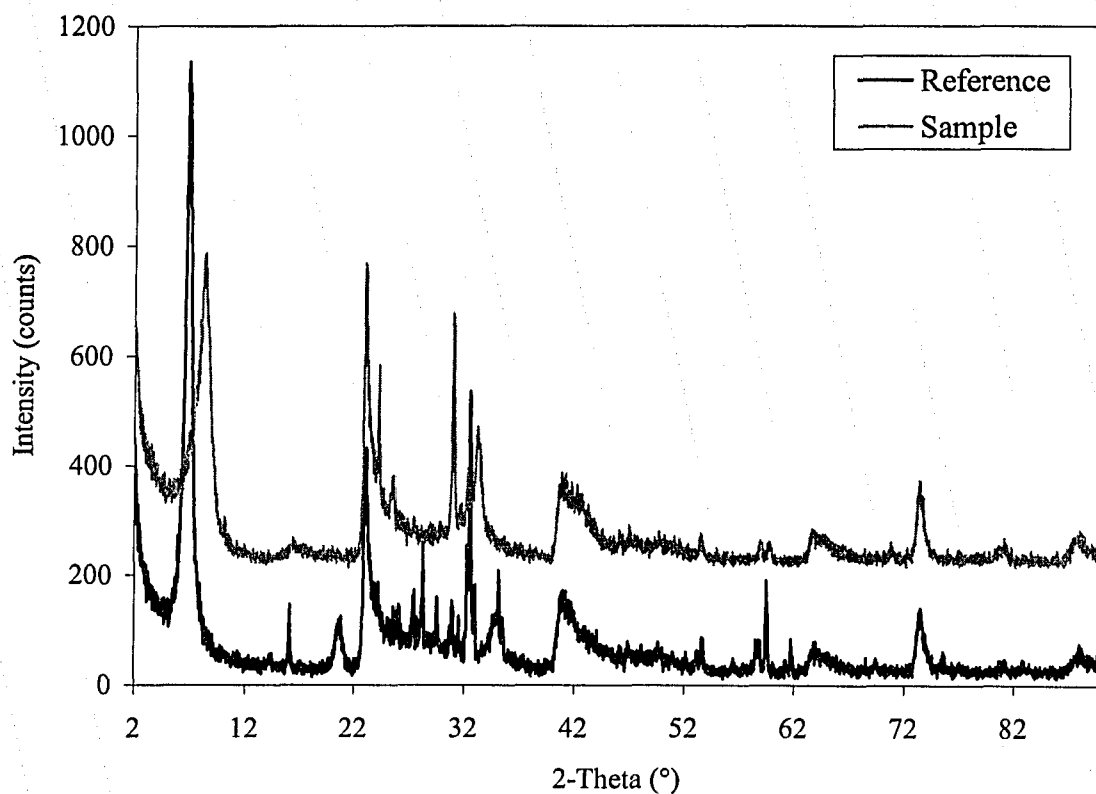
Figure 4.8. Comparison between the XRD spectra of pure montmorillonite (reference) and the commercial sample of montmorillonite

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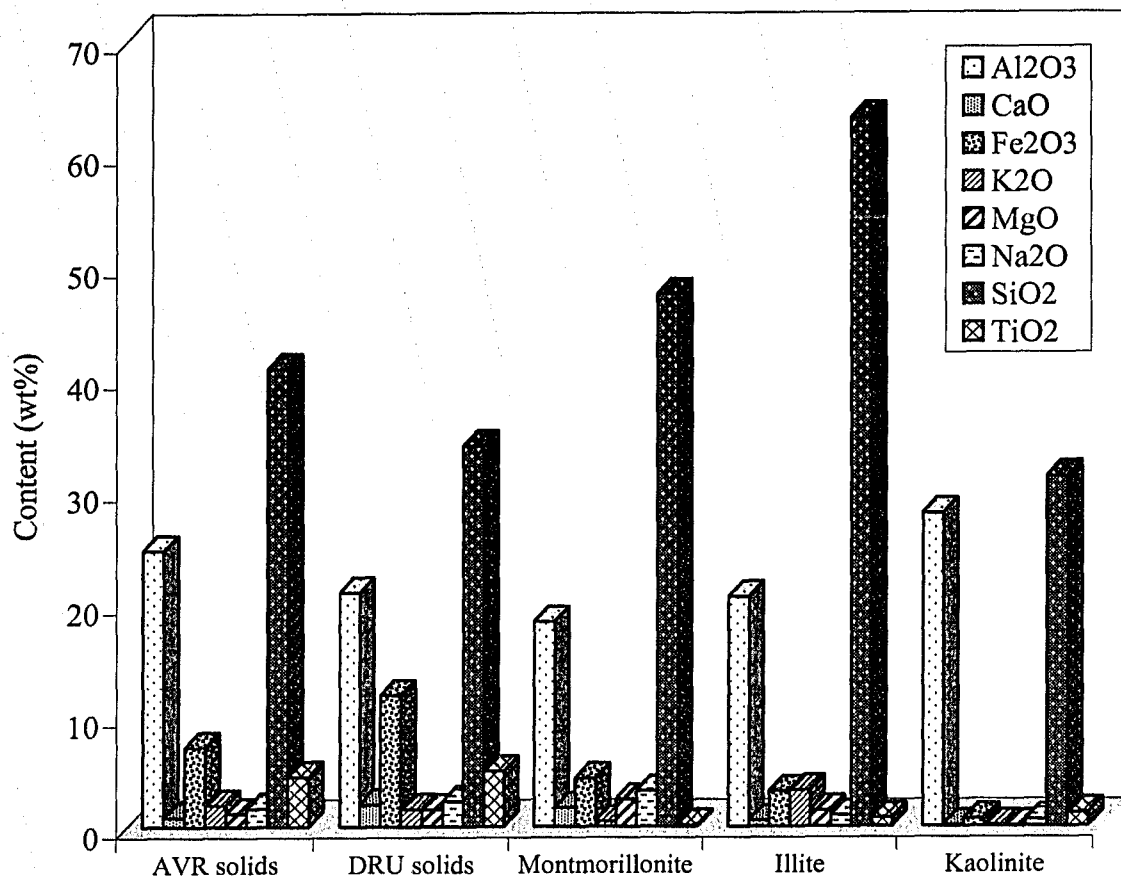
Figure 4.9. ICP analysis results for bitumen solids and standard clays

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equipment and with corrosion in transport lines and process vessels. It should be noticed that even the standard clays had a small amount of ferric oxide, but the level was much higher in the DRU and AVR solids.

4.2 Model Solids

The main objective of this research was to understand the role of fine solids in bitumen upgrading. To reach that objective it was necessary to extract a relatively large amount of bitumen solids from AVR feed for characterization and for studying their behavior under coking conditions. The procedure for obtaining bitumen solids is laborious. The results of the five different analytical techniques used in the characterization of bitumen solids were combined to create a model mixture of clays that could be used in place of bitumen solids for controlled coking experiments. The model mixture of clays was tested at coking reaction conditions, and the results compared with those obtained from original bitumen solids and standard clays.

Once the main clays forming the AVR solids were identified, and the mineral composition of bitumen solids and standard clays elucidated by the ICP-MS analyses, the best combination of standard clays was calculated using the method of least squares.

As noted in the ICP-MS analysis results, the composition of fines and clays was obtained in terms of oxides and trace of metals. The eight major oxides, which compiled over 92% of the total composition reported for each sample, were chosen as the data for creating the best combination of standard clays to obtain a fair representation of the AVR bitumen solids. With the use of the least squares method, the proportions of standard

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clays were calculated based on their contribution to the oxides composition while minimizing the differences with the AVR solids composition (see Appendix II).

Two different models were obtained from the information gathered from the characterization stage. The proportion of each one of the clays for both models was plotted in Figure 4.10. The Model 1 agrees with previous work done on characterization of bitumen solids (Hendrickson, 1975; Omotoso & Mikula, 2004; Tu et al., 2004), but it is in disagreement with the results from the XRD analysis presented earlier, since it contains 5 wt% of montmorillonite. The Model 2 is the best combination of clays in agreement with the results obtained from the characterization stage of this research.

Model 2 was prepared and tested under fluid-coking reaction conditions. The results are presented in detail in the next section.

4.3 Coking Reactions

4.3.1 Delayed Coking and Fluid Coking Conditions

As explained earlier in the literature review, there are two major technologies being used in a commercial scale for the secondary upgrading of Athabasca bitumen, delayed coking and fluid coking.

Bitumen solids have been previously studied under delayed-coking-type conditions (Liu, 2002; Tanabe & Gray, 1997). For reproducing this type of conditions, a pool of bitumen and solvent (cumene or tetralin) is mixed in a microbatch reactor under 1 atm of nitrogen or hydrogen and reacted at moderate temperature (430 °C) for periods of time between 10 to 90 min. Bitumen solids have been shown to reduce the amount of coke formed under this type of conditions. The use of thin films of bitumen reacted on a

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Model 1

3.34% 5.32%

30.69%

60.65%

Model 2

3.40%

33.65%

62.95%

	Montmorillonite		Kaolinite
	Illite		Rutile
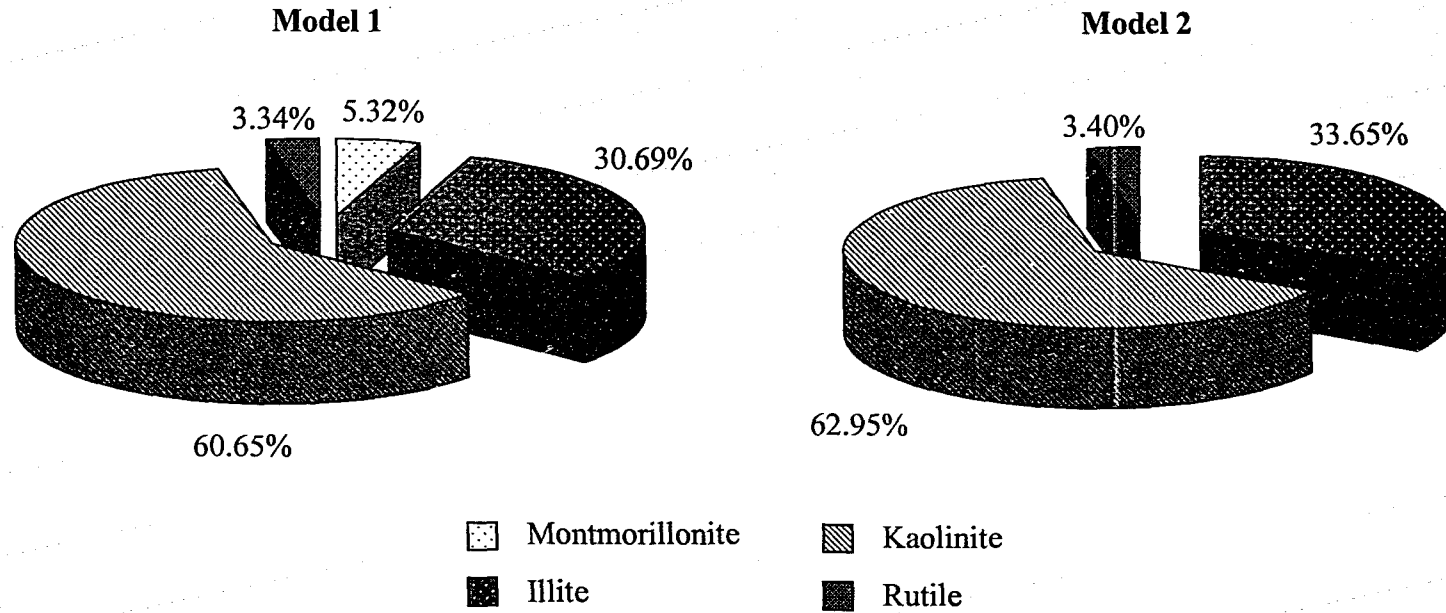
Figure 4.10. Models of fine solids obtained from analysis of AVR solids

metallic surface is the experimental approach used for reproducing the conditions of a fluid coker. For this type of conditions, rapid heating rates are used to reach temperatures ranging between 500 and 530 °C. A very thin film of bitumen on the strip reacted at very short reaction times (10 to 240 s), reproduces the reactions occurring to a film of bitumen covering a coke particle inside the coker. The thin film technique has been used for the study of the kinetics of Athabasca bitumen (Soundararajan, 2001); however there has been relatively little work done on the influence of bitumen solids under fluid-coking-type conditions. Based on the knowledge that coke yield is generally path dependant, affected by heat up rate, reactor geometry, etc., the ongoing research focuses on the effect of fines on coke and products yields under the latest type of conditions.

4.3.2 Coking Reactions with No Solids Added

Initially, solids-free AVR was reacted at four different reaction times and a minimum of three repetitions per experimental condition. Coke and extractables yields were calculated for each case (see formulas 3.3 and 3.4). This was done with the aim of determining the reaction time at which the best repeatability was obtained for both extractables and coke yields. These results can be seen in Figures 4.11 and 4.12. After performing these experiments, a reaction time of 15 s was chosen for the rest of the following coking reactions.

According to previously reported experimental results of the heating time of Curie point strips in the induction furnace (Soundararajan, 2001), the time to reach 350°C (temperature at which cracking starts taking place) is 3 s, and the time to move from 350
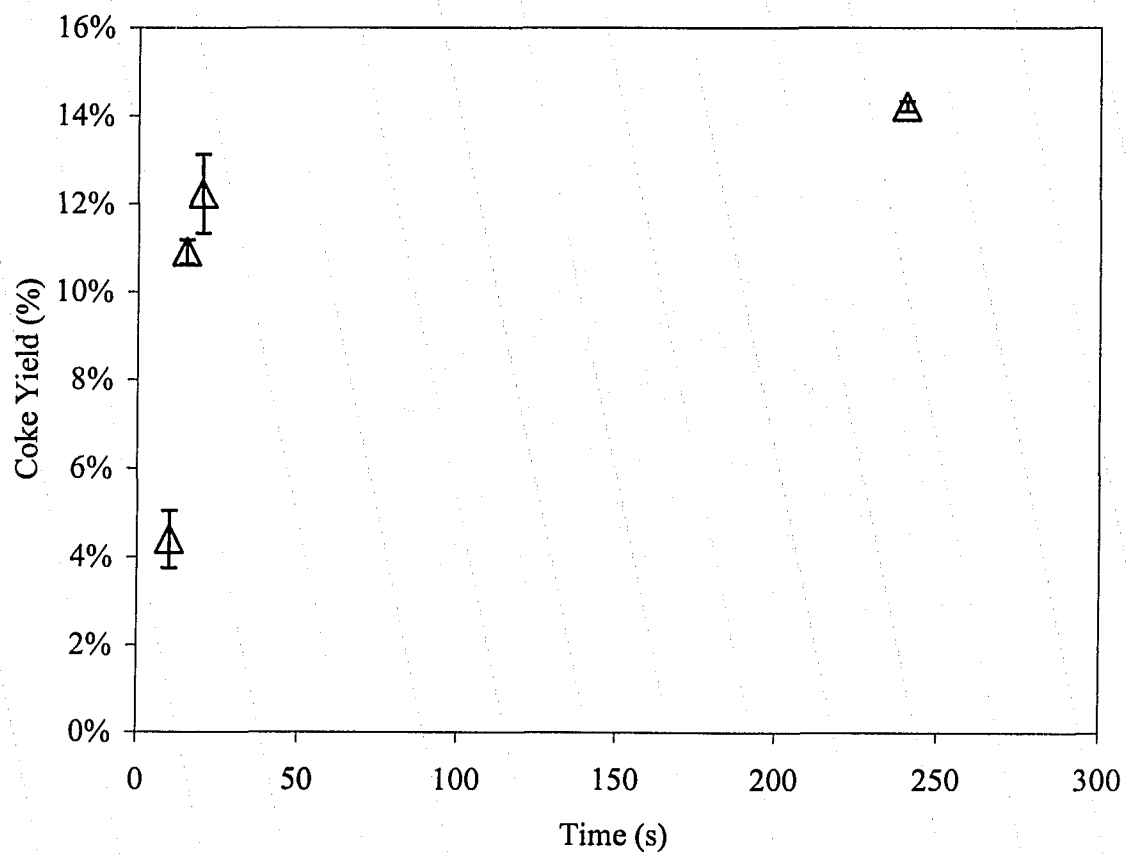
Figure 4.11. Coke yield of AVR solids free using the curie-point strip technique at 510 °C

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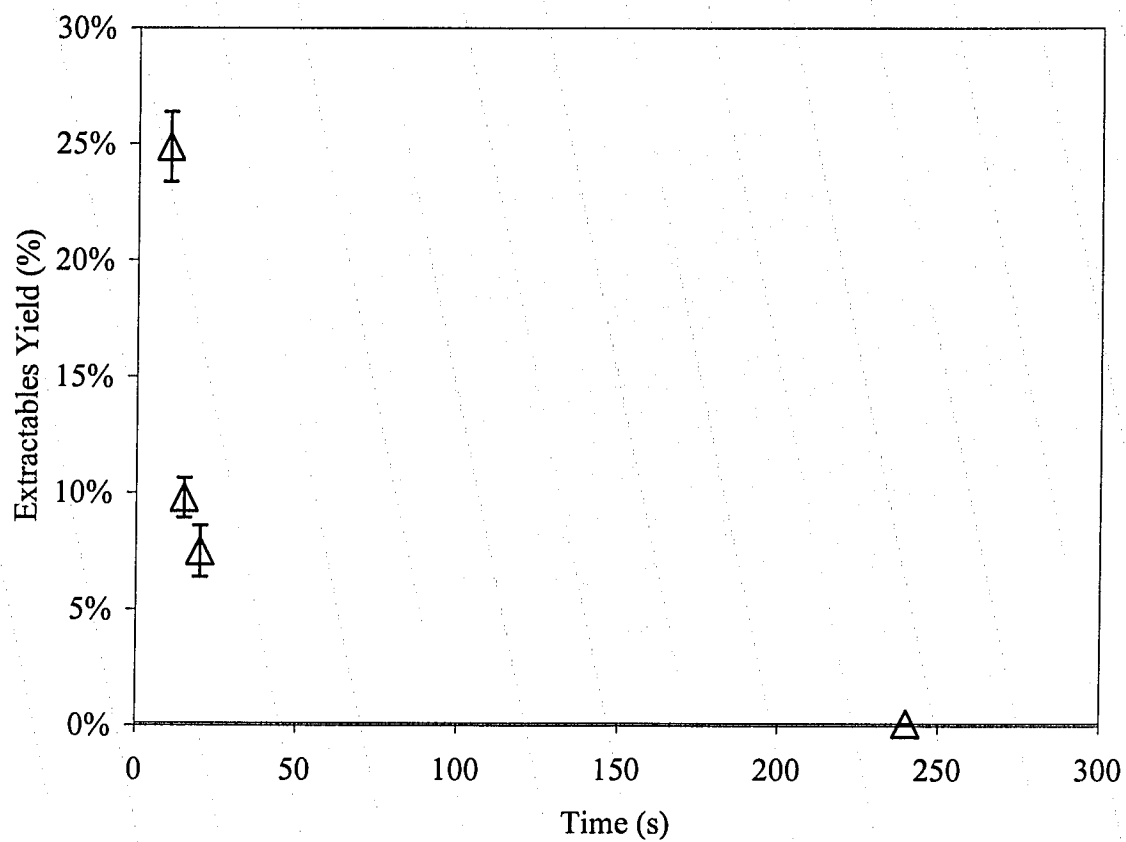
Figure 4.12. Extractable yield of AVR solids free using the curie-point strip technique at 510 °C

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°C to reaction temperature (510 °C) is 1.6 s. However, results are reported at the total time of reaction from the start of heating.

4.3.3 Variation of Coke and Extractables Yield with Type and Concentration of Bitumen Solids

The effect of bitumen solids associated with AVR was previously studied (Liu, 2002), showing that for delayed-coking-type conditions, the coke yield decreased to a minimum corresponding to half of the theoretical solids concentration of the AVR (approximately 1 wt%). It has also been reported (Tababe & Gray, 1997) that under very similar conditions, the presence of fine solids in the residue inhibited coke formation.

For this research, the yields of coke and extractables (unreacted material) were studied at five concentrations of bitumen solids (original solids), from solids-free feed (0 wt%) to the original solids content of AVR (1.4 wt%) under fluid-coking-type conditions (510 °C and 15 s). These results are presented in Figures 4.13 and 4.14. Additionally, model solids were added to solids-free AVR at the same five concentrations mentioned above in order to compare the previous results with the effect of model solids on coke and extractables yield as well as the effectiveness of the model at reproducing the behavior of bitumen solids (see Figures 4.15 and 4.16). Finally, one last group of coking reactions was performed with commercial clay minerals, treated bitumen solids (named AVR clean solids) and fine carbon at a concentration of 1.4 wt%. Three different clay minerals were used: kaolinite, illite, and rutile (the components of the model solids). The AVR clean solids consisted of fines obtained from AVR, reacted for removing the organic coating as shown in Section 3.3, coated with asphaltenes as indicated in Section

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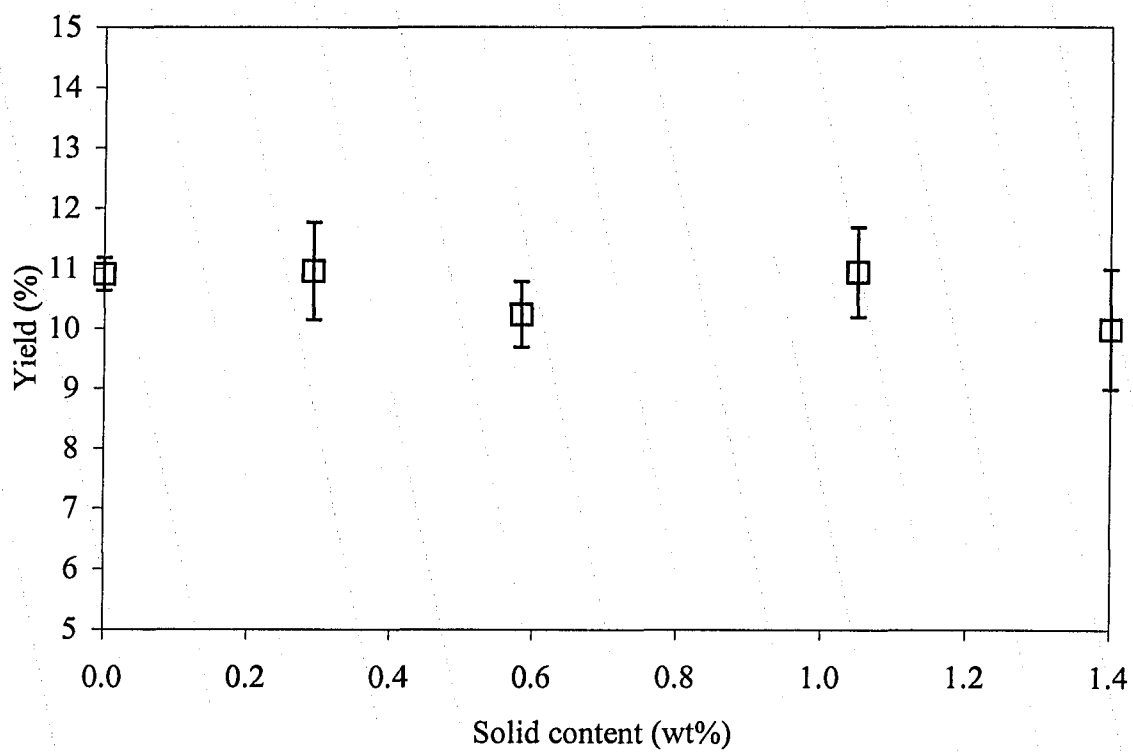
Figure 4.13. Coke yield of AVR at 510 °C and 15 s of reaction using curie-point strip technique

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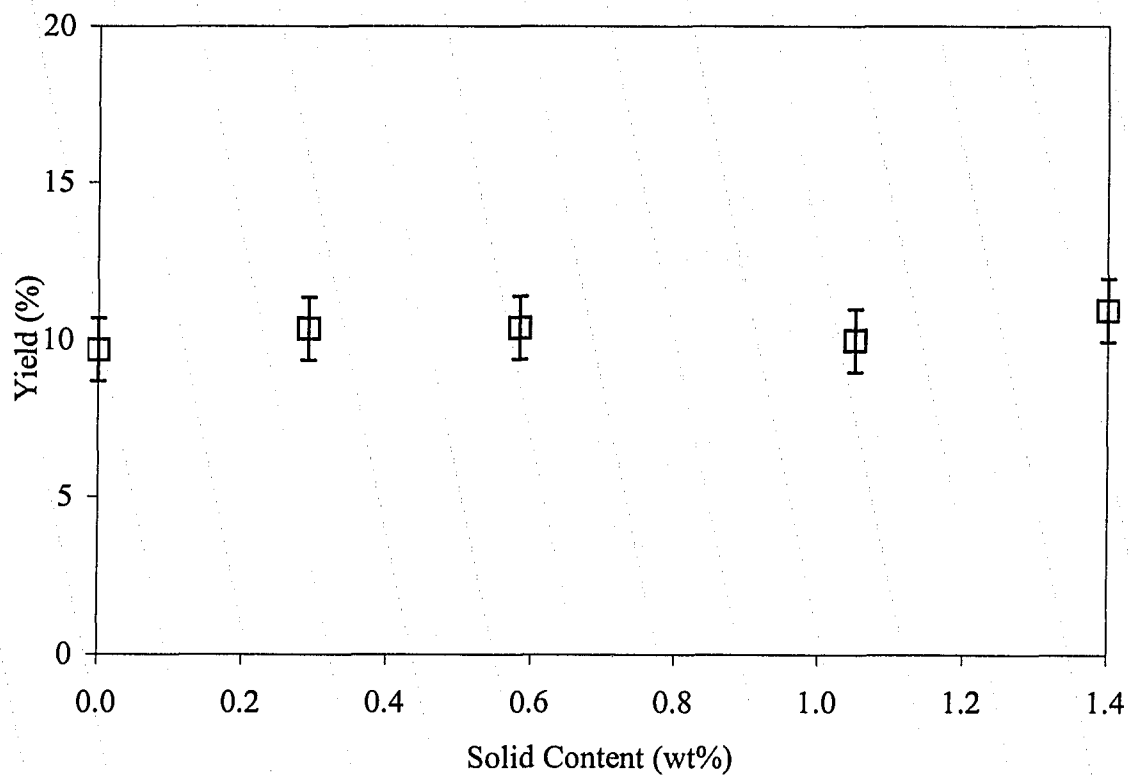
Figure 4.14. Extractable yield of AVR at 510 °C and 15 s of reaction using curie-point strip technique

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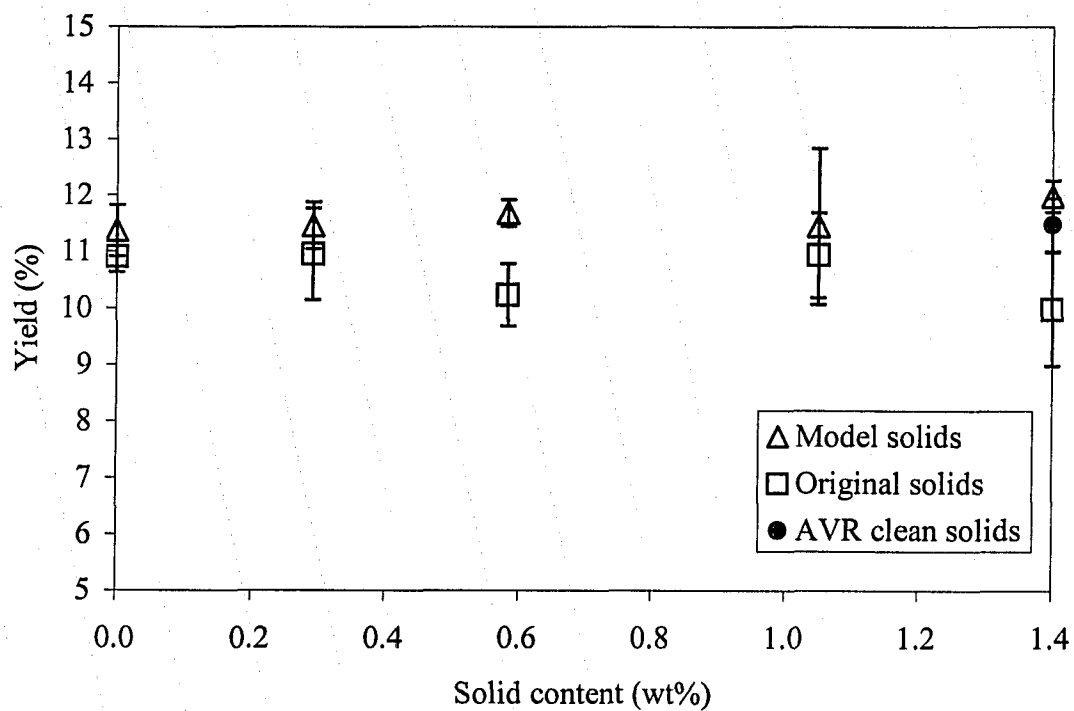
Figure 4.15. Coke yield of AVR with original, model and AVR clean
solids at 510 °C and 15 s

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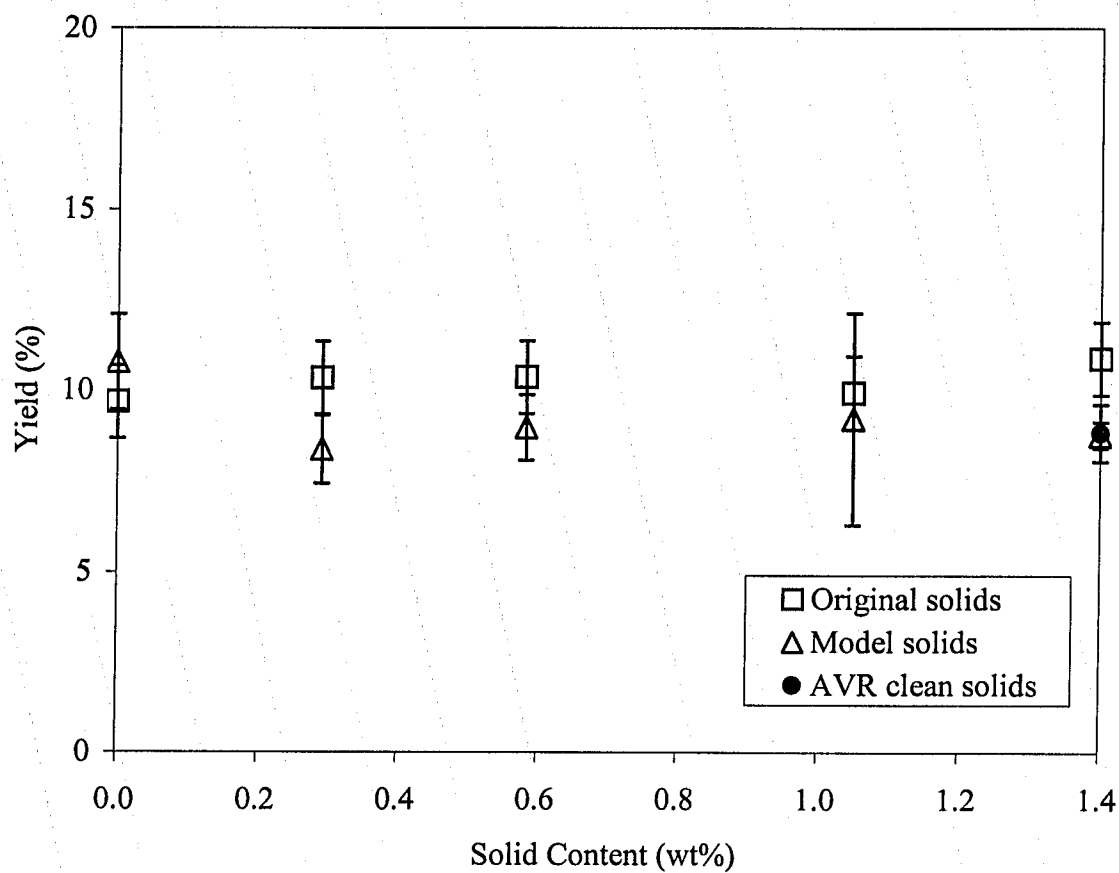
Figure 4.16. Extractable yield of AVR with original, model and
AVR clean solids at 510 °C and 15 s

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3.5., and finally reincorporated to a solids-free feed. This reaction with AVR clean solids was done looking for similarities in the effect of an intermediate type of solids that share common characteristics with both original and model solids as the clay matrix and the asphaltene coating respectively. The effect of the solids organic coating was also being proven. The results are presented Figures 4.17 and 4.18.

In order to create an organic coating similar to the one present in bitumen solids, the commercial clays used to create the model solids as well as those used separately were coated with AVR-asphaltenes prior to the coking reaction. It is important to recognize that for obtaining the closest resemblance to the bitumen solids behavior, not only the types and amounts of clays should be taken into consideration, but also the organic coating present in the original bitumen solids. As mentioned earlier in this chapter, the organic coating may be responsible for the behavior of the solids under certain reaction conditions, making them potential contributors to coke formation in reactor vessels and catalysts surfaces (Li et al., 2004). As described earlier (Kotlyar et al., 1998), the bitumen solids organic coating is a strongly bound toluene insoluble material that has characteristics similar to those of asphaltenes, which is the reason for the pre-treatment of the model solids with AVR-asphaltenes.

In contrast with the results obtained by Liu and Tanabe, a statistically constant trend can be observed for the coke yield when the reaction occurs in the presence of the original solids as well as the model solids. Similarly, a statistically constant trend can be observed on the extractables yield. The statistical test applied to both results (coke and extractables yields) consisted of performing linear regression analysis by using the least squares method to determine of the slope of the regression line.

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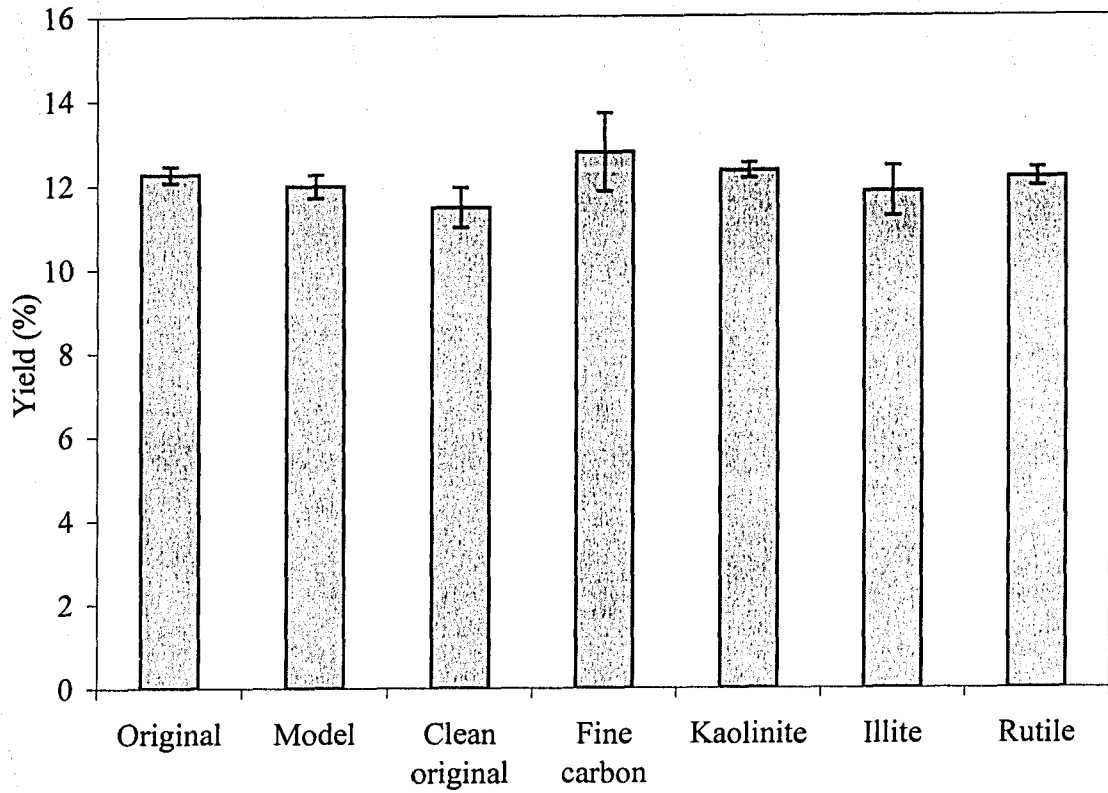
Figure 4.17. Coke yields of AVR at 1.4wt% solid content, using different types of solids

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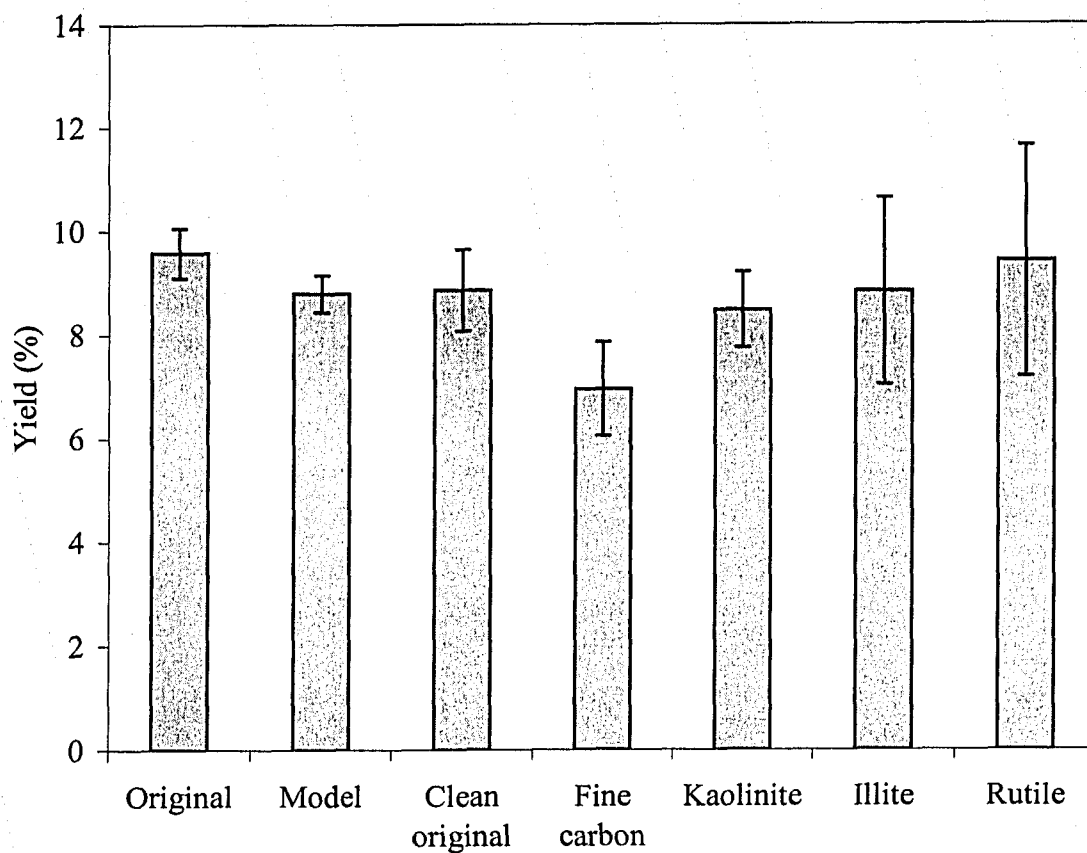
Figure 4.18. Extractable yields of AVR at 1.4wt% solid content, using different types of solids

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One of the differences of the present study when comparing with the pool of feed used in the micro-batch reactor is that the mass transfer effect within the feed was greatly minimized by using 20μm of film thickness of AVR on the strips (Soundararajan, 2001). These results proved that the model designed for bitumen solids behaves in a very similar way to that of the original solids, so these model solids can be used for further studies of the effect of solids on bitumen processability.

It can also be observed (Figures 4.15 and 4.16) that the presence of organic coating does not affect significantly the yield of coke and extractables under the specified reaction conditions. In this case, a t-test was performed to compare the results at 1.4 wt% solids, obtaining (within a 95% of level of confidence) that the values corresponding to AVR clean solids keep the trend of the original solids in both coke and extractables yields.

The set of experiments using standard clays and fine carbon were carried out with the objective of studying the effect of each clay separately. As mentioned in the literature (Grim, 1953), mineral clays have a potential catalytic effect when they take part in reactions along with organic compounds. This group of reactions was done trying to measure if there was any effect on the yields caused by the presence of specific ions as components of the clays or minerals. The results can be observed in Figures 4.17 and 4.18, in which statistically similar values were obtained for the different clays and minerals tested.

4.3.4 Effect of the Type and Concentration of Solids in the Yield of Distillate and Gas

In addition to the determination of coke and extractables yields, distillate products were recovered and the yield calculated for each composition of model solids on solids-free feed. The distillate yield was calculated according to the formula 3.2 presented in Section 3.5.5. A summary of the values used for the statistical analysis is presented in Table 4.4.

Table 4.4. Summary of data used for statistical analysis of distillate yield

Solids concentration (wt%)	Distillate yield (%)	Mean (%)	Standard deviation	Number of repetitions
0.00	79.523 74.825 74.449	76.266	2.827	3
0.29	77.571 82.384 78.258	79.404	2.603	3
0.58	76.040 77.785 73.139 78.118	76.271	2.278	4
1.05	70.378 74.090 75.115	73.194	2.492	3
1.40	67.500 65.980 70.965	68.148	2.555	3

As seen in the results presented in Figure 4.19, and based on the statistical analysis, the distillate yield decreases with the increase of the concentration of model solids, with a maximum yield at 0.3 wt% of solids. Distillate products were also recovered from reactions of original AVR (1.4 wt% solids) and AVR clean solids (also at 1.4 wt% solids). Both results were statistically consistent with that for the model solids.

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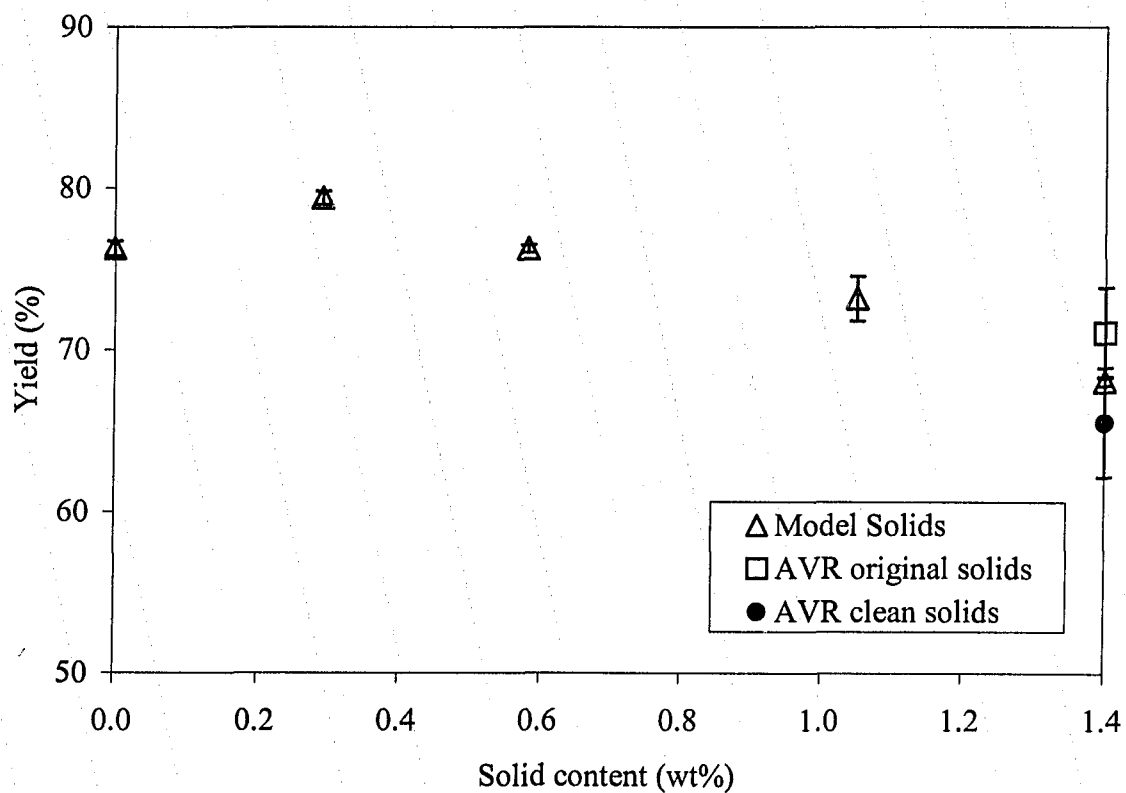
Figure 4.19. Distillated yield of AVR with original, model and AVR clean solids at 510 °C and 15 s

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The fact that the distillate yields decreases with the increase in the concentration of solids has important process implications. Among the various products from coking reaction, i.e. distillate, gas and coke, distillates is the most valuable; a reduction in its yield may have a negative impact in the upgrading process.

The distillate yields obtained for standard clays, minerals, and AVR clean solids were comparable to that of original and model bitumen solids, as shown in Figure 4.20. These results agreed with those presented for coke and extractables yield, which implies that none of the solids used in these experiments were catalytic under the experimental conditions.

Finally, the gas yield was computed as the result of a 100% mass balance after calculating the yields of coke, extractables and distillate. The results are presented in Figure 4.21. A tendency to the increase of the gas yield can be observed from the plot, with the increase of the concentration of model solids. These results contrast with those previously found (Liu, 2002), in which a constant trend for the gas yield was obtained with the increase of solids concentration on a delayed-coking-type reaction. There are two important factors, however, to note here. First, the reaction conditions that lead to each result are different, being of the delayed-coking type for Liu's work and fluid-coking type for this work. The time of reaction is significantly greater for the delayed-coking case. Second, the gases were collected and analyzed in the first case while for this research the gases were calculated as a difference between a 100% material recovery and the yields of coke, extractables, and distillate. These two factors may be attributable to the differences between the constant and increasing trends of both studies.
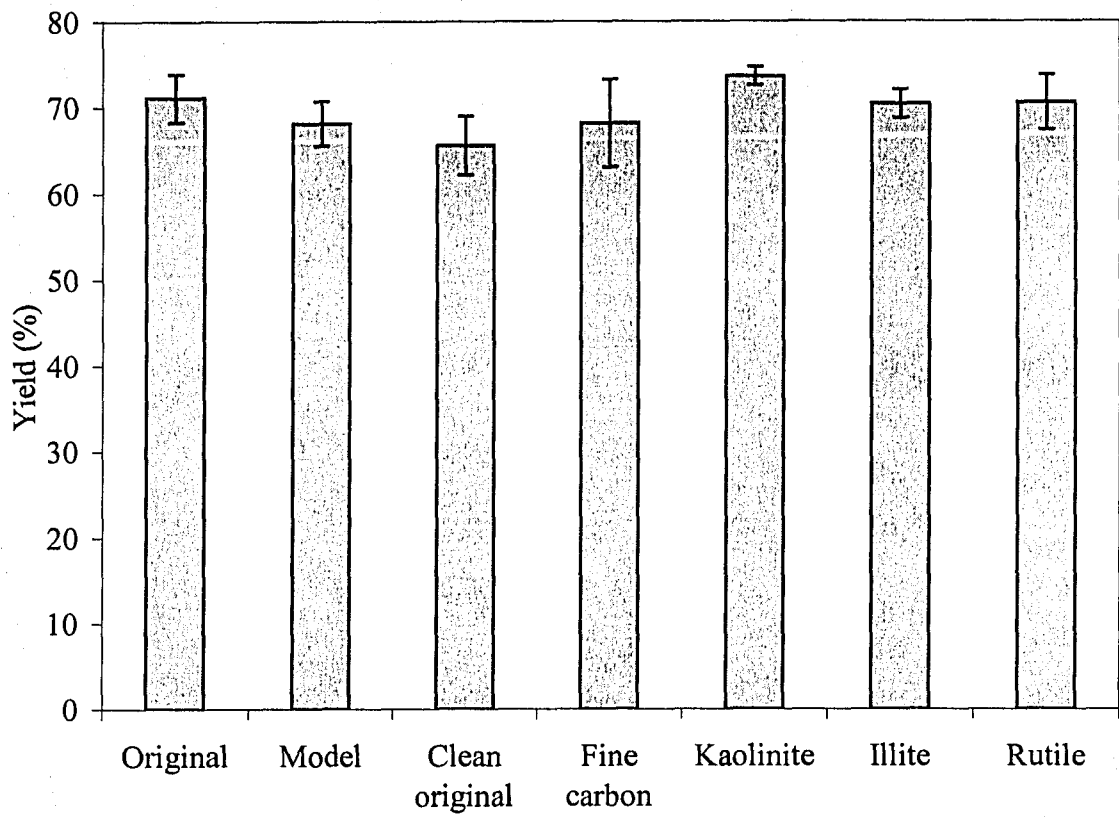
Figure 4.20. Distillate yields of AVR at 1.4wt% solid content, using different types of solids

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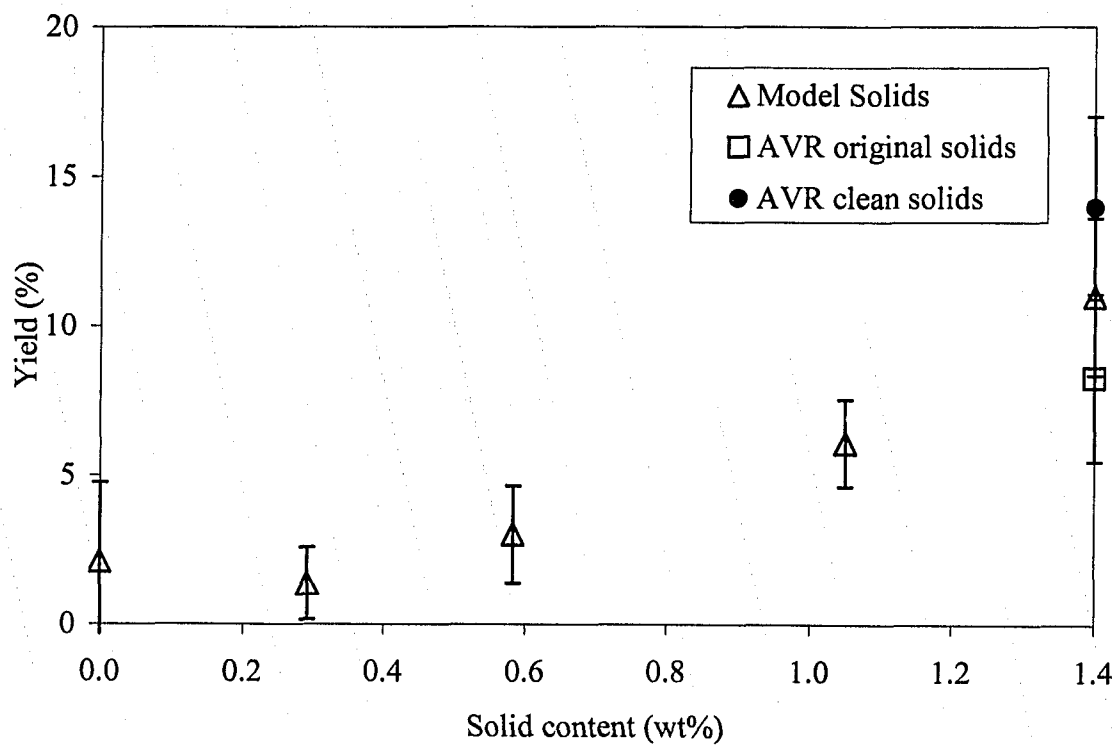
Figure 4.21. Gas yield of AVR with original, model and AVR clean
solids at 510 °C and 15 s

Contrarily to the results obtained for coke, extractables and distillate yields, a greater variability occurred when calculating gas yields using pure standard clays and minerals. As observed in Figure 4.22, kaolinite is the clay for which the minimum gas yield occurred. However, it is important to highlight that this yield carries out the experimental errors associated with the determination of the other three yields, which is observable by the large error bars (the largest among the yields) in Figure 4.22.

4.4. Process Implications

The results obtained from the study of the effect of fine solids on coking reactions have the following implications for the overall performance of the fluid coking upgrading processes:

1. Among the various products from coking reactions (i.e. distillate, gas and coke), distillate is the most valuable, and therefore an increase in its yield may have a positive impact on the upgrading process. If all the bitumen solids are eliminated from the feed, there could be an improvement of up to 8 % in distillate yield. Moreover, the partial elimination of bitumen solids could lead to an even higher efficiency of the coking process.

2. An additional benefit of reducing or completely removing the solids in the coking unit feed is that plugging of downstream units and catalysts will also be reduced.
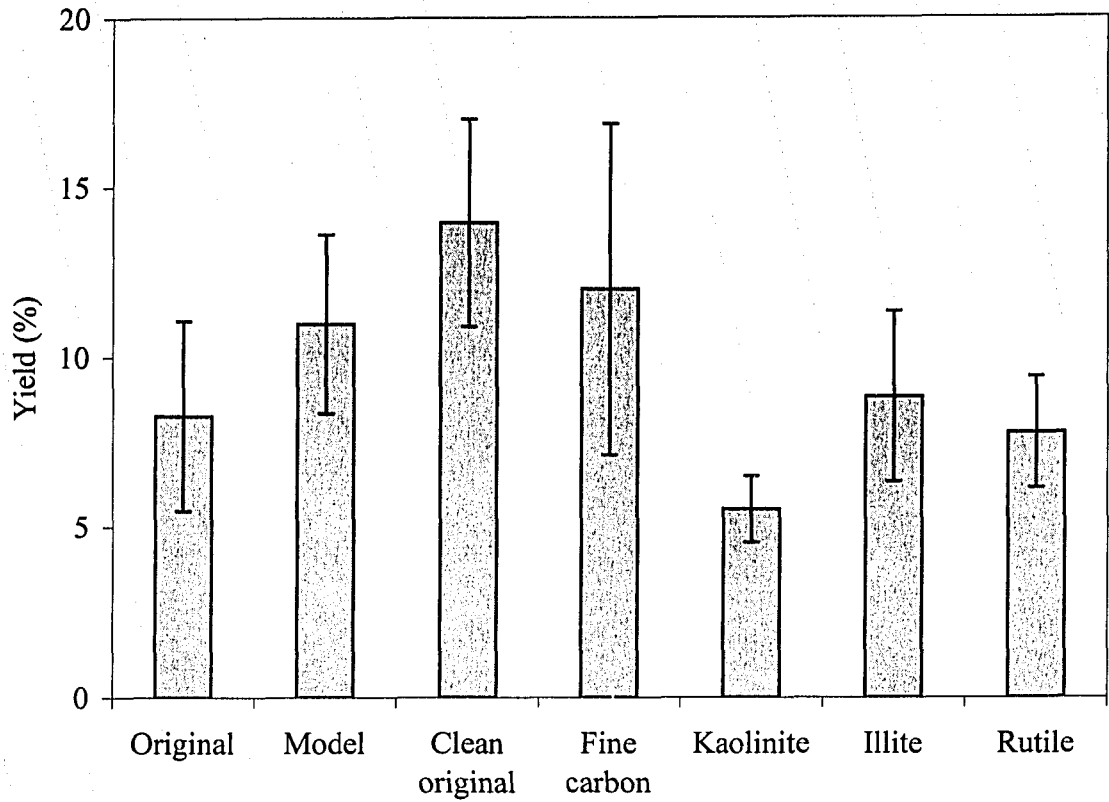
Figure 4.22. Gas yields of AVR at 1.4wt% solid content, using different types of solids

CHAPTER 5
CONCLUSIONS AND RECOMMENDATIONS

5.1. Conclusions

Based on the results obtained from the characterization of Athabasca vacuum residue (AVR) bitumen solids and the study of the effects of these solids in coking reactions, the following conclusions can be drawn:

1. When comparing the amount of organic material coating the fine bitumen solids from Diluent recovery unit (DRU) feed and AVR, it can be concluded that this toluene-insoluble coating does not increase significantly in its amount from extraction to upgrading. Thermogravimetric analysis showed that the amount of organic material burned from DRU feed and AVR solids remained relatively similar.

2. The structure of bitumen solids revealed through the Scanning Electron Microscope and Energy Dispersive X-ray analysis shows a great difference between DRU feed solids and AVR solids in terms of size and composition, most likely due to the time between collecting both samples . The composition of AVR solids revealed through EDX analysis is in agreement with the composition of mineral clays.

3. According to the results obtained from the X-ray diffraction analysis (XRD), kaolinite and illite are the predominant clays present in fine solids. The amount of montmorillonite present was likely lower than 2% since there was no evidence of montmorillonite from the XRD spectra.

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4. Bitumen solids have no significant effect on coke or extractables yields under fluid-coking-type reaction conditions. According to the results obtained for different types of solids, neither the organic coating nor the nature of the solids have an effect on the amount of coke produced or the amount of unreacted material left after the reaction for the conditions specified above.

5. Bitumen solids seem to have an effect on the yield of distillate products and gas produced at 510 °C. The amount of distillate product increased up to a maximum when the concentration of solids in the feed increased from 0 to 0.3 wt%. However, after this maximum, the yield declined in value when the concentration of solids increased. The opposite trend was observed for the yield of gas. The overall change in gas and distillate yields was around 8 wt% when solids were added to the feed.

6. According to the effect of bitumen solids on distillate yield, an optimum solids concentration of 0.3 wt% is desirable for upgrading, with a maximum increase of 11 wt% in the yield of distillate being reached.

7. The use of the model solids was proven to be effective in the study of the role of bitumen solids on coking reactions. According to the results obtained for coke, extractables, distillate and gas yields, the behavior of the model solids agreed with that of bitumen solids extracted from Athabasca vacuum residue.

8. According to the results obtained for the standard clays, there is no evidence of a catalytic effect of any particular clay in coking reactions at fluid-coking-type reaction conditions.

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5.2. Recommendations

The following recommendations are proposed for the extension of this research:

1. A more extensive characterization of the bitumen solids, focusing on the clay mineral fraction, will allow for a better understanding of the role they represent in the different reactions taking place during bitumen upgrading. More importantly, specific tests for the identification of montmorillonite should be performed.

2. Since the variability of the results for the yield of gas was relatively high, it is recommended that the amount of gas produced during the coking reaction be quantified for the various concentrations and types of solids.

3. The characterization of the coke formed at different solids concentration levels will allow the expansion of the scope of the effect that fines may have on coking reactions.

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APPENDICES

APPENDIX I : LOG SHEET FOR COKING REACTION EXPERIMENTS

Experiment	Spray # 16 - AVR 0.291 Wt %
Strip Temperature (°C)	509
Feed	AVR - 0.291 Wt % - Model Solids
Time of reaction (s)	15
Solids content (mass fraction)	0.003
Organic mat. on solids (%)	38.4%

Reaction # 3
Coke Yield

Strip #	Bitumen (g)	Bitume S.Free (g)	Solids (g)	Clay content (g)	Strip Wt. after Reaction (g)	Strip Wt. after ultras. Bath (g)	Filter paper Wt. before filt. (g)	Filter paper Wt. after filt. (g)	Coke+solids (g)	Coke+solids yield (%)	Solids free Coke (g)	Solids free Coke yield (%)
4	0.210	0.209	0.00061	0.0004	26.988	26.945	1.228	1.248	0.022	10.476	0.022	10.315
9	0.210	0.209	0.00061	0.0004	27.100	27.063	1.230	1.253	0.025	11.905	0.025	11.747
13	0.217	0.216	0.00063	0.0004	26.854	26.815	1.221	1.245	0.027	12.442	0.027	12.285
16	0.208	0.207	0.00061	0.0004	26.989	26.953	1.225	1.246	0.025	12.019	0.025	11.861
20	0.221	0.220	0.00064	0.0004	26.856	26.817	1.228	1.249	0.026	11.765	0.026	11.606
25	0.209	0.208	0.00061	0.0004	27.085	27.049	1.238	1.256	0.022	10.526	0.022	10.366

	Bitumen (g)	Bitume S.Free (g)	Solids (g)	Clay content (g)	Strip Wt. after Reaction (g)	Strip Wt. after ultras. Bath (g)	Filter paper Wt. before filt. (g)	Filter paper Wt. after filt. (g)	Coke+solids (g)	Coke+solids yield (%)	Solids free Coke (g)	Solids free Coke yield (%)
Sum	1.275	1.271	0.004	0.002	161.872	161.642	7.370	7.497	0.147	-	0.145	-
Total mass of empty strips					161.622			AVERAGE	0.024	11.522	0.024	11.363
								Std. Dev.	0.002	0.823	0.002	0.824

Extractables Yield

Ext. mass on strips (g)	Yield (%)
0.103	8.093

Distillate Yield

Component	Weight (g)		
	Initial	Final	Difference
1: Flange+sstube+1st T	922.400	922.440	0.040
2: sstube+2nd T+vent	285.490	285.560	0.070
3: Inlet flex tube	229.390	229.460	0.070
4: U tube	530.000	530.380	0.380
5: Oulet flex tube	228.640	228.680	0.040
Ceramic holders	92.448	92.512	0.064
Cooper tube	22.966	22.968	0.002
Strings	0.986	0.989	0.003
Kimwipes	3.031	3.358	0.327
Total mass of liquid products (g)			0.996
Yield (%)			78.26%

Mass Balance (%)	97.725
Gas yield (%)	2.275

APPENDIX II: LEAST SQUARE METHOD - SPREAD SHEET
FOR MODEL SOLID COMPOSITION

Table II.1. Data from Iductively Coupled Plasma analysis (Loring Laboratories Ltd., Calgary AB)

Sample	Oxide content (mass fraction)							Sub-Total	Others* (mass fraction)
	Al_2O_3	CaO	K_2O	MgO	Na_2O	SiO_2	TiO_2		
AVR solids	0.2456	0.0078	0.0189	0.0116	0.016	0.4072	0.0442	**0.7513**	0.2487
Montmorillonite	0.1827	0.0166	0.0046	0.024	0.0314	0.4738	0.0012	**0.7343**	0.2657
Illite	0.2049	0.005	0.0321	0.0142	0.0099	0.6306	0.0076	**0.9043**	0.0957
Kaolinite	0.2786	0.0009	0.0009	0.0004	0.0057	0.3112	0.012	**0.6097**	0.3903
Rutile	0	0	0	0	0	0	1	**1**	0

* Includes minor amounts of metals (Cr, Cu, Li, V, etc.) as well as iron oxide. Only the sub-total was taken into account for calculations.

Based on the sub-total, the proportions of oxides were recalculated for AVR solids.

Table II.2. Recalculated proportions of oxides on AVR solids

	Oxide proportion (%)						
	Al_2O_3	CaO	K_2O	MgO	Na_2O	SiO_2	TiO_2
AVR solids	32.6900	1.0382	2.5156	1.5440	2.1296	54.1994	5.8831

Table II.3. Mass fraction of clay in the model of AVR bitumen solids

Model	Montmorillonite	Illite	Kaolinite	Rutile
1	0.053	0.307	0.606	0.033
2	0.000	0.335	0.631	0.034

The values of the mass fraction of standard clays on the model of bitumen solids were obtained by modifying the mass fraction of illite and kaolinite to minimize the total square error.

The predicted composition of oxides on bitumen solids was obtained based on the contribution of each standard clay for the correspondent model.

The standard error is the difference between the real oxide composition of AVR solids and the composition predicted by the model.

Table II.4. Composition of each oxide in the bitumen solids predicted from Model 1

	Al_2O_3	CaO	K_2O	MgO	Na_2O	SiO_2	TiO_2
Composition (%)	0.2416	0.0030	0.0106	0.0059	0.0082	0.4075	0.0431
Standard error	0.0040	0.0048	0.0083	0.0057	0.0078	-0.0003	0.0011
Square error	1.625E-05	2.339E-05	6.820E-05	3.274E-05	6.137E-05	7.502E-08	1.231E-06
Total square error	**8.576E-05**						

Table II.5. Composition of each oxide in the bitumen solids predicted from Model 2

	Al_2O_3	CaO	K_2O	MgO	Na_2O	SiO_2	TiO_2
Composition (%)	0.2445	0.0022	0.0113	0.0050	0.0069	0.4077	0.0440
Standard error	0.0011	0.0056	0.0076	0.0066	0.0091	-0.0005	0.0002
Square error	1.301E-06	3.088E-05	5.740E-05	4.342E-05	8.255E-05	2.254E-07	3.195E-08
Total square error	**5.895E-05**						

Table II.6. Summary of results for model solids composition

Clay / Mineral	Composition (Wt%)	
	MODEL 1	MODEL 2
Montmorillonite	5.32%	0
Illite	30.69%	33.65%
Kaolinite	60.65%	62.95%
Rutile	3.34%	3.40%
Total	**100.00%**	**100.00%**
Sum square	**8.6E-05**	**5.9E-05**

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