University of Alberta

Effect of Solids on Coke Formation from Athabasca Bitumen and Vacuum Residue

by ©

Liming Liu

A thesis submitted to the Faculty of Graduate Studies and Research in partial fulfillment of the Requirements for the degree of Doctor of Philosophy

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The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies and Research for acceptance, a thesis entitled Effect of Solids on Coke Formation from Athabasca Bitumen and Vacuum Residue submitted by Liming Liu in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Chemical Engineering.

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Abstract

Canada has the world's largest reserve of oilsands containing over one trillion barrels of bitumen. In the upgrading of the bitumen, however, coke formation causes a considerable loss of the hydrocarbon resource and numerous operational problems. Furthermore, the bitumen produced *via* surface mining, currently the predominant method of bitumen production, contains high content of fine solids called bitumen solids. The effect of the bitumen solids on coke formation is still not well known.

In this thesis, the mechanism of coke formation at thermal upgrading conditions was studied, and kinetic models were developed. The effects of the bitumen solids and other added fine solids were investigated. The coke produced at coking conditions of low to moderate severity behaved as a viscous liquid at the reaction temperatures, was mainly isotropic under cross-polarized light, and was soluble in quinoline. Upon reheating or at longer reaction times, the coke could be partially transformed to mesophase. Two kinetic models were developed to give improved modeling of the induction phenomenon and the formation of quinoline insoluble from quinoline soluble coke. In model (I), Wiehe's (1993) phase separation model was modified to combine with modeling of quinoline insoluble coke. Model (II) was a lumped kinetic model with a model parameter for the induction time. The mechanism of the coke formation is discussed. The bitumen solids in the Athabasca bitumen reduced coke formation at coking conditions. With increasing concentration of these solids, the coke yield first decreased and then increased after passing a minimum. Bitumen solids were found to have weak catalytic activities towards dehydrogenation and hydrogen shuttling. Added fine solids with oleophilic surfaces, such as carbon black and asphaltene-treated kaolin were also found to reduce coke formation, but only monotonically. Oleophobic solids such as kaolin and ultrafine silica had no significant effect on coking. The mechanism of the effect of bitumen solids on coke formation is discussed and the effect is attributed to the combination of two factors: enhanced mass transfer due to the coating of liquid phase coke on oleophillic surfaces, and the dehydrogenation effect of bitumen solids under coking conditions.

Acknowledgement

I would like to thank my thesis advisors, Dr. Murray R. Gray and Dr. William C. McCaffrey for their guidance and support throughout my doctoral program. Their advice, inspiration and encouragement were crucial to the completion of this thesis. Much of the work in this thesis has also benefited from discussions with Dr. Phillip Choi and Dr. Keng Chung.

Many others have also contributed to the work in this thesis. I would like to thank two summer students, Mr. Matt Stevens and Mr. Kurtis Mattson, for doing much of the kinetic and quinoline extraction experiments. I am also grateful to Ms. Tina Barker for her help in SEM and EDX, and Ms. Marlene Tychkowsky of Syncrude Research for her help in petrography.

My colleagues in the Heavy Oil Upgrading Research Group have been a great help on a daily basis, in particular, Dr. Yingxian Zhao, Ms. Tuyet Le, Dr. Sanyi Wang, Dr. Srini Srinivasan, Ms. Samina Rahmani, Dr. Dwijen Banerjee, Dr. Richard Dutta, Mr. Ko Aoyagi, Mr. Jeff Sheremata and Mr. Shakir Japanwala. I would also like to thank many people working in the Department of Chemical and Materials Engineering for their assistance throughout my research here, especially Mr. Walter Boddez and Ms. Andree Koenig.

Finally, I would like to thank my wife, Ms. Julia Yanjuan Chu and my parents, Mr. Yuquan Liu and Ms. Bobi Zhao, for their support, encouragement, and tolerance during the tough time when I had to work and write this thesis at the same time.

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Chapter 1

Introduction and Thesis Outline

1.1 Introduction

As the world's supply of conventional crude oil declines, heavy oils and bitumen are becoming increasingly more important to meet the world's growing demands for fuels and petrochemicals. Heavy oils and bitumen are abundant in the world and the total reserves far exceed that of the conventional crude (Speight, 1991). These heavy hydrocarbon resources, however, contain high concentrations (up to 50% for bitumen) of non-distillable residues, and usually require upgrading or dilution before they can be pipelined to a refinery. Residues are of little market value, and usually are also upgraded to lighter, more valuable oil products in refineries. The study of upgrading of bitumen and residues is therefore of great practical importance.

Heavy oils and bitumens are defined by their physical properties. Conventional crude oil usually has API gravities higher than 20. Heavy oils have viscosities between 10^2-10^5 mPa·s and API gravities between 20-10, while bitumens have viscosities over 10^5 mPa •s and API gravities lower than 10 (Meyer and de Witt, 1990). Vacuum residuum, or simply called residue, is the fraction of conventional crude oils, heavy oils or bitumen that does not distill under vacuum. Vacuum residues are the bottom products of a typical refinery vacuum distillation tower, and usually correspond to boiling range of 525 ^oC+ (Gray 1994).

Oilsands are a major source for bitumen (Demaison, 1977). Major oil sands deposits have been found in Canada, Venezuela, and the United States (Phizackerley and

Scott, 1967; Demaison, 1977; Meyer and Dietzman, 1981). Canada has the world's largest proven reserve of oilsands. The total bitumen contained in the oil sands deposits in northern Alberta is estimated to contain 1.3 trillion barrels of bitumen, and the largest single deposit, in Athabasca area, is estimated to contain 830 billion barrels of bitumen (Outrim and Evens, 1977). In total, about 300 billion barrels of bitumen in northern Alberta are recoverable commercially by current technologies (Precht and Rokosh, 1998). The development of Alberta oil sands has been growing very rapidly and this growth is projected to continue for the next four to five years (Figure 1.1). Currently the oilsands bitumen contributes about 26% of Canada's oil supply, and it is expected to grow to about 50% by year 2005 (Lachambre, 1998).

The properties of Athabasca bitumen are markedly different from those of conventional crudes (Table 1.1) and cannot be fed directly to a conventional oil refinery. The current strategy used by Syncrude and Suncor, the two largest producers of oilsands bitumen, is to upgrade the bitumen into lighter fractions and then blend these fractions to produce a synthetic crude oil (SCO). Currently the combined SCO production from Suncor and Syncrude accounts for more than 18% of total Canadian oil supply. The SCO has characteristics similar to conventional crude oil and is pipelined to existing refineries. The SCO also has lower heteroatoms such as nitrogen, sulfur and metals, and has lower concentration of fine solids. The combined production of SCO accounts for over half of all oilsands bitumen produced. The rest is often diluted with natural gas condensate to meet the pipeline specifications. The diluted bitumen is then pipelined to refineries where the bitumen is upgraded.

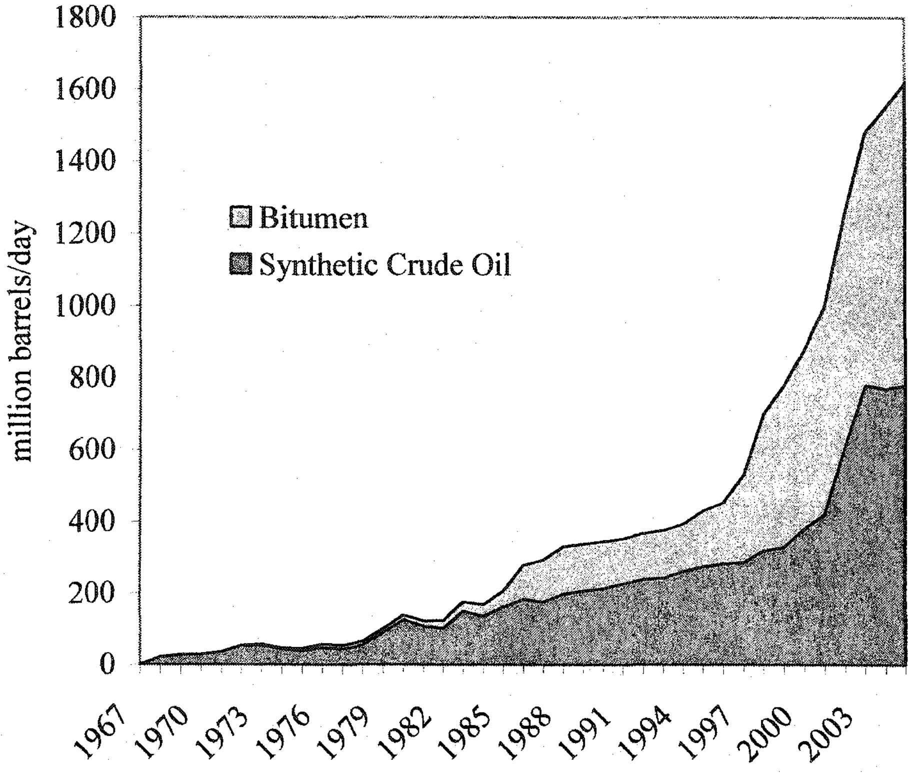

Figure 1.1 Development of Alberta Oil Sands — History and outlook (Precht and Rokosh, 1998).

Table 1.1 Comparison of properties of Athabasca bitumen with those of conventional crude oil (Speight, 1991).

		Bitumen	Conventional Crude
Gravity, °API		8.6	25-37
Distillation, °C	Vol%		
	5	221	
	10	293	-
	30	438	
	50	543	<343
Viscosity@38°C, centistokes		7,500	<6.4
Elemental Analysis, wt%			
Carbon		83.1	86
Hydrogen		10.6	13.5
Sulfur		4.8	0.1-2.0
Nitrogen		0.4	0.2
Oxygen		1.1	
Hydrocarbon type, wt%			
Asphaltenes		19	<10
Resins		32	
Oils		49	>60
Metals, ppm			
Vanadium		250	
Nickel		100	
Iron		75	2-10
Copper		5	
Ash, wt%		0.75	0
Conradson Carbon, wt%		13.5	1-2

The goal of upgrading bitumen and residues is to produce petroleum fractions with lower boiling ranges, lower concentrations of heteroatoms such as sulfur, nitrogen and metals, and higher H/C ratios. According to the approaches to achieve higher H/C ratios, the upgrading processes can be classified into two categories: those with hydrogen addition and those with carbon rejection. In hydrogen addition processes, hydrogen atoms are added to the hydrocarbon molecules to increase the H/C ratio. Hydrogen addition processes that can be used to upgrade bitumen and residues include ebulated bed hydrocracking such as the LC-Fining™ (van Driesen, 1986) and H-Oil™ (Wisdom *et al.*, 1985) processes, slurry phase hydrocracking such as CANMET (Lunin *et al.*, 1985) and Combi-Cracking™ (Dickenson *et al.*, 1998), and the water based Aqua-Conversion™ (Carrazza *et al.*, 1997) process. In contrast, carbon rejection processes achieve higher H/C ratios by rejecting a percentage of carbon from the feed. Processes using this approach include resid FCC, solvent deasphalting such as the ROSE™ process (Low *et al.* 1995; Gearhart and Garwin, 1976) and coking (including delayed coking and fluid coking™). Hydrogen addition processes usually give higher quality and higher yield of the desirable products. These processes, however, require hydrogen and catalysts and are operated at high pressures, which result in higher capital and operating costs compared with carbon rejection processes. Coking is currently the most commonly employed technology to upgrade bitumen into SCO. At present, 80% of the oil sands bitumen produced in Canada is processed by coking technologies as the primary upgrading process, while the rest is processed by ebullated hydrocracking.

Upgrading processes, including delayed coking, fluid coking, and hydrocracking, all involve a formation of a solid carbonaceous material generally called coke. In hydrocracking, coke formation causes deactivation of catalyst and shortens the run length and thus it has to be minimized. Coke formation is also responsible for the fouling of furnace tubes and other process vessels (Watkinson and Wilson, 1997; Lemke and Stephenson, 1998, Nandi *et al.*, 1977). In both delayed and fluid coking, the formation of coke is necessary for the process to operate properly and coke is accepted as a byproduct. Excessive coke formation, however, is economically undesirable since coke is of much lower value than distillates. Therefore, coke formation has to be controlled in order to maximize distillates yield. For example, in Syncrude Canada, which operates two of the world's largest fluid cokers to process oil sands bitumen, the coke has been stockpiled since so far there is no market for this coke.

Currently the majority of Athabasca bitumen is produced by surface mining combined with hot water extraction technologies. This bitumen contains a high content of fine solids called bitumen solids. These bitumen solids cause numerous operational problems such as plugging of hydrotreaters and contribute to the fouling of process vessels. The effect of bitumen solids on coking, however, is not well known, and study of the role of these solids in coking is important to fully assess process options to abate the problems associated with them. Fouling is an operational problem in all the above-mentioned upgrading process and is closely associated with coke formation on hot surfaces. Severe fouling often leads to costly unscheduled shutdowns and increased downtime during scheduled shutdowns. Therefore, study of the mechanism of coke formation is of great interest, so that coke formation can be minimized and where it forms can be controlled.

1.2 Thesis Outline

The objective of this thesis is to study the mechanism of coke formation, including interactions between coke formation and bitumen solids during the coking of Athabasca bitumen. Chapter one serves as an introduction to the subject of upgrading Athabasca oilsands bitumen. The principles and relevant literature in thermal upgrading are reviewed in Chapter two. The review includes the physical and chemical nature of the constituents of bitumen and residue, *i.e.* saturates, aromatics, resins and asphaltenes, some basic principles of thermal cracking reactions, earlier work on mechanism of coke and mesophase formation, earlier work on the effect of bitumen solids, kinetic modeling, and relevant industrial thermal upgrading processes. The intent of Chapter two is to provide the background necessary to put the subsequent chapters in context.

The body of this thesis is presented in paper format in two chapters: chapter three and chapter four. In Chapter three, the phase behavior of coke and the mechanism of phase transition in coke are discussed, and kinetic models are developed using two different approaches with emphasis on improving modeling of the induction phenomenon in coke formation, and the formation of quinoline soluble coke and quinoline insoluble coke. In model (I), Wiehe's (1993, 1997) phase separation model was modified to combine with modeling of quinoline insoluble coke. Model (II) was a lumped kinetic model with five pseudo-components—gases, maltenes, asphaltenes, quinoline soluble coke, and quinoline insoluble coke, and a model parameter for the induction time. In both models, the formation of quinoline insoluble coke from quinoline soluble coke was modeled as a reaction of shifting order, from first order at low quinoline soluble concentration to zeroth order at high concentration of quinoline soluble coke. Some interesting phenomena are presented which indicate that coke passes through a liquid phase prior to becoming a solid, and even after it is separated, coke may still behave as a thermoplastic polymer which could behave as a high viscosity liquid upon heating. The formation of mesophase and the transition from isotropic coke to mesophase coke are also described in this chapter. Chapter four investigates the role of the fine solids in coking. This chapter shows that the bitumen solids reduced coke formation under coking conditions, and there was an optimum solids concentration at which the coke yield displayed a minimum. The possibility of the bitumen solids having catalytic effects were tested using model reactions but were found not responsible for the coke reduction. Other fine solids with oleophilic surfaces, including carbon black and asphaltene-treated kaolin powder were found to have similar reduction in coke yield as the bitumen solids did, while fine solids with oleophobic surface, such as kaolin and ultrafine silica powder, were not found to have any significant effect on coking. The mechanism of the effect of the fine solids are discussed and a mass transfer hypothesis is proposed to explain the coke reduction, and the combination of the catalytic effect and the mass transfer effect is proposed to be the cause of the minimum coke yield at intermediate solids concentration.

Chapter five provides a synthesis of the preceding chapters. Also presented are further discussions on the mechanism of coke formation and process implications of thermal upgrading based on the combination of the results and discussion of preceding chapters. Some recommendations for further study on this topic are also made in this Chapter.

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Chapter 2

Review of Basic Principles and Relevant Literature

2.1 Composition of Bitumen and Residue: Saturates, Aromatics, Resins, and Asphaltenes

The processibility of bitumen and residue depends on their chemical composition. Bitumen and residues are very complex mixtures containing thousands, perhaps even millions of compounds (Wiehe and Liang, 1996; Greinke, 1994; Zander, 1987). Therefore, the analysis on a molecular basis is impossible. Structural group analysis, *i.e.* identification of key structures from analytical data that characterize a complex mixture (Petrakis *et al.*, 1983), can provide a quantitative description of the types and distribution of the functional groups. For example, Gray *et al.* (1989) have detailed the structural group composition of Athabasca bitumen and several of its residues of different boiling ranges. This approach, however, is very expensive and time-consuming. The most widely used approach to characterize bitumen is to divide the components into solubility classes. Bitumen or residue is first separated into asphaltenes and maltenes by aliphatic solvents such as n-heptane or n-pentane. Asphaltenes are the class of compounds that are insoluble in n-heptane or n-pentane but soluble in toluene; while maltenes are the class of compounds that are soluble in n-heptane or n-pentane. By propane extraction or adsorption chromatography, maltenes can be further separated into resins (propane insoluble) and oils (propane soluble). The physical and chemical properties of the resins are somewhat intermediate between the asphaltenes and the oils. Resins separated using chromatography are sometimes also called polars and are slightly different from resins separated using propane. One characteristic of chromatography-separated resins is that they have the highest oxygen content. Although the contents of S, N, and metals in resins are much lower than in asphaltenes (Speight, 1991; Banerjee *et al.*, 1985), the oxygen content in resins can be several times higher than in asphaltenes (Banerjee *et al.*, 1985). In chromatography, the adsorbent is usually silica or alumina and the separation is achieved by elution with different solvents. Maltenes are thus separated into saturates (elution with heptane), aromatics (elution with benzene) and resins (elution with benzene/methanol). The products from this separation is commonly known as SARA (Saturates, Aromatics, Resins and Asphaltenes) fractions. The separation sequence is illustrated in Figure 2.1. It should be noted that the solubility classes separated using different methods differ slightly in composition although they are called the same names. Therefore, when referring to these solubility classes, it is important that the separation methods be explicitly specified, for example, pentane-insoluble asphaltenes *vs.* heptane-insoluble asphaltenes.

In thermal upgradings of bitumen or residues, asphaltenes are the major contributor to coke formation. Asphaltenes are not only the most reactive chemically (Wiehe, 1993), but also the least stable physically due to possible flocculation or precipitation. Physical changes of the asphaltenes during thermal reactions could alter the interactions between asphaltenes and other fractions, which in turn may affect the reaction kinetics and product properties.

As stated previously, asphaltenes are very complex mixtures and it is impossible to obtain an exact molecular description using current analytical techniques. Some information about the chemical and physical structures, however, can be elucidated by

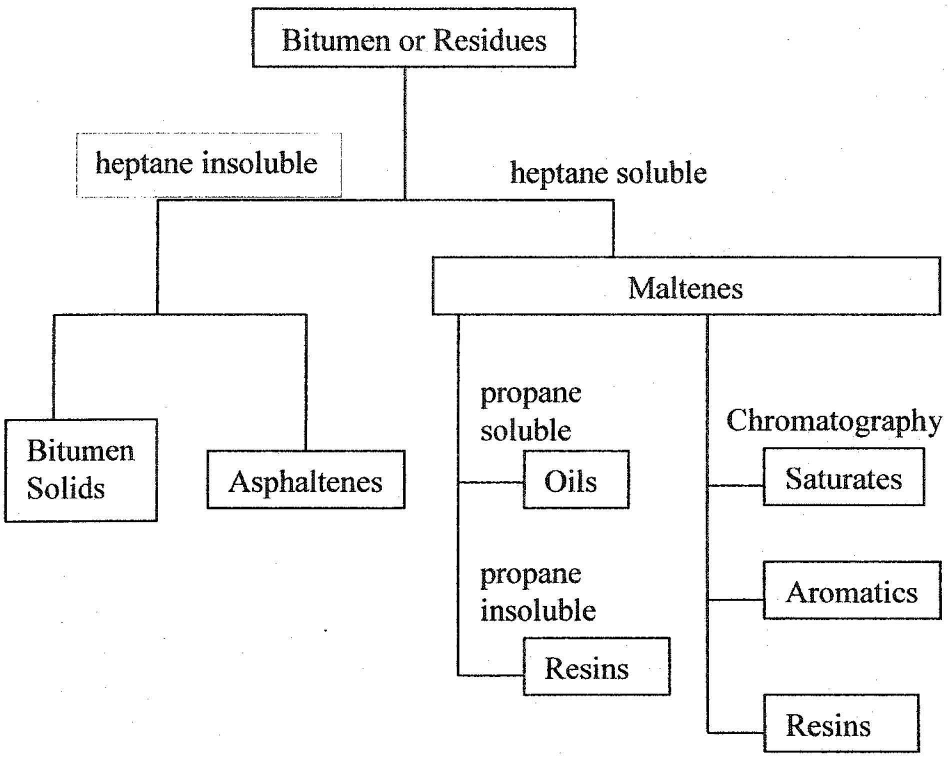


Figure 2.1 Schematics of the separation of bitumen or residues into solubility classes.

methods such as elemental analysis (Speight and Moschopedis, 1981), reactions with model reagents (Speight, 1991; Peng *et al.*, 1997), FTIR (Moschopedis and Speight, 1992; Lian *et al.*, 1994), ^{13}C and H-NMR (Storm *et al.*, 1994), rheology (Storm *et al.*, 1991; Sheu *et al.*, 1992c; Storm *et al.*, 1995b; Storm *et al.*, 1996), surface tension (Sheu *et al.* 1992a), small angle X-ray scattering (Storm *et al.*, 1993; Herzog *et al.*, 1988) and small angle neutron scattering (Sheu *et al.*, 1992c; Storm *et al.*, 1994; Thiyagarajan *et al.*, 1995; Ravey at al., 1988). Petroleum asphaltenes are widely reported to be polynuclear aromatics linked to aliphatic and naphthenic chains, with various functionalities, and heteroatomic moieties.

Strausz and co-workers have made extensive effort to construct hypothetical chemical structures of asphaltenes based on analytical data (Strausz, 1989; Murgich *et al.*, 1999). Their model of an asphaltene molecule in Athabasca bitumen is shown in Figure 2.2. (Murgich *et al.*, 1999). Asphaltenes have a high tendency of self-association which has made molecular weight measurements in the past vary considerably from around 500 to as high as 100,000 depending on the method and conditions of the measurement (Moschopedis *et al.*, 1976). For example, the molecular weight of asphaltenes from Athabasca bitumen has been reported to range from 885 to 10,910 (Champagne *et al.*, 1985). The high values are not the true molecular weights of the asphaltenes, but the average "molecular weight" of the self-associated asphaltenes aggregates. The most reliable number average molecular weights of asphaltenes have been obtained by vapor pressure osmometry (VPO) measurements in highly dissociating solvent such as nitrobenzene, pyridine and orthodichlorobenzene at the highest feasible temperatures and lowest feasible concentrations (Speight *et al.* 1985; Wiehe, 1993). At

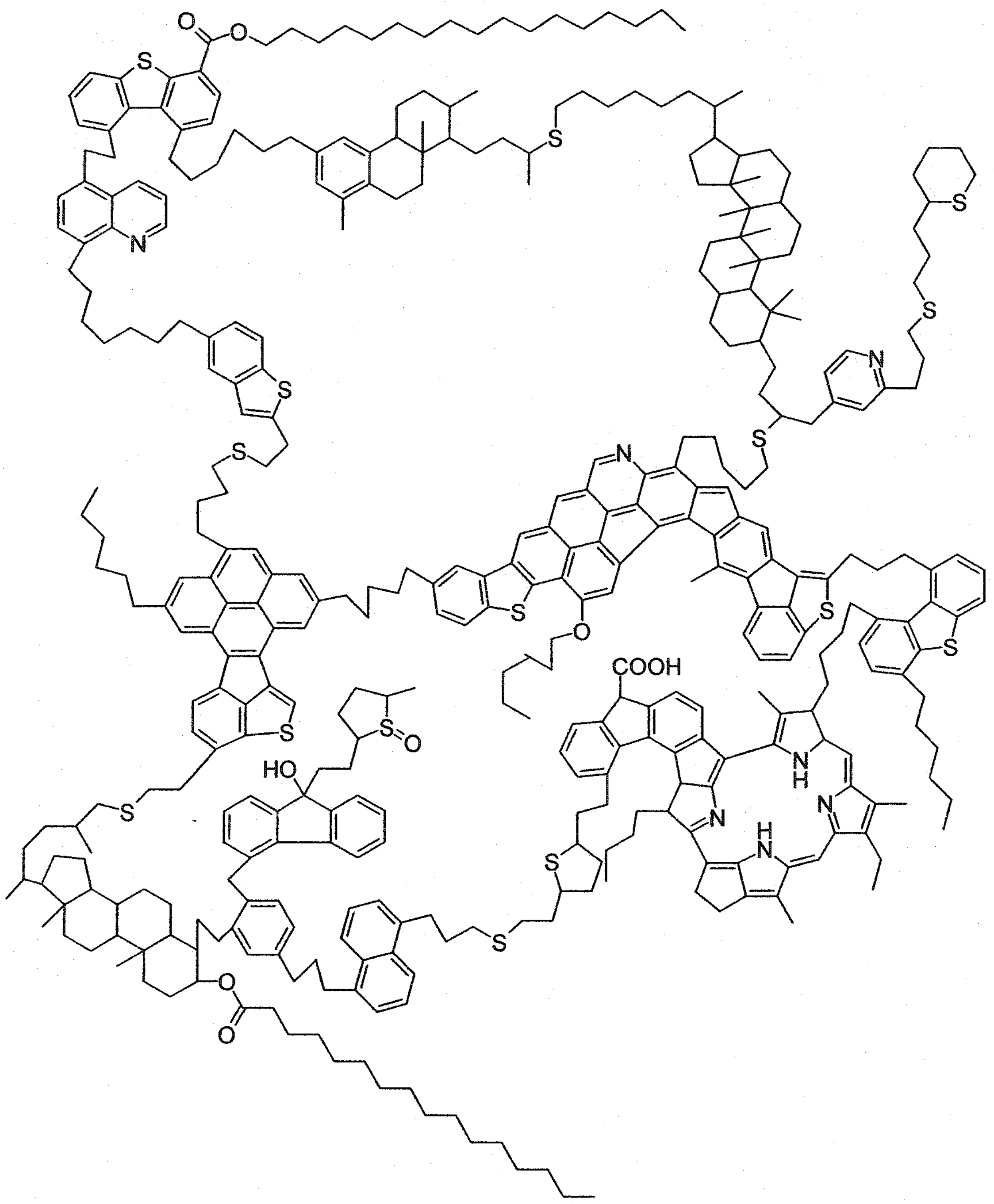


Figure 2.2 A hypothetical asphaltene molecule from Athabasca Bitumen (Murgoch *et al.*, 1999)

these conditions, asphaltenes are the least associated compared with other methods, and give the molecular weight values (number average), usually in the range 1,000-4,000.

Despite the apparent homogeneity, residues or bitumen are not in a true solution state, but rather a colloidal dispersion of asphaltenes in resins and oils (Pfeiffer and Saal, 1940; Bardon *et al.*, 1996; Speight and Long, 1996; Loeber, 1998; Li *et al.*, 1999). Usually, after the resins are removed, the asphaltenes become insoluble in the oils fraction. It is possible, however, to bring about a stable dispersion of asphaltenes in their corresponding oils fraction merely by addition of resins (Koots and Speight, 1975). By small angle X-ray scattering, it was reported that the asphaltenes existed in oils as dispersed particles on the order of 100 Å in diameter (Storm *et al.*, 1993). It was also found that for an asphaltene/oil mixture there was a critical concentration of resins. When resins are above this critical concentration, asphaltenes could be dispersed to form a stable dispersion, while below this critical concentration asphaltenes could not be dispersed and would precipitate (Swanson, 1942; Licha, 1977). A commonly used model to describe this behavior was proposed by Pfeiffer and Saal (1940). In this model, the asphaltenes adsorb resins on their surface to form a stable dispersion (Figure 2.3). When there are sufficient resins to cover the surfaces of asphaltenes, asphaltenes are fully peptized to form a stable dispersion which behaves as a Newtonian fluid (Storm, 1996). Yen (Dickie and Yen, 1967; Yen *at al.*, 1961) proposed that asphaltenes were aggregates of "stacks" of polycyclic aromatics as shown in Figure 2.4. Each "stack" was formed by π–π bonding of the aromatic cores of about four or five asphaltenic molecules and then the stacks formed aggregates by hydrogen bonding or other dipole-dipole interactions. Surface tension measurements on solutions of asphaltenes (Sheu *et al.* 1992a, Menon and

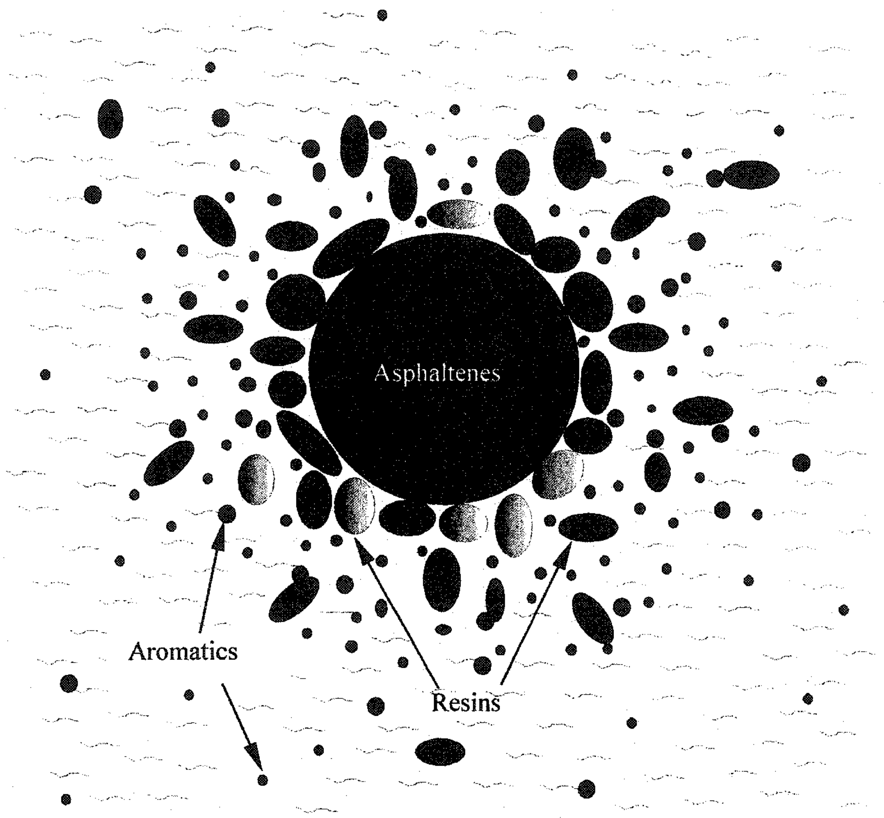


Figure 2.3 Pfeiffer and Saal's (1940) model of asphaltenes micelles in heavy oils.

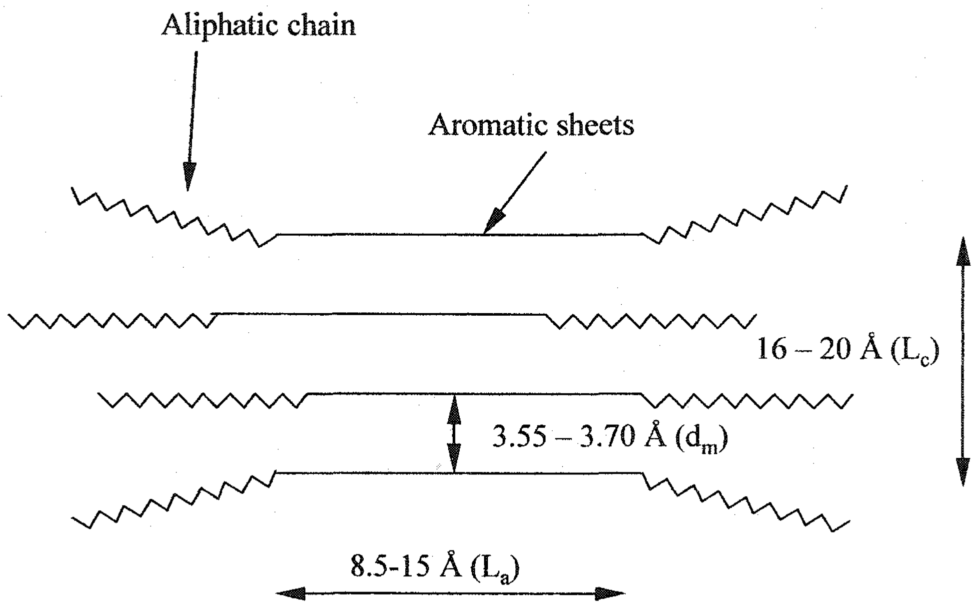


Figure 2.4 Model of an asphaltene "stack" (Yen *et al.*, 1961). D_m = inter-Layer distance, L_c = Diameter of aromatic sheet perpendicular to plane of Sheet, L_a = diameter of aromatic sheet.

Wasan, 1986, Rogacheva *et al.* 1980) revealed that there was a distinctive discontinuity point in the surface tension as a function of asphaltenes concentration in various solvents. This is an identifying phenomenon of surfactant solutions and the discontinuity point is the critical micelle concentration (CMC). When the concentration is above CMC, micelles begin to form in the bulk phase. Sheu (1996) further showed that at low concentrations, the asphaltenes were largely in a molecular state. Above the CMC, however, these asphaltenes molecules started to form micelles similar to aqueous surfactant systems. The CMCs for asphaltenes in the solvents are rather low. For instance, in pyridine it is about 0.2 wt% and about 0.025 wt% in nitrobenzene at 25°C (Sheu *et al.*, 1992a). These values are far below any asphaltene concentrations in bitumen or residues. Therefore, the asphaltenes should exist in bitumen or residues as micelles rather than individual molecules at conditions similar to these CMC test conditions (Sheu *et al.*, 1992a).

To better understand the solubility of asphaltenes and appreciate the hypotheses of micellar structure of asphaltenes, it is important to distinguish between true solutions, micelle formation and phase formation. In a true solution, the solute is dispersed at molecular level while micelles are aggregates of the solute molecules. Micellization differs from phase separation in that it can be described as a kinetic equilibrium between single solute molecules and the micellar species. Unlike phase separation, it does not lead to infinite aggregation of the solute molecules (Anderson and Birdi, 1991). A conventional micellar mixture is an optically transparent single phase, like a true solution, while its thermodynamic properties resemble those of a two-phase system such as colloids (Shinoda, 1978). The structure within each micelle is ordered: one side of it "likes" the solvent and tends to have a maximum possible contact with it while the other side "dislikes" the solvent and tends to avoid contact with it. The inter-micellar structure, however, is not ordered, *i.e.* the micelles themselves can diffuse randomly in the bulk of the solution. Therefore, unlike a liquid crystal, a micellar solution does not exhibit anisotropic physical properties (Collings and Hird, 1997) as will be discussed in more detail later in this thesis. Conventional micellar systems are surfactant solutions, where strong hydrophobic-hydrophilic interactions cause the ordering in structure and electrostatic repulsive forces keep the micelles dispersed. The asphaltene micelles resemble the surfactant micelles in that the asphaltene-resin aggregates or asphaltene-asphaltene aggregates are partially ordered structures due to $\pi-\pi$ bonding, hydrogen bonding and other dipole-dipole interactions. Steric barriers of aliphatic side chains of varying length are suggested to be responsible for the dispersion of the micelles (Leontaritis, 1989; Wilhelms and Larter, 1994), thus preventing the asphaltenes from precipitating (*i.e.* phase separation). Speight (Speight *et al.* 1985; Mitchell and Speight, 1973) has proposed that the asphaltene micelles are reverse micelles in which the polar moieties are associated in the center of the micelles, surrounded by the nonpolar moieties of the same molecule. In heavy oil or residues, it can be envisaged that the aggregation of asphaltenes takes place according to the following scheme (Andersen and Birdi, 1991):

asphaltenes molecules→(particles→micelles)→aggregates

In this scheme, the particles are related to the model of Dickie and Yen (1967) as the stacks, each of which consists of about four or five asphaltene molecules. Micelles can be formed by associations of these stacks through hydrogen bonding or other dipole-dipole interactions. Larger aggregates can be formed by association of the micelles.

Finally, the asphaltenes micelles and aggregates are peptized in the oil by absorbing resins surrounding their surfaces (Andersen and Birdi, 1991; Leontaritis, 1989; Sadeghi *et al.*, 1989).

2.2 Physical Behavior of Asphaltenes at Elevated Temperatures

At thermal upgrading conditions, the physical behavior of the colloidal asphaltenes/maltenes system could play a pivotal role in coke formation (Laux *et al.*, 1995). The precipitation or flocculation of asphaltenes was speculated to trigger the onset of coke formation (Storm, 1996; Wiehe, 1993). However, it is very difficult, if not completely impossible, to directly measure the behavior of asphaltenes under such conditions. This is because of the coupling of physical behavior and chemical reactions, and because of the difficulty in unambiguously distinguishing between asphaltenes precipitate and early coke formation. So far the hypotheses regarding the behavior of asphaltenes at elevated temperatures are all based on indirect experimental evidence, such as rheology (Storm *et al.*, 1996, 1995b), Small Angle X-ray Scattering (SAXS) (Bardon *et al.*, 1996) and Small Angle Neutron Scattering (SANS) (Thiyagarajan *et al.*, 1995; Overfield *et al.*, 1989).

Storm *et al.* (1995b, 1996) made rheological measurements at a series of temperatures and found that at 93 °C vacuum residue was essentially a Newtonian fluid. At temperatures higher than 93 °C, shear thickening was observed. When the temperature was raised to 250 °C the shear thickening was very significant. These observations were attributed to the flocculation of asphaltenes. Shear thickening is usually indicative of a structure that became entangled due to the flow (Storm *et al.*, 1996). Assuming the asphaltene particles as hard spheres that are stabilized by an adsorption layer, they fit the relative viscosities and the weight fractions of asphaltenes into a hard-sphere dispersion model, and calculated the thickness of the adsorption layer at 300 °C to be only about 2-3 Å. Then assuming the asphaltenes to have a Hamaker constant similar to that of polystyrene, 7.9×10^{-20}, and the diameter of the asphaltenes to be 66 Å based on their small angle X-ray scattering measurement, they estimated van der Waals force between two asphaltene particles in terms of potential to be about 12 kT. Therefore, the attractive van der Waals force was dominant and the dispersion was unstable towards flocculation. They concluded that at ambient temperatures the asphaltenes were dispersed in the vacuum residue by adsorbing a non-asphaltenic species to form a protective layer. This protective layer was dissipated at higher temperature, leading to flocculation of the asphaltenes. These flocs of asphaltenes would trigger the onset of coke formation.

Thiyagarajan *et al.* (1995) used small angle neutron scattering (SANS) and entropy analysis to investigate the structural changes of asphaltenes dispersed in pre-deuterated methyl-naphthalene at elevated temperatures. They found that at room temperature, the asphaltenes aggregated as rod-like particles whose radius was 18 Å, but lengths could vary beyond 500 Å. As the temperature was increased up to 100 °C, the radius decreased slightly but the length of the aggregates decreased significantly with a simultaneous increase in the concentration of the smaller particles. At 150 °C two types of particles, spherical particles with a radius of 12 Å and ellipsoidal particles with semi-axes of 3.3 and 12 Å were observed. At 340 and 400 °C only spherical particles were seen with a radius of 12 Å. Thiyagarajan *et al.* (1995)'s observations are consistent with the earlier observations by Overfield *et al.* (1989). Overfield *et al.* (1989)'s SANS results showed that the aggregated asphaltenes dissolved in pre-deuterated toluene were elongated in shape. When the temperature was raised from 25 °C to 250 °C the radius of gyration decreased from 116 Å to 53 Å and the apparent molecular weight, *i.e.* the "molecular" weight of the aggregates, decreased from >500,000 to 6,000. One interesting result was that the molecular weight by VPO method for these asphaltenes in o-dichlorobenzene, (a highly dissociating solvent) was also 6,000. These results suggest that although at ambient temperatures asphaltenes exist in a solvent as aggregates, as temperature rises the aggregates tend to dissociate into individual asphaltenes molecules. This hypothesis is in complete contradiction with the conclusions by Storm *et al.* (1996) as outlined in the previous paragraph. The exact physical behavior of asphaltenes at elevated temperatures remains not well understood and the existing hypotheses remain controversial.

2.3 Thermal Cracking Reactions

The upgrading of bitumen or residues is achieved by cracking reactions, *i.e.* decompositions of larger molecules into smaller molecules by bond breakage. Thermal cracking of heavy hydrocarbon mixtures occurs spontaneously at significant rates at temperatures higher than 400 °C (Gray, 1994; Yang *et al.*, 1993; Poutsma, 1990). The cleavage of carbon-carbon bonds is achieved mainly via free radical chain reactions. Free radicals are neutral species with unpaired electrons. The relative degree of difficulty in breaking a particular bond to form free radicals can be partially described by the bond dissociation energies. For a bond between two atoms A-B, the bond dissociation energy for homolytic scission is defined as the enthalpy of the reaction

$$A\text{-}B \rightarrow A\bullet + B\bullet$$

and is a measurement of the intrinsic strength of a chemical bond (Loudon, 1995).

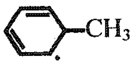
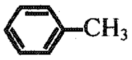
Table 2.1 Bond dissociation energies of some typical bonds (Benson, 1965)

Bond	Dissociation energy kJ/mol	Bond	Dissociation energy kJ/mol
C_2H_5-C_2H_5	343	CH_3S-H	368
C_6H_5- C_2H_5	378	C_6H_5 S-CH_3	251
CH_3-H	435	C_6H_5-$N(CH_3)_2$	339
C_6H_5-H	431	C_6H_5-OH	431

Table 2.1 gives the examples of the bond dissociation energies of several common bonds (Benson, 1965). It is noteworthy that C-S bonds are considerably weaker than C-C bonds and C-H bonds and thus are the first to break. C-C bonds in aromatic compounds are generally much stronger because of the resonance stabilization, which makes aromatics stable at normal process temperatures (< 600°C) until the aromatic character is destroyed by hydrogenation (Gray, 1994).

Hydrocarbon macro-radicals can still be subject to further bond breakage if thermodynamically and kinetically favored. By comparing the bond dissociation energies of radicals it is noteworthy that the bonds at the β-position to the free radical site have much lower dissociation energies. For example, The bond dissociation energy of CH_3CH_2-CH_3 is 355 kJ/mol. When there is an unpaired electron in the α-position, as $\bullet CH_2CH_2$-CH_3, where the dot "•" denotes the location of the unpaired electron, the bond dissociation energy is lowered to 107 kJ/mol (see Table 2.2). Therefore, the β-scission reaction, *i.e.* the free radical splits at the β-position to produce an olefin and a child free radical, is strongly favored in thermal cracking.

Table 2.2 Comparison of bond dissociation energies of free radicals with those of molecules

Bond in free radical	Dissociation energy kJ/mol	Bond in molecule	Dissociation energy kJ/mol
$\bullet CH_2$-H	443	CH_3-H	435
$\bullet CH_2CH_2$-H	163	CH_3CH_2-H	410
$\bullet CH_2CH_2$-CH_3	107	CH_3CH_2-CH_3	355
	146		389

The stability of hydrocarbon free radicals follows the order benzylic > 3° > 2° > 1°. Homolytic scission reactions favor the formation of the most stable radical species. Therefore, formation of a t-butyl radical is energetically much more favorable than the formation of an ethyl radical. Delocalization or resonance also enhance the stability of radicals such as in the case of the benzyl radical.

Like other free radical chain reactions, thermal cracking goes through initiation, propagation and termination steps (Gray, 1994):

Initiation: $M \longrightarrow 2R\bullet$

Propagation: Chain transfer: $R\bullet + M \longrightarrow RH + M\bullet$

β–scission: $M\bullet \longrightarrow R\bullet + \text{olefin}$

Termination: Recombination: $R\bullet + R\bullet \longrightarrow RR$

Disproportionation: $R\bullet + R\bullet \longrightarrow R{=}CH_2 + RH$

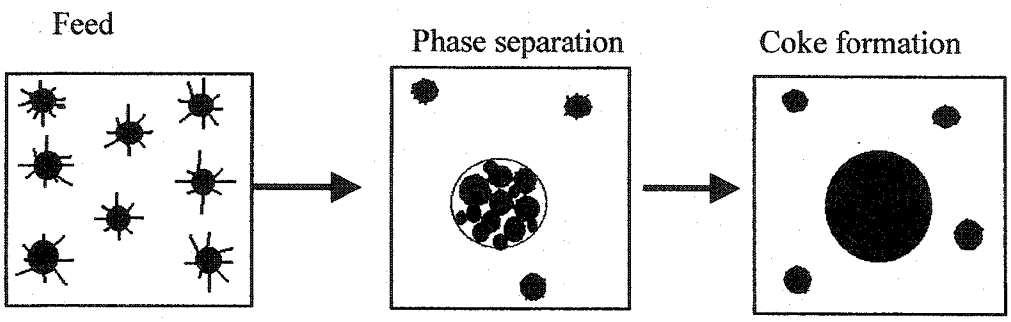
Here M is the parent compound, and R• is a hydrocarbon radical. Similar to free radical polymerizations, the free radicals in cracking reactions quickly reach pseudo-steady state at a low concentration. This mechanism was developed by Kossiakoff and Rice (1943) and has been the basis for understanding of thermal cracking reactions.

Alkyl-aromatics, alkyl-naphthenes and alkyl-hydroaromatics are the most abundant constituents of residues. The cracking of the labile aliphatic groups in these compounds constitute the bulk of the thermal cracking reactions. The thermal cracking pathways and kinetics of several alkylaromatics (e.g. n-butylbenzene, n-dodecylbenzene, n-pentadecylbenzene), alkylnaphthenes (e.g. n-butyl-cylcohexane, n-tri-decyl-cyclohexane) and alkyl-hydroaromatics (e.g. 2-ethyltetralin) have been reported (Savage and Klein, 1987a, b; Savage and Klein, 1988; Savage, 1986; Mushrush and Hazlett, 1984; Fabuss *et al.*, 1985; Blouri *et al.*, 1985). Pyrolysis of long chain alkylbenzenes usually produces two pairs of major products (toluene plus a corresponding olefin, and styrene plus a corresponding alkane) and numerous minor products. Gray *et al.* (1991) studied the quantitative structure-reactivity relationships of Athabasca bitumen over Ni/Mo on γ-alumina catalyst. Their research concluded that the only variable that correlated the observed rate of residue conversion was the concentration of carbons α to an aromatic ring in the feeds. Similar to alkyl-aromatics, pyrolysis of alkyl-cyclohexane usually produces cyclohexane as major products plus a corresponding olefin and methylene cyclohexane plus a corresponding alkane. At higher pyrolysis temperatures and without sufficient hydrogen pressure, the naphthenic groups can form aromatics *via* dehydrogenation. For example, pyrolysis of tridecylcyclohexane at 450 ^{o}C produced toluene as a significant product, but at lower temperatures, no toluene was detected and no other aromatics were observed (Savage and Klein, 1988). The most important reaction of hydroaromatics during thermal cracking is hydrogen donation. For example, tetralin can donate its four hydrogen atoms and form a stable naphthalene molecule. Catalytic hydrogenation of naphthalene can then regenerate the tetralin. Addition of hydroaromatics can provide significant hydrogen to the reacting species, thus achieving the benefits of hydrogenation such as improved product quality and suppression of coke formation, while avoiding the use of catalysts. In recent years, research on the upgrading of petroleum residues and coal liquefaction with hydrogen donors have been very active (Yoshida *et al.*, 1999; Miki and Sugimoto, 1998; Kubo, 1998; Tomic and Schobert, 1997; Ishihara *et al.*, 1995; Badger *et al.*, 1994; Smith and Savage, 1994; Shen and Iino, 1994; Wang and Curtis, 1994; Gioia and Murena, 1993).

2.4 Formation of Coke and Carbonaceous Mesophase

Coke is the carbonaceous solid product from thermal conversion of petroleum residues, coal tar pitch or other hydrocarbon or hydrocarbon derivatives. Coke has a low value compared with other petroleum products; therefore, excessive coke formation is economically undesirable. Coke formation also contributes to the fouling in process vessels (Watkinson and Wilson, 1997; Lemke and Stephenson, 1998). In petroleum refining and upgrading, coke is usually defined as a carbonaceous material that is insoluble in aromatic solvents such as toluene (Gray, 1994). Therefore, similar to asphaltenes and maltenes discussed earlier, coke is also a solubility class consisting of a complex mixture of components. It should be noted that in pyrolysis of materials other than petroleum, coke is usually defined differently. For example, in pyrolysis of coal tar pitch, where the feed itself is largely insoluble in toluene, coke is usually defined as THF insoluble or quinoline insoluble.

The formation of solid coke (at room temperature) from liquid bitumen or residues requires that there must be a phase separation step during or after its formation. Coke formation is usually attributed to condensation and polymerization of aromatic components, eventually producing a carbon-rich material (Levinter *et al.*, 1966 &1967; Wiehe, 1993). Magaril *et al.* (1968) postulated that coke formed by condensation and polymerization in a new solid phase that was formed by precipitation of the asphaltenes. Yan (1987) introduced a phase separation step in his kinetic model for visbreaking. Wiehe (1993) proposed that during thermal cracking, asphaltenes cracked off their aliphatic side-chains to form asphaltene cores. These asphaltene cores were initially dissolved in the maltenes. While the thermal cracking reactions further progressed, more asphaltene cores were formed while the amount of maltenes decreased. When the relative amount of asphaltene cores and maltenes reached the solubility limit, the excess asphaltene cores precipitated to form a new phase. In this new phase, the asphaltene cores rapidly reacted to form coke. Storm *et al.* (1996) proposed that asphaltenes were dispersed in oil by a layer of absorbed non-asphaltene molecules. At elevated temperatures, this protection layer was dissipated, and the asphaltenes flocculated due to the loss of the protective layer. They proposed that these asphaltene flocs were the precursors of coke and were what Wiehe's phase separation model referred to as the new phase. The comparison of the hypotheses of Wiehe (1993) and Storm (1996) are schematically illustrated in Figure 2.5.



Wiehe (1993):	Solution of asphaltenes	Precipitation due to solubility limit	Coke formation
Storm (1996):	Dispersion of asphaltenes	Flocculation due to loss of dispersants	Coke formation

Figure 2.5 Schematic representation of Wiehe's (1993) model and Storm's (1996) model of mechanism of coke formation.

A characteristic of coke formation in bitumen or residues is an induction period during which thermal cracking reactions occur but no coke is formed. The induction phenomenon has been observed by a number of investigators using a variety of feeds and under different coking conditions (Schucker *et al.* 1980; Savage *et al.* 1985, 1988; Wiehe, 1993; Srinivasan and McKnight, 1994; Tanabe and Gray, 1997). Wiehe's (1993) solubility-limit model of coke formation explained the induction period as the time needed to reach the solubility limit. The solubility limit hypothesis was also consistent with his observation that during the period of coke formation, the ratio of the asphaltene concentration to the concentration of maltene approached a constant, as shown in Figure 2.6.

Since coke formation is believed to result from free radical polymerization and condensation, factors that affect the initiation, propagation or termination of the free radicals will be very important to the kinetics of coke formation. There are noteworthy similarities between coke formation and free radical polymerizations. One example is the induction phenomenon. In polymerizations, the induction period is attributed to "impurities" that act as free radical inhibitors (or scavengers). Only after the inhibitors are consumed by the free radicals can polymerization start. Thorough purification and de-oxygenation can eliminate the induction period in these polymerizations (Barrett, 1975).

During prolonged reactions at thermal cracking conditions, the produced coke may further undergo physical and chemical changes, and may go through a carbonaceous mesophase stage (Marsh and Cornford, 1975; Marsh and Walker, 1978; Marsh and Diez, 1994). Mesophase is a term equivalent to liquid crystal (Gray, 1973), and was introduced to replace the self-contradictory term liquid crystal. Carbonaceous mesophase is usually

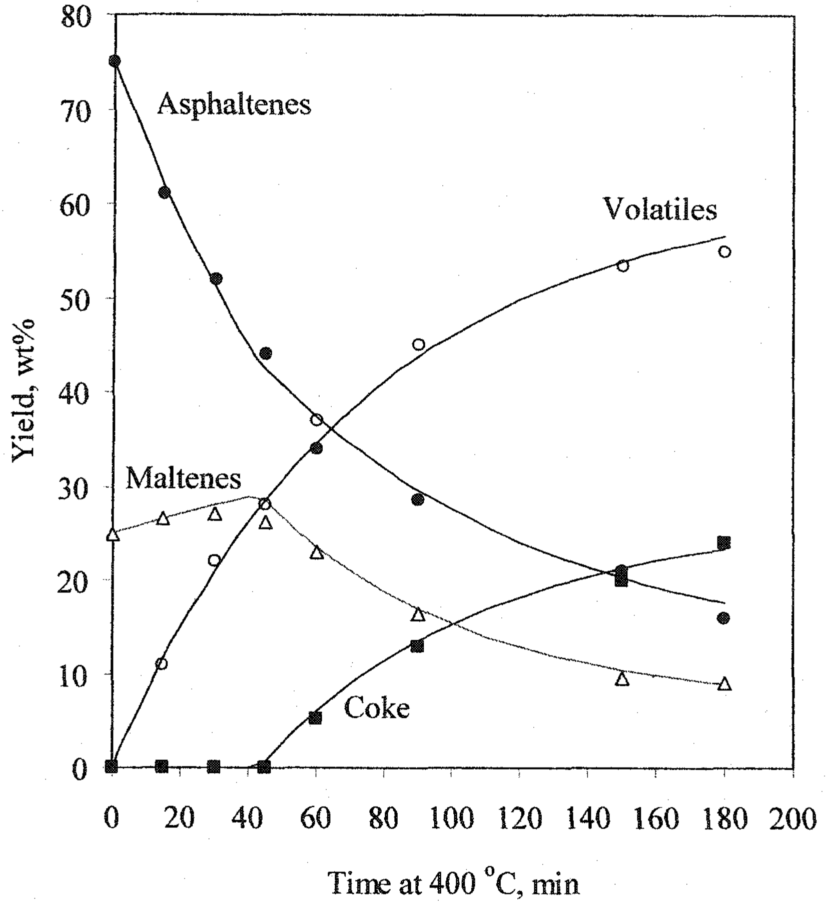


Figure 2.6 Temporal variation in the four product classes from thermolysis of Cold Lake vacuum residue (Wiehe, 1993).

observed with optical microscopy as micron-sized spheres during coal tar pitch pyrolysis (Brooks and Taylor 1965, Mochida *et al.* 1988, Braun *et al.* 1995, Korai *et al.* 1996, Alain *et al.* 1996), and during coking of petroluem residues (Kapustin *et al.*, 1983; Wiehe, 1993). Studies on pyrolysis of coal tar pitch showed the formation of mesophase coke, which appeared as spherules and was insoluble in quinoline. These mesophase spheres appear anisotropic under cross-polarized light microscopy, indicating ordering in structure. The thermotropic liquid crystalline behavior of carbonaceous mesophase was demonstrated by Lewis (1971). Using a hot stage microscopy, he observed anisotropic mesophase spheres at 350 ^{o}C in a pitch produced from pyrolysis of naphthalene. These spheres disappeared when the pitch was heated rapidly from 350 ^{o}C to 450 ^{o}C but could reappear when the pitch was allowed to cool to the original temperature of 350 ^{o}C. Heating rate plays an important role in formation of mesophase spheres. Abramski and Mackowsky in 1952 concluded (Brooks and Taylor, 1968) that slow but long periods of heating with compacting pressure tended to give more complete ordering than fast heating and moderate pressure. They also found the heating rate should not be too slow. For example, when heated at 1 ^{o}C/min, coal did not reach the same degree of ordering as when heated at 3 ^{o}C/min.

It should be noted that carbonaceous mesophase is far more complicated and differs from classical liquid crystals in several ways. Classical liquid crystals are usually created from pure compounds which possess functional groups with considerable polarity such as hydroxyl, nitrile, carboxylic, heterocyclic oxygen and nitrogen, out-of-ring nitrogen, and metallic groupings (Marsh *et al.* 1999). The resulting liquid crystals are either Calamitic (*i.e.* rod-shaped) or discotic (*i.e.* disc-shaped). The mesophase-forming compounds in petroleum residues are complex mixtures and do not have strong polarity and thus rely on the π-π interactions of its aromaticity to form only discotic structures. The temperatures at which carbonaceous mesophase forms and exists are usually from 350 °C to 500 °C (Alain *et al.*, 1996; Korai *et al.*, 1996; Braun *et al.*, 1995, Dubois *et al.* 1997). These are significantly higher than the temperatures for classical liquid crystals, which are often near room temperature. Classical liquid crystals are stable end products, while carbonaceous mesophases are only intermediates which tend to continue to react into solid products under the conditions of their formation. The chemical composition and structure of classical liquid crystals are well defined, whereas the structure and composition of carbonaceous mesophase are not well understood and are indeed far more difficult to investigate than the classical liquid crystals. Murakami *et al.* (1996) have been able to obtain hydrogen distribution information of a carbonaceous mesophase using high-temperature ^{13}C-NMR at 300 °C and using pyrene as solvent. Since petroleum residues or coal tar pitches vary considerably in chemical composition, so does the resulting carbonaceous mesophase.

2.5 Effects of Fine Solids on Coke Formation

Athabasca bitumen and its residues contain relatively high content (usually more than 1 wt %) of fine toluene insoluble solids (bitumen solids) resulting from the surface mining – hot water extraction processes. These bitumen solids are potentially important in affecting both the phase behavior and free radical reactions. Bitumen solids may act as nucleation sites during phase separation, or act as emulsion stabilizers preventing the dispersed new phase from coalescing. Bitumen solids are also known for their ability to scavenge free radicals by providing large surface area, and there have been studies showing that free radical scavengers could reduce coke formation in FCC transfer lines (Edgerton and Sapre, 1993). Previous investigations found that bitumen solids contained a substantial content of metal elements such as iron (Kotlyar *et al.* 1988, 1998), which might act as a hydrogenation catalyst. The aluminosilicate clays contained in the bitumen solids included kaolinite, illite and smectite (Carrier *et al.* 1987; Gunter *et al.* 1994), which, when subjected to certain treatments, were also reported to have catalytic activities (Breen *et al.* 1997) or to a synergistic effect with hydrogenation catalyst (Attala *et al.* 1990). There have not been many studies on the effect of fine solids on coke formation under coking conditions. Additionally, most of the previous studies were conducted under hydroconversion conditions, and the observed effects were often attributed to catalytic activity of the solids towards hydrogenation, or synergistic effect between the solids and the hydrogenation catalyst (Attalla *et al.* 1990). Wolk (1974) patented the use of the bitumen solids from oil sands bitumen to suppress coke formation in a hydroconversion process. Nandi *et al.* (1978) found that by adding coal powder to Athabasca bitumen it was possible to control coke precursors during hydrogenation reactions. Marked improvement in the process operability was observed with the addition of coal and increased distillate yields were obtained at low coal concentration (Fouda *et al.*, 1989). No significant penalties were observed in terms of product qualities by adding coal in the feed, while the inhibition of coke formation and the enhancement of metals removal were observed. Rosa-Brussin (1995) reviewed the use of clays for hydrotreatment of heavy crude oils and concluded that clays adsorbed hydrogen on iron center sites and thus promoted hydrogenation. Belinko *et al.* (1977) also found that added coal powder acted as nuclei for agglomerated particles in the form of spheres as revealed by optical micrographs.

Very little work has been done on effect of fine solids on coke formation in the absence of hydrogen pressure. Girolami (1963) investigated the effects of fine calcined petroleum coke particles on the coking of coal tar pitch in the absence of hydrogen pressure. He also found that coke yield increased when petroleum coke particles, molecular sieve or Fuller's earth was added. He observed the increase in coke yield was dependent on the amount of surface area added and the concentration of petroleum coke powder and molecular sieves. Glass powder had no detectable effect. This result was explained to be due to a lack of surface activity. With a preheating procedure at 200 °C and 300 °C, respectively, there was a sharp jump in the coke yield at certain concentration of the solids. He attributed this phenomenon to the possibility that the preheating allowed the pitch to dispatch the air or other gases absorbed by the solids particles. Beuther *et al.* (1980) found that fine acidic catalyst solids, γ-alumina and η-alumina, inhibited the formation of large domains of mesophase and only very small domains were observed. They attributed this effect to the formation of coke on the surface of the alumina. An alternative explanation was proposed earlier by Dubois *et al.* (1970) and Bradford *et al.* (1971) that the addition of fine solids interfered with the coalescence of the mesophase. Marsh and Walker (1979) found that the presence of carbon black in the carbonization systems increased the number of mesophase single spherules. These foreign solids might enhance the formation of spheres through its active surface and restrict their growth and coalescence through its adsorption on their surface (Korai *et al.* 1996). Tanabe and Gray (1996) found that the fine solids in Athabasca vacuum residue reduced coke formation compared with the solid-free feeds (Figure 2.7). A hypothesis was proposed that the fine solids accumulated on the interface of a new phase of coke precursor and thereby stabilized the coke precursors from coalescence, analogous to the stabilization of oil-in-water or water-in-oil emulsions (see Figure 2.8). A better dispersed coke phase would have more contact with hydrogen donor compounds in the oil phase, which in turn would lead to reduced rate of coke formation. Rahimi *et al.* (1999) studied the interaction of solid particles with mesophase formation under thermal upgrading conditions. A hot-stage microscope was used to study the effect of clays (kaolinite, illite and montmorillonite) on mesophase formation. The clay additives prolonged the mesophase induction period and suppressed the growth and coalescence of mesophase spheres. Wang *et al.* (1998) studied the interaction of added fine solids with the toluene insoluble (TI) spheres formed from Athabasca coker gas oil. They found the interaction depended on the hydrophobicity of the solid surface. Little interaction was observed between TI spheres and kaolin particles. Addition of particles with non-polar surface groups (carbon black and asphaltene-coated kaolin), however, suppressed the formation of the separate TI spheres. In this case, the TI formed primarily on the surface of the added solids.

2.6 Kinetic Models For Coking of Bitumen and Residue

Because of the complexity in composition of residues, thermal cracking of these feeds can not be modeled based on the true reactions of each molecular constituent of the feed. Modeling thermal cracking of residues based on structural group compositions is a

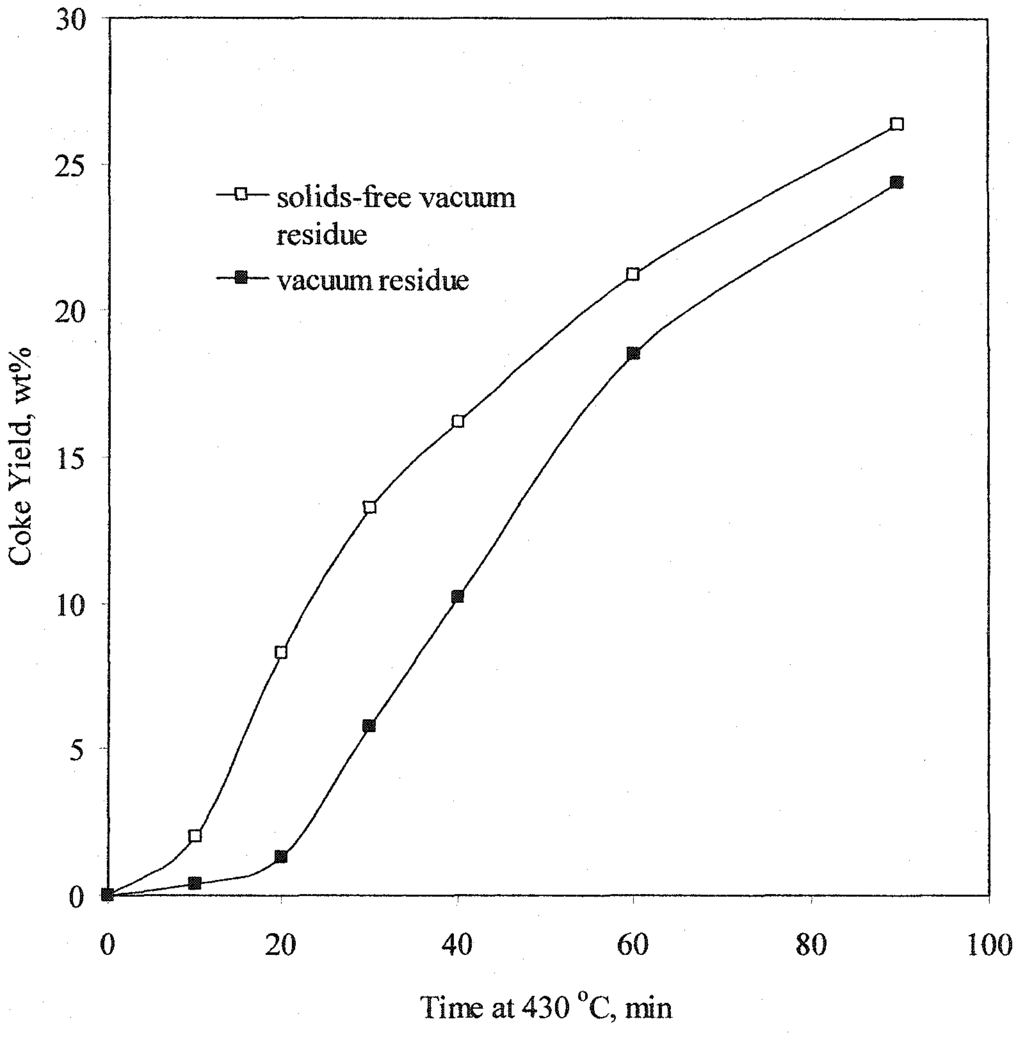


Figure 2.7 Effect of fine solids on coke yield of Athabasca vacuum residue. (Tanabe and Gray, 1997).

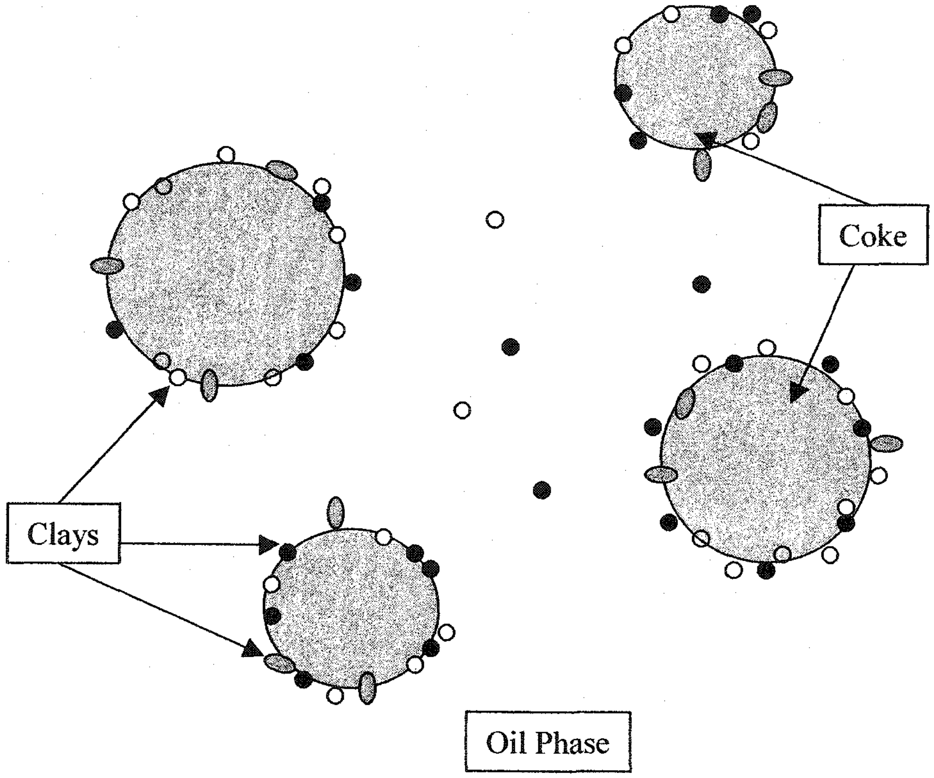


Figure 2.8 Schematic diagram of clays at interfaces of thermoplastic coke dispersed in oil. (Tanabe and Gray, 1997).

possible alternative. Savage and Klein (1989) developed a very sophiscated Monte Carlo simulation to model the pyrolysis reactions of asphaltenes using asphaltene structural information and model compound kinetics. Neurock *et al.* (1990) developed a Monte Carlo simulation of cracking of heavy oils, and then assembled the 10,000+ product molecules into asphaltenes, maltenes, gas, and coke to compare with experimental results. Developing and using this type of models, however, is extremely time consuming. A more practical and widely used approach is the so-called lumped kinetic modeling, *i.e.* dividing the feed and product into a few pseudo-components (lumps) and modeling the "reactions" between these pseudo-components. The selection of pseudo-components must be readily quantifiable by simple separation procedures for the model to be useful for practical purpose.

Lumped kinetic models have been very successful in describing and predicting the cracking of distillates. For coking of residues and bitumen, this same approach is so far still unsuccessful in predicting product yields and distribution. One possible reason is that the boiling range cuts, which are usually used as the basis for the pseudo-components for modeling cracking of distillates, have a close relationship with molecular weight. Residues, on the other hand, are non-distillable, and thus solubility classes such as asphaltenes and maltenes have to be used as the pseduo-components. Solubility classes, although easy to quantify, do not reflect or represent the reactivity behaviors of their components very well. First order is usually assumed as a satisfactory approximation for all the reactions between the pseudo-components. As mentioned earlier these models do not perform well in predicting yields or product distribution for feeds and reaction conditions different from those from which the model was developed.

Del Bianco *et al.* (1992) developed a simple kinetic model for thermal cracking of a vacuum residue of Belaym (Egypt) crude. They combined volatiles and gas into one lump termed distillables, and introduced an imaginary intermediate lump to account for the induction period of coke formation (Figure 2.9). In this model, coke was defined as tetrahydrofuran (THF) insoluble. The amount of vacuum residue (VR) after each reaction was measured as the THF-soluble fraction of the nondistillable product. VR was considered to consist of two parts, the unconverted vacuum residue (VR*) and the intermediate (I). Thus VR*+I = VR. VR* and I were not measured but calculated by fitting the experimental data. Though simple, this model agreed with their experimental data very well. Takatsuka *et al.* (1989) developed a very comprehensive model involving eight lumps, including dividing coke into quinoline soluble and quinoline insoluble fractions. The reaction network is shown in Figure 2.10. The models of Phillips *et al.* (1985), Neurock *et al.* (1991) and Trauth *et al.* (1992) (Figure 2.11, Figure 2.12 and Figure 2.13 respectively) all involved essentially only asphaltenes, maltenes, coke and gas. Wiehe's (1993) phase separation model is a semi-theoretical kinetic model mainly focused on describing coke formation. He used six lumps: reactant asphaltenes, reactant maltenes, reacted asphaltene cores, product nonvolatile maltenes, volatile products and coke. He proposed that coke formation be triggered by a phase separation of asphaltene cores from maltenes when the solubility limit of the asphaltene cores were exceeded. This model, as it appears in the publication, was based on coking at one temperature 400 °C only and the publication did not indicate any attempt to obtain Arhrenius parameters. The objective of this model seems mainly to support the solubility-limited phase separation hypothesis and the emphasis was not on the kinetics *per se*. Nevertheless, this model

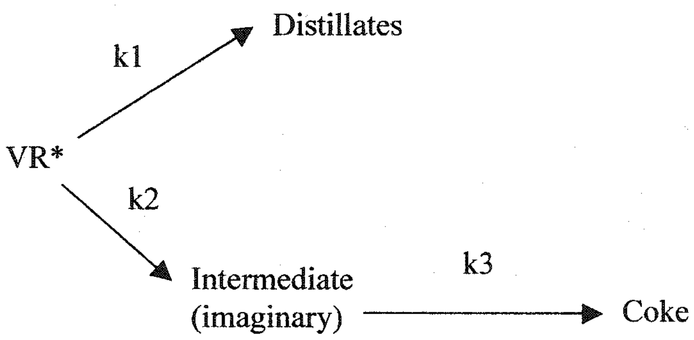


Figure 2.9 A kinetic model of thermal cracking of an Egypt vacuum residue (Del Bianco *et al.*, 1992).

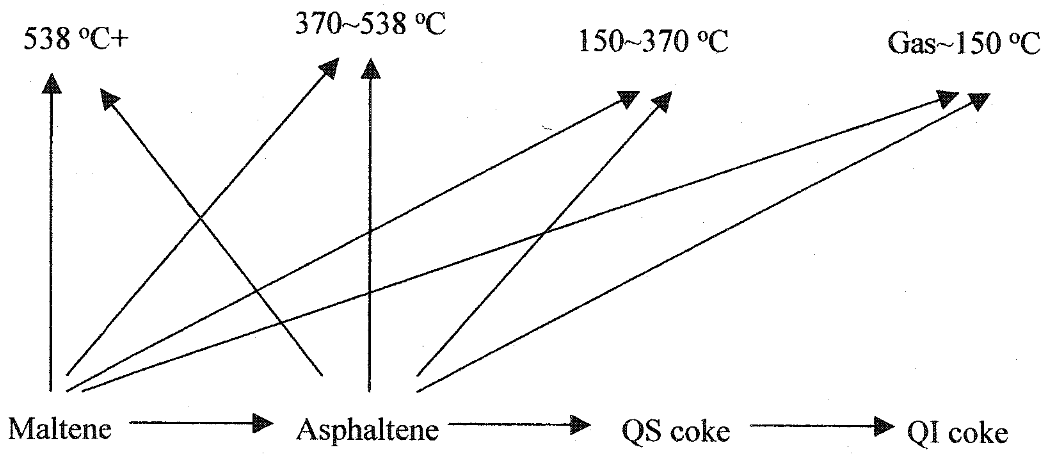


Figure 2.10 Kinetic model of cracking of residual oils (Takatsuka *et al.*, 1989).

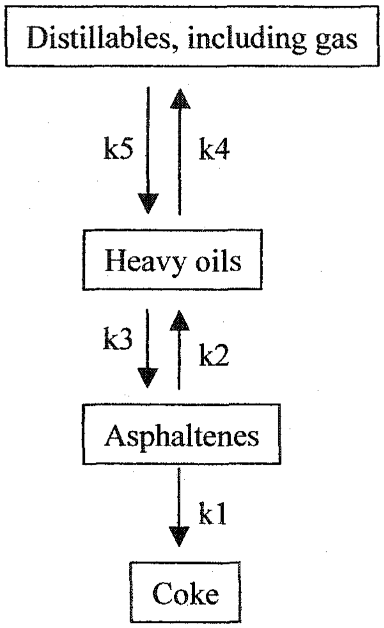


Figure 2.11 Lumped kinetic model for thermal cracking of Athabasca bitumen (Phillips *et al.*, 1985).

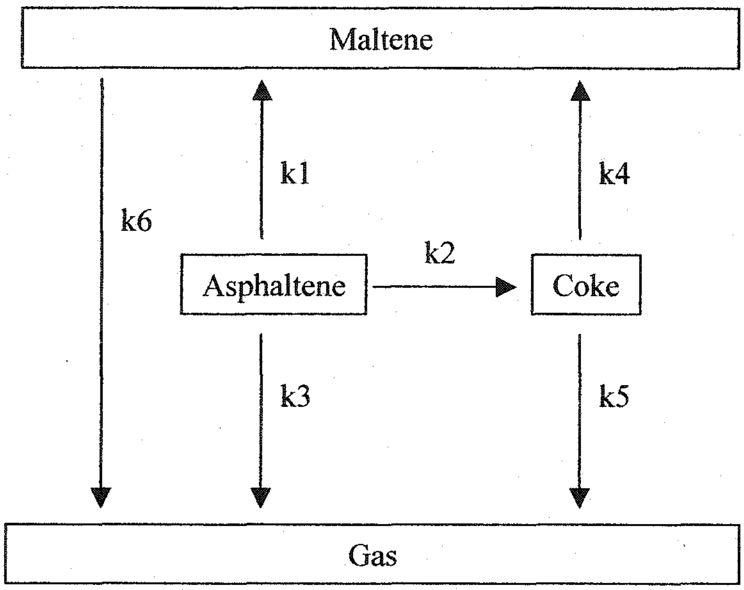


Figure 2.12 Asphaltene pyrolysis pathways model (Neurock *et al.,* 1991).

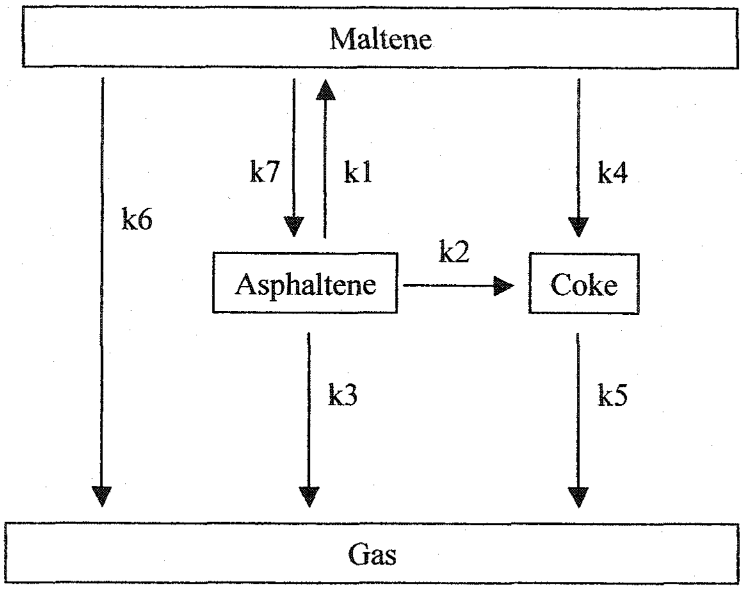


Figure 2.13 Asphaltene pyrolysis pathways model (Trauth *et al*, 1992).

provides a very good basis for more comprehensive kinetic studies. The model is as follows:

$$H^{+} \xrightarrow{k_H} aA^{*} + (1 - a)V$$

$$A^{+} \xrightarrow{k_A} mA^{*} + nH^{*} + (1 - m - n)V$$

Solubility limit: $$A^{*}_{max} = S_L(H^{+} + H^{*})$$

$$A^{*}_{ex} = A^{*} - A^{*}_{max}$$

$$A^{*}_{ex} \xrightarrow{\infty} (1 - y)TI + yH^{*}$$

where H^{+} = reactant maltenes (heptane solubles); H^{*} = product maltenes; A^{+} = reactant asphaltenes; A^{*} = asphaltene cores; V = volatile products; A^{*}_{ex} = asphaltene cores that exceed the solubility limit; S_L denotes solubility limit and a, m, n, and y are stoichiometric coefficients; and TI = toluene insoluble (coke).

2.7 Industrial Processes for Thermal Upgrading Bitumen and Residues

Thermal cracking is the oldest but still the most widely used technology for upgrading petroleum residues. When petroleum fractions are heated to temperatures over ca. 400 °C, thermal or free radical reactions start to give cracking of the mixture at significant rates (Gray, 1994; Yang *et al.*, 1993). The conversion and product characteristics from thermal upgrading are mainly determined by the severity of the process, which is the combination of reaction time and temperature. Usually, there is a trade-off between reaction time and temperature. If no side reactions occur, longer reaction times at lower temperatures should be equivalent to shorter times at higher temperatures (Gray, 1994). Commercial thermal upgrading processes for bitumen and residues include visbreaking, delayed coking and fluid coking. The typical operating conditions for visbreaking, delayed coking and fluid coking are listed in Table 2.3.

2.7.1 Visbreaking. Visbreaking is a mild treatment of residues mainly for reducing the viscosity to meet the fuel oil specifications, while also producing additional light products for catalytic cracking feedstock. Vis breaking is operated at a relatively lower severity, usually 425-510 °C and 0.3-2.1 MPa at the heater outlet and reaction time of several minutes (Speight, 1991). If the severity is too high, coke will begin to form and the resulting products will be unstable and form sediments or sludge during storage. Table 2.3 gives a typical time-temperature relationship for a visbreaking.

Table 2.3 Summary of reaction conditions of industrial thermal upgrading processes

Process	Severity	Reaction time	Temperature, °C	Pressure MPa	Conversion
Visbreaking	Low	60-180 sec	425-510 °C	0.3-2.1	Low
Delayed coking	High	24 hour Semibatch	435-480 °C	~0.6	High
Fluid coking	High	~25 sec	510-560 °C	~0.06	High

There are two types of visbreaking operations, furnace visbreaking, also called coil visbreaking, and soaker visbreaking. Furnace visbreaking uses higher temperatures (475-500 °C at furnace outlet) but shorter reaction times (60-180 seconds), while soaker visbreaking uses lower furnace outlet temperatures (425-440 °C) and longer reaction times. In furnace visbreaking, the feed is introduced to a furnace and heated up to reaction temperature and immediately quenched with gas oil at the exit of the furnace. In soaker visbreaking operation, after leaving the furnace the feed passes through a soaker drum, which provides additional reaction time, and then is quenched at the exit of the soaker drum. A process flow diagram for furnace visbreaking is shown in Figure 2.14.

2.7.2 Coking. Coking is a high severity process with a high conversion to achieve maximum distillate liquid yields by allowing a solid coke formation. Two types of coking processes are widely used commercially, *i.e.* delayed coking, and fluid coking. Both types of coking are capable of processing oils with high contents of heteroatomic compounds and metal impurities at a lower cost than catalytic upgrading processes such as LC-Fining or the H-Oil processes. The feedstock of coking can be vacuum residues, atmospheric residues, bitumen, cracked residues or even waste oils. This high tolerance of low grade feeds at a low operating cost has earned it the historic nickname--the garbage can of a refinery. Coking is an old process but is becoming more important as the conventional crude is becoming heavier, and heavy oils and bitumen are gaining more market share (Elliott, 1992). As the sulfur, nitrogen, metals, and Conradson carbon residues of crudes increase, coking is becoming more popular to many refiners, since the process not only can tolerate these impurities (catalyst poisons) but concentrate them in the coke. Therefore, coking should be called "catalyst poison rejection" process rather than just a "carbon rejection" process, because a principal reason for coking is to improve the liquids for further upgrading by catalytic processing (Wiehe, 1995). Thus, in the present day economic environment, the coker is frequently the most important unit in the refinery (Lieberman, 1981).

The products of coking are gases, naphtha, light gas oil, heavy gas oil and coke. In a typical refinery, gas oils usually are the major products of a coking operation (Speight, 1991). For coking in a conventional refinery, the gas oil serves primarily as a

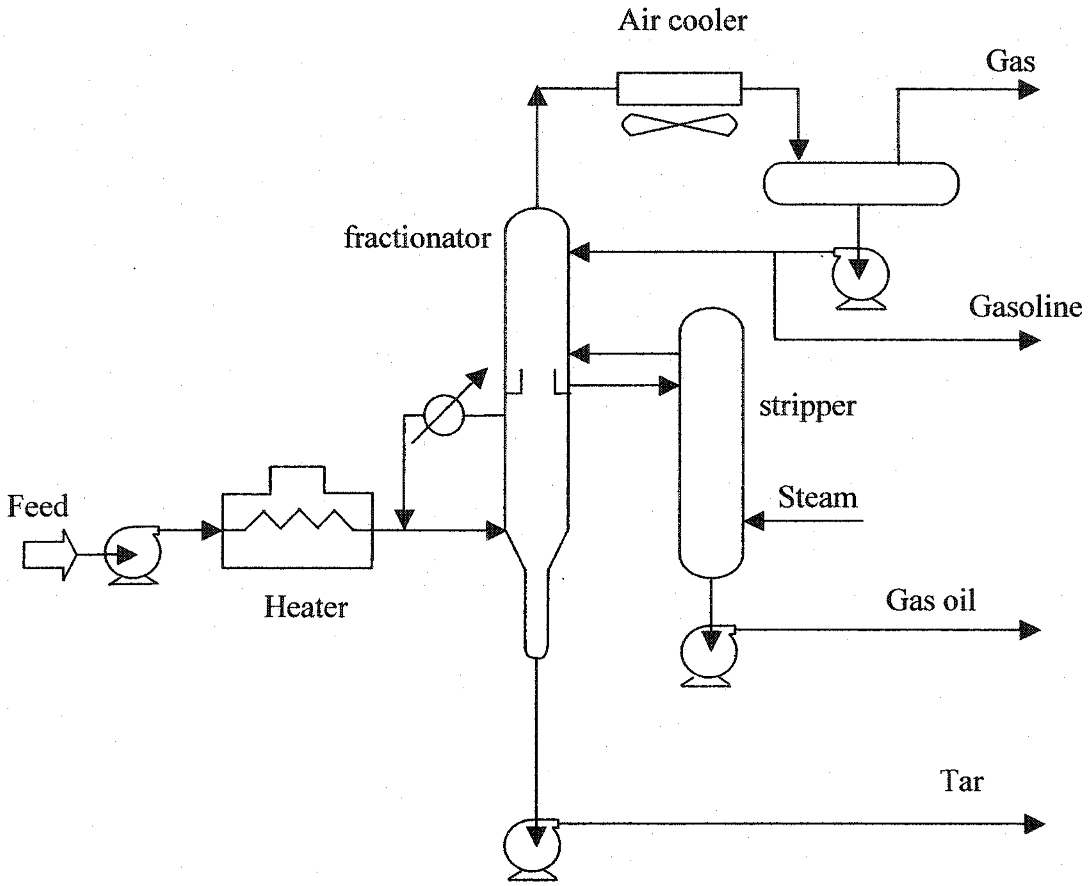


Figure 2.14 Simplified flow diagram of a typical furnace visbreaking process.

feedstock for fluid catalytic cracking (FCC) units (Le Page *et al.* 1992). In oil sands bitumen operations, however, the gas oils are blended to produce the synthetic crude oil (SCO). The coke obtained is usually used as fuel, electrode and metallurgical coke, depending on the properties and quality of the coke. At present, Athabasca coke is stockpiled for future use due to the unattractive current market and due to a high level of impurities.

2.7.3 Delayed Coking. Delayed coking is a semibatch process and is by far the most widely used among all commercial coking processes. Figure 2.15 illustrates a simplified flow diagram of a typical delayed coker. Hot feed is charged to the fractionation tower two or four trays above the bottom flash zone. The bottom of the fractionation tower acts as a surge drum from which the feed is pumped to the coking heater. The heater raises the temperature of the feed to about 480 °C and the feed then flows into one of a pair of coke drums. Steam is introduced to the heater tubes to increase the velocity and thus minimize coke deposition in the heater tubes. The coke formation is thus "delayed" until the feed enters the coke drum which provides the sufficient retention time for the coke formation to take place — hence the term delayed coking.

The coke gradually fills the drum, usually over a period of 24 hours, while the cracked lighter products such as gas, naphtha, and gas oil exit as vapor to the fractionation tower. Since the coking reaction is endothermic, the vapors leaving the top of the coke drum are roughly 40 °C lower than the heater outlet temperature (Lieberman, 1981). The temperature in the coke drum usually ranges from 415 to 450 °C at pressures from 0.1-0.6 MPa (Speight, 1991). In the fractionation tower, the coke drum vapors are

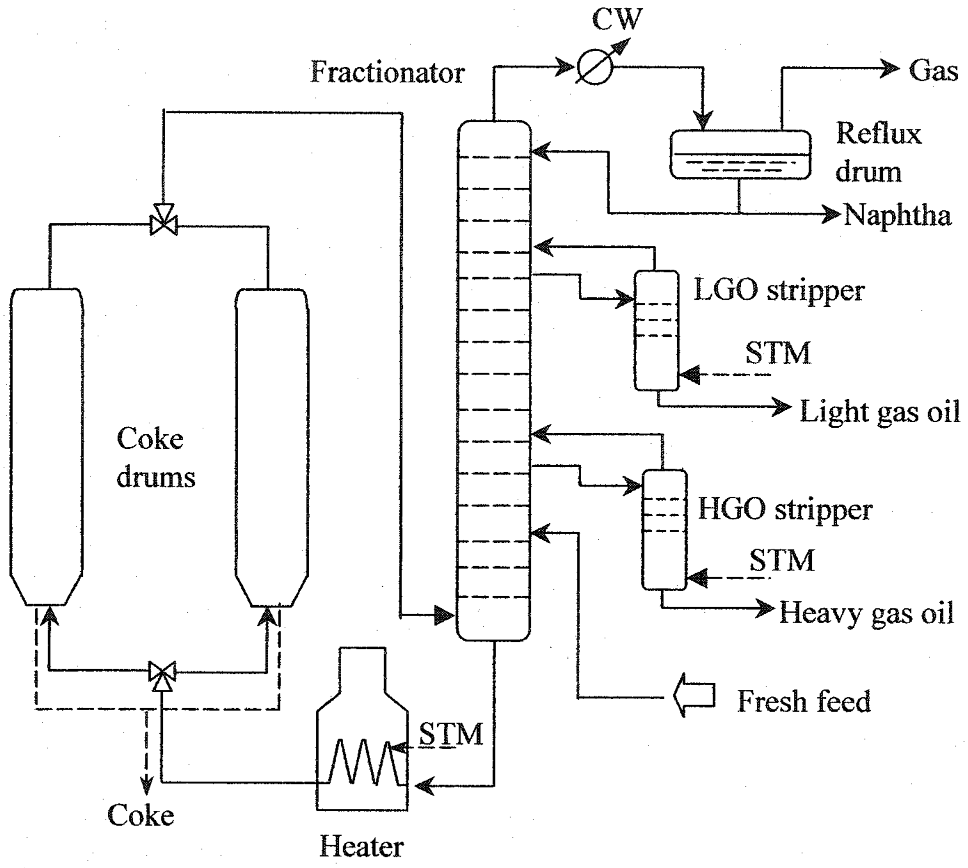


Figure 2.15 Simplified flow diagram of a typical delayed coking process.

condensed and fractionated into gas, naphtha, and gas oil. When the coke drum is filled to a safe margin from the top, the heater effluent is switched to the empty coke drum and the full drum is then steamed to remove hydrocarbon vapors, cooled by water, opened, drained, and the coke is removed by high-pressure water (Gary and Handwerk, 1984).

2.7.4 Fluid coking. Fluid coking is a continuous fluidized-bed coking process, thus the name fluid coking. Fluid coking consists of a reactor and a burner, both holding fine coke particles fluidized by steam introduced at the bottom of the vessels. The feed is sprayed into the reactor and coking takes place on the surface of the fluidized coke particles. The temperature is usually maintained at 510-560 °C and the pressure is substantially atmospheric to allow a quicker vaporization of the cracked product and lighter fraction of the incoming feed. The vapor, which consist of gases and distillates, passes through cyclones at the top of the reactor to remove entrained coke particles, and is discharged into the bottom of a scrubber where the vapor is quenched by gas oil. The upper portion of the scrubber is a fractionation zone from which the coker gas oil is withdrawn and the gases are charged to condensers. The coke particles flow down through the reactor into a stripping zone, where steam strips the product vapor off the coke particles. The coke is then blown through a riser by steam to the fluidized burner where a portion of the coke is burned to supply the heat for the reactor. Air is added as needed to maintain the temperature of the burner. The temperature in the burner is usually 590-650°C and pressure may range from 0.035-0.17 MPa. Hot coke from the burner returns to the reactor by a second riser assembly and the extra coke is withdrawn from the burner as net coke production. Figure 2.16 illustrates a simplified flow diagram of a fluid coking process.

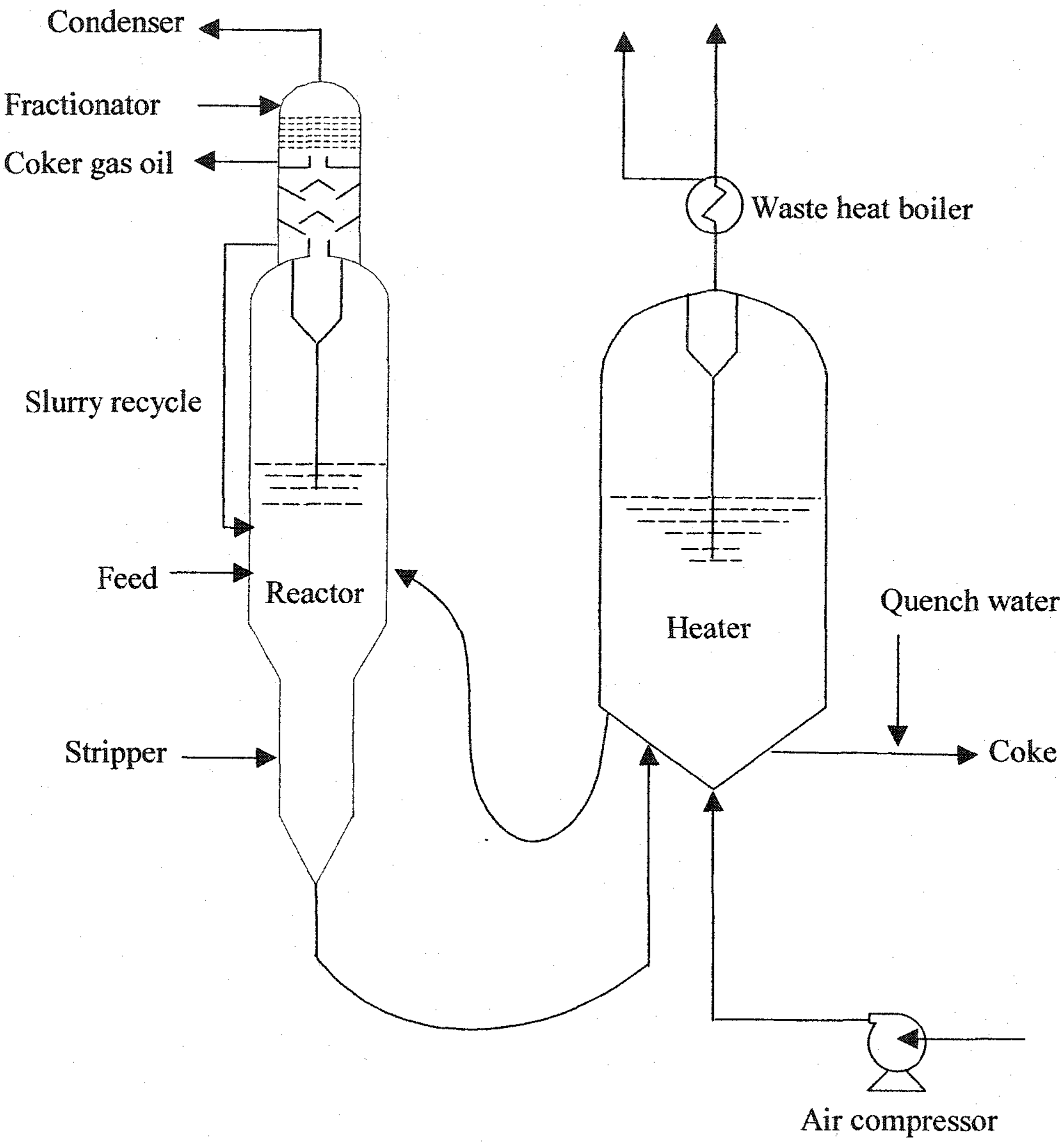


Figure 2.16 Simplified flow diagram of a typical fluid coking process.

Compared with delayed coking, fluid coking has the advantage of continuous flow, which eliminates the manpower intensive efforts involved in the decoking of each cycle. In addition, due to its fluidized bed reaction nature, fluid coking permits higher coking reaction temperatures and shorter contact times than those can be used in delayed coking. The higher temperature and shorter time result in less coke yield and more distillates yields. The main disadvantage of fluid coking is the necessity of burning the coke to generate process heat which liberates sulfur as sulfur dioxide. Besides, fluid coking can not be used to produce high-quality coke for production of metallurgical coke or electrodes. The former disadvantage can be overcome by adding a fluidized-bed coke gasifier to fluid coking to convert the excess coke to a mixture of CO, CO_2 and H_2. The fluid coking so revised is known as Flexicoking.

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Chapter 3

Phase Behavior and Kinetics of Coke Formation in Coking of Athabasca Bitumen and Vacuum Residues

3.1 Introduction

In petroleum refining, coke is usually defined as a carbonaceous solid (at room temperature) that is insoluble in toluene. Coke formation is usually attributed to condensation and polymerization of aromatic components, eventually producing a carbon-rich material (Levinter *et al.*, 1966, 1967). The formation of solid coke from a liquid feed requires that there must be a phase separation step at certain stage of the reaction. There are several different theories of how this step occurs, such as that proposed by Storm *et al.* (1996) and that by Wiehe (1993), as outlined in the previous chapter. Solid coke usually passes through a carbonaceous mesophase stage (Marsh and Cornford, 1975; Marsh and Walker, 1978; Marsh and Diez, 1994). Carbonaceous mesophase appears anisotropic under cross-polarized light (an indication of ordered structure), and is insoluble in quinoline. With optical microscopy, carbonaceous mesophase is usually observed as spheres during coal tar pitch pyrolysis (Brooks and Taylor 1965, Mochida *et al.* 1988, Braun *et al.* 1995, Korai *et al.* 1996, Alain *et al.* 1996), and also during coking of petroleum residues (Kapustin *et al.*, 1983; Wiehe, 1993; Rahimi, 1998). Wang *et al.* (1998) observed that micron-sized, toluene insoluble carbonaceous spheres were produced from gas oil under hydrotreating conditions. These spheres, however, were completely soluble in quinoline, indicating that they may not be mesophase. It should be noted that the conditions at which these toluene insoluble microspheres were produced were considerably milder than coking conditions, but these microspheres, being insoluble in toluene, fell into the definition of coke and might well be precursors to mesophase, if they were not mesophase themselves. At conditions of very high severity such as that in a commercial fluid coker, coke is usually a mosaic of anisotropic domains in an isotropic matrix. It was also reported that higher process severity usually results in higher percentage of anisotropic coke (Nowlan and Srinivasan, 1996). These observations raise the question whether there are additional phase transitions within the coke after it is first formed, and how these transitions occur during coking reactions.

In coking, thousands, maybe even millions of reactions take place simultaneously (Zander, 1987; Greinke, 1994), including cracking of large molecules into smaller ones, and combination of smaller molecules into larger ones *via* condensation, oligomerization and polymerization, and hydrogen shuttling, to name a few. Because of the complexity in the reactions and the composition, the coking kinetics of bitumen and residues cannot be directly modeled on a molecular basis. Consequently, an empirical approach, the so-called lumped kinetic modeling, is usually used for such feeds. By dividing the feed and products into a few pseudo-components (lumps) based on physical properties, the kinetics can be modeled as if the reactions were between these pseudo-components. Ideally, the choice of the physical properties should reflect the reactivity of the components in such a way that the molecules in each pseudo-component share common reactivity, and it should be relatively easy to quantify the pseudo-components for experimental considerations. Unfortunately, the most common method used to fractionate bitumen, residues and coke is by their solubility in different solvents. This approach is necessary due to the difficulty in fractionating such heavy materials by other methods. Fractionation by solubility is easy to operate, but solubility does not generally reflect reactivity very well.

A number of lumped kinetic models with varying complexity for thermal cracking of residues have been developed (Phillips *et al.*, 1985; Takatsuka *et al.*, 1989; Neurock *et al.*, 1991; Del Bianco *et al.*, 1992 and Trauth *et al.*, 1992, Wiehe, 1993, 1997) as discussed in details in the previous chapter. First order kinetics is usually employed as satisfactory approximations for all the reactions between the pseudo-components. Variation in mass rather than moles of each pseudo-component was used in the formulation of the models.

One interesting phenomenon widely reported in the coking literature is the induction period. During the early stage in the coking reaction, no coke is produced but significant production of gases and changes in asphaltene concentration are still observed. Only after this induction period has passed does significant coke formation begin. This induction phenomenon in coking was observed by a number of investigators (Schucker *et al.* 1980; Savage *et al.* 1985, 1988; Wiehe, 1993; Srinivasan and McKnight, 1994; Tanabe and Gray, 1997; Li *et al.* 1997). Among the above-mentioned kinetic models, however, only Del Bianco (1992) and Wiehe (1993) included modeling for the induction period. The omission of induction period from a kinetic model adversely affects the fitting during and near the induction period; more importantly, it usually also results in an overestimated yield of coke at longer reactions for a simple first-order reaction kinetics.

The kinetics of formation of quinoline insoluble (QI) coke from quinoline soluble coke (QS) is a potentially important indicator of how the phase transition takes place during coke formation. Most coking kinetic models in the literature, however, do not describe this step. Takatsuka *et al.* (1989) modeled QI formation but their approach of considering QI formation as a first-order reaction from QS seemed inadequate to describe the experimental data. The fitting of QI was far poorer than the other reactions such as gas formation and TI formation (Takatsuka *et al.*, 1989).

The objective of this study was to experimentally investigate the phase behavior and kinetics of coke formation. Athabasca bitumen, its vacuum residue, and a mixture of asphaltene-rich fraction of Athabasca vacuum residue in gas oil were used as the feeds. The coking reactions were carried out in a closed micro-batch reactor at 430 °C to 475 °C. Scanning electron microscopy (SEM) and petrography were used as the main tools for examining the phase behavior. Kinetic models were developed to describe the coking reactions of Athabasca vacuum residue with an emphasis on improved modeling of the induction period and the formation of QI from QS. To avoid the interference of the bitumen solids, these solids were removed prior to reactions.

3.2 Development of Kinetic Models.

Theoretically, the reaction network for lumped kinetics modeling can include all possible reactions among the pseudo-components, and the insignificant reactions can be identified as the ones with very low rate constants. Because of unavoidable experimental errors and a limited number of experimentally measure parameters, however, leaving too many unknown variables to be determined by data fitting is often very unreliable. Therefore, one has to select only the major reactions while neglecting the minor ones based on known reaction mechanisms.

As discussed in the previous chapter, QI can consist of both mesophase and non-mesophase. Formation of ordered structure such as mesophase from a non-ordered structure or from a structure of different ordering is essentially a phase change. The rate of a phase change is limited by energy flux and is independent of concentration, a scenario that usually indicates zero-order kinetics. As a general rule, when the concentration of the reactant is lowered, a zero-order reaction usually shifts to higher orders (Levenspiel, 1972). During the formation of QI from QS, the cracking reactions of the side-chains on the QS molecules and cross-linking of the QS molecules also take place. These reactions are concentration-dependent and accordingly, kinetics of an order of higher than zero is expected. It should be noted, however, that much of the cracking and cross-linking occur within the phase boundaries of QS and QI. For instance, some of the cracking of QS molecules could give a product that is still soluble in quinoline, and the product of cracking and cross-linking of QI will remain as QI. These reactions cannot be reflected in the lumped kinetic model.

According to the above analysis, the kinetics of QI formation from QS can be best described as a reaction of shifting orders between 0 and 1. As for modeling, this type of kinetics of shifting orders can be described as:

$$\frac{dQI}{dt} = \frac{k_1 QS}{1 + k_2 QS} \tag{3.1}$$

Thus at higher QS concentrations, $k_2 \cdot QS >> 1$, eq. (3.1) reduces to $\frac{dQI}{dt} = k_1/k_2$ and the reaction becomes zero-th order with a rate constant of k_1/k_2; at low QS concentrations such that $k_2 \cdot QS \ll 1$, eq. (3.1) becomes $\frac{dQI}{dt} = k_1 \cdot QS$, and the reaction becomes first order with a rate constant of k_1.

As for the modeling of the induction period, Del Bianco's (1992) approach of modeling the induction period by introducing an imaginary intermediate provided potentially better prediction at longer reactions, but has been found to be inadequate to account for the induction period itself. This is because adding an intermediate step only artificially slows down the calculated rate of coke formation at the very early stage but does not give a delay in the coke formation, while in coking there is an actual delay of coke formation. Wiehe's (1993, 1997) phase separation model is a semi-mechanistic kinetic model mainly focused on describing coke formation. He proposed that coke formation was triggered by a phase separation of asphaltene cores from maltenes when the solubility limit of the asphaltene cores was exceeded. The induction period is thus the time it takes the concentration of the asphaltene core to reach the solubility limit of the maltenes. This model, as it appears in the publication, was based on coking at one temperature only (400 °C), and no attempt was made to obtain Arrhenius parameters. The objective of this model was mainly to verify the solubility-limit phase separation hypothesis and the emphasis was not on the kinetics *per se*. An advantage of Wiehe's model is that it has the potential to predict the induction time if the solubility behavior at coking conditions can be accurately predicted from known thermodynamic data. At present, however, the solubility limit S_L and the stoichiometric coefficients in his model can only be obtained by fitting the experimental data. Moreover, the solubility limit is dependent on temperature; thus at each temperature a different solubility limit must be obtained, again, by fitting the experimental data. This essentially reduces Wiehe's model to an empirical model. The functionality of the model, however, gives an excellent fit to experimental data.

Model I. Considering the success of Wiehe's (1993) approach of modeling the induction period and the potential advantage of predicting model parameters based on thermodynamic data, his approach was used in this study but his model was modified for the experimental conditions in this study and to include modeling of QI formation.

$$M^{+} \xrightarrow{k_M} aA^{*} + (1 - a)G \tag{3.2}$$

$$A^{+} \xrightarrow{k_A} mA^{*} + nM^{*} + (1 - m - n)G \tag{3.3}$$

$$A = A^{+} + A^{*} \tag{3.4}$$

$$M = M^{+} + M^{*} \tag{3.5}$$

Induction period ends when

$$A^{*} \geq S_L \cdot M \tag{3.6}$$

Thereafter

$$C = A^{*} - S_L \cdot M \tag{3.7}$$

$$QS = C - QI \tag{3.8}$$

$$\frac{dQI}{dt} = \frac{k_1 QS}{1 + k_2 QS} \tag{3.9}$$

where M^{+} = the reactant maltenes; A^{*} = asphaltene cores; G = gas yield; A^{+} = reactant asphaltenes; A = asphaltenes yield; M^{*} = product maltenes; M = maltenes yield; C = overall coke yield, QS = the yield of quinoline soluble coke; QI = the yield of quinoline insoluble coke; S_L = solubility limit; and a, m, and n are stoichiometric coefficients.

Model II. An alternative approach to model the induction period is to directly introduce an empirical model parameter for the induction time, τ, which can be determined by fitting the experimental data.

Five pseudo-components, asphaltenes (A), maltenes (M), gases (G), QS and QI were selected for this model. Under the experimental conditions, the gases were end products and could not act as reactants to form other pseudo-components. Asphaltenes could crack to produce gases, maltenes, and coke. Maltenes could react to form asphaltenes, gases and coke. The formation of coke from maltenes was assumed to go through asphaltenes as a transition. First order is assumed for these reactions. Second order reactions and additional reaction pathways including QS → gases, QI → gases, asphaltenes → QI were also tested, but the resultant model did not yield an improvement in fitting, and was therefore rejected. The final selection of reaction pathways in Figure 3.1 was a result of compromise between simplicity, reliability and prediction accuracy.

During coke induction period:

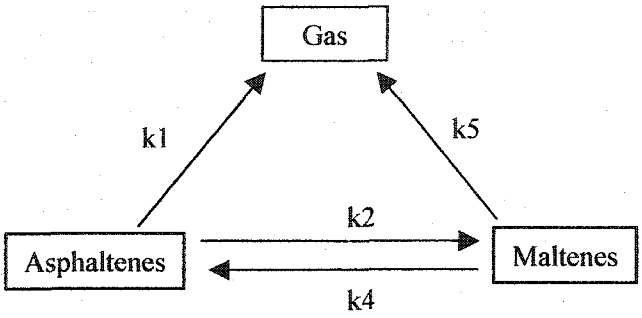
$$\frac{dA}{dt} = -(k_1 + k_2)A + k_4 \cdot M \tag{3.10}$$

$$\frac{dM}{dt} = k_2 \cdot A - (k_4 + k_5)M \tag{3.11}$$

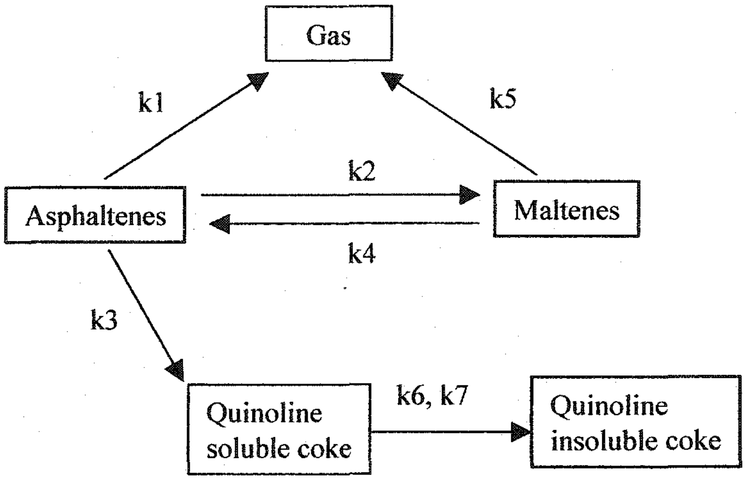
$$\frac{dG}{dt} = k_1 \cdot A + k_5 \cdot M \tag{3.12}$$

$$\frac{dQS}{dt} = 0 \tag{3.13}$$

$$\frac{dQI}{dt} = 0 \tag{3.14}$$



(a) The reaction pathway of coking during coke induction period



(b) The reaction pathway of coking after coke induction period

Figure 3.1 The reaction pathways of coking of Athabasca vacuum residue.

Induction period ends when $t > \tau$. Thereafter,

$$\frac{dA}{dt} = -(k_1 + k_2 + k_3)A + k_4 \cdot M \tag{3.15}$$

$$\frac{dM}{dt} = k_2 \cdot A - (k_4 + k_5)M \tag{3.16}$$

$$\frac{dG}{dt} = k_1 \cdot A + k_5 \cdot M \tag{3.17}$$

$$\frac{dQS}{dt} = k_3 \cdot A \tag{3.18}$$

$$\frac{dQI}{dt} = \frac{k_6 QS}{1 + k_7 QS} \tag{3.19}$$

$$C = QS + QI \tag{3.20}$$

where A = asphaltenes, M = maltenes, G = gases, QS = quinoline soluble coke, QI quinoline insoluble coke, C = total coke.

A Matlab™ program was written to calculate the model parameters for both model I and model II described above. Runge-Kutta method of the 4th order was used to solve the differential equations numerically. The model parameters were computed by using a Simplex optimization method to minimize Eq 3.21 (Neurock *et al.*, 1991):

$$\chi^2 = \sum_{i=1}^{n} [(YE_i - YM(\vec{x})_i / \sigma_i]^2 \tag{3.21}$$

where χ is the overall deviation of the model calculation from the experimental data, n is the number of experimental data points, YE_i is the i-th experimental data point, $YM(\vec{x})_i$

is the calculated value using the model at the i-th experimental point, $\vec{x}$ is the vector of the model parameters, and σ_i are the standard deviation of the i-th experimental point.

3.3 Experimental

3.3.1 Materials. The properties of Athabasca bitumen, vacuum residue, gas oil, and endcut (all provided by Syncrude Canada, Ltd.) are listed in Table 3.1. The endcut contains 88.5% asphaltenes and is the heaviest fraction from extraction of Athabasca vacuum residue with supercritical pentane and represents approximately 42 wt% of the residue (Chung *et al.*, 1998).

Table 3.1 Properties of Feeds Used for Coking Reaction

Property	Vacuum Residue	Bitumen	Gas Oil	Endcut
Toluene insoluble, wt%	1.8	1.1	0.025	4.9
Asphaltenes, wt%	31	15	0.6	88.4
MCR, wt%	27.8	14	0.10	48.9
Average Molecular Weight	1191	544	-	4662
Aromatic C, %	38.7	31.6	14.9	49.0
Density, g/cm^3 @15.6 °C	1.0868 [a]	1.016	0.9208	1.0887
Boiling range, °C	524+	IBP-524+	275-540	-
S, wt%	5.72	4.65	0.1	6.51
N, ppm	7206	4300	460	10500
Total carbon, wt%	81.59	85.48	87.5	78.48
Total hydrogen, wt%	9.62	11.02	12.3	8.00

[a] Density at 20 °C

The toluene insoluble solids in bitumen and vacuum residue were removed by dissolving the bitumen and vacuum residue in 40 parts of toluene followed by filtration with a 0.22 μm Millipore™ membrane and evaporation of the solvent. The same method could not be used to remove the toluene insoluble solids from the endcut due to plugging of the pores of the filter membrane. The plugging was mainly due to gum-like material, possibly formed by partial oxidation of the asphaltenes during storage of the endcut when the asphaltenes, which are porous solids at ambient conditions, contacted oxygen in the air (Speight and Moschopedis, 1981). Therefore, centrifugation was used instead of filtration to remove most of the toluene insoluble solids from endcut. The endcut was dissolved in 40 parts of toluene at 70 °C for 2 hours. The hot solution was then centrifuged at 3100 rpm for 1 hour, followed by evaporation of the toluene from the supernatant to remove most of the toluene insoluble solids from the endcut. The "solid-free" endcut was then mixed with the gas oil using sonication for 15 minutes to give an apparently homogeneous mixture with an endcut concentration of 10 wt%. This mixture of gas oil and endcut was used as feed.

3.3.2 Coking Reactions. Coking reactions were carried out in a 15 ml autoclave batch reactor made from stainless-steel Swagelok™ tubing and fittings. For each experiment, the reactor was loaded with approximately 3 g of feed, pressure tested at 20 MPa, purged of oxygen with nitrogen at 20 MPa three times, and closed at 1 atm nitrogen pressure at room temperature to provide an inert reaction atmosphere. The reactor was then immersed in a fluidized sand bath that was preheated to the reaction temperature. The reactor was agitated at 1 Hz during the reaction to ensure temperature uniformity.

A test was performed to check the actual reaction temperature. A thermocouple was inserted directly into the reactor. The tip of the thermocouple was in direct contact with the vacuum residue feed but not in direct contact with the reactor bottom. The reactor was then sealed and immersed in the preheated sandbath and agitated at 1 Hz. The temperature was recorded versus the time elapsed after the reactor was immersed in the sandbath (see Figure 3.2). Reaction temperature was achieved within 5 minutes of immersion and was maintained within ±1°C of the reaction temperature by a temperature controller. After the desired reaction time had elapsed, the reactor was quenched in cold water to terminate the reaction.

3.3.3 Separation of Products. After the reactor was quenched at the end of the reaction, the gas was vented. The difference in mass before and after venting the gas was taken as the mass of gaseous product. The liquid and solid products were recovered by washing with 120 ml of toluene. The mixture was sonicated for 30 minutes to maximize extraction. The coke (toluene insoluble solid product) was separated from the liquid by filtering the mixture using a 0.22 micron Millipore™ membrane filter. The resultant filter cake was washed with toluene several times until the toluene passed through the filter without color. The filter cake was then vacuum dried at 70 °C for 2 hours. Any coke that was still attached to the reactor walls after the toluene extraction was removed by scrubbing the inside wall. The amount of the attached coke was included in the coke yield calculation. The toluene in the filtrate was removed with a rotary evaporator. This concentrated filtrate was then mixed with 120 ml of heptane to precipitate the asphaltenes. The mixture was sonicated for 5 minutes and then filtered with a 0.22

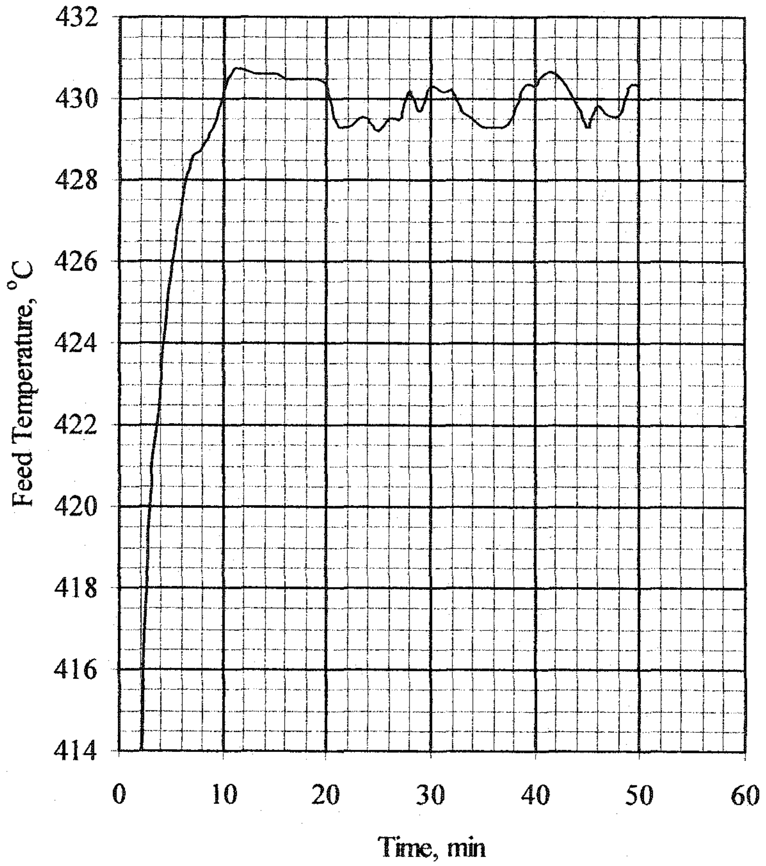


Figure 3.2 Temperature response of the reactant at setpoint of 430°C.

micron Millipore™ membrane. The filter cake was washed with heptane three times and then vacuum dried at 70 °C for 2 hours to determine the concentration of asphaltenes.

3.3.4 Aging of Isolated Coke. Approximately 100 mg of coke was loaded into a 2 mL glass vial. The vial was then inserted into the micro-reactor described earlier. Similar to coking reactions, the reactor was purged of oxygen with nitrogen three times, and closed at 1 atm nitrogen pressure at room temperature. The reactor was then immersed in the fluidized sand bath that was preheated to the desired temperature. Unlike the coking reactions, the reactor was not agitated for the aging experiments. After a predetermined time elapsed, the reactor was quenched in cold water to terminate the aging experiment.

3.3.5 Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray (EDX) Analysis. Approximately 2 mg of coke was mixed with 5 ml of ethanol by sonicating for 5 minutes. One drop of the dispersion was pipetted onto a SEM sample holder. The ethanol was then evaporated in the air, leaving the coke particles well distributed on the sample holder. The sample was sputter-coated with gold when only SEM was needed. The sample was coated with carbon when EDX was also required. The coated sample was then analyzed using a Hitachi S-2700 SEM with a Princeton Gamma-Tech EDX.

3.3.6 Quinoline Extraction. Coke samples were separated into quinoline insoluble (QI) and quinoline soluble (QS) fractions. Approximately 100 mg of coke was mixed with 8 g of quinoline in a sonication bath for 30 minutes. The mixture was then filtered through a Whatman Glass Microfibre filter. The filter cake was washed with quinoline three times followed by rinsing with toluene to remove the residual quinoline.

The filter cake containing the quinoline insoluble fraction was then dried in a vacuum oven at 70 ^{o}C for 2 hours to remove any residual toluene. The proportion of the mass of the filter cake to the coke sample prior to quinoline extraction was used to calculate the overall yield of QS and QI fractions of the coke. For each coke sample, four or five repeats of quinoline extractions were conducted in order to give more accurate QI data.

3.3.7 Coke Petrography. Coke and the QI fraction were mounted in epoxy resin and polished according to standard grinding and polishing procedures for petrography (Craig and Vaughan, 1994). The polished surface was imaged using an optical microscope with 650× magnification under cross-polarized light to examine the anisotropy of the coke. A Lamda plate was used to convert the degree of birefringence into different colors for better contrast (Wahlstrom, 1979).

3.4 Results and Discussions

3.4.1 Formation of Liquid Phase Coke. Under SEM, the majority of the toluene insoluble coke collected from the coking of Athabasca bitumen and vacuum residue at 430 ^{o}C and 40 min appeared to be agglomerated particles of deformed viscous liquid droplets (Figure 3.3). Separate spheres were also observed, and in some areas of the coke sample the separate spheres were even predominant (Figure 3.4). The coke collected from the coking of a mixture of 10wt% of endcut in gas oil at 15 minutes showed similar morphology, but had higher percentage of separate spheres (Figure 3.5), probably due to the lower probability of coalescence in this dilute system. The average diameter of the spheres was approximately 1μm, with a distribution mainly in the 0.5~5 μm range. Spheres that were relatively smaller tended to grow independently, while as the particles

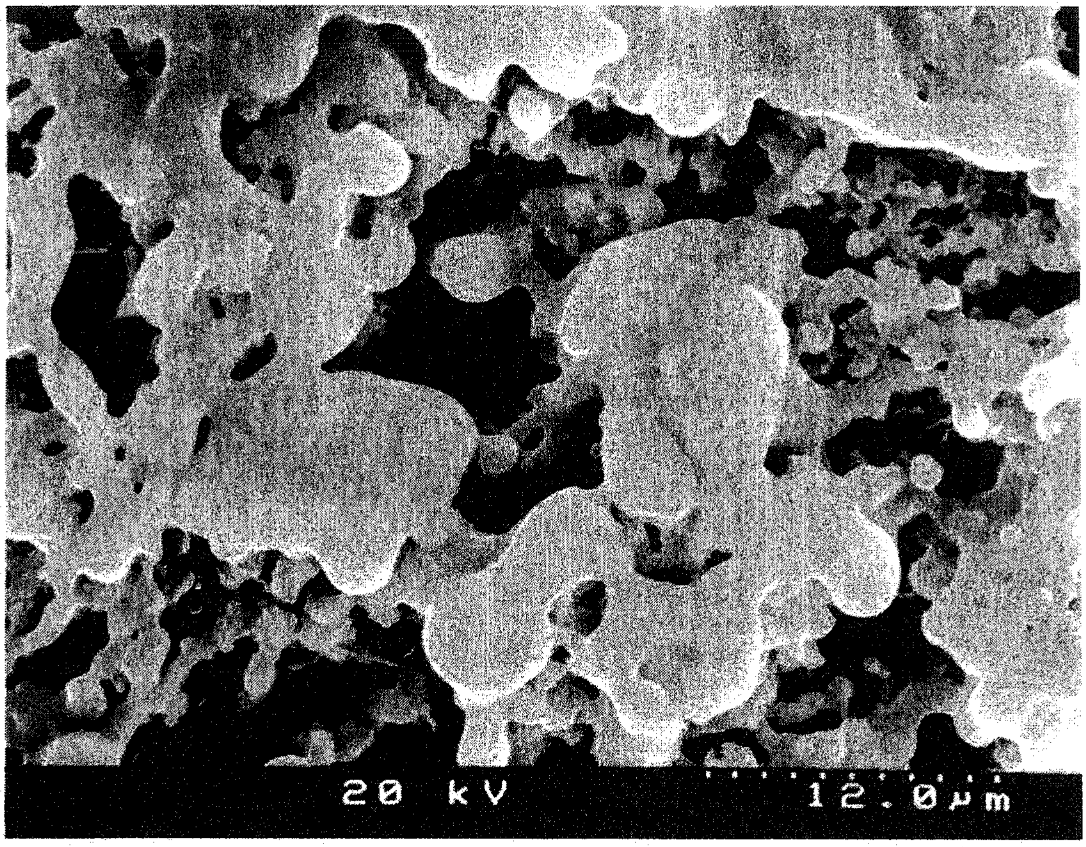


Figure 3.3 SEM micrograph of flowing features of coke collected from the coking of bitumen at 430°C and 40 min.

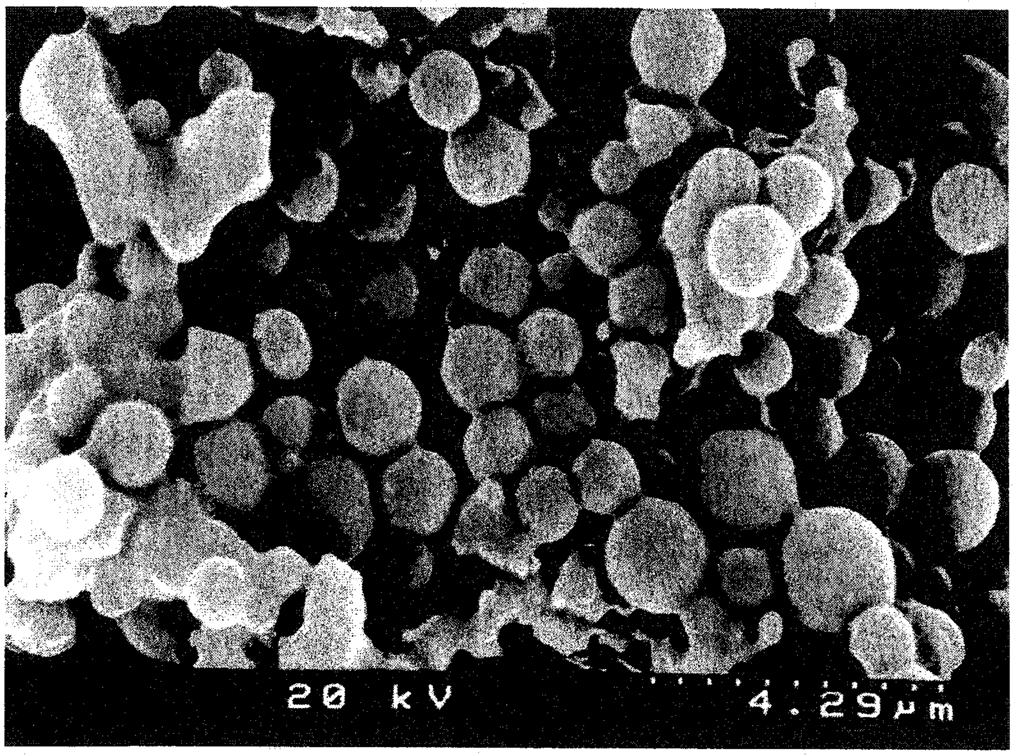


Figure 3.4 SEM micrograph of coke collected from the coking of bitumen at 430°C and 40 min.

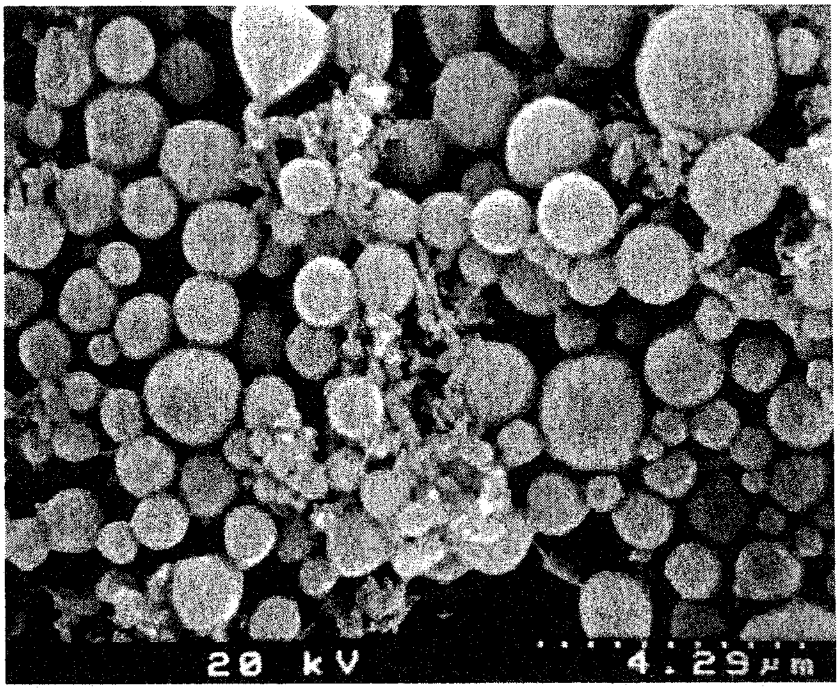


Figure 3.5 SEM micrograph of coke microspheres from the coking of endcut/gas oil mixture at 430°C and 15 min.

grew in size, the likelihood of coalescence increased. The morphology of the coke had evident flowing features with smooth and rounded surfaces (see Figure 3.3). The spheres, agglomerated spheres and especially flowing features are compelling evidence that at some stage of coking the coke was a liquid. Analogous to emulsion systems, droplets of a dispersed liquid phase in a liquid media tend to be spherical to minimize the interfacial free energy. When the droplets coalesce, the interfacial tension will act as the driving force for the droplets to merge and regain spherical morphology, while the viscosity will act as the resistance to the flow during the merger. As a result a relaxation time is required for the coalescing droplets to transform into a single sphere. The rapid temperature drop upon quenching of the coking reaction in cold water must have been faster than the relaxation time and thus froze the deformed shapes.

As shown in Figure 3.3, Figure 3.4 and Figure 3.5, the surfaces of the coke spheres and agglomerates were very smooth. Although toluene extraction with sonication was used to separate the coke, there was no sign of etching on the coke surface. This is strong evidence that at reaction conditions the coke spheres actually existed as a separate liquid phase with a well-defined phase boundary — all materials inside this boundary were toluene insoluble materials while the surrounding materials were all soluble in toluene. When phase separation first takes place, it can be argued that the new phase is asphaltenes or asphaltene cores separated from the bulk phase due to solubility limit (Wiehe, 1993). It is also likely that the new phase actually is coke (materials that are insoluble in toluene at room temperature) from the very beginning of the formation of this new phase. If the new phase is initially asphaltene cores, the reaction of the asphaltene cores to coke must be almost instantaneous, considering temperature drop was so rapid during the quenching in cold water. Otherwise there should have been etching on the surface of some of the coke spheres or agglomerates. This is consistent with Wiehe (1997)'s model, where he assigned an infinite rate constant to the reaction of asphaltene cores to coke.

3.4.2 Formation of Mesophase Coke. The coke produced from Athabasca bitumen at 430 °C and 40 min, as shown in Figures 3.3 and 3.4, was found to be mostly soluble in quinoline, with only 9.8wt% of the coke being QI. Since mesophase coke has been reported to be insoluble in quinoline, the coke produced at these conditions was probably not mesophase. Figure 3.6 shows the temporal variations of coke yield and QI as a fraction of total coke. The coke produced at shorter reaction times was mainly soluble in quinoline. As the reaction time increased, the QI, as a fraction of total coke, also increased, roughly in a linear manner. Under cross-polarized light, the QI of the coke produced from coking of bitumen at 80 minutes was almost completely anisotropic, as shown in Figure 3.7. (The several isotropic "chunks" at the bottom edge of Figure 3.7 were probably due to quinoline soluble fraction that was not dissolved during quinoline extraction and filtration). Coke from short coking reactions was almost completely isotropic, with only sporadically embedded anisotropic "spots", such as the coke produced from vacuum residue at 30 minute and 430 °C shown in Figure 3.8 (top). As the reaction time increased, more and larger anisotropic domains were observed. These anisotropic domains were often spherical, typical for mesophase, as shown in Figure 3.8 (bottom) for the coke produced from vacuum residue at 120 minutes and 430 °C. The increase in anisotropic coke was, at least qualitatively, consistent with the increase in percentage of QI in total coke. This indicates that at such temperatures, increasingly more

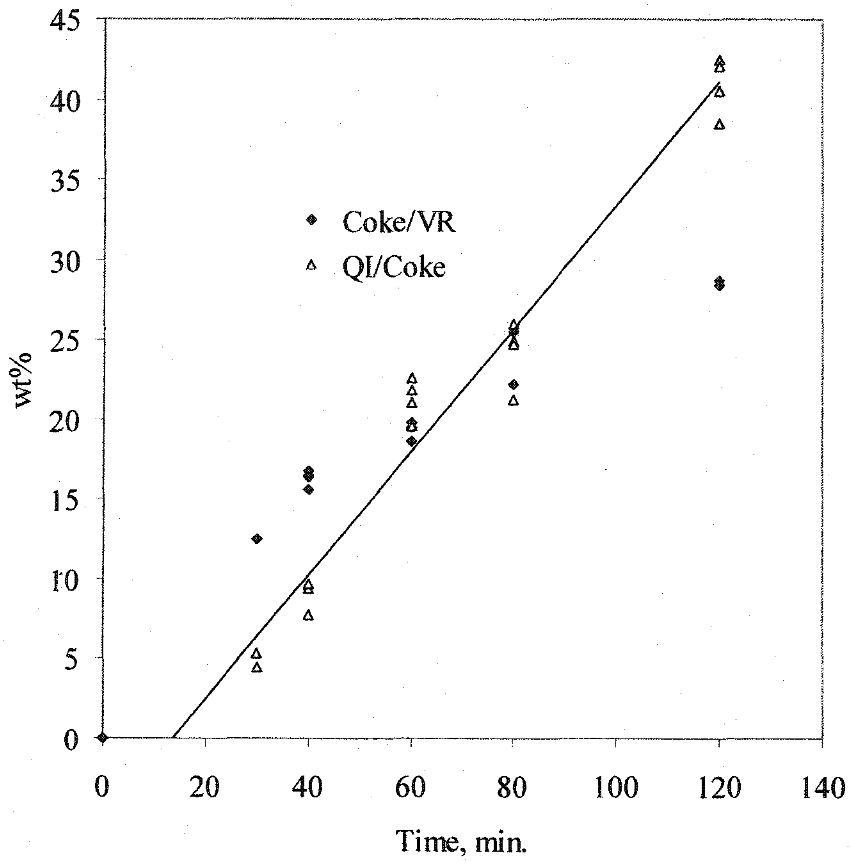


Figure 3.6 Temporal variation of coke and QI fraction of coke for coking of vacuum residue at 430°C. The straight line is the linear trendline for QI/Coke only.

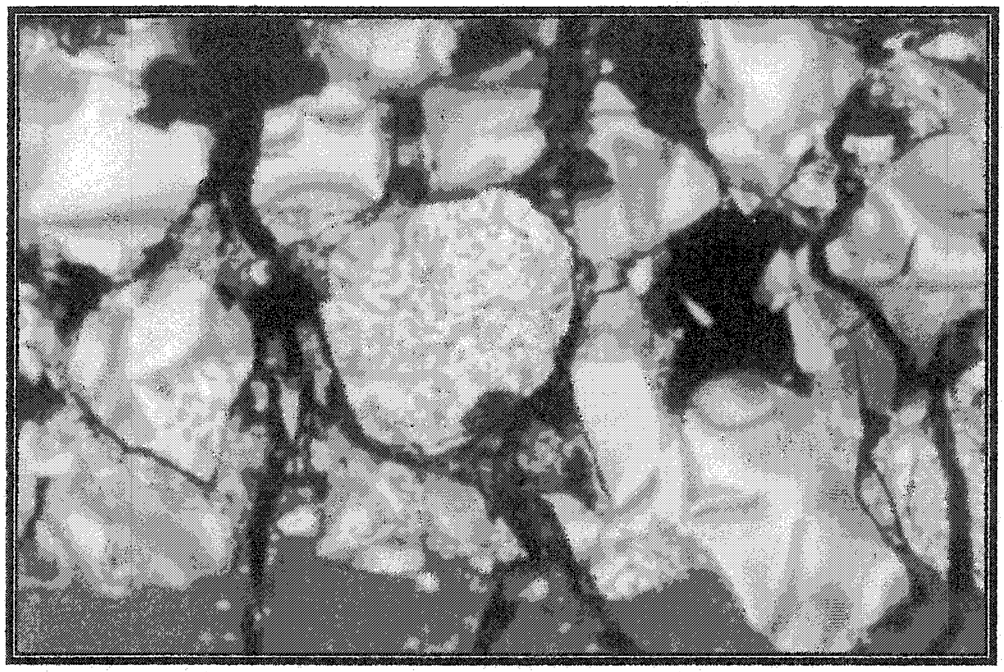
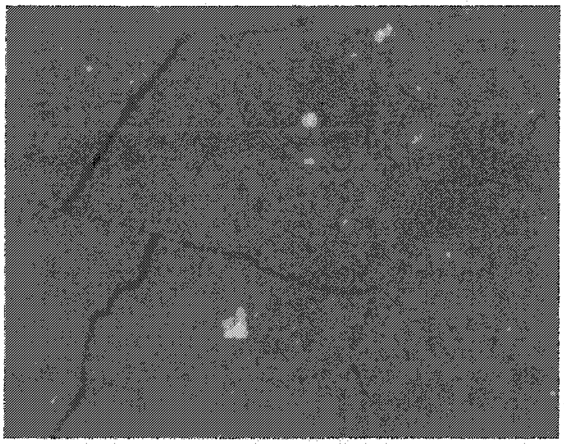
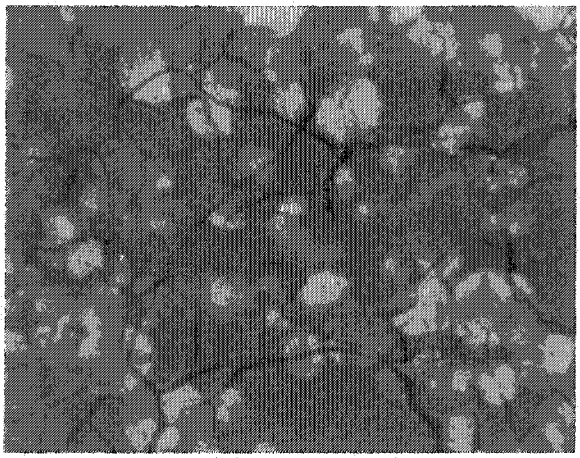


Figure 3.7 Micrograph of petrography of the quinoline insoluble (QI) fraction of coke. The QI was mainly mesophase which appeared anisotropic under cross polarized light



30min



120min

Figure 3.8 Petrography micrographs of coke from coking of vacuum residue at 430°C and 30 min (top) and 120 min (bottom).

mesophase coke was formed as coking time increased. Increasing reaction temperature from 430 °C to 450 °C and then to 475 °C at 40 minutes also increased QI and anisotropic coke formation.

3.4.3 Aging of Isolated Coke. The coke collected from coking of vacuum residue at 40 minutes and 430 °C was reheated (aged) to 430 °C to examine the phase behavior of isolated coke without interference from additional coke formation. After terminating the aging reaction by quenching in cold water, oil condensate was observed on the top portion of the wall of the vial, and the total weight loss of the solid coke was recorded as a measurement of the cracking reaction of the coke (see Figure 3.9). It was noted that the heat transfer to the coke was not very efficient. Especially for the 5-minute aging experiment, at the end of the aging reaction, even the sandbath temperature had just returned to the 430 °C setpoint. Therefore the temporal variation in weight loss should not be used as quantitative kinetic study. Nevertheless, it is evident, qualitatively, that the cracking of isolated coke was quickly approaching completion.

Aging also quickly transformed the mainly quinoline soluble coke into quinoline insoluble coke. The quinoline insoluble fraction increased from 9.8% to 55% after 5 minutes of aging process, and became completely insoluble in quinoline after 10 minutes of aging. If compared with the temporal variation of quinoline insoluble fraction and total coke (Figure 3.6) it is evident that the transformation from quinoline solubles to quinoline insolubles was much faster in isolated coke than if the coke was in the coke-forming media. In other words, the hydrogen rich reaction media inhibited the fast transformation of the quinoline soluble coke into QI. This is compelling evidence that there is a significant interaction between the spheres and the liquid medium during the reactions.

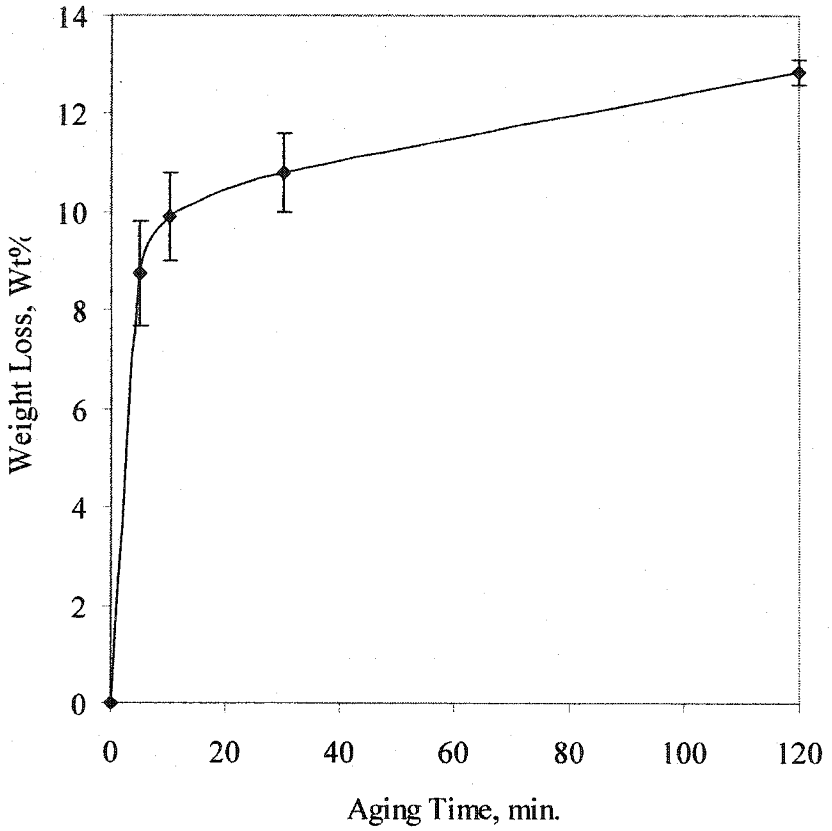
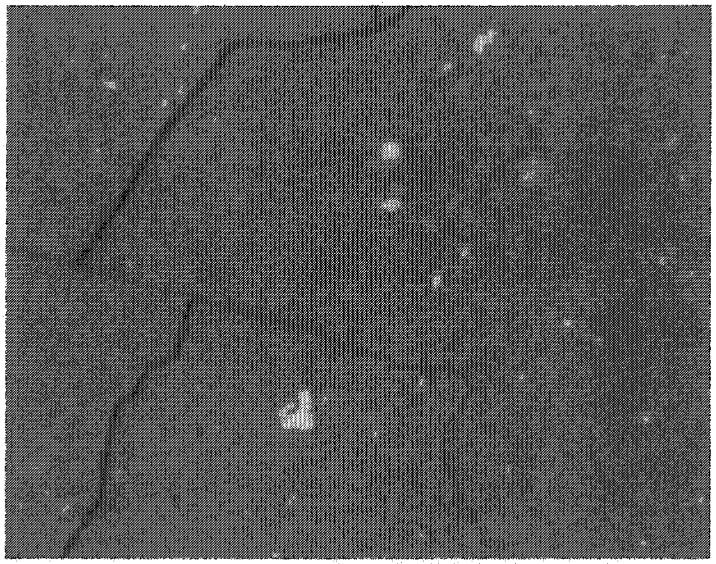


Figure 3.9 Further cracking of coke upon reheating to 430 °C as measured by the weight loss of the coke.

After aging, more and larger domains of anisotropic coke could be found that were not observed before aging, indicating that aging could partially transform isotropic coke into anisotropic coke. These anisotropic domains showed evident fusing behavior (see Figure 3.10), implying that the isolated coke could at least partly be softened and melted. This was further supported by SEM analysis of the coke after aging. After 120 minutes of aging at 430 ^{o}C, widespread holes were observed on the surface of the coke grains (see Figure 3.11), and macroscopically the coke became sponge-like porous solids. This morphology is much like the sponge coke produced from commercial delayed coker. These holes were presumably produced by gaseous cracking products escaping from the interior of the coke upon reheating. But the fact that the escaping gases left behind round holes rather than cracks indicated that isolated, cooled coke could return to high-viscosity fluid upon reheating. Thus, coke produced from coking at moderate severity behaves to some extent as a thermoplastic polymer which could be readily deformed upon heating to higher temperature.

3.4.4 Mechanism of Coke Formation. At ambient temperatures asphaltenes exist as micellar aggregates in bitumen or petroleum residues (Dickie and Yen 1967, Sheu *et al.*, 1992). Unlike in a true solution where the solute is dispersed at molecular level, micelles are aggregates of the molecules. Micellization differs from phase separation in that it can be described as a kinetic equilibrium between single solute molecules and the micellar species and it does not lead to infinite aggregation number (Anderson *et al.*, 1991). There has been experimental evidence that the micellar aggregates of asphaltenes dissociate when temperature is increased (Thiyagarajan *et al.* 1995; Overfield *et al.* 1989) as discussed in Chapter 2. At coking temperatures, the micellar asphaltenes may have



Before aging

After aging

Figure 3.10 Petrography micrographs of coke before and after aging experiment (reheating at 430 °C and 10 min).

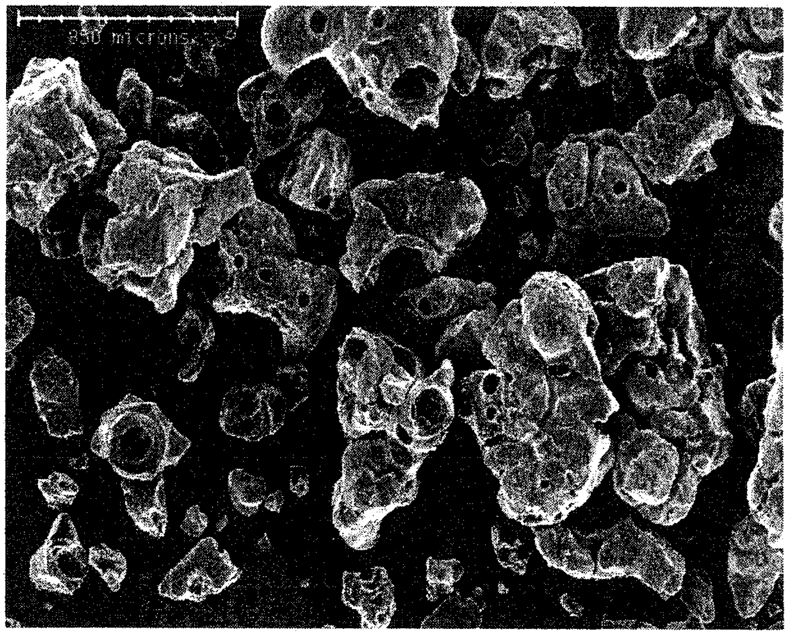


Figure 3.11 SEM micrograph of coke (from coking of vacuum residue at 430°C) after being reheated for 120 min at 430°C

dissociated to such an extent that they behave as solutes in a true solution. A true solution state is also implied by Wiehe (1993) in his phase separation hypothesis. At coking conditions, asphaltenes react to form asphaltene cores due to thermal cracking. The asphaltene cores remain dissolved in the maltenes until the concentration reaches the solubility limit (Wiehe, 1993). At that point the asphaltene cores phase separate to form a new phase. In the new phase, the asphaltene cores quickly react to form coke by molecular weight growth that can be characterized as oligomerization (Wiehe, 1993). In the early period of coke formation, the molecular weight of the coke is relatively low. Wiehe (1993) reported that the coke produced by coking of Cold Lake vacuum residue at 400 °C had a molecular weight (measured using o-dichlorobenzene vapor pressure osmometry at 130 °C) of about 4600 at 30 minutes and about 7500 at 60 minutes. The melting point of the coke having molecular weight of such order of magnitude is very likely to be below the coking temperature. Thus the coke behaves as a viscous liquid suspended in the bulk liquid phase as shown in Figure 3.3 to 3.5. The behavior of coke at such conditions resembles a thermoplastic polymer at a temperature above its melting point. The partial melting and deformation during reheating of isolated coke, as shown in Figure 3.11, again demonstrates the thermoplastic property of coke. This thermoplastic coke is not stable at coking temperature, and is simultaneously subject to polymerization and thermolysis reactions, which result in progressively growing molecular weight (Wiehe, 1993), increased degree of crosslinking, and progressively decreasing H/C ratio (Srinivasan and McKnight, 1994). As a result, the viscosity of the liquid coke will grow, along with its melting point, and the coke gradually becomes a solid.

At room temperature, the asphaltene micelles are believed to be aggregates of "stacks" of polycyclic aromatics. Each "stack" was formed by $\pi-\pi$ bonding of the polycyclic aromatic cores of about five asphaltenic molecules and then the stacks formed aggregates by hydrogen bonding or other dipole-dipole interaction (Dickie and Yen 1967). Discotic liquid crystals that have an aromatic core with aliphatic side chains also tend to display similar stacking behavior (Wiehe, 1994). Therefore, it is very likely that at the early stage of coke formation, the coke molecules are relatively flexible and also form stacks via $\pi-\pi$ bonding of the polycyclic aromatic cores. If these stacks are large enough they will become ordered domains discernable by physical devices such as optical microscope and will appear anisotropic, similar to nematic, discotic liquid crystals (mesophase). When there is still a high concentration of side chains and heteroatoms in the coke molecules, stacking of the aromatics is inhibited and the formation of large domains of ordered structures is reduced. As a result, the coke will appear isotropic even though local order exists. As coking progresses, the coke molecules gradually lose their sidechains, allowing for better stacking. Moderate coking conditions also provide the time and energy necessary for the polycyclic aromatic "sheets" to readjust and align. Therefore the fraction of mesophase in coke increased with coking reaction time. However, cracking also brings about loss of aliphatic bridges and higher crosslinking, both leading to increased molecular rigidity which hinders or prevents re-ordering of the polycyclic aromatic units. Therefore the transformation of isotropic coke to mesophase is dependent on the coking conditions. If the conditions are severe, the coke quickly becomes crosslinked. Crosslinking effectively "freezes" the relatively random structure of the polycyclic aromatic units, resulting in isotropic, amorphous solid. This is consistent with the conclusion, drawn by Abramski and Mackowsky in 1952, that slow but long periods of heating with compacting pressure tended to give more complete ordering than fast heating and moderate pressure (Brooks and Taylor, 1968). Gentle re-heating of isolated coke could also allow the ordering of coke molecules; therefore, re-heating could partially transform isotropic coke into anisotropic coke as shown in Figure 3.10. However, due to the lack of a media to terminate the free radicals left by side-chain cracking, the coke is quickly crosslinked. Consequently re-heating is less effective in transforming isotropic coke into anisotropic coke than prolonged heating in the presence of lighter, hydrogen-rich media which can terminate some of the free radicals and inhibit crosslinking. This is also consistent with the usual observations that higher pressure of closed coking system promotes mesophase formation (Brooks and Taylor, 1968), since increased pressure would keep more lighter, hydrogen-rich molecules in the bulk liquid phase which is in good contact with the coke.

The mechanism of coke formation can be schematically summarized as in Figure 3.12. At ambient temperatures, bitumen or petroleum residues are dispersions of micellar asphaltenes aggregates. These aggregates dissociate at elevated temperatures and become truly dissolved at coking temperatures. At coking conditions, the asphaltenes gradually lose some of their side chains to form asphaltene cores due to thermal cracking. These asphaltene cores remain dissolved in the maltenes media, until the concentration exceeds the solubility limit. At this point the asphaltene cores phase separate to form a second liquid phase where the asphaltene cores combine with one another to form coke. The coke was initially of low molecular weight and low degree of crosslinking, and thus is a liquid under coking conditions. The coke formed at this stage is also isotropic under

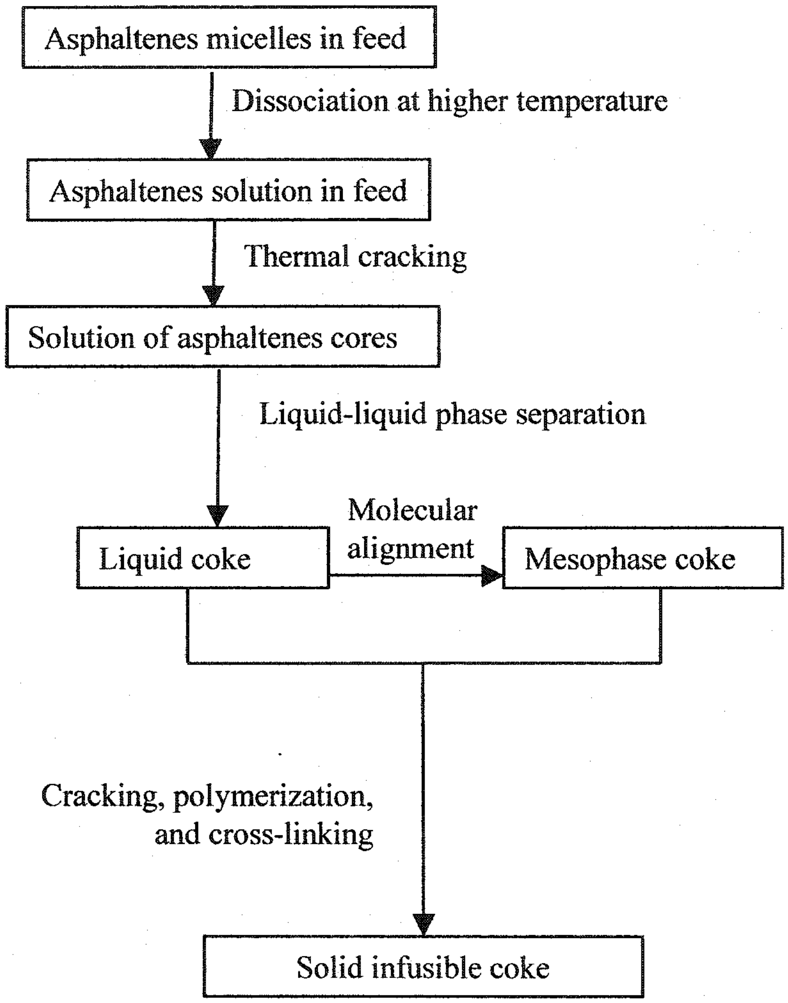


Figure 3.12 Proposed mechanism of coke formation

cross-polarized light microscopy and soluble in quinoline at room temperature and thus is not mesophase. Some of the coke molecules in this liquid coke are still flexible, and could form mesophase by self-assembling into stacks via π-π bonding between the polycyclic aromatic "unit sheets". Other coke molecules in the liquid isotropic coke gradually became rigid due to increased crosslinking before they can self-assemble into stacks of sufficient size, and thus gradually transform into isotropic solid coke. Crosslinking also renders coke insoluble in strong solvents such as quinoline. Mesophase further undergoes crosslinking and molecular growth to form anisotropic solids. Eventually coke becomes a fused mixture composed of both isotropic and anisotropic coke, with isotropic coke usually forming the continuous phase with embedded anisotropic domains which vary in amount depending on the coking condition.

3.4.5 Models of Coking Kinetics. As discussed above, the transformation from QS to QI involves phase transition, which has zero order kinetics, and cracking and cross-linking, which have kinetics of order higher than zero. As shown in Figures 3.13 and 3.14, zero order behavior is evident in a wide range of QI formation as the plot of QI yield *vs.* time falls on a straight line. The data deviates from zero-order to higher order only at short reaction times and very long reaction times, both when QS concentration is low. This is consistent with the hypothesis that the majority of QS must go through the phase transition (zero order) to form QI.

The fitting of model (I) and model (II) with the experimental data is illustrated from Figure 3.15 to 3.18. Residual variance s^2, defined in Eq. (3.22), is used to measure the goodness of the fit:

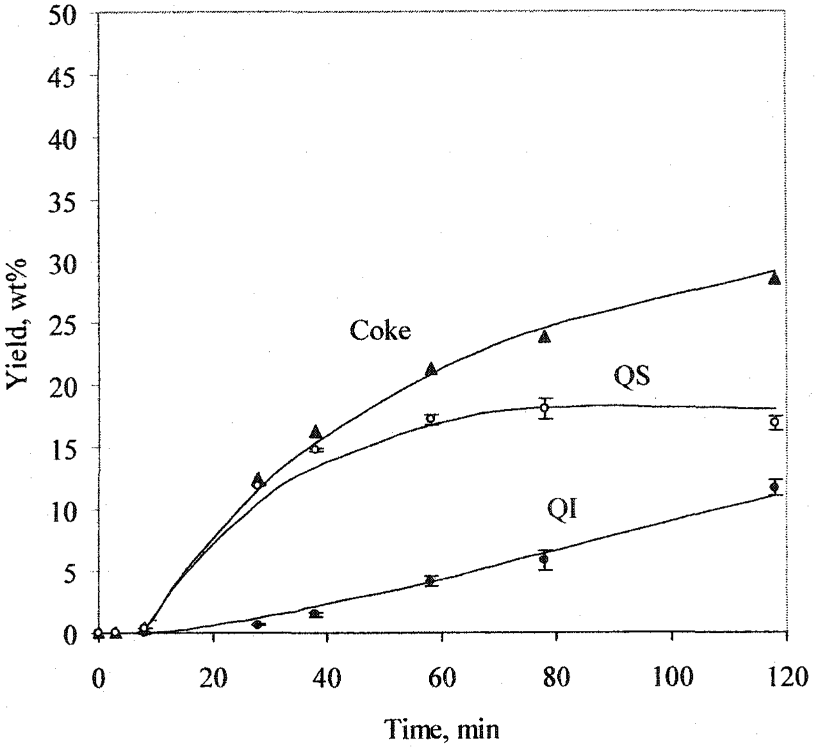


Figure 3.13 Temporal variation of quinoline soluble coke (QS), quinoline insoluble Coke (QI) and total coke at 430°C. Symbol = experimental; curve=calculated using model (II).

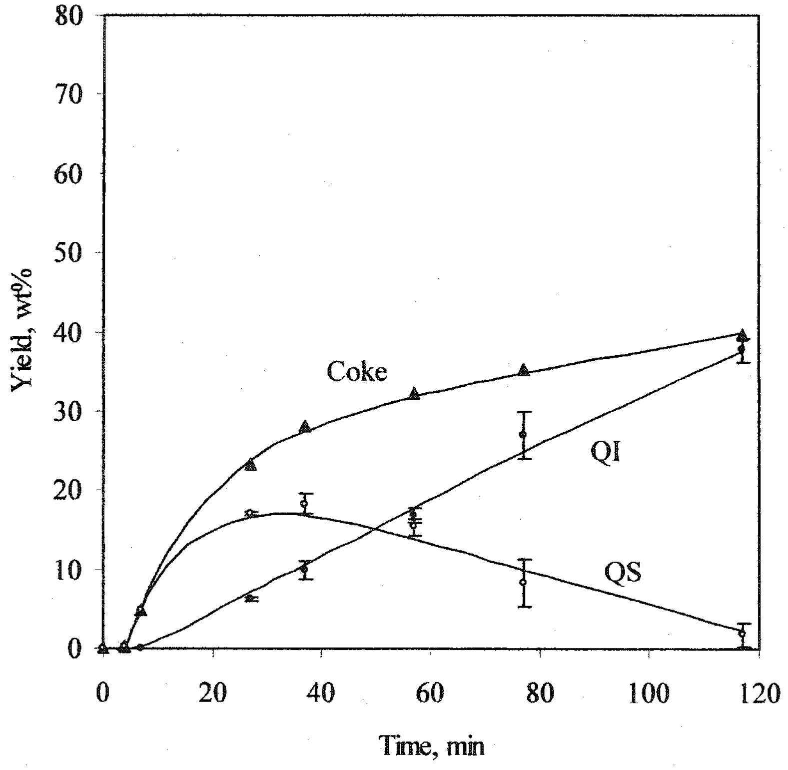


Figure 3.14 Temporal variation of coke, QS and QI at 450 °C. Symbol=experimental; curve=calculated using model (II).

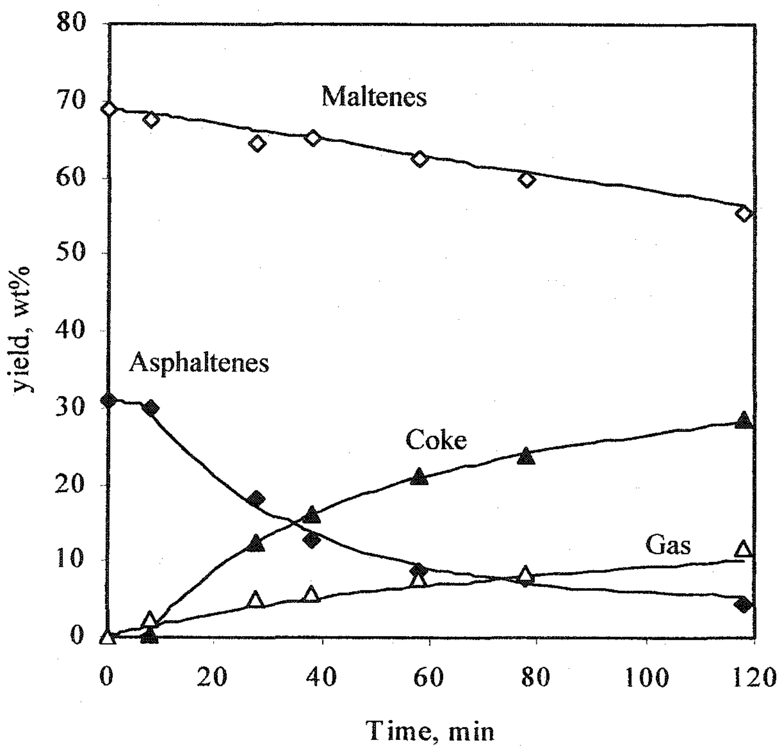


Figure 3.15 Temporal variation of asphaltenes, gas and coke at 430 °C. Symbols = experimental; curves = calculated using model (I).

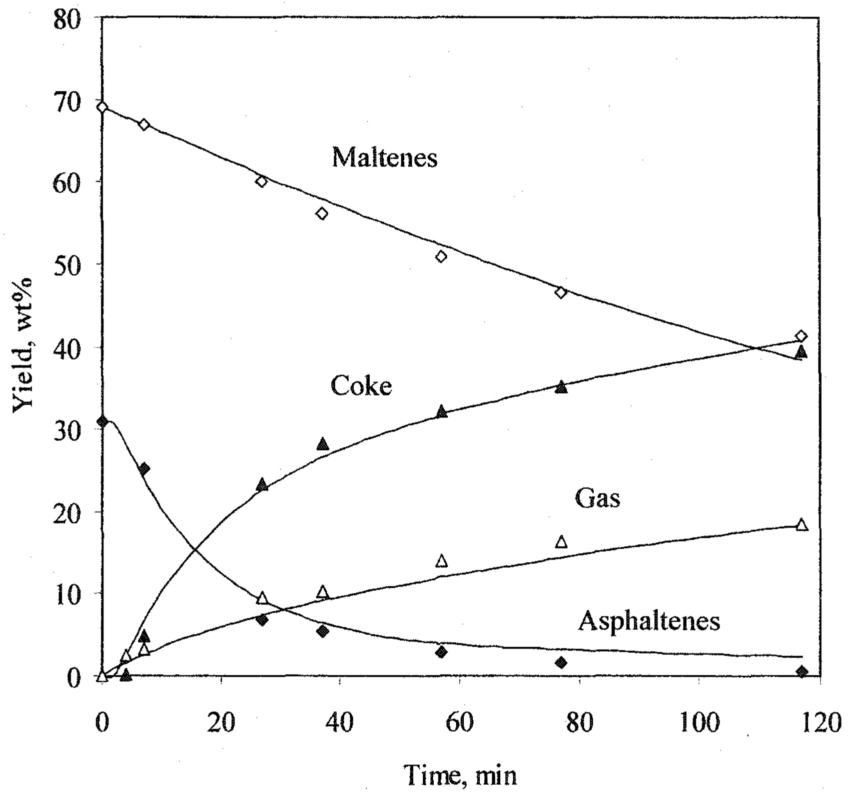


Figure 3.16 Temporal variation of asphaltenes, gas, and coke at 450 °C. Symbols = experimental; curves = calculated using model I.

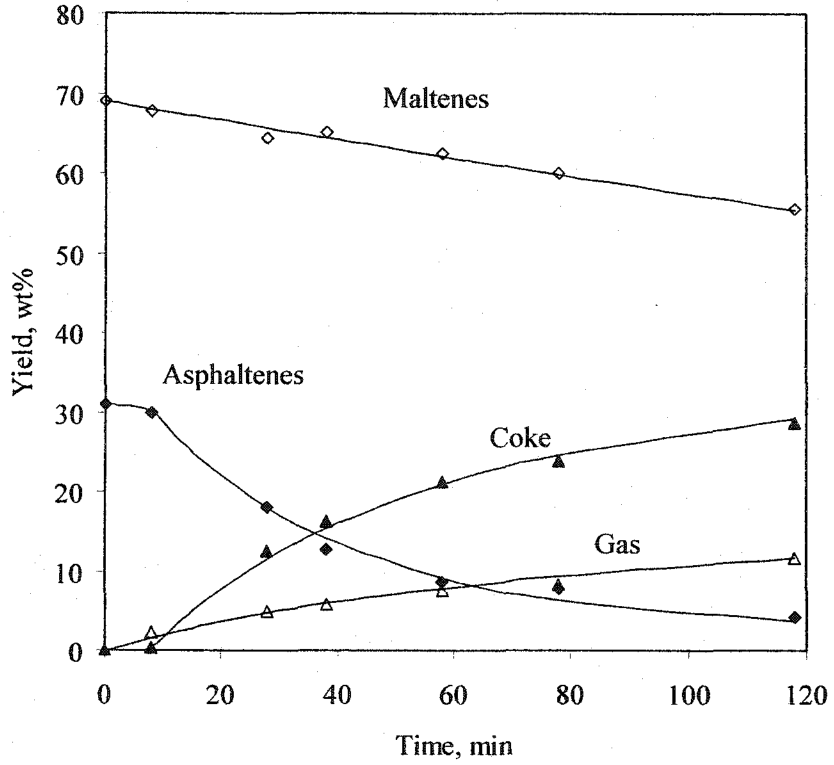


Figure 3.17 Temporal variation of asphaltenes, gas and coke at 430 °C. Symbols = experimental; curves = calculated using model (II)

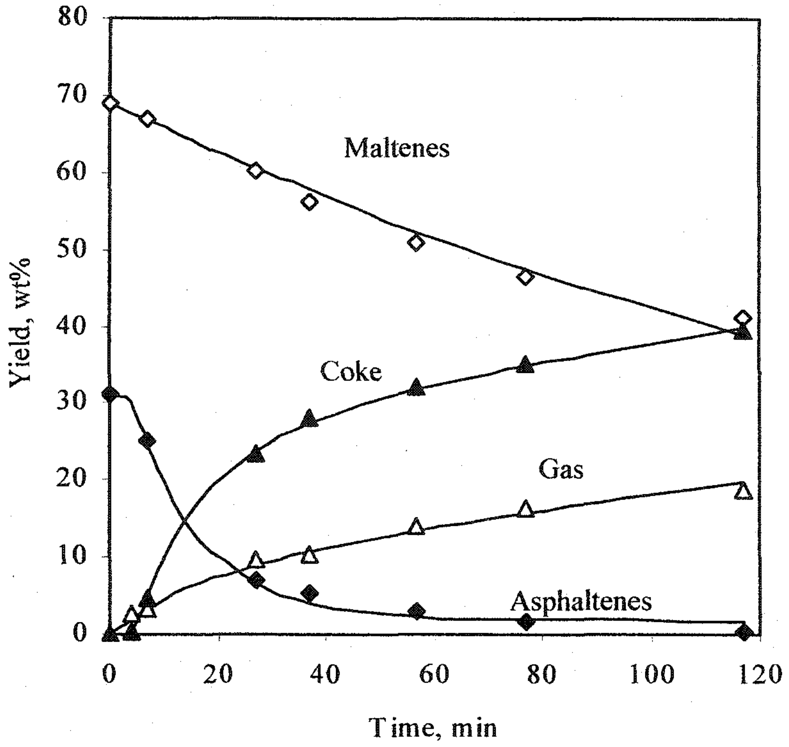


Figure 3.18 Temporal variation of asphaltenes, gas and coke at 450 °C. Symbols = experimental; curves = calculated using model (II)

$$s^2 = \frac{1}{n}\sum_{i=1}^{n}[(YE_i - YM(\vec{x})_i]^2 \tag{3.22}$$

where s^2 is the residual variance; n is the total number of data points; YE_i is the experimental value at point i; and $YM(\vec{x})_i$ is the calculated value using the model at point i. The residual variances for model I at 430 °C and 450 °C are 1.14 $(wt\%)^2$ and 5.03 $(wt\%)^2$, respectively, while the residual variances for model II at 430 °C and 450 °C are 0.437 $(wt\%)^2$ and 0.623 $(wt\%)^2$, respectively. Therefore model (II) fits the experimental data better.

The parameters for model I is listed in Table 3.2. The solubility parameter S_L decreased from 0.0854 at 430 °C to 0.0624 at 450 °C. This is probably because at higher temperatures the maltenes (including dissolved hydrocarbon gases) held in the reactor

Table 3.2 Calculated parameters for model (I). (E_A and E_M are activation energies for thermolysis of asphaltenes and maltenes, respectively; k_{0A} and k_{0M} are the frequency factors for thermolysis of asphaltenes and maltenes, respectively)

Parameter	Value	Parameter	Value
a	0.547	E_A, kJ/mol	131.3
m	0.83	E_M, kJ/mol	218.5
n	0.04	k_{0A}, min^{-1}	2.00×10^8
S_L (430 °C)	0.0854	k_{0M}, min^{-1}	3.23×10^{13}
S_L (450 °C)	0.0624		

were richer in low boiling aliphatic hydrocarbons which are poor solvents for asphaltene cores. This can also explain the much lower values of S_L obtained in this study compared with Wiehe (1993)'s value of 0.61 at 400 °C for the coking of Cold Lake bitumen with open reactors. With the reactors open to the atmosphere, the lighter hydrocarbon products would escape from the reactor, leaving only heavier, probably more aromatic hydrocarbons (good solvents for asphaltene cores) in the reactor. The activation energy and frequency factors for model (II) are listed in Table 3.3. k_6 and k_7 were calculated to be 0.036 and 0.29 at 430 °C, and 0.33 and 0.86 at 450 °C. Therefore, in the majority of the reaction time region the overall order of reaction is far from first order as was assumed in model of Takatsuka *et al.* (1989).

Table 3.3 Parameters for model (II)

Reaction No. i	Reaction	Activation energy E_i, kJ/mol	Frequency factor k_{0i}, min^{-1}
1	$A \rightarrow G$	187.3	4.173×10^{11}
2	$A \rightarrow M$	171.5	1.975×10^{9}
3	$A \rightarrow QS$	226.5	1.615×10^{15}
4	$M \rightarrow A$	181.5	4.104×10^{10}
5	$M \rightarrow G$	232.2	1.067×10^{14}
6	$QS \rightarrow QI$	470.7	3.317×10^{33}
7	$QS \rightarrow QI$	227.3	2.260×10^{16} (dimensionless)
τ (430 °C)	7.3 min	τ (450 °C)	4.1 min

3.5 Conclusions

SEM characterization showed that coke produced from bitumen, vacuum residue, and endcut/gas oil mixtures under coking conditions of moderate severity were composed of agglomerated microspheres and particles that resembled deformed viscous liquid droplets. The agglomerates showed evident flowing features. The surface of the coke was very smooth and no sign of etching was observed although the coke had gone through toluene extraction. These phenomena are compelling evidence that coke under coking conditions of moderate severity was in a second liquid phase which had a well defined phase boundary. Coke produced under these conditions behaved like a thermoplastic polymer after isolation, as indicated by the holes on the surface of the coke after reheating due to the release of gaseous cracking products. The coke produced from short coking reactions (30 and 40 minutes) was mostly soluble in quinoline and was isotropic, indicating mesophase formation was insignificant at such conditions. As the reaction time increased, mesophase formation significantly increased, as indicated by increased formation of QI fraction and more anisotropic spheres. Reheating of the coke caused further thermal cracking and weight loss that quickly approached completion. Reheating also slightly transformed the isotropic coke into anisotropic coke, and more rapidly transformed quinoline soluble coke into quinoline insoluble coke.

Coking kinetics of solid-free Athabasca vacuum residue was modeled using (I) a slightly modified Wiehe (1993) model, and (II) a five-pseudocomponent lumped kinetic model. In both models, the formation of quinoline insoluble coke (QI) from quinoline soluble coke (QS) was described as a reaction with shifting orders from first order at low QS concentration to zero order at higher QS concentration. In model (I), as in the original

Wiehe's (1993) model, the induction period was determined by a solubility parameter. In model II the induction period was modeled by directly introducing a time delay for the coke formation step as a model parameter. Both models fitted the experimental data fairly well with model (II) slightly better than model (I).

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Chapter 4

Effect of Fine Solids on Coking of Athabasca Bitumen and Vacuum Residue

4.1 Introduction

Currently about two thirds of Athabasca oil sands bitumen is produced by surface mining and water-based extraction, with the rest produced by *in-situ* steam injection technologies (Precht and Rokosh, 1998). The Athabasca bitumen produced by surface mining usually contains a high content (about 1 wt%) of fine solids usually called bitumen solids. These bitumen solids are mainly aluminosilicate clay particles coated with strongly bound toluene insoluble organic material that has the characteristics of asphaltenes (Kotlyar *et al.* 1998). Bitumen solids cause numerous downstream operational problems, such as fouling of process vessels and plugging of hydrotreater beds. One option to solve these problems is to completely remove these solids prior to upgrading. This can be achieved by using paraffinic diluents in the extraction process. The effect of bitumen solids on coke formation, however, is not well understood. Therefore, study on the effect of bitumen solids on coking is of considerable practical importance in evaluating process options.

So far, there have been very few studies on the effect of bitumen solids on upgrading reactions. Most of the earlier work investigating bitumen solids was conducted under hydroconversion conditions. Wolk (1974) patented the use of the bitumen solids from oil sands bitumen to suppress coke formation in a hydroconversion process. This effect was speculated to be due to hydrogenation catalytic effect of the solids. Previous investigations also found that bitumen solids contained substantial content of metal elements such as iron (Kotlyar *et al.* 1998), which could act as hydrogenation catalysts. The aluminosilicate clays contained in the bitumen solids include kaolinite, illite and montmorillonite (Carrier *et al.* 1987; Gunter *et al.* 1994) which were also reported to have catalytic activities (Breen *et al.* 1997) or synergistic effects with hydrogenation catalysts (Attala *et al.* 1990). These studies reinforced the speculation that the effect of bitumen solids on coke formation is due to their catalytic activity towards hydrogenation. So far in the literature, however, there have been no experimental studies to prove this speculation. Tanabe and Gray (1997) investigated the effect of bitumen solids under coking conditions. They found that removal of the bitumen solids from vacuum residue of Athabasca bitumen caused increased coke formation. In other words, the presence of the bitumen solids reduced coke formation compared with the solids-free feed. This observation showed that there might be a non-catalytic effect that was responsible for the reduction in coke formation since the reduction in coke yield was observed in the absence of hydrogen. A hypothesis was proposed that the fine solids stabilized a new phase of coke precursor from coalescence and consequently reduced the rate of coke formation.

Coking is a thermal process where the cracking reactions are free radical chain reactions in nature (Kossiakoff and Rice, 1943; Gray, 1994). Coke formation is generally attributed to condensation and polymerization of polynuclear aromatics, eventually producing a carbon-rich material (Levinter *et al.*, 1966, 1967). Coke formation also involves a phase separation process as discussed in the preceding chapters. Prior to phase separation there is an induction period during which there is little or no coke formation. Once the new phase separates from the bulk phase, coke starts to form rapidly in the new phase (Wiehe, 1993). The preceding chapter has provided evidence to the phase separation hypothesis, and demonstrated that the new phase is a liquid phase. Thus at an early stage of the coking reaction, the system might behave as an oil-in-oil emulsion. Fine solids are potentially important in affecting both the liquid phase behavior and free radical reactions. Possible roles of the solids are: nucleation sites during phase separation, or act as emulsion stabilizers which prevent the dispersed new phase from coalescing. Fine solids are also known for their ability to scavenge free radicals by providing high surface area, thereby reducing the formation of coke that is a product of the free radical condensation and polymerization. Use of free radical scavengers to reduce coke formation in FCC transfer lines has been patented (Edgerton and Sapre, 1993). Considering the estimate of the 1.3 trillion barrels of bitumen in the oil sands deposits in northern Alberta (Outrim and Evans, 1977), even a 0.1% of reduction in coke formation would translate into a huge economic reward. Therefore, the study of the mechanism of the effect of fine solids on coke formation is of both academic and practical importance.

The objectives of this study were to investigate the effect of bitumen solids on coke formation under coking conditions, and to elucidate the mechanism of interaction between fine solids and coke-forming media. Experiments were carried out using Athabasca bitumen and its vacuum residue with and without the bitumen solids. Cumene, phenanthrene and tetralin were used as model compounds to examine possible catalytic activities of bitumen solids toward hydrogenation, dehydrogenation, acidic cracking and hydrogen shuttling. Fine solids foreign to the bitumen and vacuum residue, including carbon black, kaolin powders with different surface wetabilities, and an ultrafine silica powder, were used to verify the hypotheses of the effect of bitumen solids, and to further elucidate the mechanism of the interaction between fine solids and coke-forming media in general.

4.2 Experimental

4.2.1 Materials. The properties of Athabasca bitumen and its vacuum residue (provided by Syncrude Canada, Ltd.) are listed in Table 3.1. The phenanthrene (98% purity), tetralin (99% purity) and cumene (99% purity) used for model reactions were obtained from Aldrich Chemical Co. and used as delivered. The methylene chloride (HPLC grade) used as the solvent for GC analysis was obtained from Fisher Scientific Co. The oil soluble hydrogenation catalyst, molybdenum 2-ethylhexanoate was from OMG Americas, Inc. The carbon black powder (from Fisher Scientific Co.) had a mean particle size of 0.2 μm and an elemental composition of 97.44% C, 0.86% of S, 0.39% H and 0.31% N. The silica (from Aldrich) was 99.8 % purity fumed SiO_2 in the form of ultrafine particles having sizes on the order of 10 nanometers and a surface area of 380 m^2/g. The kaolin (from Georgia Hydrite) had a mean particle size of 0.5 μm. Its chemical composition is listed in Table 4.1.

4.2.2 Preparation of Solids-Free Feed. One part of bitumen or vacuum residue was dissolved in 40 parts of toluene, followed by heating on a hotplate at 70 °C for 12 hours to ensure dissolution. The solids were then filtered using a 0.22 μm Millipore membrane filter followed by washing several times with toluene until the toluene passed the filter without color. The filter cake was dried in a vacuum oven at 70 °C for 2 hours to recover the bitumen solids. The toluene in the filtrate was removed by rotary evaporation followed by vacuum drying at 90 °C until an approximately 100% mass balance was achieved.

Table 4.1 Chemical composition of kaolin.

Compound	Wt%
Silicon oxide	45.3
Aluminum oxide	38.3
Titanium oxide	1.44
Iron oxide	0.30
Sodium oxide	0.27
Magnesium oxide	0.25
Calcium oxide	0.05
Potassium oxide	0.04
Weight loss at 950 °C (combined water)	13.97

4.2.3 Treatment of kaolin. For some experiments, the surface of the kaolin particles was rendered oleophilic by treating with asphaltenes following the method of Yan and Masliyah (1996): 1 g of asphaltenes was dissolved in 250 ml of toluene. 250 ml of heptane was then added to the solution and the mixture was sonicated for 10 minutes followed by adding 5 g of kaolin and stirring at room temperature for 24 hours. The mixture was then filtered with a 0.22 μm Millipore membrane filter and the filter cake was dried under vacuum at 50 °C for 24 hours to recover the kaolin.

4.2.4 Calcination of Carbon Black. For some experiments the carbon black was first calcined to remove any possible adsorbed oxygen. Pre-weighed carbon black was placed at the bottom of a 1-inch diameter quartz tube. The quartz tube was then heated at 500 °C for 5 hours. A continuous flow of preheated N_2 was introduced to the quartz tube during the calcinations to purge of any desorbed oxygen. The quartz tube was then cooled in the air. After the quartz tube had cooled to room temperature, a known volume of heptane was injected into the quartz tube using a syringe to avoid subsequent contact with oxygen. The carbon black/heptane mixture was then mixed with solids-free bitumen or solids-free vacuum residue following the procedure described below.

4.2.5 Mixing Fine Solids with Solids-Free Feed. One part of solids-free bitumen or solids-free vacuum residue was dissolved in one part of toluene. To this solution 10 parts of heptane was then added which turned the solution into a slurry due to precipitation of asphaltenes from the solution. The slurry was sonicated for 10 minutes. The fine solids were then added into the slurry and the mixture was sonicated for another 30 minutes. The solvents were removed in the vacuum oven until an approximately 100 % mass balance was reached. During the solvent removal, the mixture was also stirred occasionally to ensure a uniform mixture.

4.2.6 Coking Reactions. The coking reactions were carried out using both open and closed reactors. The procedure for the closed reactor reactions was the same as that described in Chapter 3. An open quartz test tube reactor system shown in Figure 4.1was also used in order to obtain ultimate coke yields. The quartz test tube was loaded with approximately 1 g of feed. A flow of preheated nitrogen was introduced into the loaded quartz tube for 10 minutes to remove any trace oxygen. The reactor assembly was then

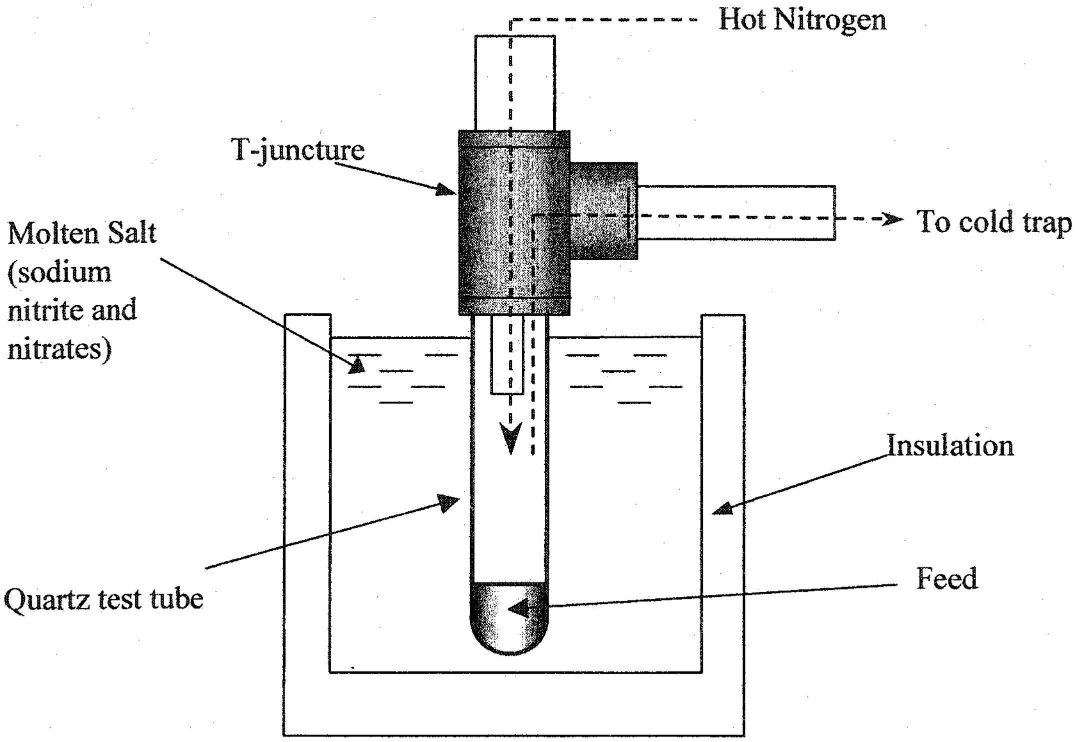

Figure 4.1 Schematic illustration of quartz tube open reactor system.

inserted into a molten salt-bath that was preheated to the predetermined reaction temperature. The sweep gas of preheated nitrogen was introduced throughout the reaction in order to remove the volatile products and to avoid reflux. The reaction was terminated by quenching the quartz tube in cold water after the desired reaction time had elapsed.

4.2.7 Separation of Products. For the closed reactor system, the gas product was vented and collected with a gasbag. Composition of the gas product was analyzed using a HP5840A Gas Chromatograph with a 0.125 inch stainless steel column packed with molecular sieve and an FID detector. Gas yield from the closed reactor was determined by measuring the difference between the weight of the reactor before and that after venting the product gas. No attempt was made to determine the gas yield from the open reactor. The liquid and solid products were recovered by extraction with 120 ml of toluene. The mixture was sonicated for 30 minutes to ensure complete dissolution. Toluene insoluble (TI) solid products were separated from the liquid by filtering the mixture using a 0.22 micron Millipore membrane filter followed by washing with toluene several times until the toluene passed the filter without color. The filter cake was then vacuum dried at 70 °C. Toluene in the filtrate was removed by rotary evaporation. Asphaltenes were recovered from this oil by adding 120 ml of n-heptane and sonicating the mixture for 10 minutes. The asphaltenes precipitated by n-heptane were then isolated by 0.22μm Millipore filter followed by drying under vacuum at 70 °C for 2 hours. Yields were calculated as follows:

$$\text{Coke yield} = \frac{m_{\text{TI}} - m_{\text{bitumen solids}}}{m_{\text{feed}} - m_{\text{bitumen solids}}} \tag{4.1}$$

$$\text{Asphaltenes yield} = \frac{m_{\text{asphaltenes}}}{m_{\text{feed}} - m_{\text{bitumen solids}}} \tag{4.2}$$

$$\text{Gas yield} = \frac{m_{\text{gas}}}{m_{\text{feed}} - m_{\text{bitumen solids}}} \tag{4.3}$$

4.2.8 Elemental analysis. The elemental (C, H, N, and S) composition of the feeds and products were analyzed using Elemental Analyzer 1108 in the Microanalytical Lab at the University of Alberta. For CHNS analysis, the sample to be analyzed was placed into the sealed combustion chamber, which was packed with catalytic materials and was maintained at a temperature of around 1030 °C. As the sample entered the combustion chamber, oxygen was injected into the helium carrier gas which was flowing through the combustion tube. The resulting catalytic oxidation, or so-called "dynamic flash combustion", assured the complete oxidation of the sample. The combustion gas, N_2, CO_2, H_2O and SO_2, were swept through the reduction reactor and into the chromatographic column by helium carrier gas. Finally, the concentration of each of the gases, which had been completely separated by the chromatographic column, was determined by the TCD detector. The concentration of the combustion gases were then used to calculate the elemental composition of the sample.

4.2.9 SEM and EDX Analysis. Approximately 2 mg of the filter cake of the TI solids product from bitumen or vacuum residue was re-dispersed in 5 ml ethanol by sonicating for 5 minutes. One or two drops of the dispersion were placed onto a SEM sample holder using a pipette, and the ethanol was evaporated in the air, leaving the TI solids well distributed on the sample holder. The sample holder was then sputter-coated with gold for SEM or coated with carbon for SEM/EDX analysis.

4.2.10 Model Reactions. Catalytic activity towards hydrogenation of bitumen solids and carbon black was measured by reacting the solids with a mixture of phenanthrene and toluene (1:1 by mass). This reaction was conducted under hydrogen pressure of 1000 psig (when measured at room temperature) at 400 °C for 30 minutes. Cracking and dehydrogenation activities were measured by reacting cumene with the solids under 1 atm (when measured at room temperature) of nitrogen at 430 °C for 40 minutes. Hydrogen shuttling activity was measured by reaction of bitumen solids with a mixture of phenanthrene and tetralin (1:4 by weight) under 1000 psi (when measured at room temperature) of nitrogen at 400 °C for 30 minutes. For each of these model reactions, 0.3 g of bitumen solids were well mixed with 2.7 g of the model compounds using sonication. The mixture was then loaded into the reactor (closed system), followed by purging of oxygen and pressurizing with nitrogen or hydrogen to the prescribed pressure, as described above. After the reaction, the bitumen solids were filtered using the 0.22 μm Millipore membrane filter. The filtrate was diluted with methylene chloride and analyzed with a HP 5890 Gas Chromatograph with an OV-101 packed column and FID detector. For each of these tests, the reaction was first carried out without bitumen solids as the basis for comparison. The results of the model reactions are reported as conversion that was calculated as:

$$X = 100 \times \text{product (mol)} / \text{reactant (mol)} \tag{4.4}$$

where X denotes conversion.

Molybdenum 2-ethylhexanoate was used as a model catalyst for hydrogenation. The molybdenum 2-ethylhexanote was dissolved in solids-free bitumen by heating and occasional agitating under a nitrogen blanket at 70 °C for 2 hours to give a concentration of approximately 500 ppm Mo in bitumen. The reaction was carried out in the same manner as the coking reactions.

4.3 Results

4.3.1 Characterization of the Bitumen Solids. A characteristic of Athabasca bitumen produced from surface mining is their high content of bitumen solids. The preparation of the solids-free feed revealed a solids content of 1.13 wt% in the bitumen and 1.8% in the vacuum residue. SEM analysis of the bitumen solids showed that they were irregular particles with average size of approximately 1 micron. These solids particles were coated with organic materials, as shown in Figure 4.2. The elemental analysis revealed that the bitumen solids contained 17.62 wt% of carbon (see Table 4.2). Assuming the toluene insoluble organic materials contain mainly carbon, hydrogen, sulfur and nitrogen, the amount of these organic materials can be estimated to be about 20 wt% of the total bitumen solids. The elemental analysis also revealed an overall H/C atomic ratio of 1.24. This H/C is similar to but slightly higher than heptane-precipitated asphaltenes (Speight and Moschopedis 1981) which could be due to partial decomposition of the combined water of the mineral compounds. Reaction of the solids with cumene at 430 °C for 40 minutes under 1 atm nitrogen was used to remove the attached organic materials. After the treatment, the solids were found to be granular particles with an average size of about several hundred nanometers (see Figure 4.3).

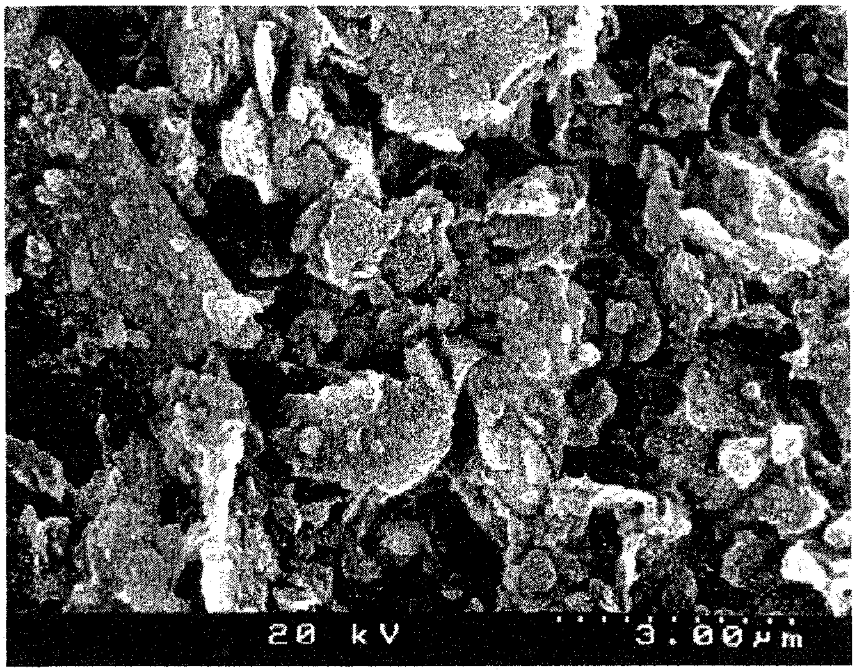

Figure 4.2 SEM micrograph of bitumen solids.

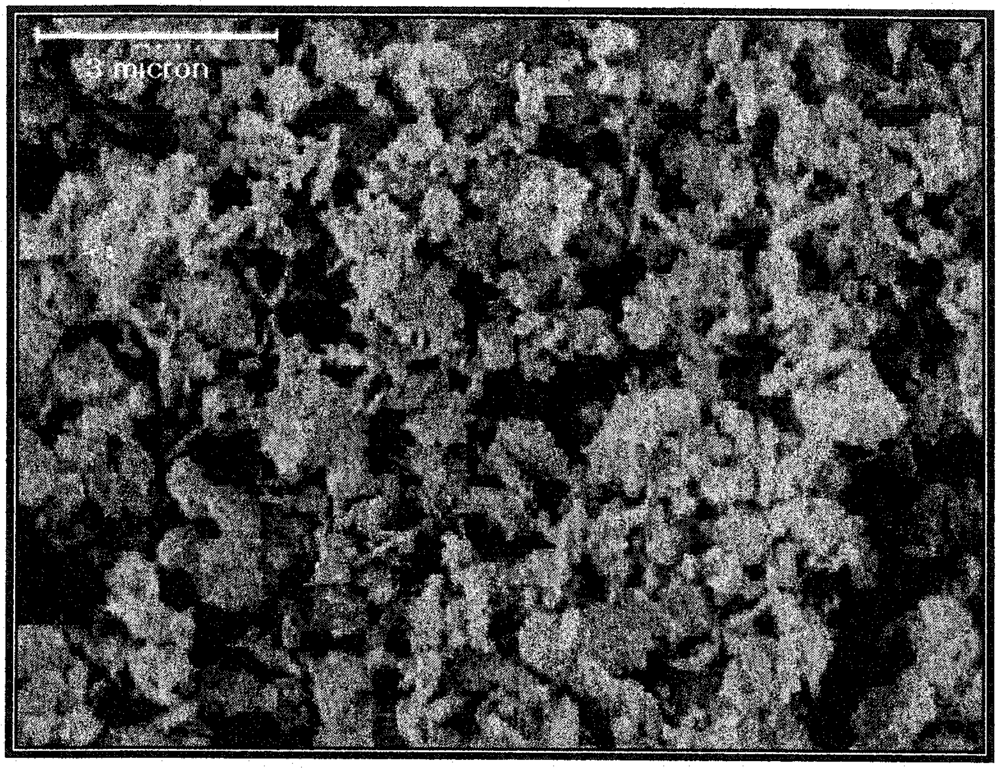

Figure 4.3 SEM micrograph of the bitumen solids after being treated with cumene at 430 °C for 40 minutes.

Major elements excluding C, H, O were measured by EDX at 20 kV electron energy as shown in Table 4.3. The ash contents of vacuum residue, solids-free vacuum residue and the bitumen solids (measured by using TGA burning at temperature up to 1000 °C) were 0.7wt%, 0.0wt%, and 69.7wt%, respectively. It is recognized that the method used to measure the ash content was not accurate at very low ash concentrations. This method tends to give a negative deviation in ash content possibly due to the loss of some of the ash to the escaping combustion products, since even solids-free vacuum residue should have some ash content due to the metals content. Nevertheless, this low ash content of solids-free vacuum residue relative to that of the full vacuum residue, indicated that the removal of the bitumen solids by filtration was very efficient.

Table 4.2 Elemental analysis of the bitumen solids from toluene extraction of Athabasca bitumen.

C, wt %	17.62
H, wt %	1.84
S, wt %	1.91
N, wt %	0.388
H/C atomic ratio	1.24

4.3.2 Effect of Bitumen Solids on Coke Yield. The effect of bitumen solids on coke yield was studied by comparing the yield of TI from bitumen and that from solids-free bitumen as a function of time (Figure 4.4). The standard deviation of the TI yield was found to be ±0.5 mg TI / g feed based on seven repeated reactions at 40 minutes.

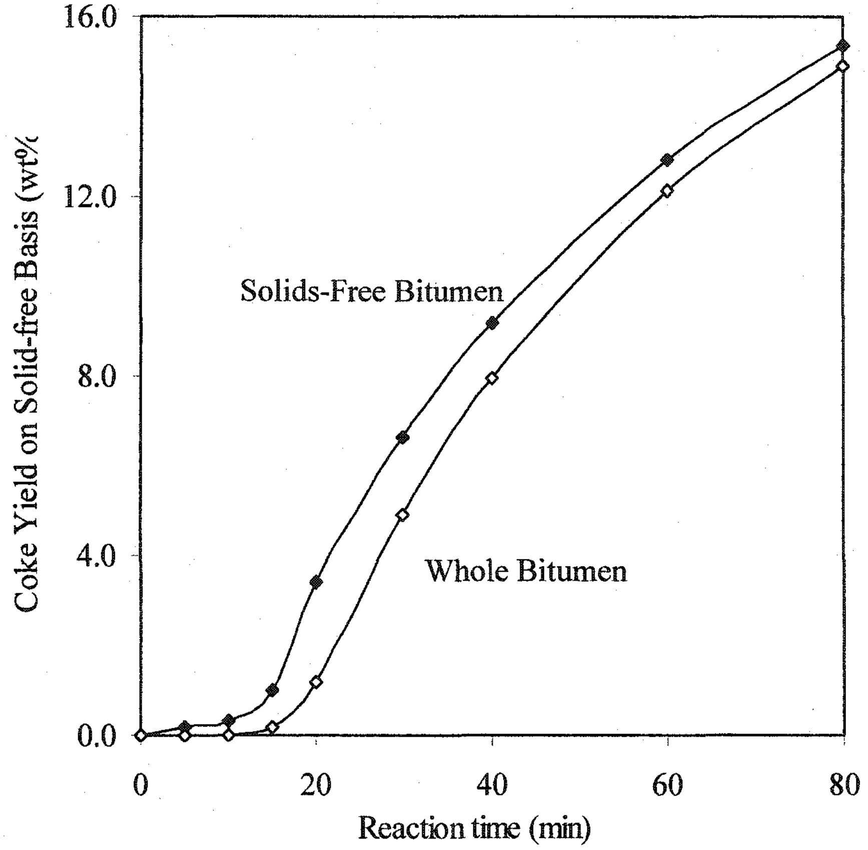

Figure 4.4 Effect of bitumen solids on coke yield from Athabasca bitumen at ca. 430 °C.

Coking of bitumen at 430 °C gave an induction time of about 10-15 minutes, before which no TI was formed; while for the coking of solids-free bitumen, there was no induction time and TI formed immediately at the beginning of the reaction. The solids-free bitumen gave a higher yield of TI than did the original bitumen at all reaction time intervals. Several control tests were conducted to check the effect of heating and dilution during the solids removal, following the same procedure of the preparation of the solids-free bitumen. Only filtration was omitted in order to keep the solids in the feed for comparison. It was found that the TI yield was unchanged. Hence the heating, dilution or sonication was not responsible for the reduction in the coke yield.

Table 4.3. Elemental composition of the bitumen solids as measured by EDX at 20kV electron energy.

Element	Content, wt%	Element	Content, wt%
Na	0.09	K	0.88
Mg	0.14	Ca	0.43
Al	4.63	Ti	1.65
Si	9.19	V	0.05
P	0.12	Cr	0.05
S	1.91	Mn	0.10
Cl	0.1	Fe	4.65

* Several elements, including C, H, O were not detectable by EDX and therefore the raw EDX data only provided relative composition. The data were calibrated by assuming sulfur content detected by EDX was equal to that determined by elemental analysis as in Table 4.2.

As shown in Figure 4.4, when bitumen solids were removed from Athabasca bitumen and vacuum residue, the coke yield increased. The removal of bitumen solids also eliminated the induction period of coke formation. These results were consistent with those of Tanabe and Gray (1997) who studied the coking of vacuum residue of Athabasca bitumen. The removal of bitumen solids from vacuum residue had the same effects except that the magnitude of the overall effect on vacuum residue were more pronounced than that on the bitumen.

Tanabe and Gray (1997) discovered that removing bitumen solids from vacuum residue could increase coke formation in the absence of hydrogen. They did not, however, confirm the reversibility of this effect, i.e. whether or not the coke yield could be reduced by adding bitumen solids back into the solids-free feed. The difficulties lay in re-dispersing the fine solids back into the solids-free feed. The revised mixing method described earlier provided two benefits in facilitating better dispersal of solids: a. the viscosity of the mixture was lowered by dissolving bitumen in heptane and by precipitating asphaltenes from the solution; b. the precipitated asphaltenes could help keep the solids dispersed during solvent removal. The results (Figure 4.5) showed that when the solids were added to the solids-free feed immediately after being filtered from the bitumen or vacuum residue without further drying, the effects could be almost completely reversed. When the solids had undergone drying after filtration, however, the effects were less pronounced. This was probably because the drying process (70 °C for 2 hours) agglomerated the solids and prevented complete re-dispersion.

Tanabe and Gray (1997) found that when reaction time increased, the difference between the coke yield from solids-free vacuum residue and from full vacuum residue

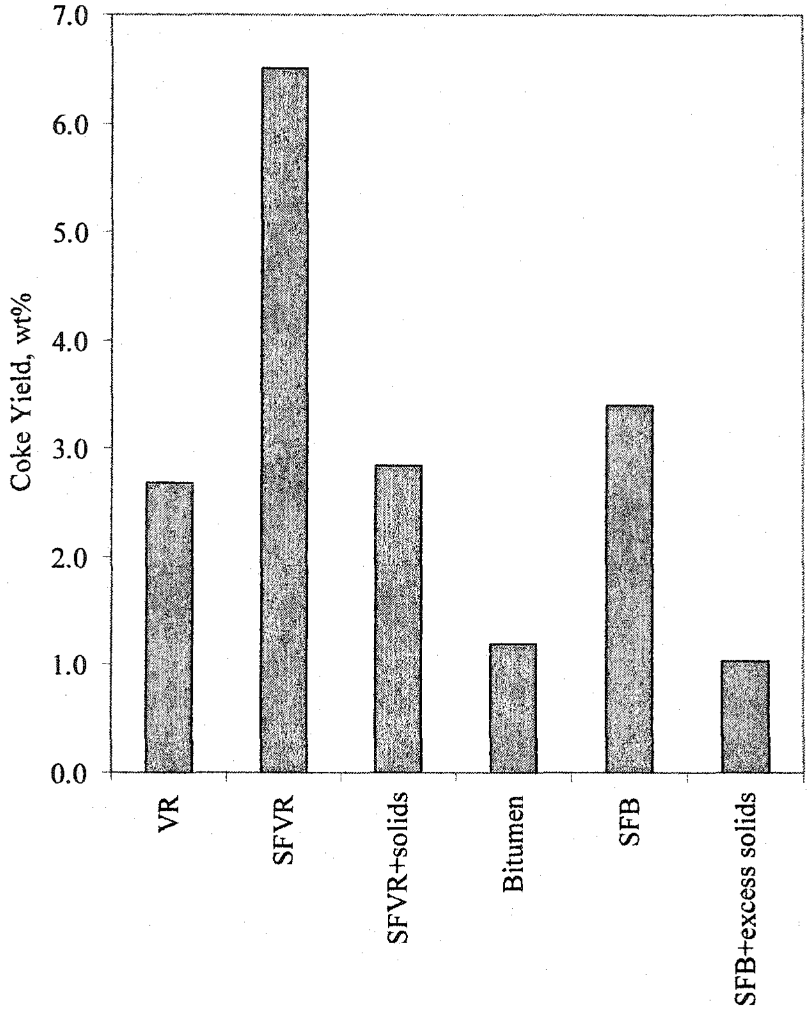

Figure 4.5 Reversibility of the effect of the bitumen solids on coke yield at ca. 430 °C and 20 min. VR = vacuum residue, SFVR = solids-free vacuum residue, SFB = solids-free bitumen.

narrowed. The result for bitumen (Figure 4.4) showed the same trend. This raised the question whether or not bitumen solids could reduce the ultimate coke yield in a commercial coking process. The narrowing of the difference in coke yield in the closed reaction system at prolonged reactions could be due to coke formation from the volatiles which in a coking process would have escaped from the reaction. The open reactor system was used to measure the ultimate coke yield. The results of coking in the open reaction system at 475 °C and 500 °C (Table 4.4) clearly showed that bitumen solids could reduce ultimate coke yield in an open reaction system as well. Hence bitumen solids reduced the yield of coke at temperatures from 430 °C to 500 °C with or without removal of volatile products.

Table 4.4. Coke yield from coking of solids-free vacuum residue (SFVR) and original vacuum residue (VR) in the open reactor system. Data at 475 °C and 10 min are mean values from 3 repeats.

Time,	Coke yield at 475 °C, wt%		Coke yield at 500 °C, wt%	
min	SFVR	VR	SFVR	VR
5	19.4	18.4	-	-
10	24.2±0.4	23.1	28.3	26.3
15	25.4	24.3	-	-
30	25.0	23.6	-	-

4.3.3 Effect of Concentration of Bitumen Solids. Solids-free vacuum residue and full vacuum residue (*i.e.* vacuum residue as received, without removal of the bitumen solids) were mixed to achieve a variation of concentration of the bitumen solids in the feed in the range of 0.0 wt% ~ 1.8 wt%. These feeds were then coked at 430 °C and 20 minutes. The coke yield as a function of the concentration of bitumen solids is shown in Figure 4.6. The effect of solids concentration is evidently nonlinear, as the coke yield was lower than linear additivity would suggest. It is especially interesting to note that there was a minimum coke yield at a solid concentration of about 1.0 wt %. As solids concentration increased from 0.0 to 1.0 wt %, the coke yield decreased from 10.3 to 5.5 wt %. Further increase in solids concentration from 1.0 wt% actually led to increased coke yield, from 5.5 wt % coke yield at solids concentration of 1.0, to 7.7 wt % coke yield at solids concentration of 1.8 %. At solids concentrations near the two ends, *i.e.* 0 % and 1.8 %, the coke yields were not far different from what would be predicted by linear additivity of solids concentration, thus the plot of coke yield versus solids concentration gives two "shoulders" (see Figure 4.6). These two "shoulders" are probably due to the poorer blending the two ends, since the different concentrations of bitumen solids were obtained by blending solids-free vacuum residue (0 % solids) with full vacuum residue (1.8 %). The poorer the blending, the more linearly additive the effect. At the extreme that there is no blending and the solids-free vacuum residue and full vacuum residue coke independently, the overall coke yield will be completely linearly additive. Another very interesting phenomenon was that although there was dramatic change in coke yield, the gas yield remained virtually constant at approximately 5 wt % throughout the range of solids concentrations from 0.0 to 1.8 wt %.

A minimum ultimate coke yield at an intermediate solids concentration would be of considerable practical interest. To test whether the ultimate coke yield would also show a minimum at an intermediate solids concentration, two series of experiments, coke yield versus reaction time with the closed reactor at 430 °C and 1.0 wt % of solids, and

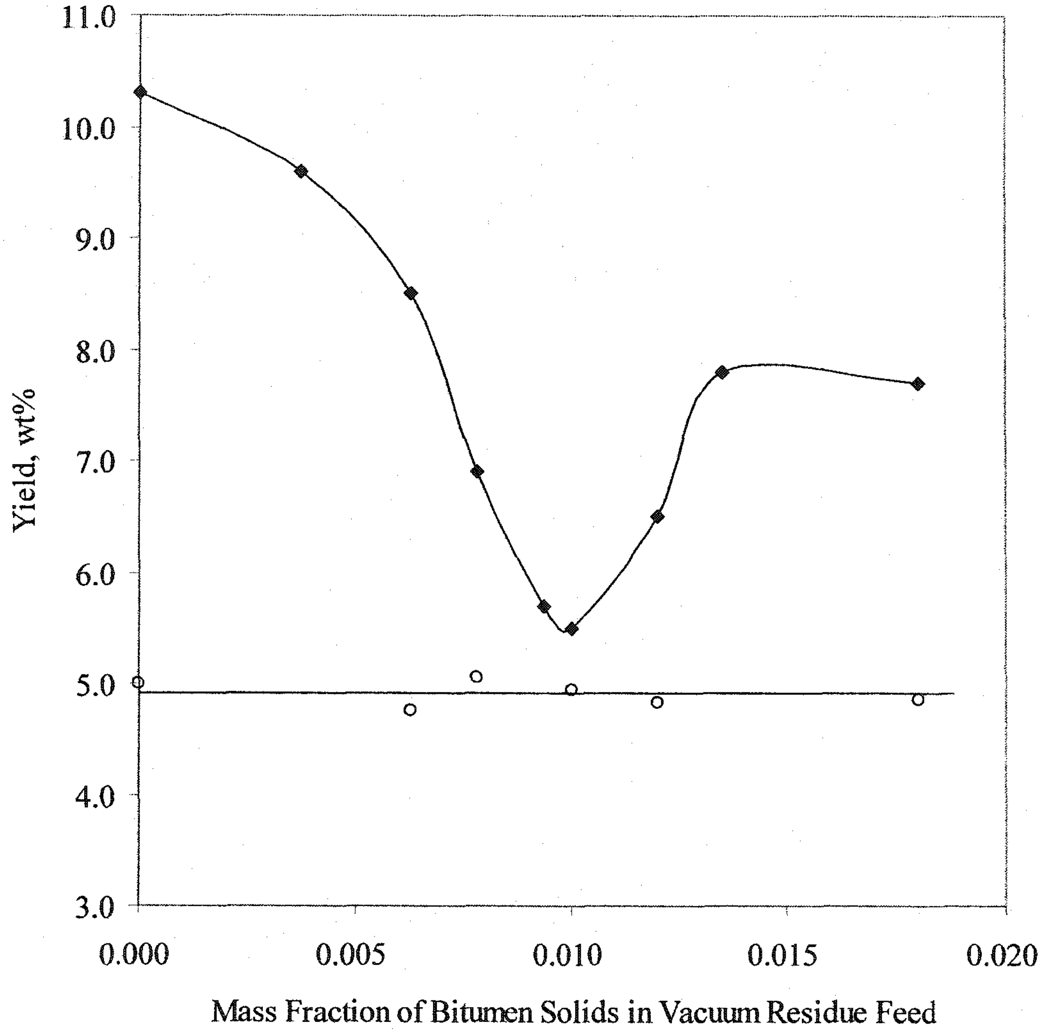

Figure 4.6 Effect of bitumen solids concentration on coke and gas yields in coking of Athabasca vacuum residue at 430 °C and 20 minutes.
◆ = coke yield; ○ = gas yield.

coke yield versus solids concentration with the open reactor at 475 °C at 12 and 30 minutes were conducted. Feeds with 1.0 wt % of bitumen solids gave a lower coke yield than the feed with 1.8 wt % bitumen solids (full vacuum residue) when the reaction time was not greater than 20 minutes (Figure 4.7). For example, at 10 min and 20 min, the coke yields were 1.5 wt % and 5.5 wt %, respectively, for the feed with 1.0 % of solids, while the coke yields of full vacuum residue were 2.3 wt % and 7.7 wt %, respectively. For longer coking reactions (higher conversions), feeds with 1.0 wt % bitumen solids and full vacuum residue gave similar coke yield, indicating that although 1.0 wt % might not give a minimum coke for long coking reactions, a higher solids concentration did not offer additional reduction in coke yield. The open reactor experiments were designed to obtain ultimate coke yield. At 475 °C, the cracking reaction was nearly completed at 12 minutes (no more bubbling or vaporization observed after 12 minutes). The reactions at 30 minutes were conducted to guarantee the coke yields were ultimate coke yields. As shown in Figure 4.8, although statistically there was still a slight reduction (an average of 1.2 % reduction) in coke yield at every tested solids concentration, there was no apparent minimum coke yield at intermediate solids concentration. Therefore, the minimum coke yield with respect to solids concentration probably only occurs at a relatively early stage of coke formation.

4.3.4 Hydrogenation Model Reaction. Hydrogenation activity was measured by reacting phenanthrene with the bitumen solids at typical hydroconversion conditions, *i.e.* hydrogen pressure of 1000 psi (when measured at room temperature) at 400 °C for 30 minutes. After reaction in the presence of bitumen solids, both 9,10-dihydro-phenanthrene and 1,2,3,4-tetrahydro-phenanthrene were detected but no other

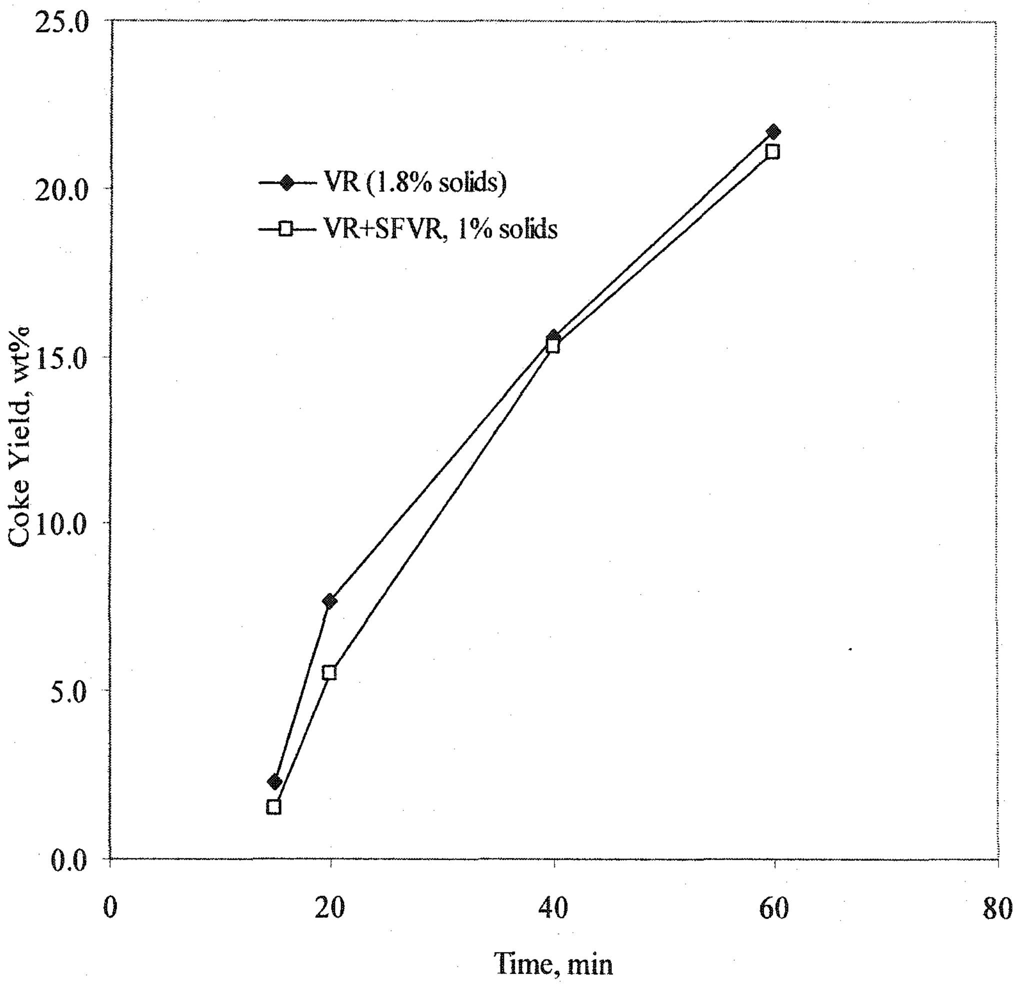

Figure 4.7 Comparison of coke yield from vacuum residue with 1.8 wt % bitumen solids and that with 1.0 wt % bitumen solids in coking at 430 °C.

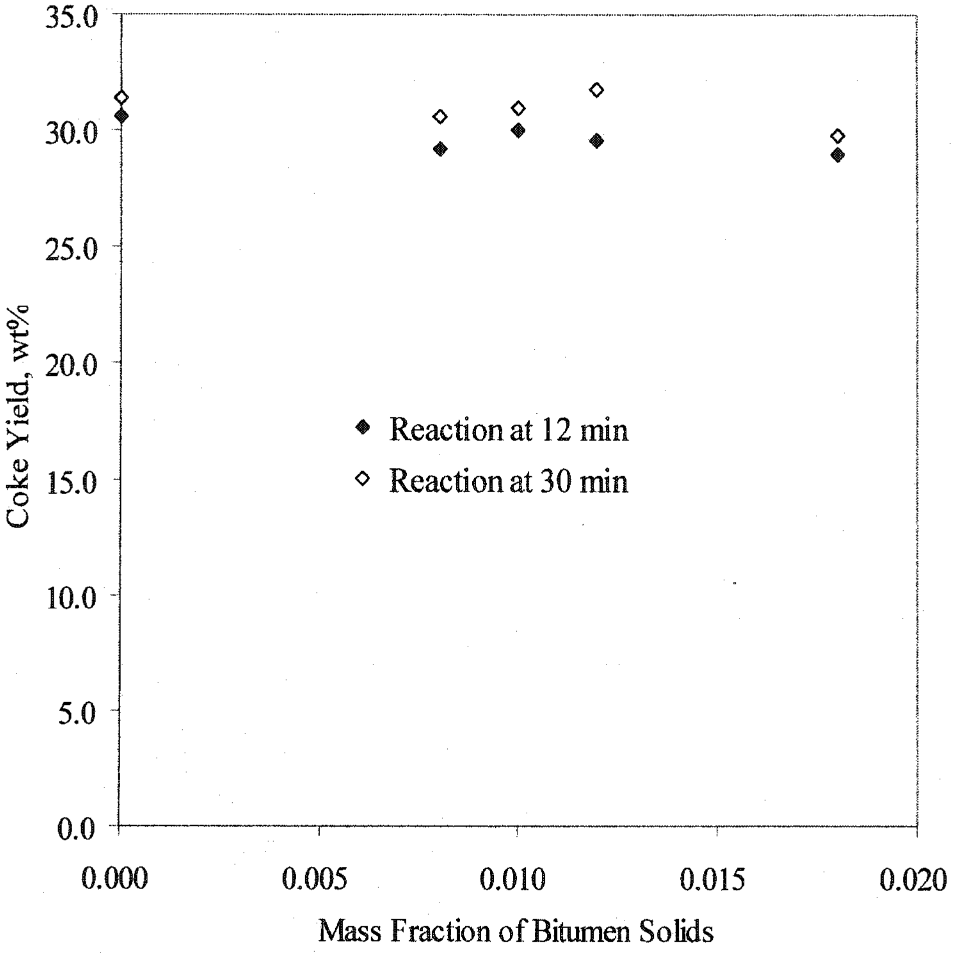

Figure 4.8 Effect of concentration of bitumen solids on the ultimate coke yield. Reactions conducted in the open reactor at 475 °C.

hydrogenation products were detected. For simplicity the products were combined in the calculation of conversion. The conversion in the presence of the solids was 4.3 % (Table 4.5). There was no conversion of phenanthrene in the absence of the fine solids. Therefore bitumen solids had mild activity towards hydrogenation, as the iron content in bitumen solids would suggest. This activity, however, was rather weak. For comparison, Suzuki *et al.*(1989), using finely dispersed FeS_2 which is generally regarded as a weak catalyst, observed a hydrogenation conversion of phenanthrene at 14.4% at 375 °C and 725 psig (when measured at room temperture) H_2.

Table 4.5 Conversions of the model compound reactions.

Reaction	Model Compound	Reaction Conditions	Conversion, %	
			Without Solids	With Solids
Hydrogenation	Phenanthrene	$P_{H2} = 1000$ psi 400 °C, 30 min	0.0	4.3
Acidic Cracking	Cumene	$P_{N2} = 1$ atm 430 °C, 40 min	Not detected	Not detected
Hydrogen Shuttling	Tetralin + phenanthrene	$P_{N2} = 1000$ psi 400 °C, 30 min	0.43	1.26
Dehydrogenation	Cumene	$P_{N2} = 1$ atm 430 °C, 40 min	0.15	0.84

As discussed earlier, bitumen solids contains about 20% of toluene insoluble organic materials with a H/C of about 1.24, i.e. similar to asphaltenes. In order to rule out the possibility that the observed hydrogenation catalytic activity was due to reaction of this organic material, asphaltenes were mixed with phenanthrene and reacted under the same conditions as those of the phenanthrene/bitumen solids model reaction. The result showed no conversion of phenanthrene. Hence the observed weak hydrogenation catalytic activity of the bitumen solids was real and was solely due to the mineral particles, not the organic material coated on them.

4.3.5 Cracking and Dehydrogenation Model Reaction. Cracking and dehydrogenation activities were measured by reacting cumene with the bitumen solids under 1 atm (when measured at room temperature) of nitrogen at 430 °C for 40 minutes. Cumene is a widely used model compound for testing dehydrogenation and acid catalytic cracking reactions because of its simple products and because it requires acid sites of medium strength for cracking to occur (Liu and Dadyburjor 1992). The reactions can be written as:

$$\text{Cracking:}\quad \underset{\text{Cumene}}{C_6H_5\text{-}C_3H_7} \rightarrow \underset{\text{Benzene}}{C_6H_6} + \underset{\text{Propylene}}{C_3H_6} \tag{4.5}$$

$$\text{Dehydrogenation:}\quad \underset{\text{Cumene}}{C_6H_5\text{-}C_3H_7} \rightarrow \underset{\alpha\text{-methyl-styrene}}{C_6H_5\text{-}C_3H_5} + H_2 \tag{4.6}$$

In all the experiments, with or without bitumen solids, benzene and propylene were not detected. The very low conversion demonstrated that bitumen solids do not have significant acidic cracking activity. As shown in Table 4.5, a negligible but non-zero dehydrogenation conversion was observed in the absence of bitumen solids. While in the presence of the solids this conversion increased slightly from 0.15 to 0.84 %.

4.3.6 Hydrogen Shuttling Model Reaction. Hydrogen shuttling was studied by reacting bitumen solids with a mixture of phenanthrene and tetralin (1:4 by mass) under 1000 psi of nitrogen at 400 °C for 30 minutes. Through hydrogen shuttling reactions, tetralin was dehydrogenated to naphthalene, while phenanthrene was hydrogenated to a mixture of 9,10-dihydro-phenanthrene and 1,2,3,4-tetrahydro-phenanthrene. The conversion was calculated on both phenanthrene and tetralin bases and gave the same results. Similar to the hydrogenation model reaction, a negligible but non-zero conversion was observed in the absence of the solids, while in the presence of the solids the conversion slightly increased from 0.43 to 1.26 %. Hence the bitumen solids have a slight activity towards promoting hydrogen shuttling reactions.

4.3.7 Reaction with Model Hydrogenation Catalyst. In order to determine if the hydrogenation catalytic activity was responsible for the reduction in coke yield at coking conditions, an oil soluble hydrogenation catalyst, molybdenum 2-ethylhexanoate was used as the model catalyst. Being soluble in the feed, this type of compound reacts with the sulfur in the feed to form *in situ* a highly dispersed molybdenum sulfide which is very efficient in hydrogenation. Compared with other metals, molybdenum based catalysts give the best hydrogenation performance. The activity of the catalyst is almost independent of the organic group bonded to the host metal as long as the organic group provides sufficient oil solubility (Del Bianco *et al* 1995; Dabkowski *et al.* 1991). A concentration of about 100 ppm of Mo is usually sufficient to achieve a high conversion (Chen *et al.* 1990).

For repeated experiments of coking of solids-free bitumen in the presence of molybdenum 2-ehthylhexanoate (500 ppm of Mo) under 1 atm (room temperature) N_2 at 430 °C and 40 minutes, no reduction in coke yield was observed when compared with the solids-free bitumen in the absence of this catalyst. Rather, a slight increase in coke yield, from an average of 9.2 % for solids-free bitumen without Mo, to an average of 10.1 % for solids-free bitumen with Mo, was observed. This increase in coke yield could be due to dehydrogenation enhanced by the hydrogenation catalyst when there was a deficit of hydrogen pressure. Hence, the reduction in coke yield by bitumen solids under coking conditions cannot be attributed to the hydrogenation catalytic activity of the solids.

4.3.8 Effect of Bitumen Solids on Formation of Gases. Removal of bitumen solids had no significant effect on gas yield. At a constant coking temperature and time, varying the solids concentrations from 0.0 to 1.8 wt % gave virtually constant gas yield, while coke yield showed dramatic change, from a high of 10.3 % at bitumen solids concentration of 0.0 wt % to a low of 5.5 % at bitumen solids concentration of 1.0 wt % (Figure 4.6). The solids-free bitumen also gave virtually the same gas yields as full bitumen (Figure 4.9).

The compositions of hydrocarbon gas products were measured for coking with and without the solids at various reaction times. In all cases, the concentration of C_4 species was very low compared with the concentration of C_1 and C_2, and methane was the predominant product (Figure 4.10). It is well established that significant formation of C_4 is characteristic of acidic catalytic cracking while thermal (non-catalytic) cracking produces predominantly C_1 and C_2. Since the presence of bitumen solids did not increase C_4 formation, it can be concluded that the fine solids did not have appreciable acidic catalytic activity. This result is consistent with the observations from model acid cracking reactions.

4.3.9 Effect of Carbon Black on Coke and Asphaltenes Yield. Carbon black was mixed with solids-free vacuum residue to give a concentration of 5.4 wt% of total solids. The coke and asphaltenes yields from solids-free vacuum residue with and without

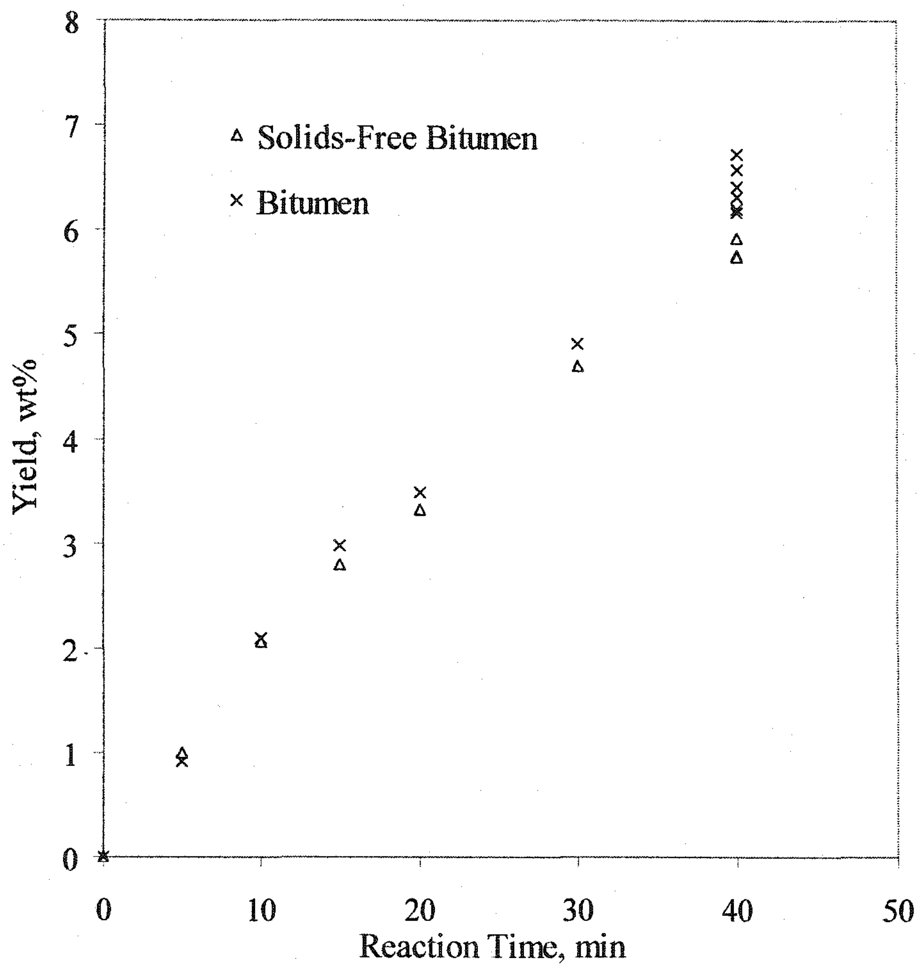

Figure 4.9 Effect of bitumen solids on gas yield in coking at 430 °C.

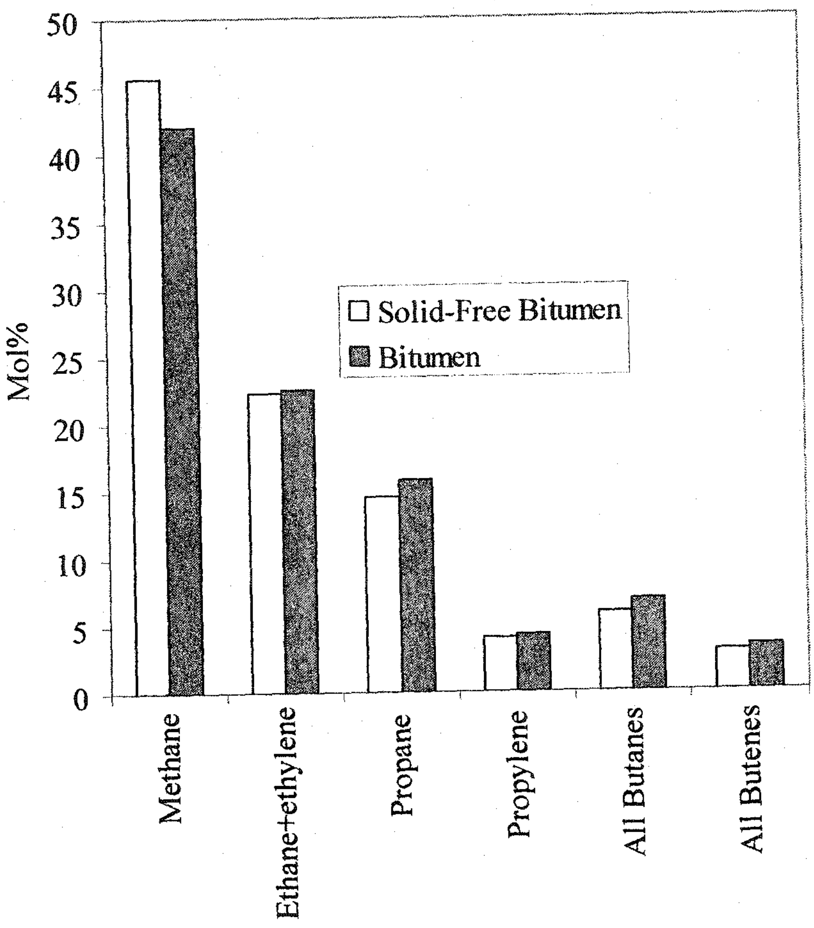

Figure 4.10 Composition of hydrocarbon products from coking of bitumen at 430 °C and 40 minutes.

carbon black are shown in Figure 4.11. At all reaction times, the addition of carbon black reduced coke yield by 1~2 wt% and increased asphaltenes yield by 1~4 wt%. The effects were more pronounced for shorter reactions but diminished with increasing reaction time. This result is consistent with the effects of bitumen solids as described earlier in this study and in the work of Tanabe and Gray (1997).

There have been reports that activated carbon has various catalytic effects, but these effects are generally attributed to adsorbed gases, most notably oxygen (Speight, 1991). The effect of carbon black on coke yield, as observed in Figure 4.11, could also be due to possible adsorbed oxygen in the carbon black powders. To investigate this possibility, the carbon black was calcined at 500 °C for 5 hours with continuous flow of nitrogen and then mixed with the solid free vacuum residue without exposure to air, as described earlier. The solids-free vacuum residue, solids-free vacuum residue with 3.0 wt % calcined carbon black and that with 3.0 wt % un-calcined carbon black, were then coked at 430 °C and 20 minutes. The feed with calcined carbon black gave the lowest coke yield, 5.5 wt %, as compared the feed without solids, 10.3 wt % and the feed with un-calcined carbon black, 7.1 %. Therefore, the reduction in coke yield was not caused by adsorbed oxygen on the carbon black. In fact, it has been reported that oxygen would increase coke yield (Speight, 1991), and this is in agreement with the result of calcination of carbon black, if the carbon black indeed adsorbed significant amount of oxygen. It is also possible that calcinations increased the total surface area of the carbon black by breaking up aggregates and higher surface area resulted in more pronounced reduction in coke yield.

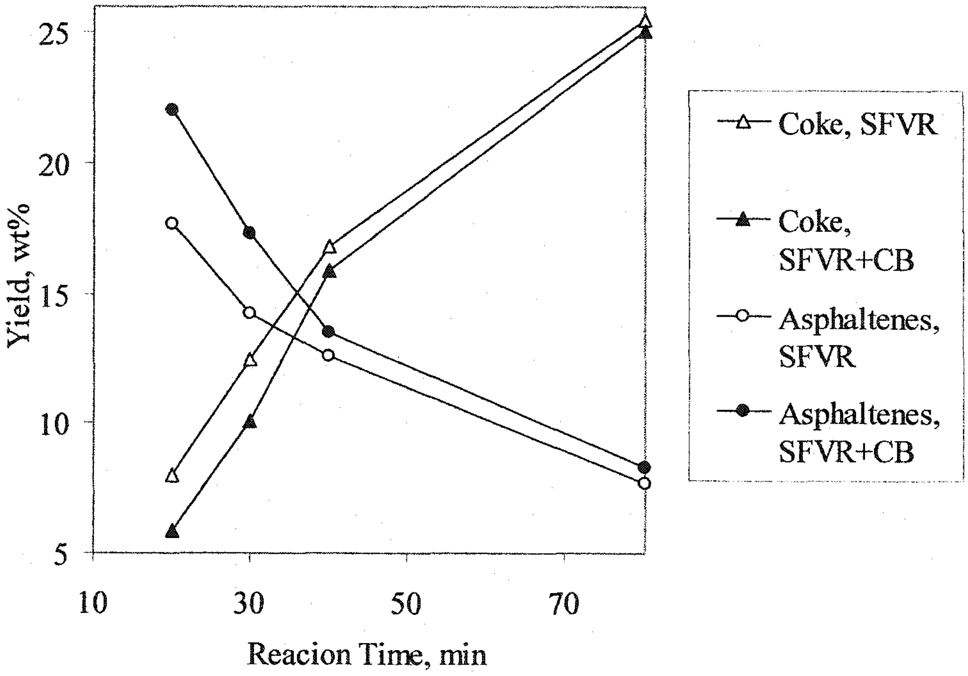

Figure 4.11 Effect of 5.4 wt % carbon black on coke and asphaltenes yield in coking of solid-free vacuum residue at 430 °C.

A control test was also conducted to check the weight loss of carbon black after the calcination. After the calcined carbon black cooled down under nitrogen, the quartz tube was carefully, but quickly, stoppered and then weighed. The calcination caused only 2.16 % of weight loss of the carbon black, possibly due to the moisture originally accumulated on the carbon black. It can then be concluded that the effect of the carbon black in reducing coke yield was not because of the weight loss of carbon black itself during coking, since this only translated into an error of $2.16\% \times 5.4\% = 0.11\%$ of coke yield on the feed basis.

4.3.10 Effect of Concentration of Carbon Black on Coke Yield. Coking reactions with different concentrations of carbon black were conducted to compare the effect of carbon black concentration with that of bitumen solids. Solids-free vacuum residue was first mixed with calcined carbon black to give a solids concentration of 2.7 wt % using the method described earlier. This mixture was then blended with "pure" solids-free vacuum residue to produce feeds with varying concentration of carbon black. Unlike bitumen solids, which gave a minimum coke yield at an intermediate concentration, the carbon black gave a monotonic decrease in coke yield, from 10.6 wt % without carbon black, to 6.4 wt % with 2.7 wt % of carbon black, as shown in Figure 4.12.

4.3.11 Effect of kaolin and asphaltene-treated kaolin. The addition of both 5 wt % and 10 wt % of 0.5 μm kaolin powder in the solids-free vacuum residue had virtually no effect on coke formation. After treating the surface of the kaolin with asphaltenes, however, the addition of kaolin reduced coke yield and increased asphaltenes yield (see Figure 4.13), similar to the effect of adding carbon black. The actual amount of asphaltenes coated on the kaolin was less than 0.1 wt % of the kaolin, as revealed from

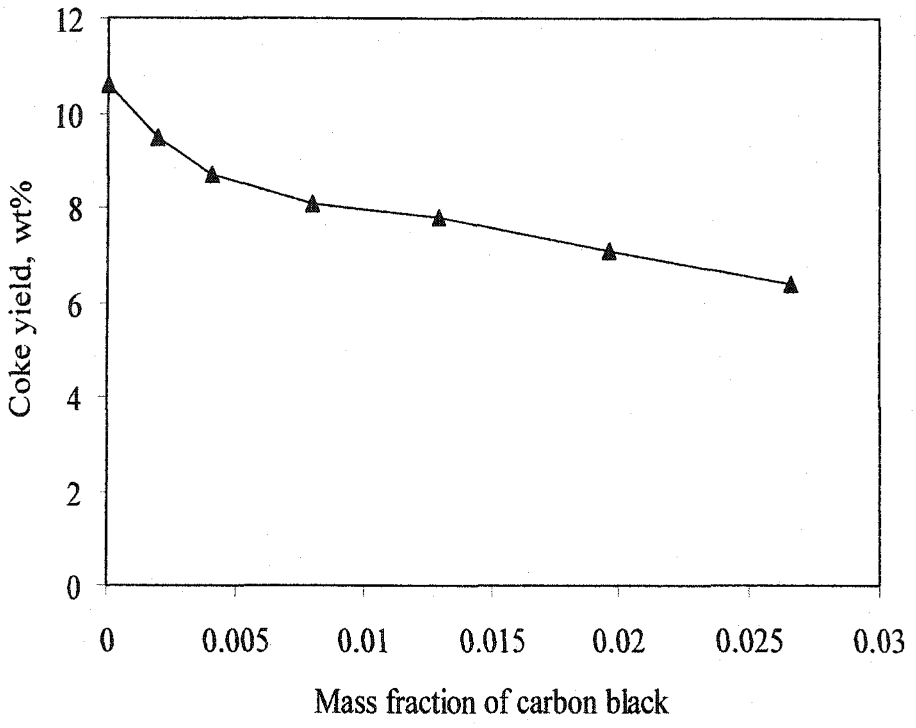

Figure 4.12 Effect of carbon black concentration added to solid free vacuum residue on the coke yield in coking at 430 °C and 20 minutes.

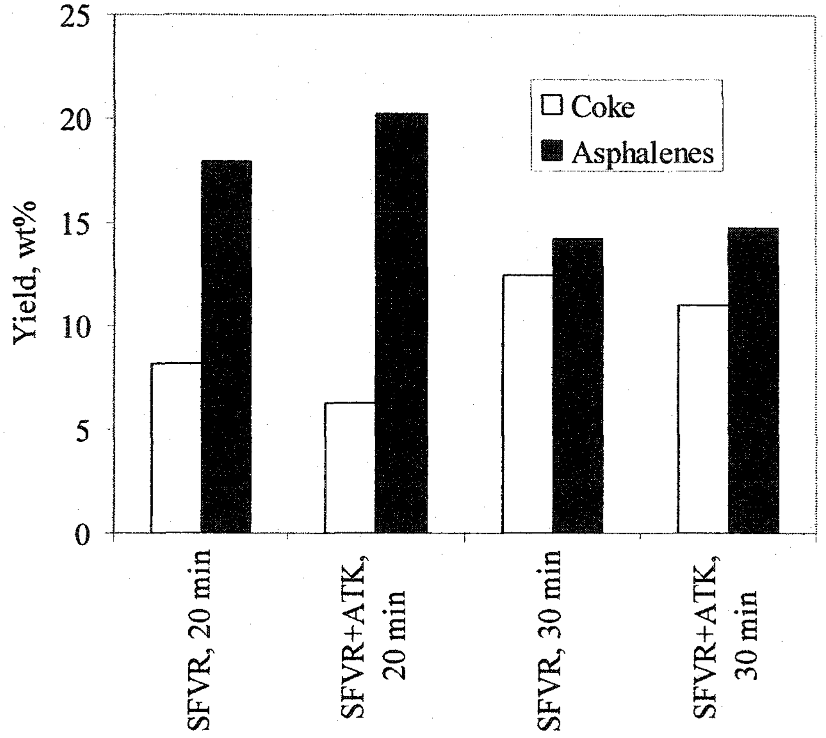

Figure 4.13 Effect of asphaltene-treated kaolin on coke and asphaltenes yield from solid-free vacuum residue.

elemental analysis. Therefore, the reduction in coke yield and increase in asphaltenes yields were real and were not due to release of the asphaltenes from the surface of the asphaltene-treated kaolin.

4.3.12 Effect of ultrafine silica powder. The ineffectiveness of kaolin powder could be due to its low surface area. To examine this possibility, 2 wt% of ultrafine silica powder was added in and well mixed with solids-free vacuum residue using the solids addition method described earlier. Like kaolin, the surface of the ultrafine silica particles is oleophobic. The major difference is that due to their extremely small particles sizes, the silica particles have a huge external surface area of 380 m^2/g. As Table 4.6 shows, however, the addition of the ultrafine silica powder had no significant effect on coking. The yield of coke, asphaltenes and gases were all virtually unchanged and the differences in the yields of coke, gas and asphaltenes were all well within their experimental errors of ±0.5 wt %.

Table 4.6 The addition of ultrafine silica powder had not significant effect on coking of solids-free vacuum residue.

	Yields (wt%)		
Feed	Coke	Gas	Asphaltenes
SFVR	16.6	6.6	12.4
SFVR+2% silica powder	16.3	6.9	12.3

It might be possible that the ultrafine silica powder was not well dispersed. If the particles were agglomerated, only a fraction of the total surface area could interact with the coking media. The observed ineffectiveness could thus be due to inadequate effective surface area that was actually interacting with the coke or coke precursors. To test this possibility, SEM / X-ray Mapping of silicon element in the coke was used to measure the distribution of silica particles in the coke produced from the coking of solids-free vacuum residue with silica powder addition. The micrograph of SEM/X-ray Mapping is shown in Figure 4.14, where the bottom half is the SEM image of coke, and the upper half is the mapping of Si signals (shown as bright spots on the image) excited by X-ray in the area of coke corresponding to the SEM image. The bright spots indicate the location Si elements. From this figure it is concluded that Si was evenly distributed throughout the sample. Had there been large agglomerates of silica particles, the Si signal would have appeared clustered or even as sporadic large bright spots. Therefore, the silica particles were well dispersed in the coking reaction media, and the lack of effectiveness must be due to their surface properties, not due to inadequate effective surface area.

4.4 Discussion

4.4.1 Possible Role of Bitumen Solids as Emulsion Stabilizers. As described earlier, removal of the bitumen solids from Athabasca bitumen and vacuum residue increased the rate of coke formation in both closed and open reaction systems, and eliminated the induction period of coke formation. When the isolated bitumen solids were added back to, and well dispersed in, the solids-free feed, the coke yield was reduced.

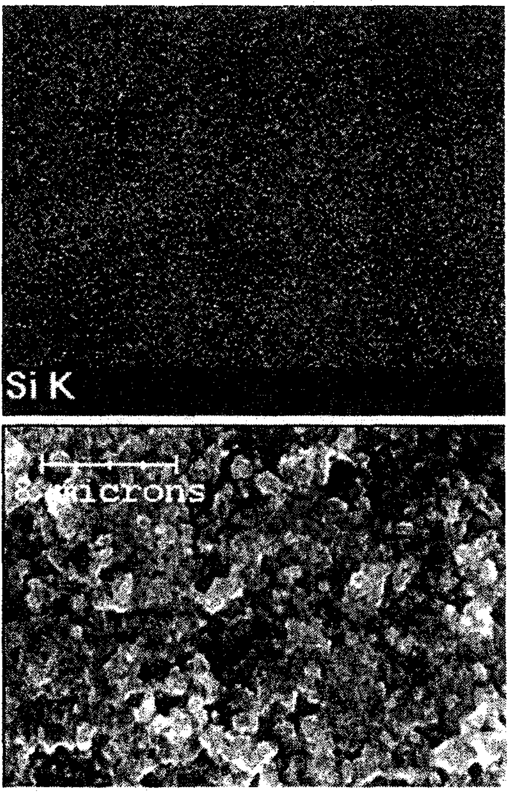

Figure 4.14 X-ray mapping of Si distribution in the coke produced from solid-free with silica powder.

The effect of solids concentration on coke yield from vacuum residue was nonlinear, with a minimum coke yield at about 1.0 wt % bitumen solids concentration. This minimum coke yield, however, was found to occur only during the early stages of coke formation.

A possible mechanism of the effect of the bitumen solids is that they act as emulsion stabilizers. As shown in Chapter 3, during early stages of coke formation, the coke behaves as spherical liquid droplets suspended in the bulk liquid media (see Figure 3.3 and Figure 3.5). Thus the reacting system is essentially an oil-in-oil emulsion. The fine bitumen solids are bi-wettabe and therefore, could accumulate at the interface between the bulk oil phase and the coke droplets. This accumulation would inhibit the coalescence of the coke droplets as described by Tanabe and Gray (1997). Scanning electron microscopy (SEM) can be used to verify this possibility. As described in Chapter 3, the toluene insoluble coke (TI) from the coking of Athabasca bitumen and vacuum residue was composed of spheres and agglomerated and coalesced spheres. The surface was very smooth, and there was no sign of etching by the toluene during the extraction of coke after the reaction. These images indicate that the coke was in a second liquid phase which had a well defined interface with the toluene soluble oil phase. In order for fine solids to stabilize emulsion droplets from coalescence, each of the solids particles must be strongly adsorbed on the interface in such a way that one side of the particle intrudes into the droplet while the other side in the bulk phase. If during coke formation, the bitumen solids accumulated on the surface of the coke spheres, the surface of the coke microspheres should appear rough under SEM after the toluene soluble oil phase was washed away with toluene. It would also be expected that the coke spheres should have either angular bitumen solids particles, or "dimples", or both, on their surfaces, depending on whether the particles remained attached to the coke spheres or were shaken away by sonication during extraction. Under SEM, however, no angular bitumen solids particles were observed on the surface of the coke microspheres. In fact, no particles, neither free nor attached, shaped like those in Figure 4.2 or Figure 4.3 were observed in the TI (which contained both coke and bitumen solids as separated by filtration) from coking of bitumen or vacuum residue. Therefore, the bitumen solids were probably completely encapsulated by the liquid coke. It is noted that although the majority of the bitumen solids have sizes of the order of several hundred nanometers as shown in Figure 4.3, the bitumen solids also contain ultrafine particles (Kotlyar *et al.*, 1998) that are too small for the resolution of the SEM to detect them. Therefore, the possibility of some ultrafine particles accumulating on the coke surface can not be completely ruled out. Nevertheless, it is very unlikely that the bitumen solids stabilized the coke precursors from coalescence by accumulating on the interface between the coke phase and the bulk oil phase.

4.4.2 Possibility of Bitumen Solids as Free Radical Scavenger. The bitumen solids could inhibit free radical chain reactions by providing a high surface area for termination of radicals, thereby reducing the formation of coke that is a product of the free radical condensation and polymerization. The elimination of the induction period due to removal of bitumen solids can be explained by free radical inhibition mechanism, analogous to the often-observed induction phenomenon in polymerization (Barrett, 1975). Inhibition of free radicals, however, would necessarily also suppress gas formation, since gas formation was mainly achieved by free radical chain reactions

(Tanabe and Gray, 1997). The fact that the gas yield was not changed with solids concentration (Figure 4.6), nor did it change with or without bitumen solids (Figure 4.9), suggests that free radical inhibition was not the cause of coke reduction by the bitumen solids. The experiments with ultrafine silica powders also prove that the reduction in coke formation with bitumen solids can not be attributed to the inhibition of free radicals. The well-dispersed ultrafine silica particles have a huge external surface area to inhibit the free radicals. Therefore, if the reduction in coke yield were due to free radical inhibition, the ultrafine silica powder should have significantly reduced coke yield. However, there was virtually no change in coke yield in the presence of these ultrafine silica particles.

4.4.3 Catalytic Activities of Bitumen Solids. The effect of bitumen solids on coke formation could be due to their weak catalytic activities. The model reactions showed that bitumen solids had mild catalytic activities toward hydrogenation, dehydrogenation, and hydrogen shuttling (Table 4.5). The model reaction of bitumen solids with cumene (see Table 4.5) gave a negligible cracking conversion, indicating that the catalytic activity of bitumen towards acidic cracking was insignificant. This was further supported by the hydrocarbon composition of the gas product from coking of bitumen and that from solids-free bitumen, which showed predominantly C_1 and C_2 while C_4 was very low. The catalytic activities towards hydrogenation, dehydrogenation and hydrogen shuttling were expected since the metallic elements contained in bitumen solids, such as iron, are possible source of catalytic activity toward hydrogenation, and catalysts that promote hydrogenation under hydrogen pressure very often promote hydrogen shuttling as well (Chadha *et al.* 1997; Badger *et al* 1994). Dehydrogenation is the reverse reaction of hydrogenation. Therefore catalysts that promote hydrogenation will also promote dehydrogenation when reaction conditions favor the reverse reaction. At coking conditions, however, the hydrogen partial pressure that is necessary for hydrogenation is absent, and therefore catalyst would only accelerate the reaction to the reverse direction, *i.e.* dehydrogenation. Hence the reduction in coke from bitumen, when reacted in the presence of bitumen solids, is not attributable to hydrogenation reactions. The role of hydrogen shuttling in coking is uncertain, since there is no external addition of hydrogen donor or hydrogen acceptor. There is no net hydrogen transfer to the reactants and the gain of hydrogen to one molecule (or molecule segment) is always at the expense of the loss of hydrogen to another molecule (or molecule segment). Dehydrogenation, however, would always contribute to increased coke formation. To verify the effect that a hydrogenation catalyst would have on coking of solids-free feed, experiments were conducted using molybdenum 2-ethyl-hexanoate. This compound is soluble in bitumen and decomposes under reaction conditions to form a very effective and highly dispersed hydrogenation catalyst. Addition of this catalyst under coking conditions, however, increased coke formation by approximately 1 wt%, rather than reducing it, as described earlier. This result is compelling evidence that the reduction in coke yield can not be attributed to the hydrogenation catalytic effect of the bitumen solids.

4.4.4 Effect of Nucleation and Enhanced Mass Transfer. Since the bitumen solids appear to be freely wettable by the liquid coke, the solids could act as nucleation sites for phase separation during coke formation. Wiehe (1993) proposed that the coke precursors were unreactive as long as they remained dissolved in the oil phase which acted as hydrogen donor and provided abstractable hydrogen. Once the coke precursors phase separated to form a second phase, however, the coke precursors quickly cracked and combined to form coke because the abstractable hydrogen was no longer available. Although nucleation helps initiate phase separation, highly dispersed nucleation sites also allow the liquid phase coke to spread on the surface of the solids once phase separation has started. The spreading of liquid phase coke on the surface of highly dispersed fine solids then provides enhanced mass transfer by offering higher interface area with the bulk oil phase and a shorter mass transfer path to and from the bulk oil phase. This hypothesis of reduction in coke yield due to enhanced mass transfer is consistent with the findings of Gray *et al.* (2001) and Dutta *et al.* (2001). Gray *et al.* (2001) coated thin films of Athabasca vacuum residue on the interior of a stainless steel tube and heated to 530 °C using induction heating. They found that the coke yield decreased as the initial film thickness was reduced from 80 to 10 μm. The mode of mass transport shifted from bubbling in thick films to diffusion through a stagnant thin film. The reduction in coke yield was attributed to the more effective transport of products out of the liquid phase. Dutta *et al.* (2001) measured the effect of mass transfer limitation on coking using a ^{13}C-labled tracer. They deposited Athabasca vacuum residue on the wall of a quartz tube reactor as a film and coked it up to over 500 °C with continuous nitrogen flushing. Coke yields decreased from 23% to 18% with decreasing initial film thickness from 150 to 15 μm. A ^{13}C-labled tracer representative of reaction fragments from bitumen was synthesized and added to the feed in order to measure the incorporation of products into the coke via retrograde reactions. A 23% decrease in overall incorporation of the tracer was observed when the initial film thickness was reduced from 150 to 15 μm.

As illustrated in Figure 4.15. When the coke first formed from the bulk phase, it coated the surface of oleophilic solids. When there were no oleophilic surfaces, such as in

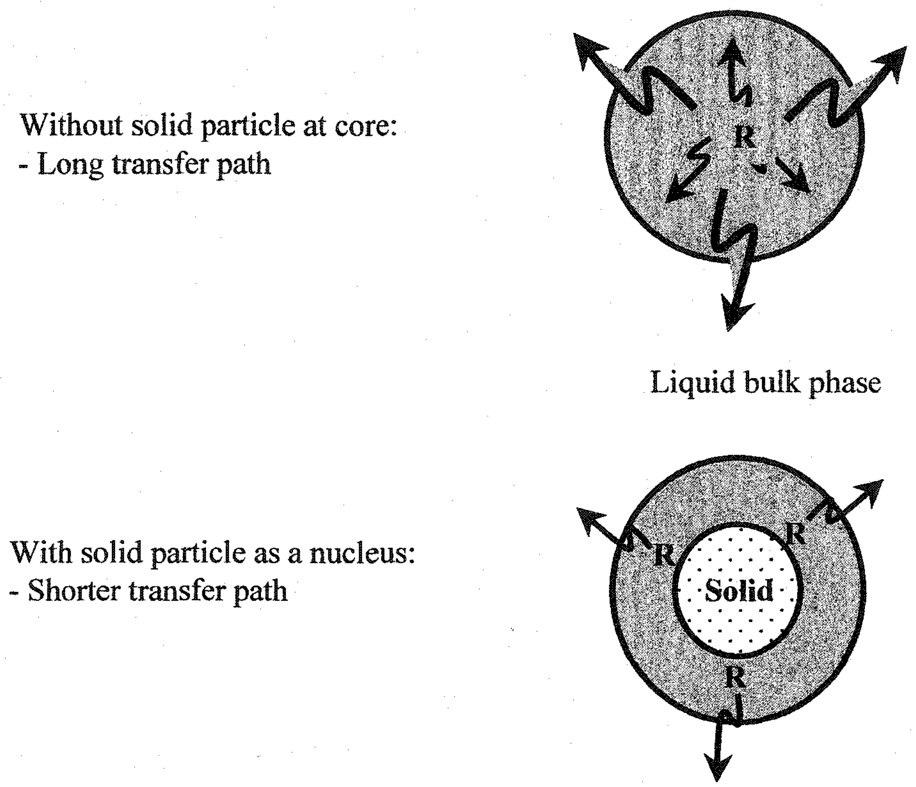

Figure 4.15 Schematic illustration of oleophilic solids facilitating mass transfer of light hydrocarbon fragments from coke phase.

the coking without fine solids or with oleophobic solids, however, the coke tended to form droplets by itself. As discussed in Chapter 3, the coke formed initially still contained substantial amount of side chains and aliphatic bridges between aromatic cores. At coking temperatures, the coke further cracked, breaking off the side chains and bridges. The release of the light cracking products gave a reduction in total coke make. The additional cracking reactions were evidenced by the substantial amount of weight loss during reheating of coke from short coking reactions, as discussed in Chapter 3. With only a thin film of liquid coke coated on the surface of oleophilic solids, the cracking products had a shorter mass transfer path and a higher mass transfer area than if the liquid coke was droplets (see Figure 4.15). These cracking products would initially take the form of free radicals. If they could not escape from coke phase fast enough, they would be incorporated into the coke as shown by Dutta *et al.* (2001). The higher interface area (mass transfer area) and shorter path afforded by the solids would also enhance hydrogen shuttling between coke phase and hydrogen donor species from the oil phase. The overall effect would be reduced coke formation.

The contrast of the effects of added fine solids with different surface wettabilities on coke yield further supported the hypothesis that the enhanced mass transfer is the cause of reduced coke formation with oleophilic fine solids. Wang *et al.* (1998) showed that the toluene insoluble carbonaceous materials (*i.e.* coke by definition) formed in a gas oil under hydrotreating conditions could wet the surfaces of carbon black and asphaltene-treated kaolin, but under the same conditions the toluene insoluble material did not wet the untreated kaolin, which was oleophobic. Ultrafine silica powder and untreated kaolin, both of which are oleophobic, showed no effect on coke yield. Similar results were observed by Sanaie *et al.* (2001), who investigated the effects of fine solids on incipient coke formation. In their work, silica, kaolinite, and Southern Alberta clay were added to Cold Lake bitumen at temperatures of about 380 — 400 °C, but no effect on coke yield was observed. As described earlier, although kaolin had no effect on coke yield, when the surface of the kaolin was rendered oleophilic by treating with asphaltenes, the asphaltene-treated kaolin reduced coke formation. Carbon black, which is oleophilic, also reduced coke formation. Therefore, the surface wettability is a very important factor, *i.e.* only fine solids with oleophilic surface can reduce coke formation.

The result that oleophobic ultrafine silica powder had no effect on coke yield also gave further evidence that the reduction in coke yield by bitumen solids, carbon black and asphaltene-treated kaolin was not due to free radical scavenging. As discussed earlier, the possibility of a free radical scavenging effect of the bitumen solids was ruled out based on the results that the gas yield from coking was unchanged with or without the bitumen solids, although the coke yield was reduced significantly with the bitumen solids and went through a minimum with increasing bitumen solids concentration. The ultrafine silica powder has a huge surface area of 380 m^2/g. If the coke reduction were caused by free radical scavenging by the fine solids, then the ultrafine silica powder would have been far more efficient in reducing coke yield since it provided a huge surface area to capture free radicals. However, the ultrafine silica powder showed no effect on coke yield.

4.4.5 Mechanism of the Effect of Fine Solids on Coke Formation. The minimum coke yield at an intermediate concentration of the bitumen solids implied that the bitumen solids could simultaneously have played two or more roles. Some of these roles tended to promote coke formation while others tended to reduce coke formation, both as functions of the solids concentration. The combined effect would then be a minimum coke yield. As discussed earlier, the most probable role the bitumen solids played to reduce coke formation was the effect of enhanced mass transfer. The most probable role of the bitumen solids in promoting coke formation was the dehydrogenation effect. As the model reactions showed, the bitumen solids promoted dehydrogenation of cumene under coking conditions, and addition of molybdenum 2-ethylhexanoate increased coke formation. The combined effect would be a minimum coke yield at an intermediate concentration of the bitumen solids. Addition of carbon black resulted in a monotonic decrease in coke yield with increasing concentration of carbon black. This was consistent with the hypothesis, since carbon black lacks the dehydrogenation catalytic activity. The minimum could also have been caused by coalescence of the bitumen solids at higher concentrations, such that the effective surface area is actually reduced at higher concentrations. But again, the fact that increasing carbon black concentration caused a monotonic decrease in coke yield indicates that coalescence was unlikely to be the cause of the minimum coke yield at intermediate concentration of the bitumen solids.

4.5 Conclusions

1. Athabasca bitumen and vacuum residue contain a relatively high content of bitumen solids. These solids were characterized to be sub-micron sized mineral particles coated with asphaltene-like but toluene insoluble organic materials.

2. Removal of bitumen solids from Athabasca bitumen or vacuum residue increased the coke yield at short coking reactions, and to a lesser degree, the ultimate coke yield as well. This effect could be reversed by adding the solids back into the solids-free feed, when the solids were well dispersed.

3. Coke yield as a function of the concentration of the bitumen solids was found to be nonlinear, with the coke yield initially decreasing with increasing concentration, passing a minimum, and then increasing.

4. As revealed by the model reactions, bitumen solids had weak catalytic activities towards hydrogenation, hydrogen shuttling and dehydrogenation. These catalytic activities, however, were not responsible for the reduction in coke yield under coking conditions. The solids did not show any appreciable acidic cracking activity.

5. The addition of oleophilic fine solids, including carbon black and asphaltene-treated kaolin, could reduce coke yield and increase asphaltene yield at coking conditions. Oleophobic solids, such as untreated kaolin and ultrafine silica powder, however, had no appreciable effect on coking. The coke yield decreased monotonously with increasing concentration of carbon black.

6. The effect of the bitumen solids in coke formation is proposed to be due to a combined effect of enhanced mass transfer and dehydrogenation. The solids acted as nucleation sites which allow coke to deposit and spread on the surface of the solids, thereby providing a higher mass transfer area and shorter mass transfer path. Enhanced mass transfer facilitated the escape of light hydrocarbon from coke phase and promoted hydrogen shuttling reactions with the hydrogen donor species from the bulk oil phase, leading to a reduced coke formation. On the other hand, the bitumen solids catalyzed

dehydrogenation reactions, which tended to increase coke formation. As both the mass transfer effect and dehydrogenation effect were functions of the concentration of the bitumen solids, the combined effect gave a minimum coke yield at an intermediate concentration.

7. The effect of foreign fine solids including carbon black, kaolin and asphaltene-treated kaolin, and ultrafine silica further verified the hypothesis that the enhanced mass transfer effect is the cause of coke reduction with bitumen solids. The coke formed initially was a liquid which could wet and coat the surface of oleophilic solids and thus form a thin film. Therefore, oleophilic solids such as carbon black and asphaltene-treated kaolin reduced coke yield. Conversely, without dispersed fine solids or with oleophobic solids, the coke tended to form droplets suspended in the bulk phase. Unlike bitumen solids, carbon black (with absorbed oxygen removed) does not have catalytic hydrogenation activity. Therefore the coke yield decreased monotonously with increasing concentration of carbon black.

4.6 References

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Chapter 5

Conclusions and Recommendations

5.1 Mechanism and Kinetics of Coke Formation

The experiments described in Chapter 3 elucidated the phase behavior and mechanism of coke formation under thermal conversion conditions. Coke produced from bitumen or residues at moderate coking severity was initially composed of microspheres that could grow and coalesce (see Figure 3.3 to 3.5). The coalescence led to agglomerates that showed evident flowing features. The surface of the coke was very smooth and no etching was observed although the coke had gone through toluene extraction. These phenomena are compelling evidence that coke under coking conditions of moderate severity was in a well-defined second liquid phase. Coke produced from these conditions remained as a thermoplastic polymer after isolation, as indicated by the deformation caused by escaping gaseous products during reheating (Figure 3.11).

The coke produced from vacuum residue at moderate severity (430 °C, <40 minutes) was mostly soluble in quinoline and was isotropic, indicating mesophase formation was insignificant. As reaction time increased, mesophase formation significantly increased. Reheating caused further thermal cracking of the coke that quickly approached completion. Reheating also slightly transformed the isotropic coke into anisotropic coke, and rapidly transformed quinoline soluble coke into quinoline insoluble coke. Increasing temperature was more effective than increasing reaction time in forming higher fraction of quinoline insoluble coke. This is consistent with the lumped kinetic model, which showed that the activation energy of forming quinoline insoluble coke was significantly higher than that of quinoline soluble coke formation (see Table 3.3).

The coke at the early stage of its formation was a liquid under coking conditions and was soluble in quinoline when isolated and cooled to room temperature. The behavior of coke at such conditions resembled a thermoplastic polymer at a temperature above its melting point. This thermoplastic coke, however, is not stable at coking temperature, and will crack off its side-chains, crosslink, and grow in molecular weight by continued polymerization. At moderate coking temperatures, the crosslinking is relatively slow, and coke can retain it thermoplastic properties upon reheating. The coke was initially of low molecular weight and low degree of cross-linking and thus was mostly isotropic. The fractions of mesophase and anisotropic solid in coke increased with coking reaction time. Eventually the coke would become a mixture of both isotropic and anisotropic solid, with isotropic coke usually forming the continuous phase with embeded anisotropic domains which varies in amount depending on the condition the coke was produced.

Coking kinetics of solid-free Athabasca vacuum residue was modeled using (I) a modified Wiehe (1997) model, and (II) a five-pseudocomponent lumped model. In both models, the formation of quinoline insoluble coke (QI) from quinoline soluble coke (QS) was described as a reaction with shifting orders from first order at low QS concentration to zero order at higher QS concentration. In model (I), as in the original Wiehe's model, the induction period was determined by a solubility parameter. In model II the induction period was modeled by directly introducing a time delay for the coke formation step as a model parameter. Both models fitted the experimental data fairly well with model (II) slightly better than model (I).

5.2 Mechanism of the Effect of Finely Dispersed Solids on Coking

Removal of bitumen solids from Athabasca bitumen or vacuum residue increased the coke yield at short coking reactions, and to a lesser degree, the ultimate coke yield as well. Addition of bitumen solids, other oleophilic solids such as carbon black and asphaltene-treated kaolin into solid-free feeds reduced coke yield while leaving gas yield unchanged. Addition of finely dispersed oleophobic solids such as untreated kaolin and ultrafine silica had no significant effect on coking. Coke yield as a function of the concentration of the bitumen solids was found to be nonlinear, with the coke yield initially decreasing with increasing concentration, passing a minimum, and then increasing. Coke yield as a function of carbon black concentration, however, decreased monotonously. As revealed by the model reactions, bitumen solids had weak catalytic activities towards hydrogenation, hydrogen shuttling and dehydrogenation. These catalytic activities, however, were not responsible for the reduction in coke yield under coking conditions. The solids did not show any appreciable acidic cracking activity.

Chapter 3 showed that coke was initially in a liquid state. This liquid-state coke can wet the oleophilic carbon black and asphaltene-treated kaolin, but does not wet the untreated kaolin and ultrafine silica, both of which are oleophobic. When the coke first starts to form out of the bulk phase, it tends to coat the surface of oleophilic solids. When there are no oleophilic surfaces, such as in the coking without fine solids or with oleophobic solids, however, the coke tends to form droplets of its own. As discussed in

Chapter 3, the coke formed initially still contained substantial amount of side chains and aliphatic bridges between aromatic cores. At sustained coking temperature, the coke molecules further undergo cracking reactions, losing the side chains and bridges. The release of the light cracking products gives a reduction in total coke yield. The coating of liquid coke on oleophilic surfaces enhances the release of the light cracking products since the coating provides larger mass transfer area and shorter mass transfer path as illustrated in Figure 4.15. The additional cracking reactions were evidenced by the substantial amount of weight loss during reheating of coke from short coking reactions, as discussed in Chapter 3. The bitumen solids also act as a weak catalyst for dehydrogenation as proved in the model reactions (see Table 4.5), which tends to increase coke yield.

5.3 Process Implications and Recommendations

The experiments presented in this thesis confirmed that coke formed at conditions of low to moderate severity is a liquid that can flow and spread on oleophilic surfaces. Very often fouling is also attributed to coke formation at low severity. Therefore, in tackling fouling problems, it would be useful to take the liquid behavior, such as adhesion, coalescence, wettability into consideration. The thermoplastic properties of isolated coke produced from low to moderate severity, could potentially also be exploited.

The reduction in coke yield by the presence of bitumen solids, and especially the minimum coke yield at intermediate concentration of the bitumen solids could have some industrial applications. The fine solids carried over to downstream products have caused operational problems, and thus there have been proposals to remove the bitumen solids completely prior to coking. As this thesis has shown, however, rather than removing the bitumen solids completely, it may be economic to partially remove these solids to a concentration that optimize the overall performance. The use of oleophilic solids such as carbon black as additives to reduce coke formation may be an interesting direction for future studies towards commercial applications.

In this thesis, the reduction in coke yield with oleophilic solids is attributed to enhanced mass transfer resulting from liquid-state coke spreading on the surface of these solids. This hypothesis can be further verified and the effect quantified if oleophilic solids with known size and size distribution are available. This can be a topic for future work.